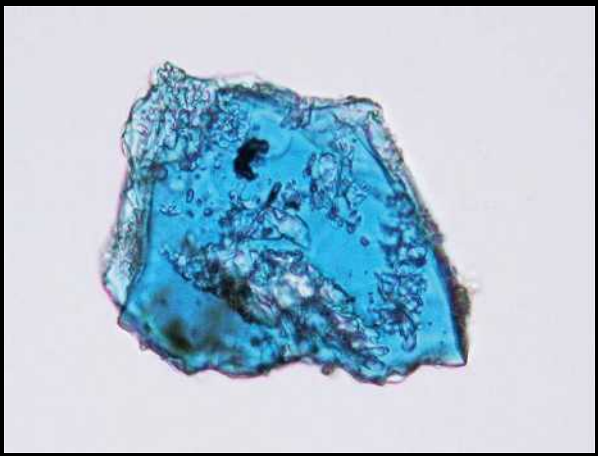
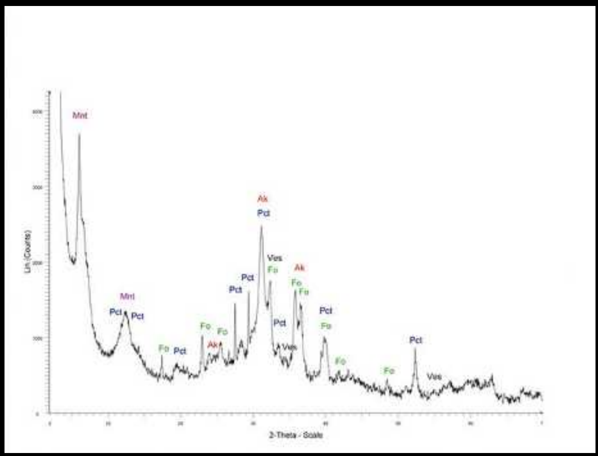
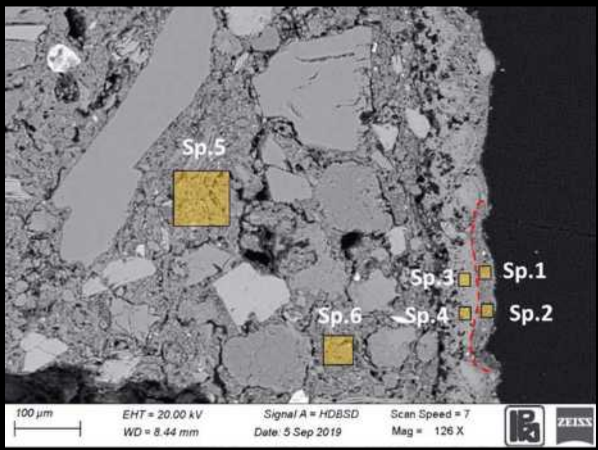
Proceedings of the 7th Symposium of the Hellenic Society for Archaeometry

Archaeology Archaeometry: 30 years later







Eleni Filippaki (ed.)

in collaboration with

Y. Bassiakos, G. Facorellis, A. Oikonomou,
M. Papageorgiou, P. Loukopoulou and M. Kaparou

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Cover images:

Upper left side: Egyptian blue grain (Βιβτένκο, Σ., Τζαναβάρη, Α. και Βασιλειάδου, Α., this volume). Upper right side: X-ray diffraction pattern of the powder obtained from a casting mould (Iliopoulos, I. and Soura, K., this volume). Lower left side: Backscattered electron image of the ceramic body of a cooking pot in cross section (Oikonomou, A., Marabea, Ch., Papachristodoulou, Ch. and Palles, D., this volume). Lower right side: Strongly tectonized marble with relics of bigger grains decaying into a groundmass of small calcite grains (Anevlavi, V., Prochaska, W. and Ladstätter, S., this volume).

Contents

Preface

The 7th Symposium of the Hellenic Society for Archaeometry was held in the premises of the Byzantine and Christian Museum in Athens in Autumn 2019 (October 9-12) and managed to bring together well- respected members of the archaeometric community from Greece and abroad.

The Hellenic Society for Archaeometry (HSA), founded in 1982, constitutes one of the oldest associations of the field in Europe, encompassing hundreds of members, Greeks and foreigners. HSA, as a scientific association dedicated to promoting the interdisciplinary field of Archaeometry, aims at enhancing this discipline scientific field, which applies Science and Technology on Archaeology, History of Art and, generally, on any field related to Cultural Heritage. Active members of the HSA are academics, researchers and students, from related institutions- scientific and academic-, the Archaeological Service and the private sector in Greece.

Since its establishment, the HSA has organized seven Symposia on Archaeometry, all of them with intense international character, as well as numerous seminars and public lectures, promoting Archaeometry in the country and abroad. Additionally, HSA is one of the founding bodies of the prestigious international Archaeometry journal "Archaeological and Anthropological Sciences" established in 2009 https://www.springer.com/earth+sciences+and+geography/journal/12520.

The 7th Symposium entitled "*Archaeology-Archaeometry: 30 years later*", commemorated the organization of the 1st Symposium of HSA back in 1990, which bore the emblematic title *"Linking Archaeology and Archaeometry"*. During the 3-day Symposium, more than 100 original papers were delivered in oral and poster presentations, all of which served as springboard for intriguing and stimulating discussions.

The Organizing Committee of the 7th Symposium consisted of Y. Bassiakos, Y. Facorellis, E. Filippaki, M. Kaparou, P. Loukopoulou, A. Oikonomou, M. Papageorgiou and G. Theodorou. The Members of the international Scientific Committee were E. Aloupi-Siotis, S. Boyatzis, H. Brekoulaki, J. Buxeda i Garrigós, A. Dellaporta, R. Jones, P. Karkanas, A. G. Karydas, V. Kassianidou, V. Kilikoglou, D. Kontopoulou, A. Kouli, I. Lyritzis, Y. Maniatis, E. Margariti, S. Pavlidis, E. Photos-Jones, Th. Rehren, C. Renfrew, M. Roumbou, A. Sarris, Z. Stos-Gale, G. Tsokas and N. Zacharias.

This volume of proceedings comprises a representative collection of the contributions presented in the Symposium, covering a wide range of fields in archaeological science, such as provenance and technology of archaeological and historical materials, geo-archaeology and bio-archaeology, dating methods and applications, landscape studies, as well as papers presenting the origins of Archaeometry in Greece.

The Organizing Committee would like to acknowledge the valuable support and the hospitality provided by The Byzantine and Christian Museum in Athens. We are also very grateful to the sponsors of the Symposium, namely NCSR "Demokritos" and Arte Solutions. Importantly, we remain indebted to the referees in Greece and abroad, as well as to the Members of the Scientific Committee who reviewed and commented on the scientific papers submitted. Finally, we cordially thank all those whose contributions have been essential in organizing the Symposium and publishing these Proceedings.

On behalf of the Editorial Committee

Eleni Filippaki, Researcher
Lab. of Archaeometry, NCSR "Demokritos"

Mineralogical and Chemical Characterization of a Casting Mould and Other Metalworking-related Finds from the LBA Settlement at Stavros, Chalandritsa in Western Achaea, Greece. Preliminary Results and their Archaeological Interpretation

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Abstract: Excavations at the LBA settlement at Stavros, Chalandritsa in Western Achaea (Greece) have provided evidence of *in situ* metalworking such as fragments of casting slag, metallurgical ceramics, a clay tuyère, and most importantly, the half of a double mould used for the casting of whole-cast socket spearheads. The significance of the latter lies not only in its meticulous manufacture, but mainly in the scarcity of such items in the Mycenaean world. In fact, the absence of stone moulds for the casting of weapons even from the most extensively-excavated Mycenaean palatial sites makes it difficult to assume that such a high-quality craft was manufactured in a peripheral village of mostly agrarian character, and suggests that the mould may have been imported into the settlement of Stavros, Chalandritsa.

Tracing the mould's origin would shed more light on the casting procedures for the manufacture of weapons during the Mycenaean period, as well as on the attested role of Achaea in the technological interaction usually referred to as a "metallurgical koinè". For the aforementioned reasons, an analytical approach based mainly upon non-destructive or minimally-destructive techniques was devised (optical microscopy, SEM/EDS, XRF/ED, XRF/WD, NIR spectroscopy, XRD). The results obtained so far have enabled us to characterize the mould by means of minero-petrographic and chemical composition and draw some preliminary conclusions about its possible provenance—the case of a local origin having at first excluded.

KEYWORDS: METALWORKING, LATE BRONZE AGE, ACHAEA, MOULD, XRD, XRF, SEM, NIR SPECTROSCOPY

Introduction

The LBA settlement of Stavros, Chalandritsa is located in Western Achaea at a distance of 20 km south-west of the city of Patras. It occupies a plateau of approximately 12 acres on the top of a hill. This was a strategic location controlling a vast fertile land and the natural passage connecting the littoral and the inland of Western Achaea (Figure 1). According to the ongoing study of the archaeological data, the site was inhabited—probably uninterruptedly—during the entire Late Helladic period (*c*.1700-1100 BC) (Soura 2017; forthcoming). The clusters of dwellings that have come to light spread over the south and southwestern part of the plateau and are arranged in successive building rings that conform to the ground slope. The portable archaeological finds relate mainly to everyday household activities and are indicative of the basically agro-pastoral character of this peripheral Mycenaean settlement (Kolonas and Gazis 2006; Kolonas 2009; Soura, forthcoming). It is, therefore, remarkable that the site has also yielded traces of *in situ* metalworking. These comprise fragments of slag and metallurgical ceramics, a clay tuyère, and the possible use of some pits within the casting procedure (Soura 2014). However, the find that stands out is the half of a double-type stone mould meant for the casting of whole-cast socket spearheads.

Chalandritsa's mould is a high-quality craft consisting of two assembling parts (Figure 2). The largest part, which bears the spearhead negative, has an oblong trapezoidal shape, a semi-circular cross-section, and measures up to 16.2*5.6*3.5 cm. The smallest part was manufactured to repair the first (larger) part after its breaking and so render it functional. It is of a rectangular shape with a semi-circular cross-section and its maximum dimensions are 5.9*3.6*2.5 cm. Traces of bindings are occasionally visible on three pairs of corresponding holes on both parts that were meant for their assemblage.[1]

The mould's casting product corresponds to a laurel leaf-shaped spearhead[2] with a short and wide whole-cast socket, a type which appeared in the Aegean by the end of LH IIIB[3] and became popular during

[1] For an analytical description of the mould, see Soura 2017.

[2] It corresponds to Group K according to O. Höckmann's classification system (Höckmann 1980: 67-76, fig.15, pl.6).

[3] Most scholars agree on a Central-European / West-Balkan origin of this type of spearhead. See e.g. Sandars 1963; Höckmann 1980: 68, 149;

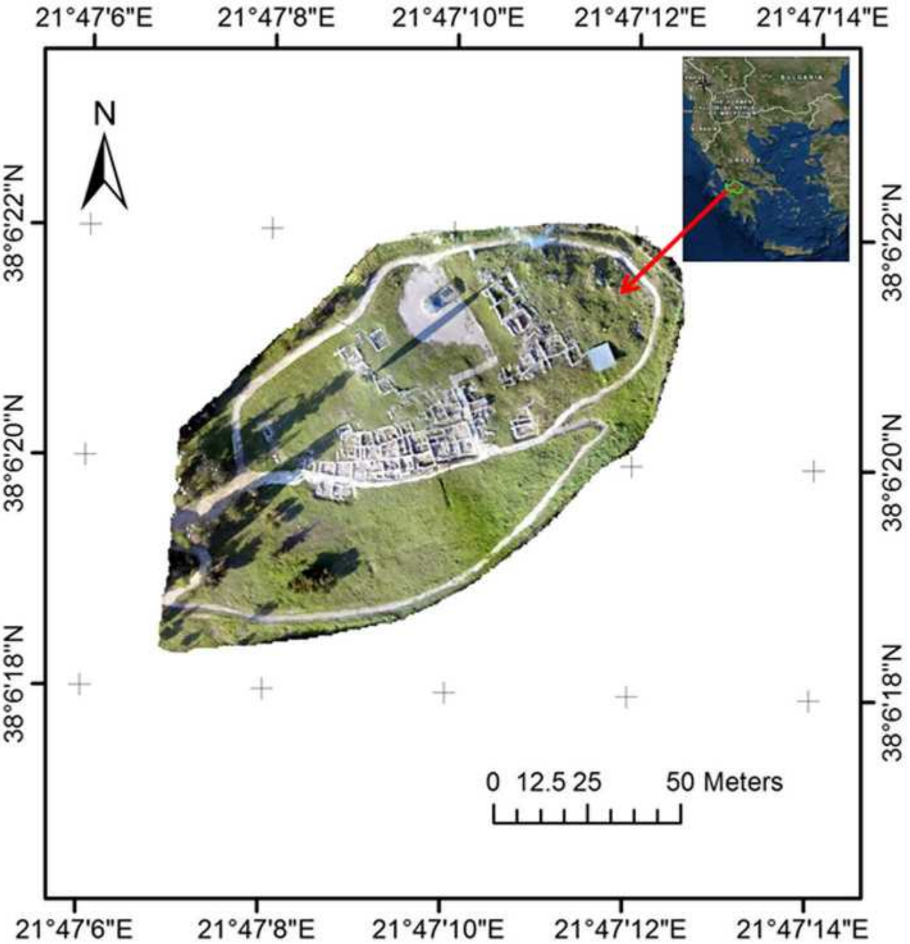

Figure 1. Oblique area view of the LBA settlement of Stavros, Chalandritsa in Western Achaea, Greece (modified after Nikolakopoulos *et al.* 2017).

the LH IIIC period.[4] Despite of the popularity of this type of spearhead, the mould itself constitutes a rare archaeological find, not only for the region of Achaea, but for the entire Mycenaean world (Soura 2017: 487). In fact, the large number of LBA weapons found in Greece stands in stark contrast to the remarkable scarceness of corresponding moulds.[5] No mould for the casting of swords has been found so far,[6] while only one stone mould from Kastanas, Macedonia was undoubtedly used for the casting of spearheads (Hochstetter 1987: 20-21, pls 5.3, 28.7).[7]

The discrepancy between the amount of other types of stone moulds and those for the casting of weapons has led many scholars to assume the use of different casting procedures for the manufacture of weapons in the Mycenaean world, clay and sand being the most probable substitute materials (Harding 1984: 259; Evely 2000: 361; Wardle and Wardle 2001: 44-45; Hakulin 2004: 25, 27; 2008: 197). In addition, the fact that the only well-identified pieces of LBA stone moulds for spearheads found in Greece (namely the moulds from Kastanas, Macedonia and Stavros, Chalandritsa) were both of the "non-Mycenaean" whole-cast socket type cannot be overlooked as coincidental, especially when

1987: 352; Bouzek 1985: 141; Hochstetter 1987: 20-21; Zucconi Galli Fonseca 1992; Sherratt 2000; Jung 2009.

4 All published spearheads of this type from the region of Achaea date to the LHIIC period. See Soura 2017: 486, n. 20 for a list of references.

5 On the contrary, numerous moulds for the casting of jewelry, tools, and implements have been found (Tournavitou 1997: 209-256; Evely 2000: 353-362; Hakulin 2004: 22-23, figs. 2, 45, Appendix IV.2; Hughes-Brock 2008: 127-151; Kleitsas 2013: 146-149).

6 A LM IIIC Early multiple stone mould from Phaistos, Crete was probably meant for the casting of daggers (Borgna 2011: 291, n. 10).

7 A fragmented mould from Pylos perhaps served the same purpose (Blegen and Rawson 1966: 284, fig. 300.4), while evidence for the use of clay moulds for the casting of spearheads has come to light at the acropolis of Tiryns (Rahmstorf 2008: 81-82, pl. 35.1789-1791). For the use of some lead spearheads as casting models, see Kilian 1983: 308.

taking into account the large number of contemporary stone moulds found in other European and Balkan regions (Soura 2017: 487, n.26 for a list of references).

Bearing in mind all the above, the finding of such a rare and high-quality tool in the peripheral village of Chalandritsa naturally raised questions regarding its provenance. Therefore, an analytical approach was devised in order to identify the mould's raw material and hopefully trace its possible origin. At the same time, analysis was scheduled for some samples of probable metallurgical ceramics aiming to shed light on the casting procedures that took place at the settlement of Stavros, Chalandritsa.

Materials and methods

The material analyzed so far includes two segments of a stone mould, a clay tuyère, and three fragments of metallurgical ceramics (Figure 2). Upon being granted permission for the transport and analysis of the abovementioned materials, they were taken to the Minerals and Rocks Research Laboratory (MRRL) at the Department of Geology, University of Patras for devising an analytical strategy. Given the nature and state of maintenance of the artifacts, a combination of non-invasive/non-destructive (Figure 3) and invasive/minimal destructive or destructive techniques was used. The non-invasive/non-destructive techniques included a macroscopic examination of the integral artifacts using a ProScope mobile microscope paired to an iPad and a hand lens, the mineral determination through Near Infra-Red Spectroscopy using a portable NIR SpecTerra system (SM-3500 Spectral Evolution portable spectrometer) under laboratory room conditions, and the chemical analysis of the studied artifacts through a benchtop X-ray fluorescence devise (XRF-ED NEX CG RIGAKU) under vacuum. The microstructure and the chemistry of the artifacts were also evaluated under high vacuum on an environmental scanning electron microscope (SEM-EDS; ZEISS EVO MA 10) at the Department of Materials Science, University of Patras.

With regard to the pair of rare archaeological artifacts, no invasive/destructive techniques were used upon the clay tuyère, while only a minimal amount (less than a few milligrams) of loose powder left over during conservation of the mould's large segment was received. The loose material obtained was further powdered in an agate mortar, and was first mounted on dedicated silicon-based low background holders, and then analysed in an X-ray powder diffraction system (BRUKER D8 ADVANCE). The diffractograms obtained were evaluated using EVA Bruker AXS software (Bruker-AXS, Madison, WI, USA) coupled with the ICDD PDF-2 database (version 2006), which permitted the identification of the mineralogical composition of the examined material. Once the mineralogical identification was completed, the same powder (weighing *c.*0.5 milligrams) was placed on special sample cells that are routinely used for the analysis of samples of very small quantity without pressing it. These cells were then chemically analyzed under vacuum in a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF; RIGACU ZSX PRIMUS II). In addition to these analytical techniques, small fragments from the

Figure 2. The archaeological artifacts considered in the present study: (a) the mould's large segment; (b) the mould's small segment; (c) archaeological drawings of the stone mould; (d) the clay tuyère (akrofysion); (e) the fragments of one of the metallurgical ceramics analyzed herein (© Ephorate of Antiquities of Achaea).

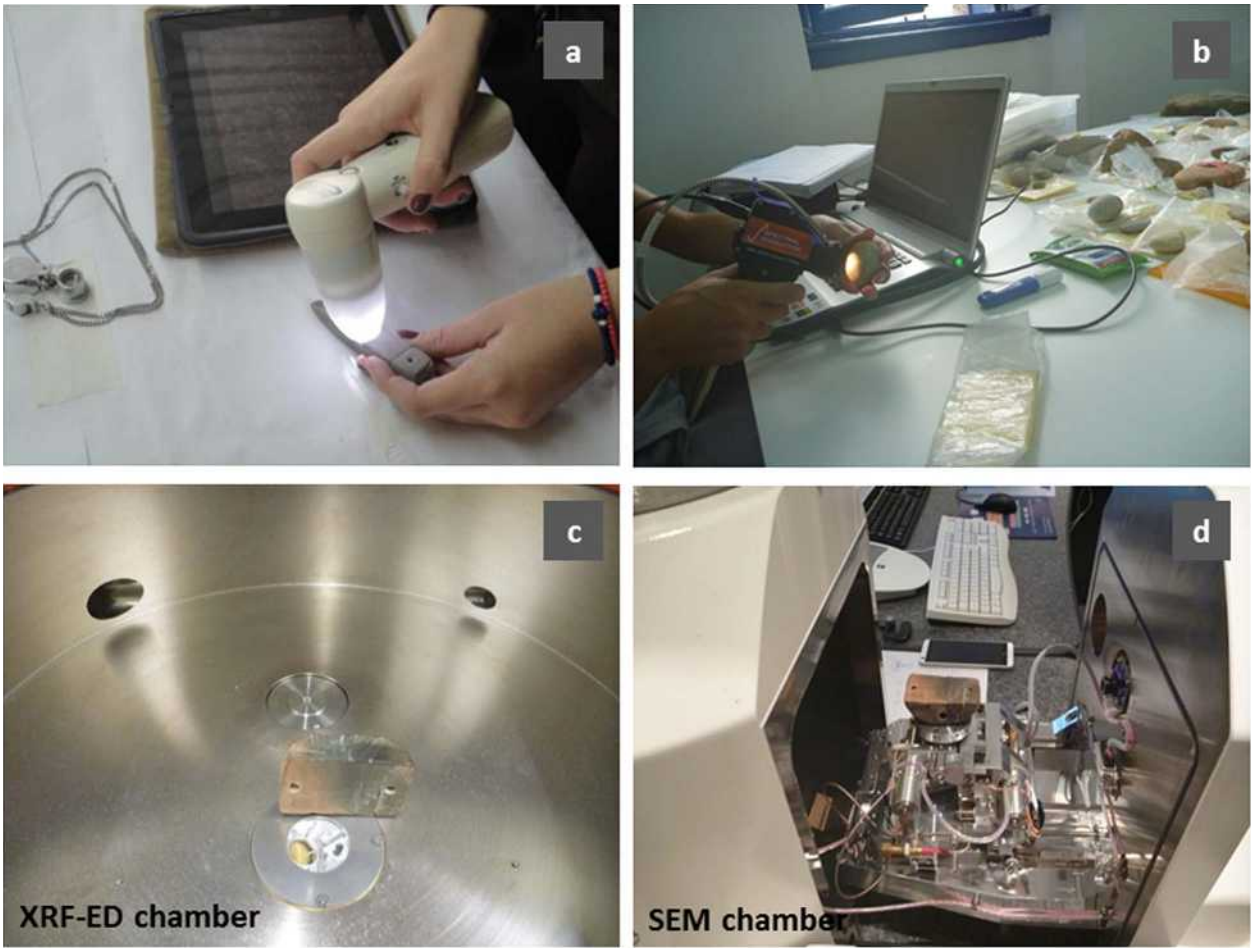

Figure 3. The non-invasive/non-destructive analytical techniques employed during this study: (a) the ProScope mobile microscope paired to an iPad, used for obtaining detailed microphotographs of the studied artefacts; (b) the NIR SpecTerra portable spectrometer, used for the mineralogic evaluation of the samples; (c) the chamber of the XRF-ED NEX CG RIGAKU system, where the small part of the stone mould was placed; (d) the chamber of the SEM/ED ZEISS EVO MA 10 system with the small part of the stone mould being fixed on the analysis holder.

probable metallurgical ceramics of a dimension around 1*1*0.5 cm were thin-sectioned and studied under a polarizing microscope (Zeiss AxioScope.A1) equipped with a Jena ProgRes C3 digital camera.

Geological background of the studied area

In order to identify the possible origin of the analyzed material, its chemical and mineralogical composition had to be compared to the local geology. The area of Chalandritsa is located southwest of the city of Patras and is characterized by the presence of alternations of limestones and flysch deposits. These belong to the Pindos and Gavrovo-Tripolis geological units that represent the Alpine basement in the study area (Tsoflias 1984). The Pindos zone comprises of: a) flysch deposits which mainly contain sandstones and rare marls with thin alternations of limestone layers; b) thin to medium platy pelagic limestones with thin siliceous intercalations; and c) radiolarites with siliceous beds which occasionally bear Mn nodules. The Gavrovo-Tripolis zone is represented in the area only by its flysch sequence, mainly containing marls, sandstones, yellow-gray clays, and conglomerates. The post-Alpine formations of the studied area comprise Pliocene marine, brackish and lacustrine sediments, which are composed of alternating layers of marls, clays, sands, and conglomerates. No metamorphic or igneous rocks are present in the area, with the exception of some rare exotic volcanic fragments occasionally found in Pindos zone (Pe-Piper and Piper 1991; Piper 2006).

Results

Characterization of the stone mould

The macroscopic examination of the two parts of the stone mould helped us to identify the strongly foliated nature of the material which is consistent with a metamorphic origin of the source material (Figure 4a, b). Towards the surface of the artifact a thin yellowish-white layer of non-foliated material was encountered.

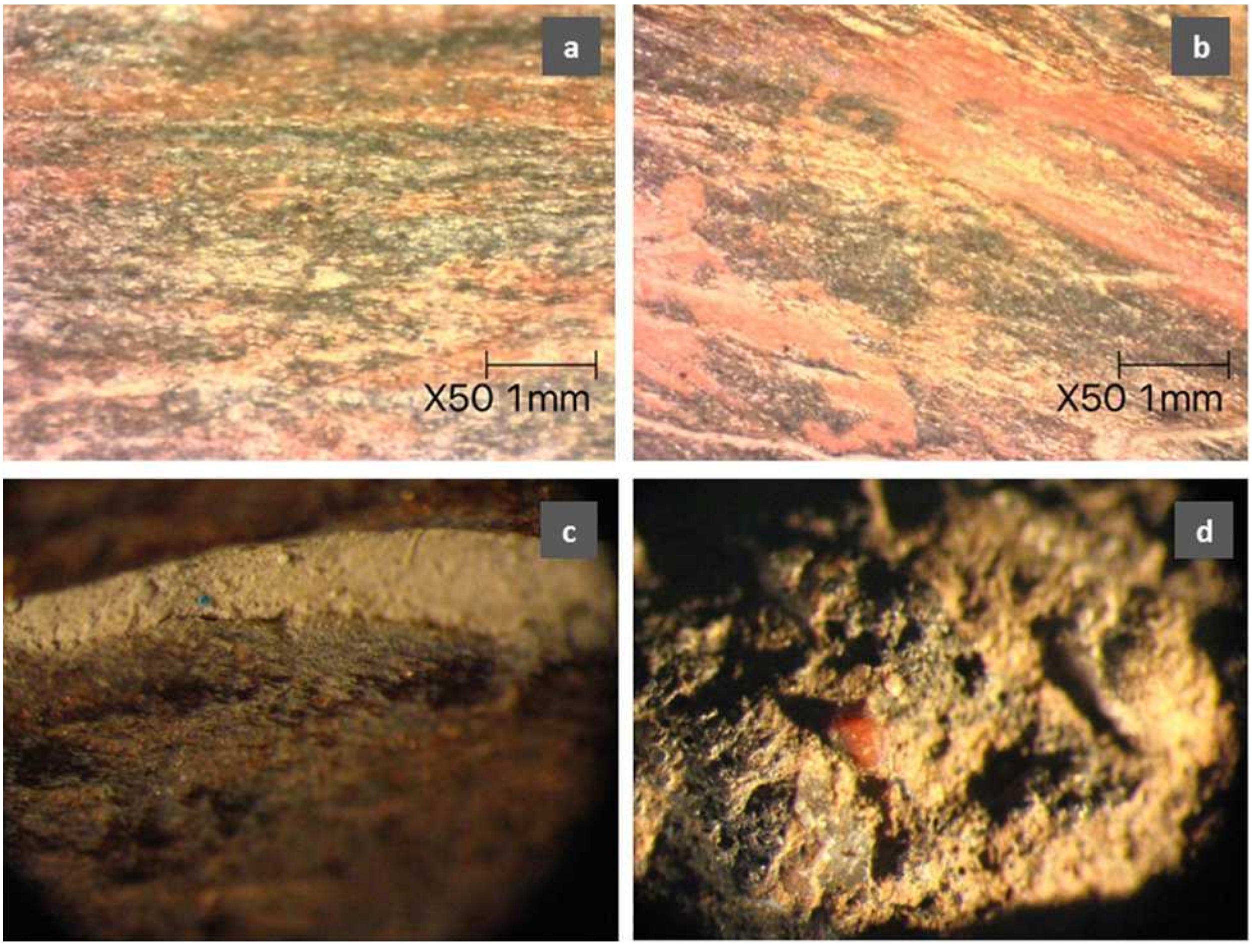

Figure 4. Representative microphotographs of the mould's large segment. The photos in the upper row were captured using the ProScope mobile microscope, whereas those in the lower row were taken using the macro lens of a normal digital camera: (a, b) the foliated matrix of the stone mould as is pronounced by the orientation of the elongated white and grey coloured mineral grains observed on the external surface of the artefact; (c) a blue colored mineral grain (possibly a variety of pectolite) identified in the whitish non-foliated matrix of the stone mould and observed close to one of the external surfaces of the artifact; (d) a red colored mineral grain (possibly vesuvianite), identified in the main matrix of the artifact.

This embodies rare occurrences of small mineral grains of blue and red color (Figure 4c, d). According to the XRD results presented below these colored minerals could possibly correspond to pectolite and vesuvianite respectively.

The evaluation of the archaeological finds using Near Infrared Spectroscopy (NIR) did not provide diagnostic information on the mineralogical composition of the stone mould. This is because the absorption characteristics in this region of the electromagnetic spectrum do not appear to be well developed and distinguishable, especially for wavelengths longer than 2100 nm (Figure 5a, b). The alteration of the physicochemical characteristics of the raw material due to the default use of the stone mould and the clay tuyère make their correct evaluation difficult. Factors that affect the raw material in this case include the possible development of amorphous or crystalline mineralogical phases due to the extensive use of the finds as well as the progressive development of secondary minerals associated with alteration processes. However, the main observations obtained by their spectral signatures helped us to formulate some first inferences about the mineralogical composition of the studied artifacts. The spectral characteristics of the stone mould consist of absorptions nearly at 450 nm, 1420 nm, and 1920 nm of the electromagnetic spectrum. From 800 nm to 1800 nm the spectra display an almost flat slope, changing to a negative slope from 2150 nm to higher wavelengths. The intensity and the depth of the absorption features as well as the reflectance values differ slightly as each measurement was applied in contact to a different surface of the material. When the absorptions at 1400 nm and 1900 nm are intense and rounded, they usually indicate the presence of H2O water molecules (Clark 1999) absorbed either on the surface of the material or embedded in its crystalline structure due to surface

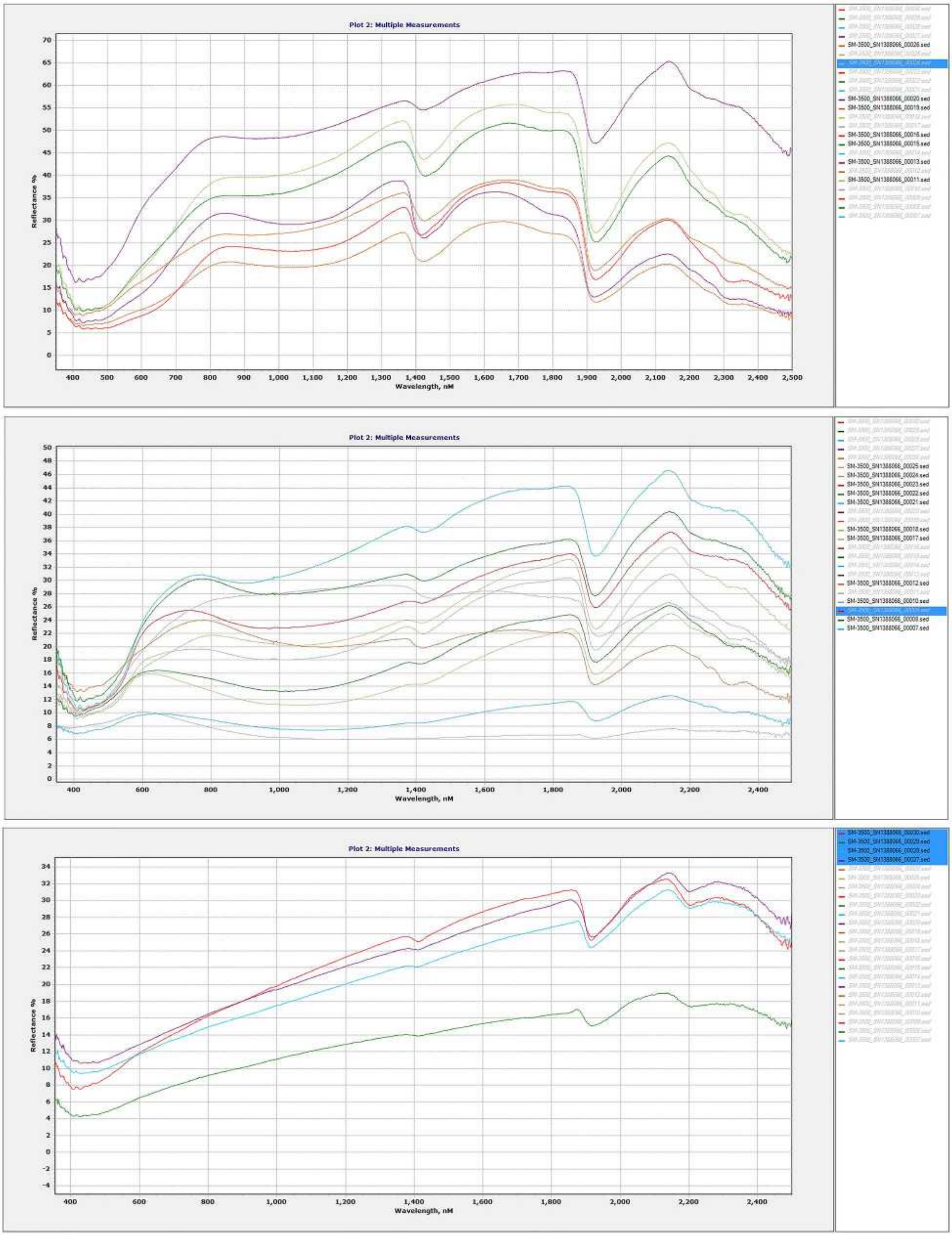

Figure 5. The NIR spectra obtained through the analysis of various domains of: (a) the mould's large segment, (b) the mould's small segment, and (c) the clay tuyère.

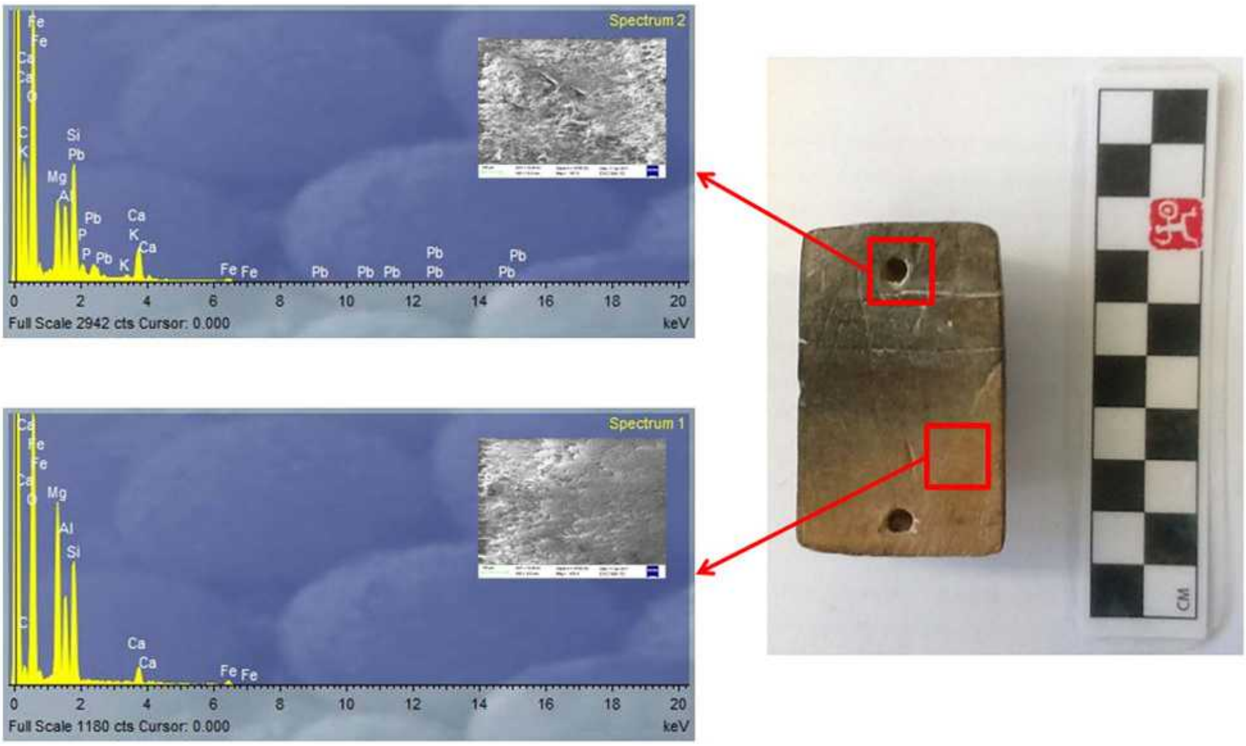

Figure 6. The ED spectra obtained through the areal microanalyses of two different micro-domains of the mould's small segment. The insets given in each spectrum are representative secondary electron micrographs from the same microdomains. Pb and Ca content is significantly higher in the area close to the assembling hole.

hydration from the exposure of the material in surface conditions. In the visible region of the electromagnetic spectrum, absorption features are mainly related to the transfer of electric charge, including Fe^{2+} and Fe^{3+}, indicative of the presence of Fe-rich minerals and oxides (Clark 1999). In several spectra we noticed a rather broad feature at 1050 nm approximately. This is attributed to the presence of olivine as verified by the X-ray Powder Diffraction Analysis (XRD). At nearly 2300 nm, a small absorption is observed in several spectra that is not only attributable to vibrations of Mg-OH molecular bonds. According to Cloutis and Gaffey (1991) and Clark (1999), olivine is characterized by broad absorption features near 1050 nm and 2300 nm in the Near Infrared region. In addition, some spectra display poorly developed features at 2200 nm approximately, which are attributed to Al-OH molecular vibrations—characteristics for clayey minerals. Through the XRD we were able to identify the presence of montmorillonite that coincides with the above observation.

The characterization of the mould's surface by means of the secondary electron micrographs obtained through SEM were rather inexplicit, probably because they were influenced by weathering and wear due to the artifact's utilization. However, the foliation of the mineralogical constituents already distinguished through the macroscopic examination could easily be reconfirmed (Figure 6). The main purpose of using SEM was to evaluate the chemical composition of the studied artifacts by EDS analysis (Table 1). The chemical microanalysis was performed on the small part of the stone mould as well as on the material obtained from the large part (the loose powder left over during conservation). In the case of the mould's small part, two sets of microanalyses were performed. The first set (5 measurements) was undertaken in proximity to one of the holes which were used for the assemblage of the two segments, and where traces of a whitish material, probable remnants of some kind of bindings, were recognized through their macroscopic examination. The second set of measurements (n=9) was performed on the main body of the small segment and far away from any of the holes. The large segment of the stone mould could not be analyzed because the microscopic analytical conditions were unattainable once the entire piece was accommodated in the microscope chamber. Thus, SEM/ED analysis of the large segment was made possible only on the loose powder (left over during conservation) obtained from that artifact. The analytical results obtained from the main body of the small piece and the material from the large piece of the stone mould were rather similar. The main discrepancy was encountered in the MgO content (*c.*15 wt% for the grinded material from the large piece versus *c.*25wt% for the main body of the small piece). The

Table 1

	Small piece (entire object)			Big piece (grinded material)		Akrofysion
	SEM-EDS		XRF-ED	SEM- EDS	XRF-WD	SEM EDS
	holes (n=5)	rest of it (n=9)	all (n=8)	L6000b	L6000-2	akrofysion
wt %	mean	mean	mean			
SiO_2	26.8	32.5	36.6	29.52	29.53	48.25
TiO_2	1.3	-	0.5	-	2.18	1.11
Al_2O_3	14.2	16.2	15.9	18	13.65	21.5
P_2O_5	4.2	-	0.1	1.7	1.75	2.05
FeO	16.6	18.0	17.0	21.48	29.09	20.03
MgO	17.9	25.2	17.8	14.97	14.03	0.67
MnO	-	-	0.3		0.69	-
CaO	16.7	9.7	7.9	11.34	4.86	2.79
K_2O	0.6	0.9	0.2	0.84	0.24	3.6
SO_3	-	-	0.35	2.15	0.19	-
NiO	-	-	0.1	-	0.23	-
ZnO	-	-	0.1	-	0.07	-
PbO	2.6	-	0.6	-	0.23	-

Table 1. Chemical analysis of the studied artifacts though SEM/EDS, XRF/ED and XRF/WD.

microanalysis of the area close to one of the holes of the small segment gave similar results for most of the analyzed elements with the exception of CaO and PbO contents, which were both significantly higher than those encountered in the main body of the same piece and the loose material obtained from the large piece. The CaO content of the area around the hole was *c*.16.7 wt% as opposed to 9.7 wt% and 11.3 wt% in the main body of the small part and the loose material obtained from the large part, respectively. The PbO content of the area close to the hole of the small segment was *c*.2.6 wt% whereas in the other two cases no PbO was revealed. The rest of the major elements exhibit only small fluctuation among the different parts of the artifacts analyzed (SiO_2 content varies from 26.8 to 32.5 wt%, Al_2O_3 from 14.2 to 18 wt% and FeO from 16.6 to 21.5 wt%).

In order to have a better insight into the chemical composition of the stone mould, the two segments of the artifact were also analyzed by means of X-ray fluorescence. The complete small segment was analyzed by placing it in the chamber of the XRF/ED system and taking various measurements (n=8) by slightly moving the object each time. The large part could not be analyzed in the XRF/ED system because the instrument repeatedly failed to achieve the necessary vacuum in the chamber once the artifact was placed in position for analysis. Thus, only the loose material obtained from the mould's large fragment could be chemically analyzed using the XRF/WD system. In both cases, the results obtained (see Table 1) were comparable to those encountered through SEM/ED analysis of the main body of the small part (with the exception of MgO content) and the loose material from the large part (with the exception of FeO and CaO contents).

The mineralogical composition of the stone mould was identified through the analysis of the loose material obtained from the artifact's large segment by means of X-ray diffraction (Figure 7a). The mineral phases recognized are montmorilonite $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O]$, forsterite (Mg_2SiO_4), pectolite $[NaCa_2(HSi_3O_9)]$, akermanite $[Ca_2Mg(Si_2O_7)]$ and vesuvianite $[(Ca,Na)_{19}(Al,Mg,Fe)_{13}(SiO_4)_{10}(Si_2O_7)_4(OH,F,O)_{10}]$. The coexistence of these minerals is rarely recognized in natural materials, while similar assemblages are rather rare worldwide. They mainly occur in skarns of high temperature, i.e. metasomatism of ultrabasic rocks under reducing conditions. Similar assemblages are also reported in areas where volcanic activity is manifested by basic and ultrabasic alkaline lithologies (Masetto 1991).

The known locations where similar rock compositions have been encountered include the regions of Maronia in northeastern Greece (Katerinopoulou *et al.* 2009), Trentino-Veneto and Lombardy in northern Italy (Camara Artigas *et al.* 2011; Boscardin *et al.* 1993),

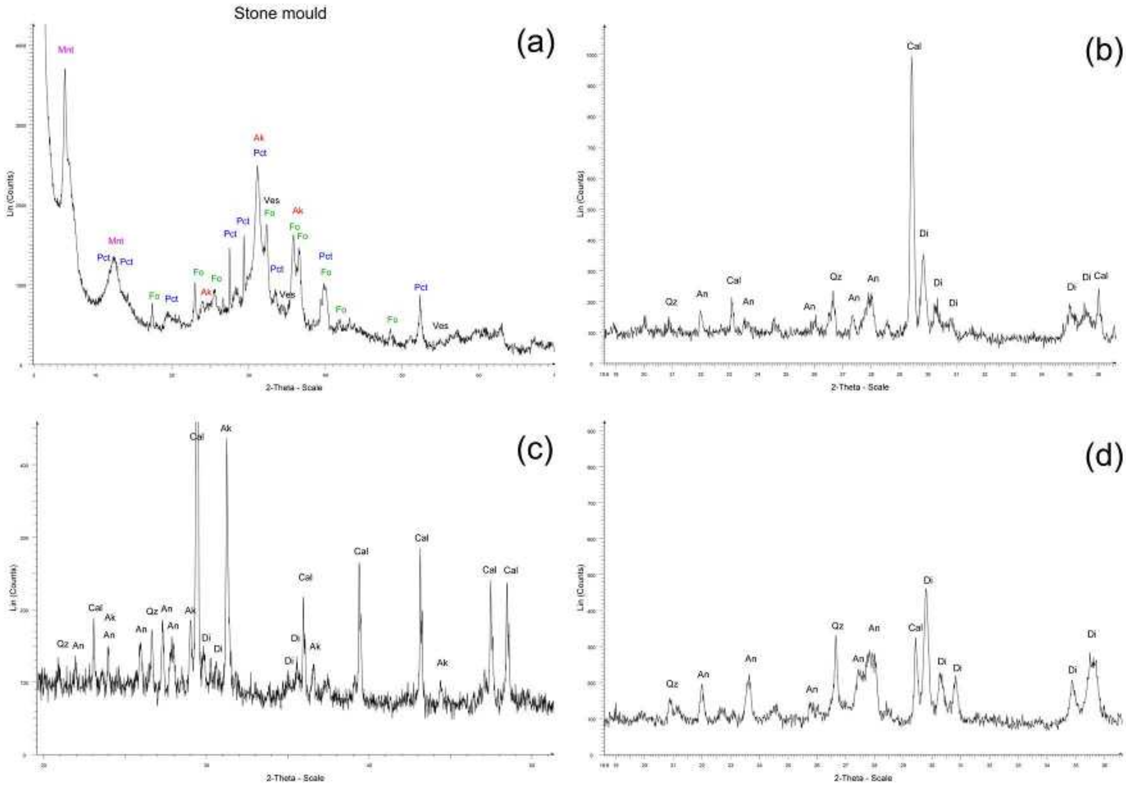

Figure 7. Representative X-ray diffraction patterns of: (a) the powder obtained from the mould’s large segment and (b, c, d) the metallurgical ceramics considered in the present study (samples X4, X7, X8, respectively).

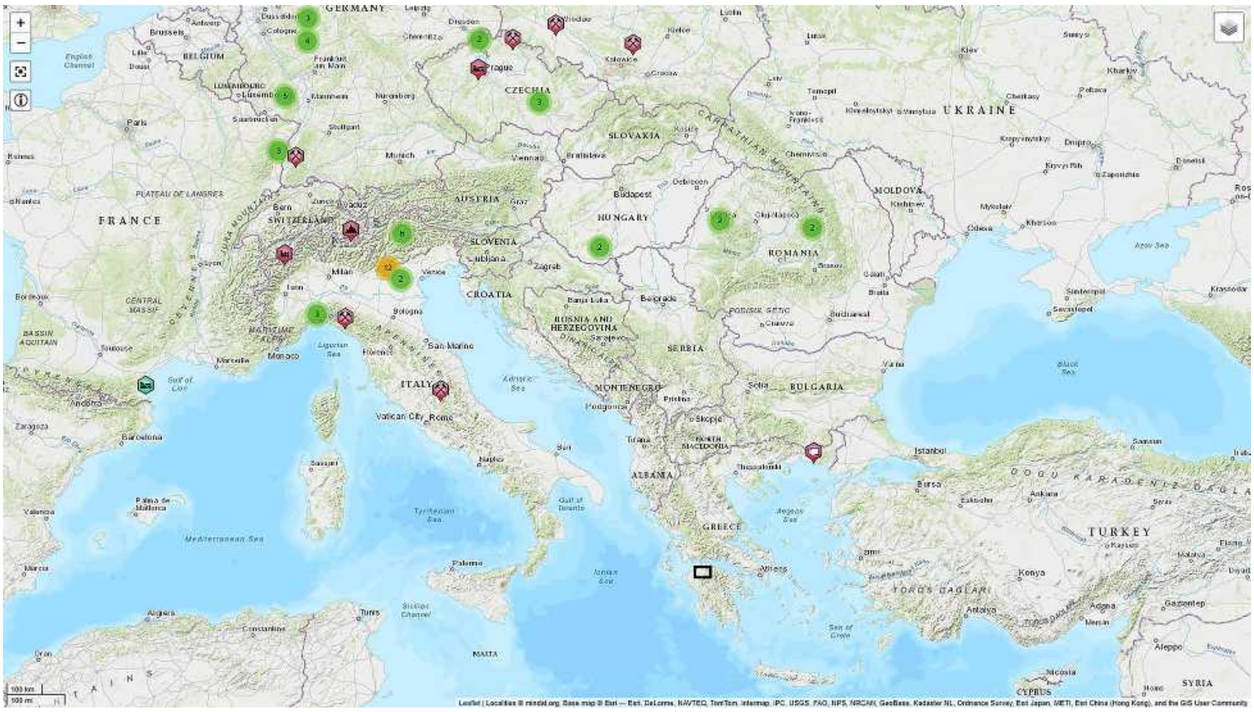

Figure 8. Main pectolite occurrences across the Southern and Southeastern Europe as traced through the mindat.org mineralogical database. Polygon symbols indicate a single occurrence and circle symbols with number denote multiple occurrences (modified after Mindat.org 2020). The rectangular frame indicates the study area.

Apuseni Mountains in Romania (Pascal *et al.* 2001), Rovina in the Czech Republic (Tasáryová *et al.* 2014) and Krivaja-Konjuh in Bosnia and Herzegovina (Segvic 2010) (Figure 8). Similar compositions are also reported from other, more remote areas such as Germany, Great Britain, Morocco, and Pakistan. The presence of olivine in the studied mould seems to rule out a "Greek" origin from Maronia (Katerinopoulou *et al.* 2009). The assemblage recorded is very similar to that described from the area of Trentino-Veneto (eg. Sano; Boscardin *et al.* 1993; Masetto 1991) as well as those encountered in Rovina, Czech Republic (Tasáryová *et al.* 2014) and the Krivaja-Konjuh ophiolite complex in NE Bosnia and Herzegovina (Tasáryová *et al.* 2014)..

Both forsterite and pectolite are refractory minerals, and thus they respond well to the thermal shock they sustain during metalworking. Montmorillonite on the other hand inherits good workability for initially engraving the mould.

Characterization of the metallurgical ceramics

In order to further document metalworking activity in the study area, we included one clay tuyère and three ceramic fragments—exhibiting signs of probable use in similar processes—to the material analyzed.

The spectroscopic characteristics of the clay tuyère (akrofysion) reflect an upward slope towards the higher wavelengths (see Figure 5c) that is indicative of its Fe-rich composition. This is verified by the geochemical analysis of the material as stated in the following paragraph. The absorption features observed through the spectroscopic study are located at 1915 nm and 2205 nm, while a small feature is rarely displayed at 1410 nm. Although the absorptions at 1410 nm and 1915 nm are most likely attributed to hydration of the material due to its exposure to surface conditions, absorption features at 2205 nm seem to be related to molecular vibrations between Al-OH bonds (Clark 1999). This feature, however, does not appear to be well developed. It could, therefore, be attributed to hydrous Al-rich minerals such as smectites. It is more possible that this feature represents the primary Al-rich nature of the raw material, which contains newly formed Al-rich mineral phases that were created under the high temperature regime that the clay tuyère (akrofysion) had sustained.

The chemical characterization of the clay tuyère was based only upon its chemical composition as determined through SEM/EDS (Table 1). The complete artifact was placed in the microscope chamber and analyzed by using the EDS attachment of the SEM. The chemical composition of the clay tuyère indicates that a non-calcareous (CaO content *c.*2.8wt%) and iron rich (FeO content *c.*20 wt%) clayey material was possibly used for its manufacture.

The fragments of probable metallurgical ceramics were studied through optical microscopy, XRD and SEM/EDS. The three fragments considered herein (samples X4, X7 and X8) exhibit clear evidence of use in ultrahigh-temperature processes like metalworking. The thin sections observed showed extensive sintering of the groundmass, well documented through the optical inactivity of the micromass and the presence of well-rounded bloating pores (Figure 9a, b, c). The latter, most of the times, contain fringes of secondary calcite deposited on their walls.

The XRD analysis of these fragments (see Figure 7c, d, e) has permitted us to identify their mineralogical composition and recognize the neoformed mineral phases developed due to the high firing of the material. The mineralogical assemblage attested (Table 2) includes diopside + anorthite + quartz ± akermanite (+calcite) and corresponds to an equivalent firing temperature greater than 1000-1050°C.

The SED/EDS analysis performed on fresh fractures obtained from these three samples has further reconfirmed the firing regime they sustained. Their microstructure is characterized by the collapsing clay plates, often coalescing, and forming extensive and interconnecting glass filaments with small pores formed in-between them (Figure 9d). Similar textures are considered indicative of the extensive vitrification stage according to Maniatis and Tite (1981).

Discussion

A first inference emerging by the analysis presented herein is that the mould does not constitute a stray find: a metalworking tradition—that may even predate the mould itself—has been recognized within the settlement of Stavros, Chalandritsa by the dispersion of relevant finds. It is also important that, at least in some cases, pyrotechnological processes (most probably small-scale casting) took place in areas of household activities as proven by the fragments of metallurgical ceramics collected from hearths inside the dwellings (Soura 2014; 2017: 483).

As far as the mould is concerned, the results of the analysis have confirmed the use of lead bindings for the attachment of the repair segment to the artifact's main body. Although the melting point of lead (327° C) is much lower than that of bronze,[8] these bindings must have had no contact with the molten alloy since they were limited to the mould's exterior facet—the stone

[8] The melting temperature of bronze, depending on its alloy, can go down to around 800o C.

sample ID	Quartz	Calcite	Diopside	Akermanite	Plagioclase	K-feldspar
X4	+	++++	+++	-	+++	-
X7	+	++++	+	+++	+	+
X8	+	+	++++	-	+++	-

-: not detected; tr: traces; +: few; ++: common; +++: frequent; ++++: dominant

Table2: Evaluation of the mineralogical composition of the metallurgical ceramics by means of X-ray diffraction analysis.

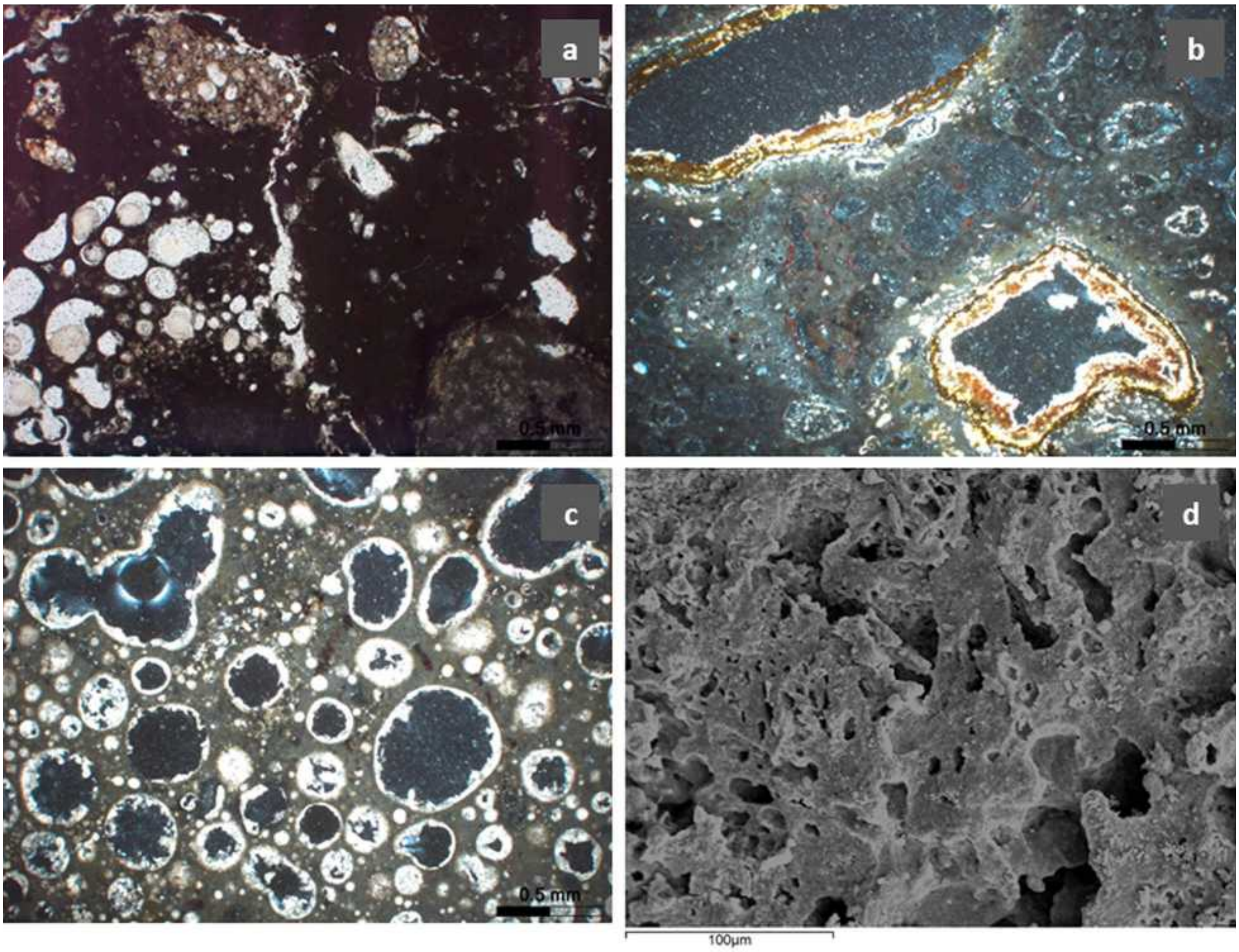

Figure 9. Representative photomicrographs (a, b, c) and a secondary electron micrograph of the metallurgical ceramics considered in the present study: (a) sample X4; (b) sample X8; (c) sample X7; (d) sample X8. All photomicrographs are taken under crossed polars Nicols prisms.

being a bad conductor of heat. Grey to blackish reduced areas on the interior surface of both segments testify to the mould having been used at least once after its repair, indicating that the lead links possibly withstood the process. The entire repair effort, so meticulously executed, further indicates how important and irreplaceable the artifact must have been considered by its owner. In addition to its utility value, the mould's importance probably also lay in its distant and the alien technology it bore provenance. In fact, the exclusion of a Greek origin of the casting mould's raw material is the most remarkable and unexpected result of the analysis conducted so far. Given that the additional segment manufactured at some point in order to repair the original artifact was of the same raw material—a material that cannot be found in the vicinity of

Achaea—the mould most probably reached the region as a finished craft rather than a piece of stone that was locally processed.

Regarding the mould's possible origin, the aforementioned regions where similar lithologies are acknowledged (with the exception of faraway Great Britain, Morocco, and Pakistan[9]) have one feature in common within the chronological frame under discussion: they belong in the territory of the so-called *metallurgical koin*è, a term referring to the LBA phenomenon of interaction on matters of technological innovations, particularly in the field of metalworking and the diffusion of similar types of bronze artifacts (also known as *Urnfield Bronzes*), in a wide geographical area comprising Central Europe, the Italian, and Balkan peninsulas (Giardino 1995; Carancini and Peroni 1997; Bettelli 2002: 132-136; Sherratt 2000). Casting moulds of technological features similar to the one from Chalandritsa, and corresponding whole-cast socket spearheads were pretty common within that wide geographical area.[10] In an advanced phase of this phenomenon, namely by the end of LH IIIB, *Urnfield* bronzes had began spreading to the Mycenaean world as well. During LH IIIC, Achaea took advantage of the liberalization of trade from the monopolistic royal control after the collapse of the Mycenaean palatial system as well as of its favorable geographical position along the western borders of the Mycenaean world, retaining an active and prominent role within this technological interaction. This has well been attested by the available archaeological data, and has lead scholars to define it as a main node on the established trade routes connecting Central Europe and the Adriatic with the Eastern Mediterranean (Eder 2003; Eder and Jung 2005; Moschos 2009; Iacono 2013).[11]

Therein probably lies the answer to how a casting mould from afar reached Chalandritsa. Artifacts related to the *metallurgical koinè* are not unknown in Achaea. On the contrary, the number of European-type bronzes that have been found in that area is quite striking when compared to other regions of the Mycenaean world (Jung, Moschos and Mehofer 2008. Cf. Paschalidis 2018: 417, n. 858).[12] These artifacts, along with other archaeological data, indicate the intense interaction of Achaea particularly with the eastern coasts of South Italy and the region of Trentino-Veneto to the north (Fisher 1991; Papadopoulos and Papadopoulou-Kontorli 2000; Bettelli, Levi and Vagnetti 2001-2; Cultraro 2005; Eder and Jung 2005; Oikonomidis 2006; Jung, Moschos and Mehofer 2008; Moschos 2009; Paschalidis and McGeorge 2009; Jung and Mehofer 2013). Although final results of our analyses will hopefully determine more precisely the mould's place of origin, it is of great interest that the source of copper used for some of the *Urnfield* bronzes found in Achaea directly relates them to the region of Trentino-Veneto (Jung, Moschos and Mehofer 2008: 88),[13] which is also one of the most probable sources of Chalandritsa mould's raw material.

In any case, the new data could prompt more discussion into the question of the Mycenaean techniques engaged for casting weapons. The suspicion that the scarcity of local corresponding moulds is not merely coincidental rises when we consider that Chalandritsa's mould seems to prove the import of not just a rare artifact but also of foreign technological know-how.

Conclusions

The analytical data obtained so far have allowed us to infer a metalworking tradition within the settlement of Stavros, Chalandritsa. The mineralogical data and the geochemical results presented herein have permitted us to exclude a Greek origin for the repaired casting mould found at the site and helped us to delineate its region of provenance within the area of Central Europe and northern Italy. Moreover, the use of the analysed ceramic fragments in pyrotechnological processes was confirmed by petrographic and mineralogical analysis. Their occasional presence in the hearths of dwellings indicates that, at least in some cases, small-scale casting took place in the same areas of other common household activities. Further analyses of the fragments of slag and metallurgical ceramics gathered at various spots of the settlement will be needed along with the completion of the study of their context in order to reach some final conclusions concerning the range and special conditions of metalworking activity at Stavros, Chalandritsa.

[9] Although the Mycenaean trading network was active all over the Mediterranean Sea and the Mycenaeans retained either direct or indirect contacts even with pretty remote areas of Europe and Asia, there are no strong indications of interaction with Morocco or Pakistan, while evidence of Mycenaean contact with the British Isles is doubtful and inconclusive (Harding 1984: 263-265). For an overview of Mycenaean expansion, see also Cline 1994; Sherratt and Sherratt 1998; Vanschoonwinkel 2006.

[10] See Soura 2017, esp. pp.485-488 for a discussion and a list of references.

[11] For possible trade routes of the *Urnfield Bronzes*, see Sherratt 2000. Also see Gazis 2017 for the role of the nearby Achaean acropolis of Teichos Dymaion as a main hub within the system of Mediterranean Bronze Age exchange networks. The midland settlement of Stavros, Chalandritsa should be seen as part of a regional network. For the role of regional networks in inter-regional systems, see Suchowska-Ducke 2018.

[12] See Sherratt 2000, fig. 5.1 and Appendix, where one can notice the striking density of European-type bronzes in Achaea, right after East Crete and the Argolid, probably indicating the main trade route from west to east. Cf. Iacono 2013.

[13] According to further analyses of bronze artifacts from various regions of Italy and Greece, Jung and Mehofer (2013) assume that interaction between the Po valley in northern Italy and Mycenaean Greece was not direct and ascribe to Southern Italy a mediating role in the transportation of products or raw materials and the dissemination of technological innovations. Cf. Eder and Jung 2005.

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The Discovery of an Ancient Roasting Furnace in the Lavreotiki and the Problem of Galena Exploitation for Silver Production

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Abstract: The question of whether ancient miners of Laurion, apart from cerussite, exploited also galena (PbS) for extracting lead and silver has been the subject of previous research. Conophagos proposed that a furnace charge mainly of cerussite with maximum 20 percent of galena could be treated directly in a reduction furnace (6) (5-9). Bachmann, Hauptmann, and other authors suggested that galena could be processed directly in a furnace without roasting. Both the above hypotheses remained uncertain, since for the production of (argentiferous) lead from galena, roasting of the ore is in principle needed before submitting to the reduction process. Nevertheless, no roasting installation had been previously identified in Lavreotiki. Recently, the remains of an ancient furnace with an unusually large diameter (2.5m) compared to the reduction furnaces (1m diameter) was discovered in Demoliaki. In the present research this furnace is characterized as a roasting furnace for removing from galena its sulfur content and transforming it into lead oxide. The characteristics, metallurgical reactions, and operation of the furnace are discussed. Regarding the archaeological and technological context, the furnace should be dated to the Hellenistic and Early Roman period.

KEYWORDS: LAURION, LAVREOTIKI, ANCIENT MINES, ANCIENT METALLURGY, LEAD, SILVER, GALENA, CERUSSITE, ORES, ROASTING, CALCINATION, SMELTING, FURNACE, DIMOLIAKI, ARI.

Introduction

This paper addresses the problem of whether galena (PbS) was extracted and employed as raw material by the ancient miners of the Lavreotiki for production of silver bearing lead and how it was processed in view of reduction in a smelting furnace.

As a matter of fact, many indications suggest that apart from cerussite ($PbCO_3$), galena (PbS) was also extracted from the mines and subsequently processed in the associated washeries at Laurion. It is, however, uncertain how it was processed metallurgically.

According an established rule in Metallurgy, in the case of sulfide ores intended for smelting in a reduction furnace, the furnace charge should consist almost entirely of oxidized ore, such as oxide or carbonate. As a consequence, galena should be converted to oxide prior to smelting by burning out the sulfur in a roasting furnace. However, neither residue of roasting activities nor remains of roasting furnaces have been identified until now in the Laurion mining area and the problem of galena processing of lead remains open.

Recently, the second of the authors of the present paper discovered in the Lavreotiki the remains of an unusually large-scale furnace. By virtue of its dimensions, geometry, and other characteristics, we recognized in it remains of an ancient roasting furnace used for galena roasting in order to convert it to oxide prior to smelting in a reduction furnace. In this respect, the present paper will discuss also the characteristics of the furnace discovered with regard to its geological, mining, metallurgical, and technological context.

Discussions on methods of galena processing in Lavreotiki

The problem of whether galena was extracted by the ancient miners in the Lavreotiki and by which method it was eventually processed has been considered by a number of researchers.

According to Conophagos (Conophagos 1980: 278) the main ore extracted and processed for the production of lead and silver in the Lavreotiki was cerussite. This view was mainly based on the fact that ancient *ekvolades* (low content ore rejected from the mines) contained only tiny amounts of galena and plynites (waste of the concentration process in the washeries), and had a very low sulfur content. Similarly, the content of sulfur in slags coming from the smelting furnaces in the Lavreotiki was very low, as a rule under 1% (Conophagos 1980: 283), suggesting that sulfur content in the charge of furnaces was very low. Conophagos, however, did not refute that ancient miners of Laurion used galena, but rather suggested that they extracted it when coming across it in their mining works and used it without roasting. For this purpose, a minor quantity of galena would be mixed with cerussite and the blend submitted directly to smelting. As a practical rule for the good operation of the reduction furnace, Conophagos proposed that the charge should not contain more than 2% sulfur. Considering that typical galena and cerussite ores from Laurion with a grade of 50% lead contained respectively about 10% and 0.2% sulfur, the percentage of galena contribution to the charge should not exceed 20% by weight.

The use of raw galena in the charge of a reduction furnace is also in agreement with Cordellas' observation that unmolten galena inclusions were sometimes present in ancient slags recovered for resmelting by the Greek Company of Laurion during the second half of the 19th century (Cordellas 1865, p.7).

Photos-Jones and J. Ellis-Jones, using mineralogical analysis on tailings of washeries uncovered during excavations at Agrileza, concluded that the silver bearing ore processed was cerussite rather than galena (Photos-Jones and Ellis Jones 1994, p.357)

Bachman (1982, p.249) based on the chemical composition of ancient slag specimens from various areas of Lavreotiki, and in particular on the fact that some of them had a relatively high sulfur content, up to 4.5%, concluded that they come mainly from galena submitted to a "roasting-reduction-reaction process". He argued, however, that according to R. Hetherington (1956, p.27) and R.F. Tylecote (1986, p.75), a roasting treatment is not necessarily required before smelting since oxidation of galena could take place in the upper part of the smelting furnace. It appears that such a one-stage process was also applied in South America (Hauptmann *et al.*1988, p.110).

Based on the mineralogical and chemical analysis of tailings from washeries, Rehren *et al.* (2002) believed that the ancients extracted and employed mainly galena, but possibly also cerussite to a limited extent. They did not enter, however, into a metallurgical discussion of the subject.

According to a signed report by John Spanos (1973), a technician native of Laurion who had worked as Chief Foreman for several decades in the French Mining Company from 1920s onwards, exhaustive galena extraction from the ancient miners was revealed when the modern underground galleries crossed ancient mining works. This occurred for all three mineralization contacts: systematic galena extraction was evidenced at Dimoliaki, which will be discussed later, at Soureza in the 1st contact and within upper marble, in Agrileza in the 1st contact and in the lower marble, in Botsari in the 1st and 3rd contact. and in the periphery of the modern shaft of Serpieri (Kamariza) up to a depth of 50 m from the surface. In this shaft, the ratio between cerussite and galena was about 20 to 1 based on the production of the years 1925-26. Also in the shaft of Jean Baptiste (near Kamariza) galena was extracted by the ancients in the 3rd contact from a vein 60 cm thick. There were also thin veins of galena near the surface that were completely recovered in antiquity.

Figure 1. A mining underground work in the proximity of Esperanza area in Lavreotiki. Tiny residues of a galena vein are observed at right. Cerussite and galena ore was extracted exhaustively at this place, leaving behind a vast room inside marble. A drift continues ahead, following the vein, in search of other ore concentrations.

Figure 1 comes from an ancient mining work in the proximity of Esperanza area in the Lavreotiki and shows tiny residues of galena left in an underground stopping where a galena vein was extracted exhaustively.

The problem of galena smelting was also examined in a paper concerning the process of lead and silver production on the island of Thasos by Hauptmann *et al.* (1988). The authors concluded, as in the case of Bachmann, that the production of lead from galena was possible inside a single furnace, where both roasting and reduction processes could take place successively.

From the above discussion, we can conclude that researchers are largely in agreement on the opinion that galena was indeed used in Laurion. They disagree, however, on whether cerussite or galena was the principal ore extracted in the mines and on the subject of how galena was processed.

In this respect, no convincing answer has been proposed for justifying the low content of sulfur in most slags of Laurion, if it is accepted that galena without roasting was used as the main constituent of a smelting furnace charge. On the contrary, the recent discovery of the roasting furnace at Dimoliaki proves that galena was actually submitted to roasting before smelting in the Lavreotiki and justifies the low content of sulfur in ancient slags. Nevertheless, this opens up new questions, in particular about the period in which it was introduced in the Lavreotiki and the conditions which imposed its use.

Description of the roasting furnace

The remains of the roasting furnace discovered recently are shown on photograph of Figure 2. The furnace is located at a distance of 300 m from the well-known complex of Dimoliaki, considered initially as an helicoidal washery by C. Conophagos and H. Mussche (1970) and shown more recently by G. Papadimitriou (2015, 2016) to be a circular mill.

The furnace belonged to a complex along with two or three other furnaces, now completely ruined (Figure 3). The architecture of the furnace complex looks like that of the Panormos (Conophagos 1980: 286) and Ari (Tsaimou 2013) smelting furnaces. They were all constructed at the back side of individual rectangular rooms, positioned side by side along the foot of a

Figure 2. The remains of the Roasting Furnace discovered at Dimoliaki-Lavreotiki. The furnace was used in the Hellenistic-Early Roman period for roasting of galena.

Figure 3. The remains of the roasting furnace at left, which formed a complex along with two or three other furnaces, now completely ruined (at right).

mound that is 2 m high in the case of the roasting furnace at Dimoliaki and about 1 m in the case of the above-mentioned smelting furnaces.

The furnace lies at the foot of a hill, at the extremity of an olive tree field, stretching in front of the furnace. On the surface of the field small pieces of oxidized ore and charcoal as well as some pieces of fused mineral foam, coming certainly from the furnace operation, are present. There are also numerous ceramic fragments, mainly of coarse ware, scattered on the surface. The latter, as well as an enormous quantity of stones, which were reused in modern times for the construction of a dry-stone enclosure in the south east side of the field, testify that apart from furnaces, settlements or buildings of industrial use, existed also in antiquity.

Behind the furnace extends an artificial plateau, which was enclosed within a wall, of which only some portions survive. The above area was most probably used by the ancient miners as a yard for raw ore and charcoal stockpiling.

The rear side wall of the furnace is preserved up to the height of the mouth, at about 2.2 meters from the ground and is supported by the mound, which apparently served also as a loading ramp between the stockyard and the furnace. No opening for wind blasting is observed, since it probably never existed. If this furnace is not considered as a roasting one, but as a reduction smelting furnace like those of Megala Pefka and Ari, then an opening for air blasting should be observed at a small height from the ground on the rear side of the wall of the furnace which remains intact until now.

The furnace is in the form of an inverted truncated cone, broadening upward with an angle of about 10 degrees. The curvature of the circular cross section of the furnace at the base of the wall, corresponds approximately to an internal diameter of about 2.5 m on the ground (Figure 4). The thickness of the wall is 80-85 cm and the stonework is made of limestone and schist irregular pieces, bonded with red clay mortar.

Few slag foams remain attached on the wall near the furnace mouth, indicating that during operation the furnace was filled up to its top and that temperatures of 800-900^{0}C prevailed locally at this uppermost zone, leading to melting of the most fusible ore components, (Figure 5). This is certainly due to the abundance of free air available in the proximity of the wide furnace mouth.

A schematic representation of the roasting furnace in operation during its charging with galena ore transported from the nearby mines is shown in Figure 6.

It is interesting to note that there are no slag pieces either between the stones fallen at the base of the furnace nor in the olive tree field in front of it. On the contrary, ore pieces of the order of 3 to 5 cm are scattered in the field and some of them contain galena inclusions. This confirms that no melting took place, only calcination of the ore. The absence of slags near the furnace contrasts sharply with their corresponding abundance in the case of ancient smelting furnaces, as for example at Panormos and Megala Pefka (Conophagos 1980: 286) and at Ari (Tsaimou 2013), where abundant pieces of slag are scattered all around them.

Furthermore, a net difference between the roasting furnace and the already known smelting furnaces resides in their dimensions. The internal diameter of the roasting furnace on the ground was 2.5 m and the one of a smelting furnace was 1 m (Figure 7). Also, assuming that both had a height of about 2.2 m, their volume should be 14.5 and 1.7 m^3 respectively.

The Dimoliaki-Ari mining area

In the adjacent mining areas of Dimoliaki-Harvalo-Ari there were considerable mining and metallurgical activities in antiquity as revealed by the remains of mining works and ancient metallurgical installations (Figure 8). This is also confirmed by the quantity of slag piles recovered in the second half of the 19th century, amounting to more than 181,000 tons in total, which were reported in the Vouyoukas report of 1865 (Conophagos 1980, p.298).

Figure 4. The roasting furnace was in the form of an inverted truncated cone broadening upward with an angle of about 10 degrees and had an internal diameter of about 2.5 m on the ground.

Figure 5. Slag foam coming from the most fusible components of the galena ore remain attached on the wall on top, near the furnace mouth.

Figure 6. Schematic representation of the roasting furnace, while charging with galena ore from the mouth.

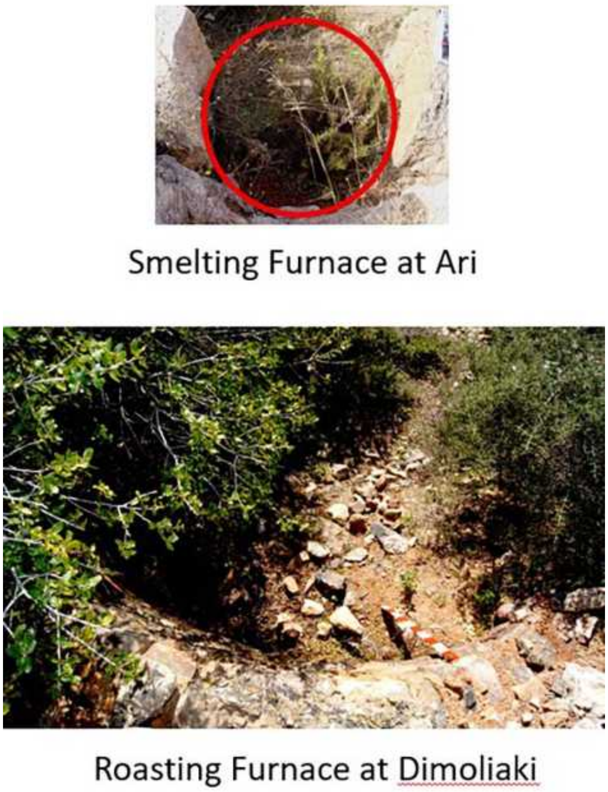

Figure 7. Comparison of dimensions of the roasting furnace of Dimoliaki (lower image) with a smelting furnace from Ari (upper image). Image scale is the same for best comparison.

The Demoliaki mining area, according to Marinos and Petrascheck (1956, p.106), was an exemplary ancient mine in the Lavreotiki. It was developed mainly in the first contact of mineralization and was very rich in sulfides, with galena very rich in silver. The map of the ancient mine is shown in Figure 9.

But apart from mining, Dimoliaki was also a metallurgical center. Although there are no remains of smelting furnaces, their existence in antiquity is deduced from the quantity of 13,000 tons of ancient slag recovered at this place in the 19th century.

The metallurgical activities in antiquity were certainly based on the sulfide ore extracted from the mines and subsequently treated in roasting furnaces before they were directed to the smelting furnaces, as well as on old stocks of litharge, ground in the circular mills and desilvered in the washeries lying next to them for recovery of metallic inclusions containing silver (Papadimitriou 2015, 2016).

Historical and chronological context of the Roasting Furnace operation

From a technological point of view, the unusually large dimensions of the furnace and its sophisticated flared shape suggest that it was a technical innovation of the Hellenistic period, and that it was introduced because of a growing use of galena for production of silver and commercial lead, exactly as the circular mill was an innovation introduced in view of the intensification of litharge recycling (Papadimitriou 2015, 2016).

In this respect, both Dimoliaki and the relatively small adjacent Ari area, despite their current toponymic distinction, should be considered as forming a single mining-metallurgical entity of the same period, which followed a common innovative path in metallurgical technology that was characteristic of the Hellenistic period (Papadimitriou 2024, this volume). This mining-metallurgical entity was certainly motivated by the existence of important galena deposits very rich in silver and by the presence of huge litharge stocks from older periods. It is worth noting that, to our knowledge, the remains of seven circular mills are preserved in this area, namely: the one of Dimoliaki, excavated by Conophagos and Mussche (1970), four mills (Ari 1 to 4) excavated by C. Tsaimou (2008), a meagre remain on Harvalo and another near the entrance of the village of Manoutso, in an area full of scattered pieces of slag and mining galleries, see above Figure 8. The last two circular mill remains at Harvalo and Manoutso are still unpublished.

As far as the time context of their mining and metallurgical activities is concerned, the sole dating available is relevant to Ary 2, an integrated recycling complex, comprising one circular mill and one washery for recovering silver from old litharge stocks, as well as a group of eight smelting furnaces (Tsaimou 2008). The smelting furnaces were probably used both for commercial lead production from desilvered litharge as well as silver bearing lead from ore coming from the mines and from *ekvolades* (Tsakiridis *et al.* 2012). Radiocarbon dating for this complex was done on charcoal pieces recovered from the above-mentioned

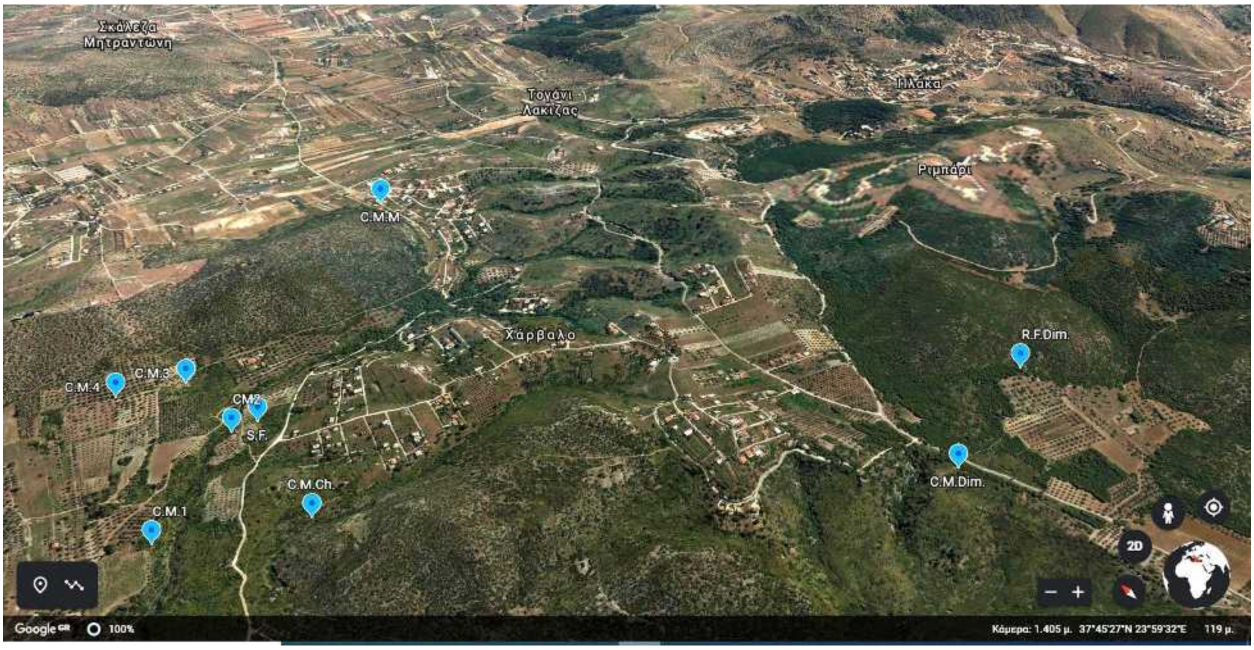

Figure 8. A view of the Dimoliaki-Harvalo-Ari mining and metallurgical area: R.F.Dim=Roasting Furnace at Dimoliaki, C.M.Dim=Circular Mill at Dimoliaki. C.M.1, C.M.2, C.M.3 and C.M.4 = Circular Mills at Ari, C.M.Ch.=Circular Mill at Charvalo, and C.M.M.= Circular Mill at Manoutso village. Adapted from a Google Earth map.

furnaces during excavations (Tsaimou *et al.* 2015). The dating gave an age (2σ) between the beginning of the 2nd and the middle of the 1st century BC (5). This dating does not tell us when the furnaces were built and or when they started their operation, but it does indicate that the furnaces and the whole recycling complex was active during the Hellenistic and the Early Roman period. The well-known passage of Strabo (Attica, 9.1.23), who visited Attika at the end of the 1st century BC, certainly refers to this kind of recycling activities.

For the particular case of the roasting furnace at Dimoliaki another approach to the dating could be deduced from a number of fine ware sherds scattered on the surface of the olive tree field in front of the furnace complex and photographed *in situ* (Figure 10). These seem to belong to the post-classical period — a date that is in agreement with the aforementioned radiocarbon dating of Ari 2. Further information is expected when radiocarbon dating of charcoal coming from the roasting furnace at Dimoliaki will be available.

The roasting reaction

The main silver minerals of Lavrion are cerussite ($PbCO_3$ -lead carbonate) and galena (PbS - lead sulfide). They usually contain 1-2 kg Ag / tn Pb, rarely up to 4 kg Ag / tn Pb.

In order to produce silver from them it was necessary at a first stage to produce silver bearing lead by reducing the ore in a smelting furnace and then, at a second stage, to recover the silver by cupellation.

In the case of cerussite, the ore was reduced using charcoal both as a fuel and reducing agent and silver bearing lead was obtained as a melt in the smelting furnace. The furnace where this process took place was a shaft furnace, such as those found, for example, at Megala Pefka, Panormos and Ari.

In the case of galena, however, the extraction of silver bearing lead by a simple reduction process was not possible because a molten phase of metal sulfides, known as "matte" forms as a distinct liquid layer between the molten metal and the slag in the smelting furnace. Lead and silver contained in matte are definitely lost because processing of matte is difficult and in any case was not practiced in the Lavriotiki.

To avoid matte formation in the smelting furnace, galena should be roasted in the presence of oxygen in order to be converted to lead oxide (PbO). At the same time, sulfur was burnt to sulfur dioxide, which was removed as a fume from the furnace mouth.

This is represented by the reaction:

$$PbS + 3/2\ O_2 \rightarrow PbO + SO_2$$

In case sulfur is completely removed from the ore, this is characterized as "dead roasting". It is, however, difficult

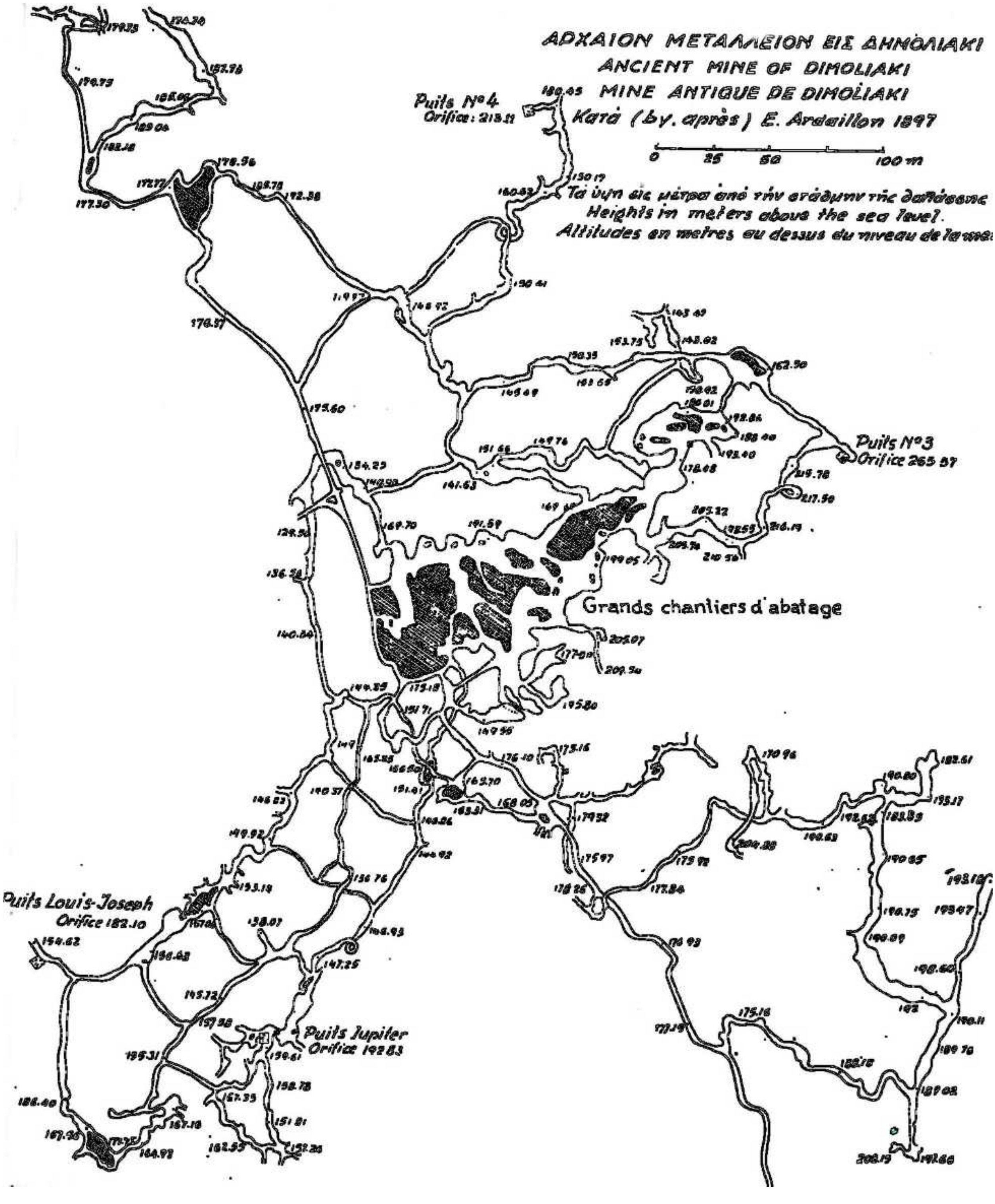

Figure 9. Ancient underground Mine of Dimoliaki, after Ardaillon 1897.

Figure 10. *In situ* photographs of some sherds laying scattered on an olive tree field extending in front of the roasting furnace.

to remove the sulfur completely and, depending on the temperature, part of galena may remain as PbS or be converted to lead sulphate according to the reaction:

$$PbS + 2O_2 \rightarrow PbSO_4$$

In the subsequent stage of smelting, the roasted charge containing lead oxide is reduced in a charcoal-fired smelting furnace, producing liquid lead according to the reactions:

$$PbO + C \rightarrow Pb + CO \text{ and}$$
$$PbO + CO \rightarrow Pb + CO_2$$

It is worth noting that small amounts of PbS and PbSO4 that may be present in the charge are not a problem for the smelting step, as they react to each other or with PbO, producing lead, according to the reactions:

$$PbSO4 + PbS \rightarrow 2Pb + 2SO_2 \text{ and}$$
$$PbS + 2PbO \rightarrow 3Pb + SO_2$$

The roasting practice before reduction smelting

The question remains regarding the processing of sulfides before the introduction of roasting furnaces as the one of Dimoliaki.

Nothing is known on the metallurgical methods used in the earliest stages of lead production in the Lavreotiki. We could, however, assume that the extraction of lead ores was carried out mainly on first contact outcrops, where cerussite largely prevailed. In this case, even when some galena was present, it was in small quantities and could be digested into the cerussite smelting charge as suggested by C. Conophagos (1980).

In classical times, however, when mining considerably advanced, it cannot be excluded that roasting of galena was practiced in one of the simplest forms of roasting installations, such as those described by Agricola for the Middle Ages (Agricola 1950, p273) and reported by Tylecote for roasting of iron ores in more recent times, until the 20th century (Tylecote 1976, p.118).

As a matter of fact, galena roasting could have been simply done in small heaps of broken ore placed on a sloped bed of charcoal and fired. In a more advanced stage, the heap was probably limited inside low walled enclosures open at their front, which are known as "stalls". These elementary constructions served mainly as barriers for keeping the heat of the fire in close contact with the charge. Several variations and examples of their operation are described by Agricola (1950: 275) and by Tylecote (1976, p.119). It is reasonable to accept that if those kind of constructions were actually used by ancient miners in the Lavreotiki, they would be extremely difficult to identify nowadays from their meagre remains.

Roasting furnaces, such as the one at Dimoliaki, became necessary near the end of the Classical/beginning of the Hellenistic period when the ancient miners went down to the third contact mineralization by means of deep shafts and galleries, where galena was more abundant. These kind of furnaces offered a high productivity and economy in charcoal consumption, which was very crucial for the deforested region of Attica.

Concerning their operation, the following characteristics should be noted.

According to the size of ore pieces scattered around the furnace, the galena ore was crushed to pieces of about 3-5 cm at maximum and transferred to the kiln for roasting. Charging the furnace was done from the top through its mouth and the roasted material was extracted from below. A little charcoal was loaded in order to ignite the furnace, then the combustion was maintained by the exothermic reaction of roasting. Usual operating temperature should have beenb about 700^0 C. The flared shape of the furnace upwards made easier the removal of sulfur dioxide during roasting. This was a crucial factor for the desulphurization reaction to be completed (dead roasting). According to R.F. Tylecote (1976: 118) processing of a charge of iron ore could take several days to weeks. This would be also indicative for the time required in case of galena. The desulfurization reaction is exothermic, so only a small amount of charcoal was added to the furnace to initiate the fire. Then the heat released by the reaction kept burning on. Except for the ignition stage of the furnace, no blasting was necessary during roasting as long as the natural draft was sufficient.

The roast-reaction process

In modern industrial practice a different process is used for the production of lead from galena. As reported in section "Previous Discussions on Methods of Galena processing in the Lavreotiki" the mechanism of the "roasting-reduction-reaction" process was invoked by H.G Bachman (1982) and by Hauptmann *et al.*(1982) for explaining how a furnace charge consisting entirely from galena could be processed inside a single furnace. For this reason a brief description of the process is given below.

In the reaction-roast process, galena is submitted only to incomplete roasting. In practice, roasting is stopped when about two thirds of galena is converted to oxide, according to the partial roasting reaction:

$$3\ PbS + 3\ O_2 \rightarrow PbS + 2\ PbO + 2\ SO_2 \text{ (partial roasting)}$$

The product obtained is then heated in another furnace in the absence of air so that a reduction reaction takes place between lead oxide and lead sulfide, producing lead, according to the reaction:

$$PbS + 2\,PbO \rightarrow 3Pb + SO_2 \text{ (reduction reaction)}$$

This process produces slags of very high sulfur, opposite to the majority of ancient slags in the Lavreotiki.

Conclusion

In the classical period and even earlier, galena ore was extracted along with cerussite in the ancient mines of the Lavreotiki and used as a minor constituent in the charge of smelting furnaces for the production of lead and silver.

From the 3rd century BC onwards, oxidized deposits occurring near the surface were almost exhausted and deeper deposits rich in galena were extracted. This imposed galena being submitted to oxidizing roasting in order to remove its sulfur and transform it to oxide, before it was subjected to the reduction process in smelting furnaces.

This conclusion is inferred from the remains of an unusually large furnace recently discovered at Dimoliaki. This was a roasting furnace, where galena ore was calcined to remove as much as possible of its sulfur before being reduced to nearby existing smelting furnaces. The furnace belonged to a complex along with two or three other furnaces, now completely ruined. The furnace had an internal diameter of 2.5 m, a height of 2.2 m, and was in the form of an inverted truncated cone, sloping upwards with an inclination of about 10 degrees.

The furnace was most probably constucted during the Hellenistic period in the context of innovations introduced in metallurgical and recycling activities at the neighboring Ari, Charvalos, and Dimoliaki mining areas, which were active in Classical times and then again during the Hellenistic and Roman periods.

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The Hellenistic Period (End of 4th to 1st Century BC) in the Laurion Region as a Period of Technological Inventions, Innovations, and Technological Transfer to Ptolemaic Egypt

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Abstract: As mining in the Lavreotiki began declining at the end of the 4th century BC, ancient miners reoriented silver and lead production toward recycling of old litharge and *ekvolades* stocks.

Recycling of litharge was initially done in the already existing ore processing installations of the *ergastiria*, where facilities were available, but at a later stage the invention of circular mills for fine and uniform grinding of litharge largely replaced them. Similarly, ore washeries were modified in order to be effective for both litharge processing and *ekvolades* enrichment.

The introduction of a roasting furnace for calcination of galena before smelting was innovation that responded to the increased quantity of galena extracted from the deepest horizons of mineralization, which were reached by means of shafts going down to a depth up to 110 m.

The above and other minor innovations probably started at the end of the 4th century BC, but their existence becomes evident to us mostly from the remains of such activities during the 2nd and the first half of the 1st century BC. Finally, since circular mill constructions, mills and ore washeries from the Ptolemaic period exist also in the gold mines of the Eastern Desert of Egypt, the problem of technology transfer between Laurion and Egypt is briefly considered.

KEYWORDS: LAURION, LAVREOTIKI, ANCIENT MINES, ANCIENT METALLURGY, LEAD, SILVER, ORES, CERUSSITE, GALENA, EKVOLADES, LITHARGE, ORE WASHERIES, CIRCULAR MILLS OF LAURION, ROASTING FURNACE, SMELTING FURNACE, DIMOLIAKI, ARI, TECHNOLOGY TRANSFER, EASTERN DESERT OF EGYPT.

Introduction

Laurion's mineral wealth was owned by the state of Athens, which leased silver/ lead mines for exploitation to Athenian lessees for a certain period of years (Crosby 1950: 190).

In 307/6 BC, concessions of mines, after 60 consecutive years, were recorded in the Agora of Athens for the last time. Obviously investor interest in the Laurion Mines had ceased to exist. As a matter of fact, mining became less profitable, since good quality mineralization near the surface was exhausted and the extraction of ore was now possible only by means of deep wells. In addition, the price of silver was reduced due to large amounts of gold brought into circulation after Alexander's conquests. The main cause of the problem, however, was of political nature, since disputes over the claim of Athens' guardianship by Alexander's descendants, led the city to political and military turmoil, resulting in economic crisis. Consequently, the mines started closing at the end of the 4th century and continued declining in the beginning of the 3rd century BC. Important mining activities probably reached their minimum in 262 BC, when the minting of the silver owls of Athens apparently stopped.

But beyond Athens, there was also in the Lavreotiki a parallel world of small entrepreneurs, craftsmen, and workers living by the Mines. Some of them were forced to abandon their city, as happened in the city of Thorikos in 295 BC (Mortier 2011, p.130). But those who stayed behind attempted to find new ways to survive, based on their own art and experience. Thus, they turned to the recycling of old mining residues and metallurgical waste (Papadimitriou 2018, pp188-192). In this way silver and lead production was never completely stopped.

Waste recycling is a fact historically attested to by Strabo's account that outlined the decline of the Laurion mines at the end of the 1st century BC, (Strabo, *Attika,* 9.1.23)

New raw materials and tentative recycling methods

The technology of the Hellenistic period in Laurion has been often implicitly considered as identical to the technology of the classical years. This is not quite true, since the production scheme underwent radical changes during the transition from one period to another, regarding both work organization and the production chain.

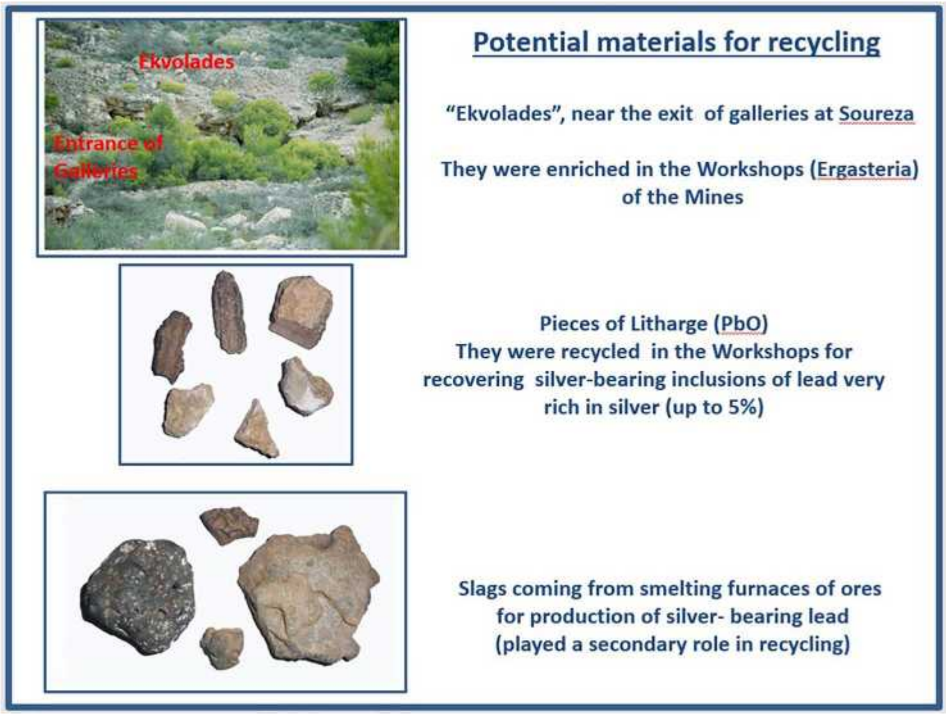

Figure 1. Potential materials for recycling in Lavreotiki after the 3rd Century BC.

With regard to work organization, after the decline of mining, a large number of workshops (*ergasteria*) associated with the mines were abandoned from their wealthy owners, and after a period of inactivity were occupied most probably by new owners interested only in the use of the old production facilities in order to secure the gains they needed to live. Such was, I assume, the situation, in the *Asklepiakon*, also known as the *Ergasterion* of Simos from Paiania (Tsaimou 1988), for which excavations have shown that it functioned in two distinct periods, in the second one on the earlier abandoned site.

With regard to recycling activities, miners had to rethink the details of their methods so as to adapt their devices to the new production chain necessary for processing materials with very low silver and/or lead content. In this context, important inventions and innovations also appeared.

At the end of the 4th century BC, potential materials for recycling, such as "*ekvolades*", furnace slag, and litharge were available in huge quantities in Lavreotiki near mines and furnaces (Figure 1).

"*Ekvolades*" refers to an ore very low in lead and silver content that was extracted in older times from the mines, but was judged as unprofitable for further metallurgical processing. It was, therefore, abandoned as waste near exits of galleries and shafts. "*Ekvolades*" have the same mineralogical and chemical composition as a good quality ore and were therefore easy to enrich with the aim of increasing their lead and silver content. When recycling started, probably in the last decade of the 4th century BC, their treatment was done in already existing workshops (*ergasteria*) using the same equipment and techniques known from the past. At first the ore was ground in order to liberate the useful mineral (cerussite or galena) from its gangue. This was done in two consecutive stages: it was broken into pieces smaller than 1 to 2 cm by means of iron hammers on stone slabs and then these pieces were reduced to sand (-3 mm grain size) in Olynthus reciprocating mills. Immediately after this sand was processed in washeries for removing the sterile minerals as a waste and obtaining a concentrate rich in lead and silver. This concentrate was driven to the smelting furnace for the production of silver bearing lead, from which silver was recovered by cupellation, Figure 2.

Slag coming from lead ore smelting of the classical period does not seem to have been substantially involved in the recycling process of the Hellenistic period. In my opinion the reason for this was that no new furnace technology was developed to make their smelting profitable, since its content in lead (12-15%Pb) and silver (less than 500 gr of silver per ton of lead) was too low. Furthermore, they had a high melting point due to their high silica content and were therefore difficult to smelt (Cordellas 1865 p. 9 and p.16).

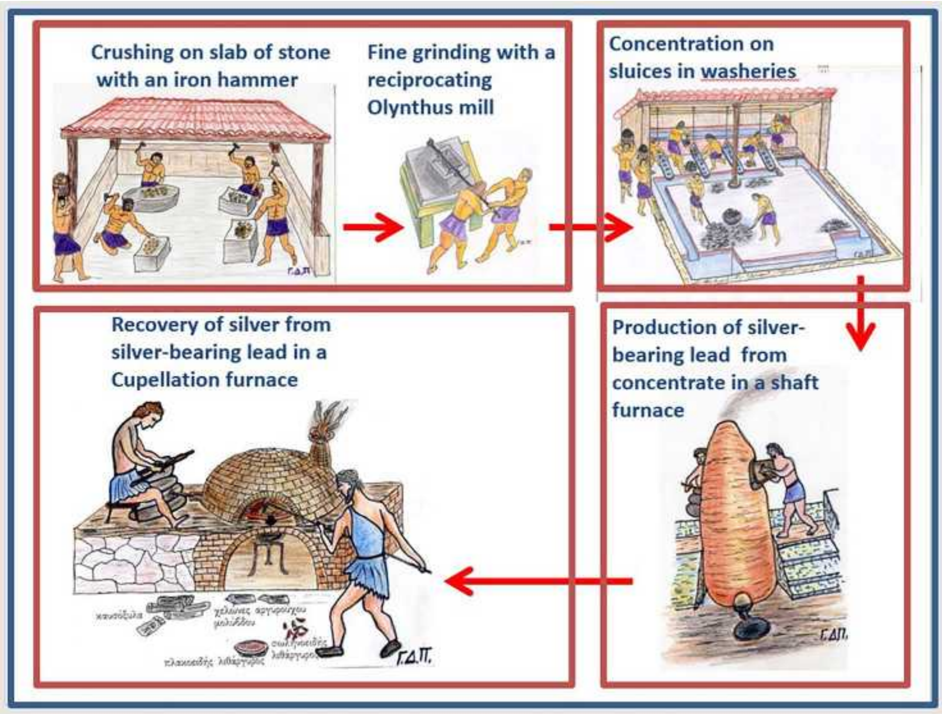

Figure 2. Production chain for silver from Ekvolades and from ore extracted from the mines

Litharge is lead oxide (PbO), a byproduct of cupellation of silver-bearing lead and its residues were certainly huge, of the order of 1 million tons or more. It contained lead silver-rich inclusions (with up to 5% Ag), varying in size: the largest ones being visible to the naked eye (1-2 mm), but most were very fine, less than half a millimeter (500 μm) (Papadimitriou 2012), Figure 3.

These inclusions could be recovered as a concentrate in the workshops (*ergasteria*): after the very fine grinding of litharge pieces — less than half of one millimeter (-0.5mm) — in order to allow inclusions to be liberated from the surrounding mass as free particles, Figure 4, they were then recovered in washeries as the heavy fraction of gravity separation, since their specific gravity is larger than that of litharge. This concentrate of silver rich inclusions was then submitted directly to cupellation in order to obtain silver. This issue presented an advantage for the miners since it did not involve smelting. For the small producers working on recycling, avoiding smelting was not only an economic advantage, but it also made them independent of the owners of furnaces.

On the other hand, the mass of the lighter fraction of separation (i.e. desilverized litharge), was not rejected but served as a raw material for the production of commercial lead after smelting in a reduction furnace.

For this reason, small to medium scale activities of both litharge and *ekvolades* recycling were practiced in a multitude of old workshops in the Lavreotiki and are evidenced from the characteristic color of their residues adhering on the drying floor of the washeries: gray for *ekvolades* and red-brown for litharge (Figure 5).

Miners' Experimentations for better recovery of silver

In the process described in the previous paragraph a problem arose: Litharge grinding by means of the old equipment of stone slab/ iron hammer crushers followed by the Olynthus reciprocating mills was not convenient for producing a powder sufficiently fine, namely with grains finer than 0.5mm, which was necessary for the liberation of the silver/lead inclusions from the mass of litharge. Hence the subsequent separation of lead/ silver inclusions in the washeries resulted in a huge loss of silver in the waste.

For this reason miners began experimenting with the addition of a third stage of more advanced grinding so as to obtain finer material and a better liberation of lead/ silver inclusions from their surrounding mass of litharge. Excavations have shown that miners tentatively used various types of mills for better grinding. For example, in *Asklepiakon* in Soureza, a large mortar (όλμος) was unveiled in excavations (Tsaimou 1980). Also, in Thorikos, next to a washery where ground litharge residues were present (Rehren *et al.* 1999), a cone-grinder very similar to that known from Pompeii was found **(**Figure 6**)**.

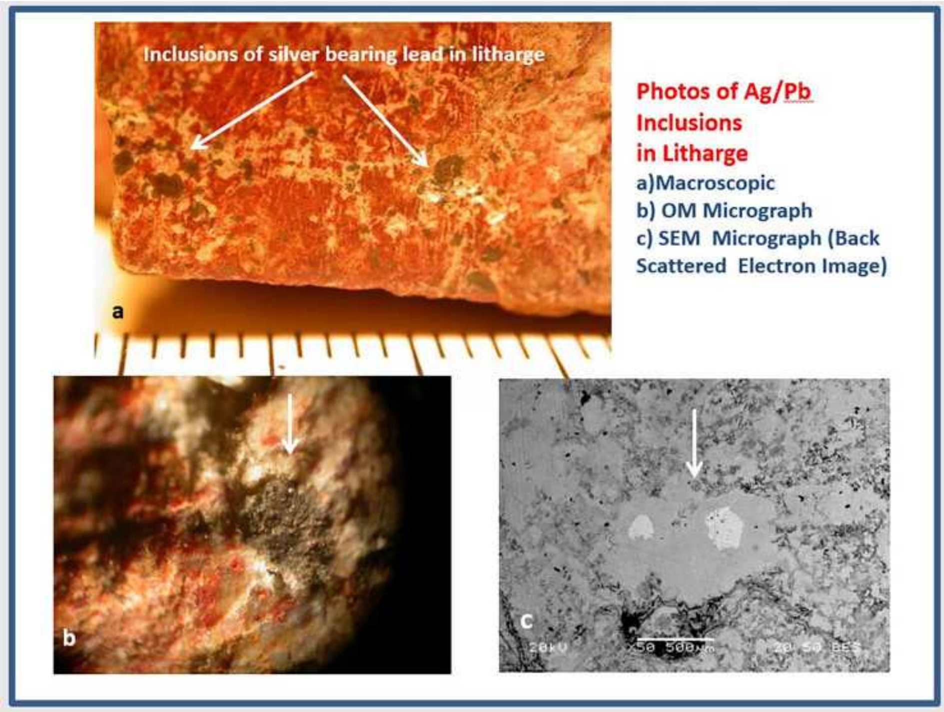

Figure 3. Evidence of inclusions in the mass of Litharge

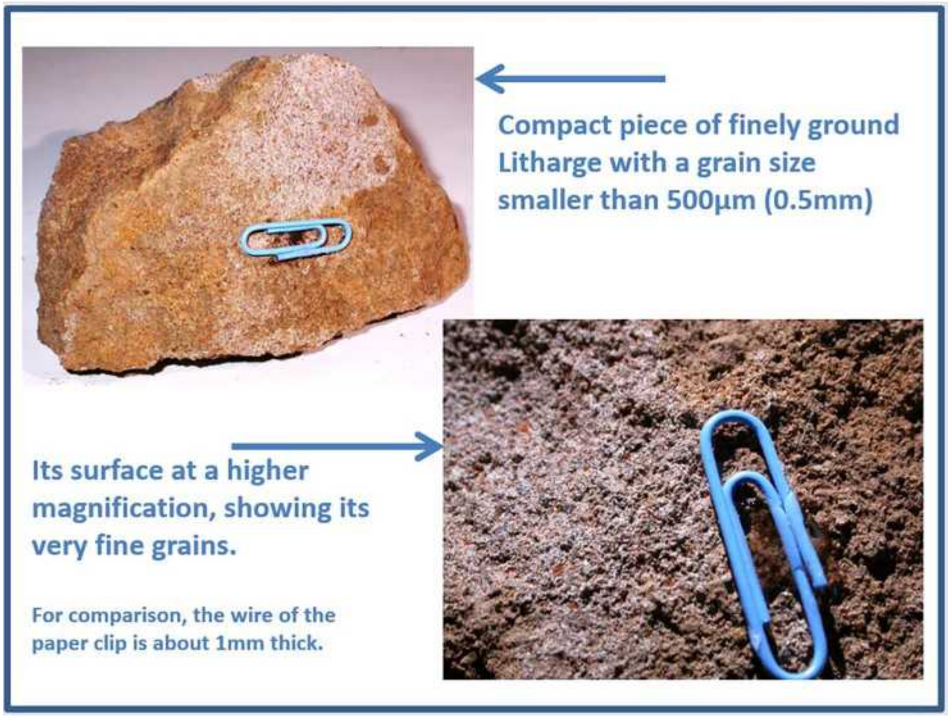

Figure 4. Piece of litharge in compact form with very fine grains

Figure 5. Remains of ekvolades waste (plynite) and of desilvered litharge on the drying floor of washeries

Other types of mills seem to have been tested by miners of the Hellenistic period, most of them of the rotating type. As a matter of fact, in the second half of the 19th century, when the Greek Metallurgical Company of Laurion was recovering slags and waste for smelting in its furnaces, it withdrew from inside their piles an appreciable number of mills. These are now displayed in the yard of the Archaeological Museum of Laurion. It should be assumed that some of these tests successfully resulted in a satisfactory fineness of ground litharge. At least with the mortar of *Asklepiakon,* the product obtained was very fine, less than half a millimeter, as I measured myself, using grain size analysis on a series of standard sieves. However, none of the types of mills tested were generally accepted most probably because they did not result in satisfactory productivity. As a matter of fact, the additional use of a third stage of grinding was a time-consuming and laborious process that delayed the entire production chain and increased costs. For this reason, although recycling litharge continued to be practiced in many workshops, this always remained a low scale production activity.

Circular mills: a new invention for higher productivity

The available litharge stocks were huge, well over 1 million tons, and their owners could hope for significant profits provided they had at their disposal a high productivity mill, capable of reducing litharge to a fine as possible uniform powder. These requirements, I assume, led to the discovery of the circular mill (Figure 7) (Papadimitriou 2015; 2016; 2017b). The starting point was probably the *trapetum* (ελαιοτρόπιον), a high productivity mill for olive crushing, where two upright millstones rotate inside a circular groove about one meter in diameter. By increasing its diameter to six meters, it was possible to increase also the size and weight of the millstone so that even large pieces of hard material could be crushed. Thus, upgrading the dimensions of *trapetum* led to the circular mill, an edge runner with upright millstone dragged into a groove by a donkey. Thanks to the multiple passes of the millstone, it can lead to very fine material. Thus, the circular mills substituted the Olynthus type mills and rendered the stone slab/ hammer crushers superfluous since they could reduce even sizable pieces of litharge directly into fine powder.

Bedding in the groove cavities of circular mills: screening the fines without... a screen!

A discovery associated with the effective grinding in a circular mill is the presence of ellipsoidal cavities carved side by side in the groove along its entire length.

The material filling of these cavities during grinding is subjected to spontaneous stratification by grain size

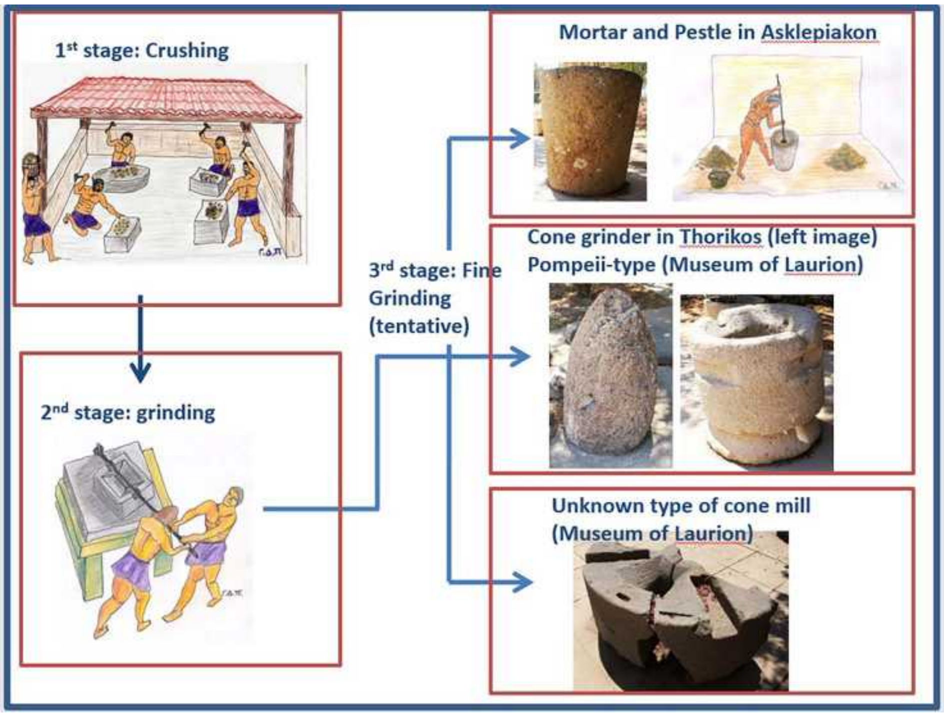

Figure 6. Addition of a third grinding stage to the already existing stages 1 and 2, for very fine grinding of litharge

Figure 7. The circular Mill of Laurion

Figure 8. Stratification inside the cavities of the groove in circular mills

(also called bedding), a phenomenon valid for granular materials, which is also observed in sedimentary clastic rocks and sands of nature. The miners certainly noticed this phenomenon when grinding minerals within a mortar by means of a pestle, where the thinnest fraction (powder) falls down into the hollow bottom of the mortar, while the thickest material remains permanently on the surface (see a simple experimental demonstration in Figure 8).

In the circular mill, the stirring action of the millstone passing over the material causes this characteristic layering, with the thinnest material going down and trapped in the bottom of the cavities. This prevents the already ground material from being over-ground, whereas unbroken and sizable pieces of the material remain exposed on the surface and are further reduced in size during the next millstone passage.

Only minor changes for the washeries in the Hellenistic Period

The washery was an old, tried-and-tested device that was used without substantial changes for nearly five centuries. Admittedly, when litharge recycling treatment began, some adjustments were made to improve its performance, but they were not generalized.

As a matter of fact, some washeries found during excavations had some of their nozzles in front of the water supply tank permanently sealed with mortar and replaced by new ones at a lower height from the floor (Figure 9 at left).

In a few other washeries, as for example in Spitharopoussi (Kakavoyiannis 1983; 1984), the nozzles seem to have been placed from the beginning at only 25 cm above the floor, instead of 40 cm which is the standard height for the classical period (Figure 9 at right).

Both of the above changes contribute to a lower inclination of the sluice, which is more convenient for the separation of litharge because of its fineness.

A second conversion was necessary for simultaneous processing of both *ekvolades* and litharge in the same washery. In this case, the light fraction of litharge separation (i.e. the fraction of desilvered litharge flowing out of a sluice) should be preserved from mixing with the waste coming from *ekvolades*. This was necessary because desilvered litharge was further used for commercial lead production, whereas the light fraction of *ekvolades* was a real waste (plynite). For this purpose, a vertical slab of stone was placed in the middle of the collecting channel, dividing it into two departments and serving at the same time both as a dam for the sediments and as an overflow for used water. This dam prevented desilvered litharge which flowed out of a sluice into the first department from advancing into the second one and from mixing with the waste of *ekvolades*. It allowed, however, for water

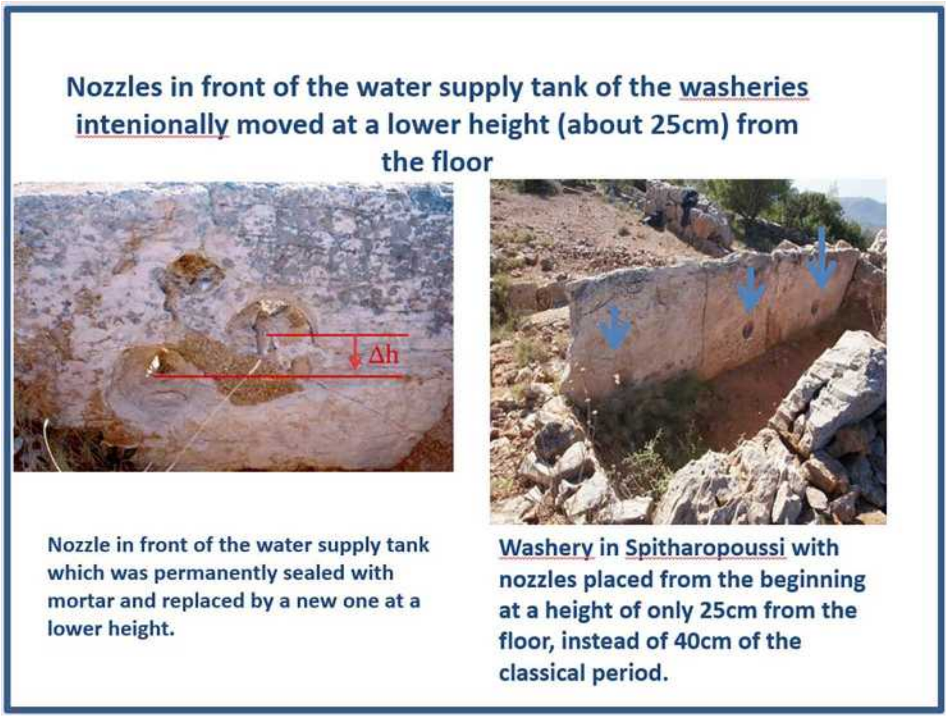

Figure 9. Transferring the water nozzles at a lower level for obtaining smaller inclination of sluices

charged with slimes to circulate freely into the water recirculation system for cleaning (Figure 10).

This simple but clever addition of a dam in the collecting channel was very important for productivity, since usually only one washery was available in each workshop. This explains why a dam is observed inside the collecting channel in a large number of washeries in the Lavreotiki. E. Kakavoyiannis (1984) reported the presence of dams in a number of washeries in the Botsari valley and considered that they were added to the original construction at a later stage, probably in the Hellenistic or Roman period. It is also worth noting that light overflow stone plates, not incorporated in the main channel, were left in the area of a number of washeries. Apparently, these plates moved dams that could be positioned at will in any place along the collecting channel or completely removed.

The advent of a Galena roasting furnace, a crucial innovation

The problem of if, and to what extent, the ancient miners exploited galena (lead sulphide) apart from cerussite (lead carbonate) was the subject of discussion of many researchers of Laurion. The origin of this problem resides in the high content of sulfur in galena, which makes smelting difficult, and in my opinion quite impossible in an ancient smelting furnace. This problem could, of course, be easily resolved if the ore was previously roasted, i.e. calcined, in order to burn out sulfur and transform galena into oxide. However, no ancient roasting furnace was found and the question remained open.

Recently a furnace, part of a compound with two or three other furnaces which are now completely destroyed, was discovered in Dimoliaki by Hercules Katsaros, (Papadimitriou and Katsaros 2024), **(**Figure 11).

We identified this construction as a galena roasting furnace. Like furnaces in the adjacent mining area of Ari, the roasting furnace probably belongs to the 2nd to 1st century BC (Tsaimou *et al.* 2015).

The use of roasting furnaces certainly played an important role in the growth of mining activity from the beginning of the 2nd century BC, when Athens started minting silver coins again: the new style tetradrachms. In particular, roasting furnaces enabled the use of galena which could be extracted from the deepest deposits of the mines. Deep galena deposits were abundant in Dimoliaki as well as in the neighboring mining area of Charvalos-Ari and had a very high content in silver. According to the testimony of a foreman who worked at the French Company of Laurion since 1920, new works

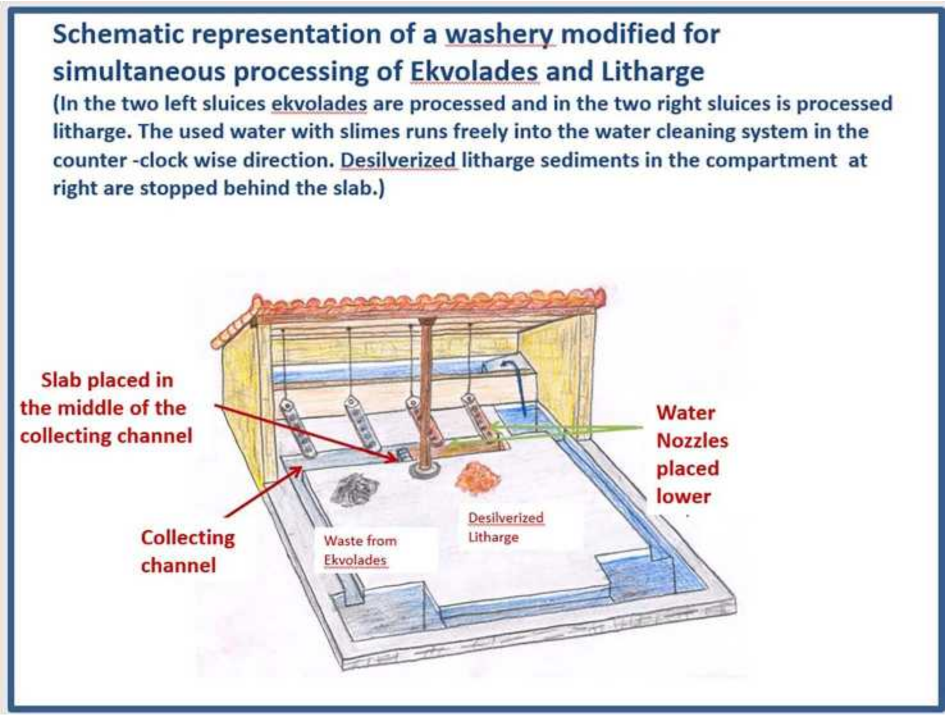

Figure 10. Modifications for processing both Ekvolades and Litharge simultaneously in the same washery

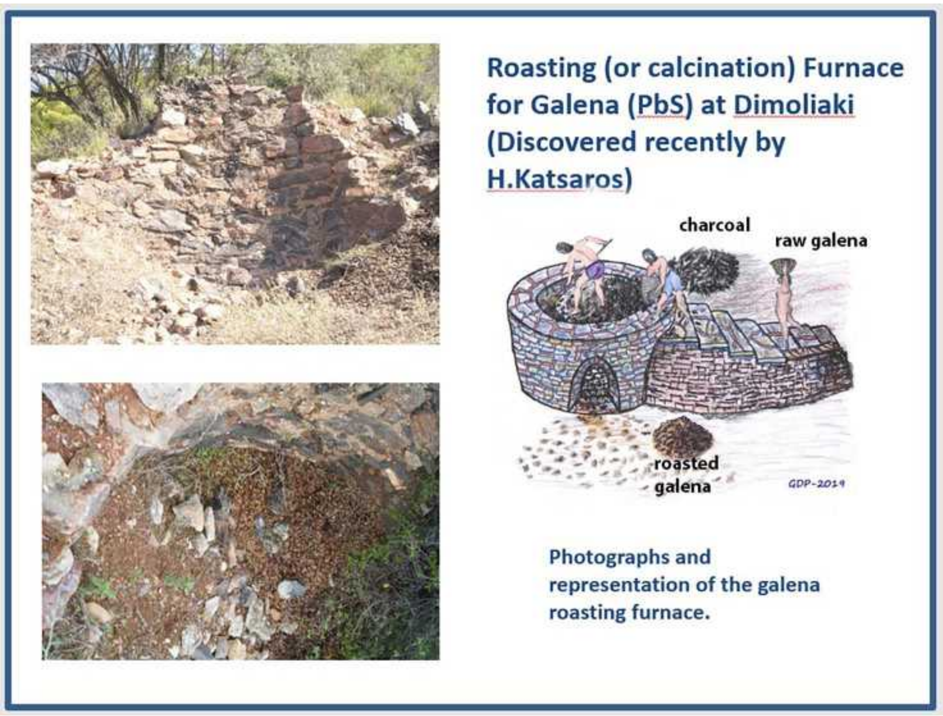

Figure 11. Roasting furnace for Galena at Dimoliaki

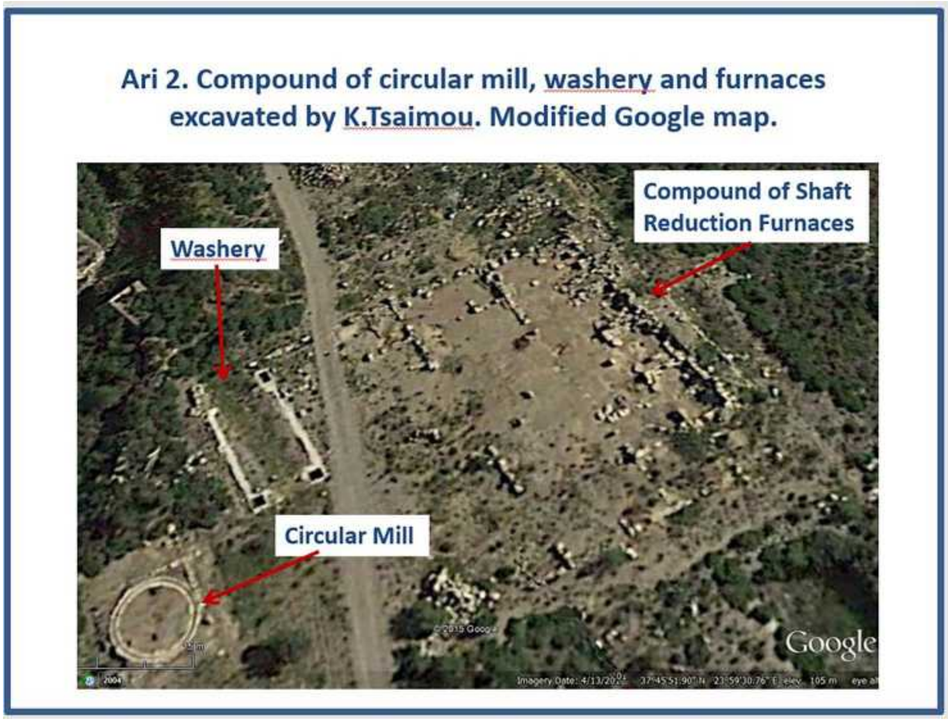

Figure 12. The compound Ari No2 excavated by Tsaimou at Ari, comprising one circular mill, one washery and one group of five or more smelting furnaces.

opened by the Company in the above regions often intersected ancient galleries, where ancient miners had exhaustively extracted galena.

I will not go further into the discussion of this furnace because it is presented in another communication in the present 7th Symposium of the Hellenic Society for Archaeometry in Athens (Papadimitriou and Katsaros 2024).

The Ary-Dimoliaki metallurgical center

The discovery of the circular mills in the Lavreotiki was a great innovation which resulted in the construction of new workshops of high production capacity adapted for recycling of litharge. These workshops were probably established by wealthy investors during the first half of the 2nd century BC, after the appearance of new style tetradrachms. Such a typical case is represented by the compound Ari2 excavated by Tsaimou at Ari, comprising one circular mill, one washery, and one group of five or more smelting furnaces (Figure 12).

The presence of very fine ground litharge is evident in several places of the compound, including the area of the circular mill and its groove and cavities where litharge residues remained attached. This litharge was compacted and partially transformed to lead carbonate under the long action of carbon dioxide of the atmosphere and of rain water, as is the case also with lime. It is important to say that this complex was dated in the time interval between 200 and 40 BC, using carbon 14 on charcoal pieces obtained from the furnaces during the excavations of Tsaimou (Tsaimou *et al.* 2015).

There is a total of five circular mills in Ari, four of them excavated by Tsaimou and a fifth one from which only a few blocks are preserved on the hill of Harvalo. A sixth one, from which only a piece of marble is preserved, is located near the entrance of the village of Manoutso, on the foot of a hill with remains of mining works and ancient slags. There is also a seventh one in Dimoliaki, at a small distance from Ari, which was one of the first unveiled circular mills in the Lavreotiki and was defined by Conophagos and Mussche as "helicoidal washery" (Conophagos 1970; 1980). All of them are of the same type and geometrical form and dimensions (diameter of about 6m), so that one could suggest that they were all active in the same period, i.e. in the Hellenistic-Roman years (Figure 13).

The astonishing high density of circular mills in the area is explained — considering the intense metallurgical activities of older times — mostly of the classical period. These earlier activities had left behind enormous quantities of mining and metallurgical waste, namely *ekvolades*, litharge and slag. Only minor

Figure 13. A view of the Dimoliaki-Harvalo-Ari mining and metallurgical area. R.F.Dim=Roasting Furnace at Dimoliaki, C.M.Dim=Circular Mill at Dimoliaki. C.M.1, C.M.2, C.M.3 and C.M.4 = Circular Mills at Ari, C.M.Ch.=Circular Mill at Charvalo, and C.M.M.= Circular Mill at Manoutso village. Adapted from a Google Earth map.

residues of them remain at present, since litharge was already exhausted in Antiquity in order to obtain silver from its metallic inclusions and commercial lead, as well as for other minor applications, whereas slag and *ekvolades* were recovered much later, in the second half of the 19th century from the Greek Metallurgical Society of Laurion, in order to be resmelted for production of lead. Quantities of ancient slag stocks which existed in the area are known from both Kordellas and from the report of the Vouyoukas Commission of 1865, which was charged from the State to record them in the Lavreotiki (Conophagos 1980).

This report accounts for the nine places in the Ari-Harvalo-Dimoliaki area with slag heaps, totaling 181,000 tons and corresponding to more than 20% of the total stocks of slag in the inland of Lavreotiki. It is evident that at least one smelting compound corresponded to each place of slags, although only one (Ari 2 of the excavations of Tsaimou) has survived to this day. Cupellation furnaces are not preserved at all, having been destroyed by scrap collectors looking for litharge and lead metal. Kordellas reports that both litharge and debris of cupellation furnaces were found mixed with slag, which means that cupellation furnaces were part of the smelting compounds. This explains why circular mills were always constructed in the proximity of older furnace compounds and slag heaps.

Another area in the Lavreotiki, with a high concentration of circular mills lies between Bertseko and Megala Pefka, where, to my knowledge four circular mills are present in a close distance to the well-known furnace compound of Megala Pefka.

The flow-sheet as well as the production chain of silver and lead in metallurgical centers after the introduction of the circular mill are represented in Figure 14. This Figure should be compared to Figure 2, which shows the production chain for silver and lead from *ekvolades*.

Comparison and Technological Transfer between Laurion and Egypt

In this part of the paper I shall try to compare the technology used for litharge processing aimed to recover its silver inclusions during the Hellenistic and early Roman period in Laurion with that used for the recovery of gold from quartz during the Ptolemaic period in the Eastern Desert of Egypt.

As a starting point I shall consider the information provided from Agatharchides of Cnidus, who reported on the production of gold in the Eastern Desert of Egypt. Agatharchides lived in the Ptolemaic Court around the end of the 2nd century BC, and his description was transmitted to us through Diodorus of Sicily (III,12-14) and the Patriarch Photius (Bibl. 250.447b.17 to

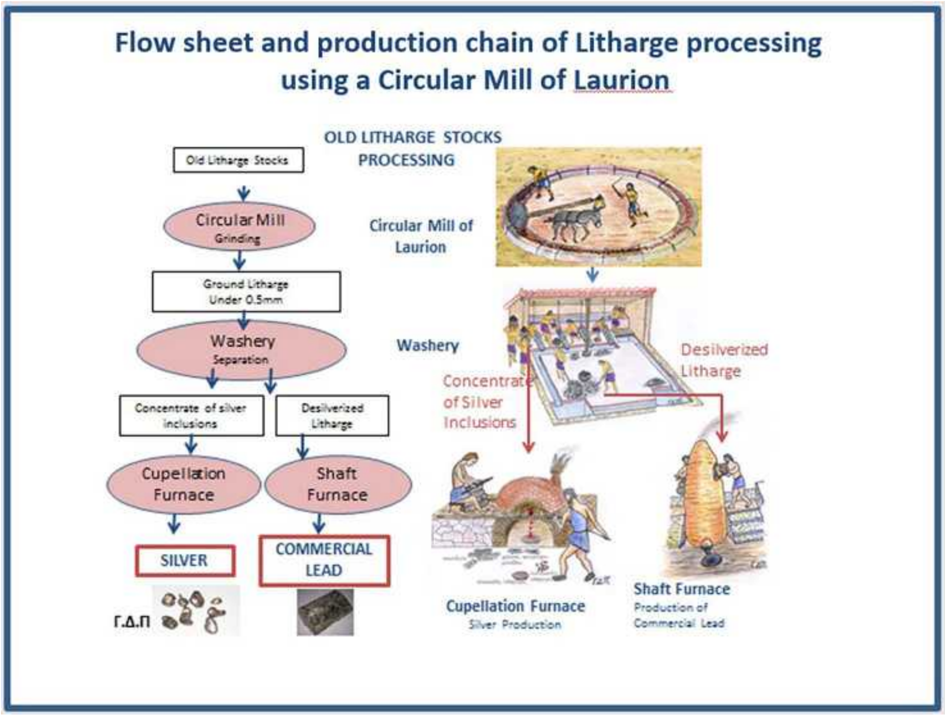

Figure 14. Flow sheet and production chain using the Circular Mill.

250.448b.35). It contains valuable information on the production chain of gold, including several technical details on the extraction of ore and the processing methods used by the miners of the Egyptian Eastern Desert.

The credibility of the information offered is confirmed by the presence of numerous remnants of mining works, crushers and grinders, washeries, immense quantities of processed ore debris of old time, as well as dwellings of workers on the mountains and in the wadis of the Eastern Desert of Egypt. Their presence came to light two decades ago in the pioneering work of Rosemarie Klemm and Dietrich Klemm (Klemm and Klemm 2013) of the University of Munich, although some isolated photographs had appeared earlier in the archaeological literature (Sidebotham and Zitterkopf 1995).

R. Klemm and D. Klemm had participated in three campaigns in the Eastern Desert of Egypt between 1989 and 1993 and recorded the sites and surface findings of more than two hundred gold mine locations in the Eastern Desert of Egypt and in Ancient Nubia (North of present day Sudan). Furthermore, they dated them based on the typology of surface findings: ceramics, stone tools, and dwellings found on the site.

In the following paragraphs I shall limit my discussion to the ore processing devices and methods, namely crushing, grinding, and recovery of gold on sluices. I will then discuss the subject of possible technological transfer from Laurion to Egypt as previously suggested by R. Klemm and D. Klemm.

The technique used to recover gold, as described by Agatharchides, is broadly similar to that used for gravity concentration in the Laurion washeries. The ore that was extracted from the mines was broken on stone slabs with iron hammers and was then reduced to a very fine powder on stone grinders. Finally, gold was separated from the ground quartz mass in a stream of water over an inclined plane of stone, covered with a wooden board.

This technique is confirmed by the findings: stone crushers and grinders as well as washing tables, i.e. stone structures with inclined plane and elementary water recycling system.

Regarding the grinding device used, Diodorus mentions that two or three women and older men worked “on the handle”, while Photius mentions only women, three “standing on one handle on each side”. Though these descriptions differ in the details they agree that many workers were necessary to activate the mill. One could speculate that Agatharchides refers to the Olynthus reciprocating mill, being driven by a number of people holding the handle. However, this seems quite unlikely since, as in the case of litharge, this mill would not be convenient for fine grinding of quartz, whose gold inclusions are extremely thin, much thinner than the inclusions in litharge. Furthermore, remains of such

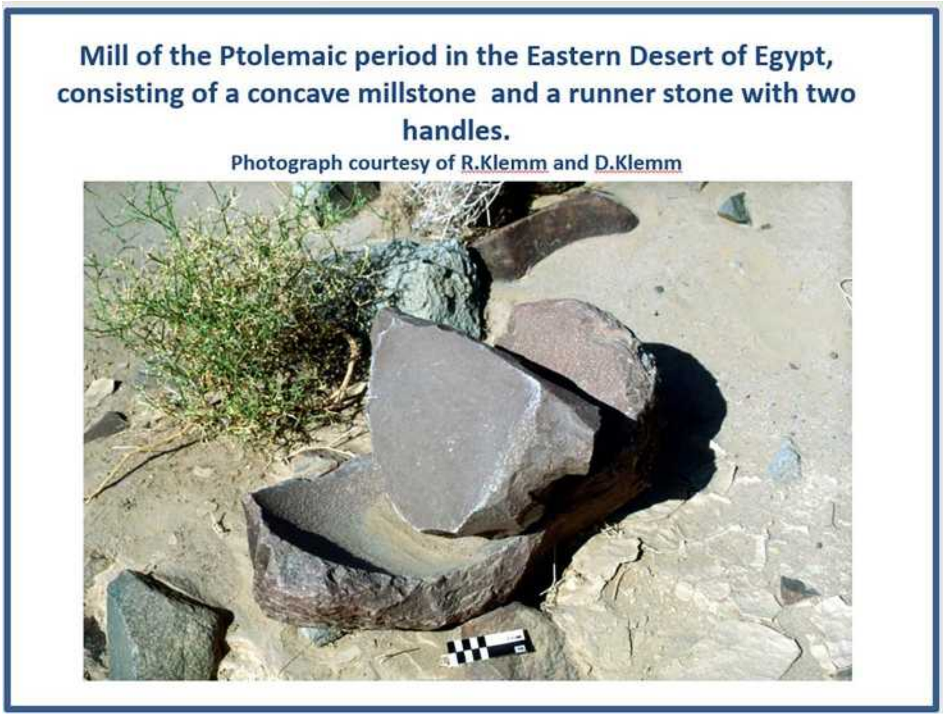

Figure 15. Ptolemaic grinding mill, whose technology was probably introduced in Egypt from Crete.

a mill have never been found anywhere in the Desert Mines.

Instead, the type of grinder found in all Ptolemaic Mines by the Klemms consisted of a concave 70-80cm long and 30-40cm wide millstone with parallel incised 2 mm deep grooves on their curved milling surface, along with a two-handle runner stone weighing between 8 and 12 kg (Figure 15). This type of mill, according to R. Klemm and D. Klemm "presumably represents a Ptolemaic import from the Aegean World" since such mills are testified in the Minoan cities of Gournia and Phestos in Crete. Despite its weight, the Klemms considered it as a grinder driven by one person. This would be possible for the sake of its "ergonomic swinging motion based on the inertial mass of the runner stone".

Should we not, however, assume that the two protrusions of the runner stone were not manual handles, but rather intended for fastening a rod which was moved back and forth by a number of two or three workers? This would be in line with Agatharchides's description and would explain how such a heavy stone could be easily moved back and forth on a curved surface. Moving the runner stone by means of a rod would be also in line with the Greek technology of the reciprocating Olynthus mill in the Hellenistic period, which was moved by means of a rod in domestic practice or alternatively by means of a lever actuated by two workers in industrial scale applications.

Another type of mill found only in four or five Ptolemaic places in the desert is the Circular Mill, similar to the Circular Mill of Laurion. There are two circular devices at Daghbag, two at a mine near Samut and several fragments of this kind of mill at Barramiya. Another is also reported at Bokari, now destroyed, and according to satellite photographs probably one at Abu Shehat. This type of mill is not mentioned by Agatharchides probably because it had escaped his attention since it was used only in a small number of mines.

Their remains were identified by R. Klemm and D. Klemm (2013), who, following the view of C. Conophagos and H. Mussche (1970), considered them as helicoidal washeries. Furthermore, based on the typology of sherds and broken tools scattered around them, they dated them to the Ptolemaic period and suggested that their technology was transferred from Laurion.

As a matter of fact, these mills seem to have been copied from Laurion, but with some minor differences that did not affect their nature and operation. In Daghbag, for example, cavities exist also, but they are carved both inside and outside of the groove. Their function was anyway the same: those lying outside of the groove served for trapping the fine material ejected during the millstone passage, whereas coarse material remaining on the surface was swept back into the groove for further milling. Finally, the dimensions reported for the mills are larger than those of Laurion, namely about 8

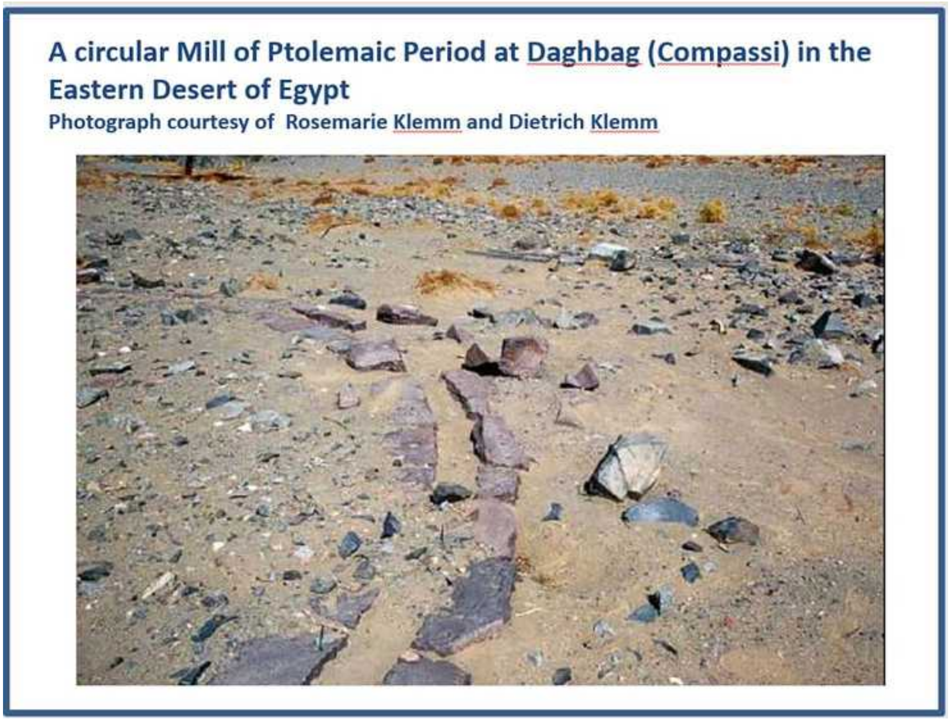

Figure 16. Ptolemaic Circular Mill, like those of Laurion, in the Eastern Desert of Egypt.

m in diameter, compared to about 6 m for Laurion. This indicates that their use aimed at a larger production than in Laurion (Figure 16).

I agree with R. Klemm and D. Klemm that this type of mill was not a local invention and that it was transferred to Egypt from Greece. In support of this hypothesis, the presence of Greeks in the mines of the Eastern Desert of Egypt, probably engineers or specialized craftsmen, is confirmed from Greek inscriptions in the Desert. Furthermore, there are some more indications in favor of this assumption: in this time period any type of rotary mill was completely unknown in Egypt. Egyptians continued using their traditional grinders consisting of a millstone with a stone runner for the grinding of any kind of materials. On the contrary, the circular mill was already known, used, and tested in the mines of Laurion and most probably also in the gold mines of Pangaion mountain in Macedonia (Papadimitriou 2015: 2016).

In my opinion, circular mill technology was transferred from Laurion to Egypt not for processing ore extracted from the mines, but as a recycling technology for processing old waste material. As a matter of fact, the circular mill was recognized as a high productivity device suitable for fine and uniform grinding of minerals. This was a guarantee of success for its use in the mines of the Desert for gold recovery from old waste, since both litharge of Laurion and old waste of ground quartz in the desert exhibit many physical characteristics in common: they are both hard and brittle materials with very fine inclusions dispersed in their mass.

Since circular mills were intended only for the recycling of old waste, it is obvious that they were installed only in very old mines, where enormous stocks of waste with appreciable gold content had accumulated over time. For this reason, I assume, they were always constructed near or amidst old waste stocks. Waste was sometimes in sizable pieces eventually mixed with sands and powders and a circular mill was able to reduce their mixture directly into fine powder without any preliminary crushing or screening.

Circular mills were not used in Egypt for grinding of ore extracted from the mines because their high capacity did not comply with the limited quantity of ore extracted daily from the mines. In this respect, the traditional manual grinder was largely sufficient. Moreover, the parallel use of circular mills and old traditional grinders in the same mine, as is demonstrated from their mutual remains near one another, may be understood only by accepting their distinct role in the production chain.

Washeries

Washeries in Egypt and Laurion both work on the same principle of gravimetric separation of minerals by water flow on an inclined plane. They differ, however, with respect to their construction details and their functional characteristics.

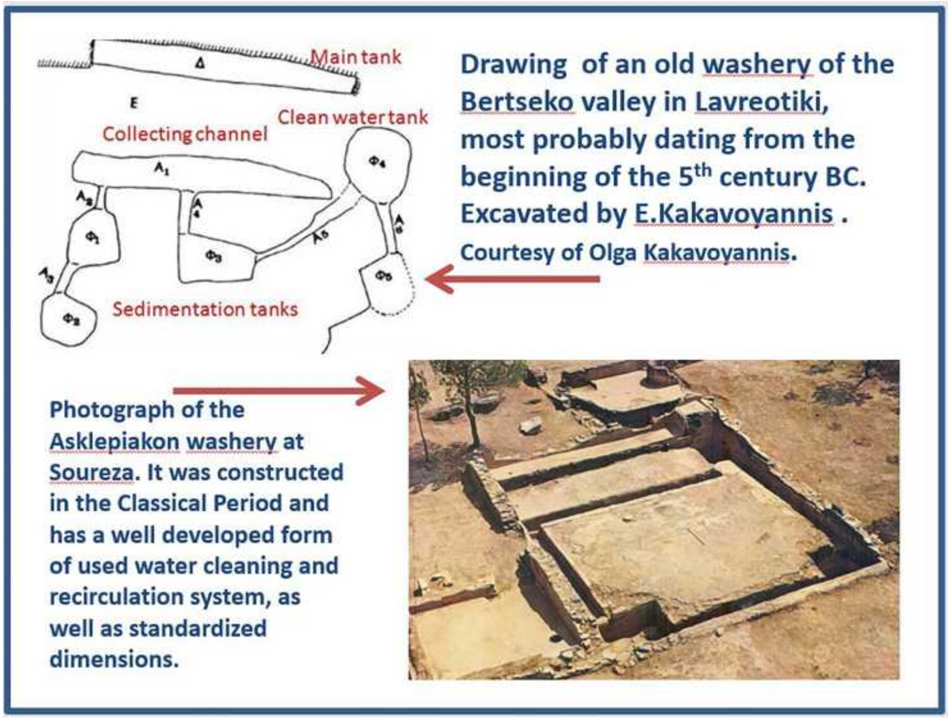

Figure 17. Evolution of ore washery at Laurion

Washeries in Laurion appeared, according to E. Kakavoyiannis (2001), in the Bertseko valley at the beginning of the 5th century BC. Their architecture was initially improvised and varied from one unit to another, but they developed rapidly into their definite form. This consisted of a well-studied ore concentration section with standard dimensions and a highly sophisticated water cleaning and recirculation system (Figure 17). For a detailed description see for example G. D. Papadimitriou (2017a).

Washeries in Egypt are testified at a very early date. R. Klemm and D. Klemm state that the oldest ones date from the New Kingdom period, which coincides roughly with the Late Mycenaean period in Greece. Although the New Kingdom Mines in the Eastern Desert of Egypt are numerous, remains of washeries of that period are rare and badly preserved. Also, from the Ptolemaic period only a small number of washeries still exist. Those, however, belonging to the Arab period (7th to 14th century AD) are abundant (Figure 18).

The Egyptian washery is a simple stone construction with a sloping plane 40-60cm wide. We may assume that this plane served as a support for the sluice, which — according to Agatharchides — was a board on which gold was separated from quartz by means of water flow and manual stirring from slaves. This plane is 80-100cm at its highest side, corresponding with an inclination angle of 15-20 degrees. This inclination is higher than that of Laurion (which was usually 11-12^{0} and in a few cases 7-8^{0}, as at Spitharopoussi), but both elevation and length of Egyptian sluices are about twice that of Laurion.

As opposed to Laurion, water was not ejected out of nozzles on the sluice, but apparently a worker poured water over the plane. Due to the strong inclination of the sluice, the water flow was certainly efficient in removing quartz, and because of its increased length, the precious gold inclusions remained longer on it and had thereafter an increased probability of being trapped.

The sluice abutted in a water recirculation circuit, consisting of a sedimentation tank and a channel conducting water back to the head of the sluice inside a feeding tank in the soil. This water cleaning system was apparently very elementary compared with that of Laurion. It was, however, certainly efficient, since ground quartz was relatively clean and did not contain much shale, as the ore in Laurion. It is also worth noting that washeries in Egypt remained unchanged from the New Kingdom to the Late Arab period.

In conclusion, washeries of Laurion and that of the Eastern Desert of Egypt are very different regarding their construction and functional details.

Ore washeries in the antiquity are currently known only from Laurion and Egypt. To my knowledge, they have not been identified either in Macedonia and Thasos

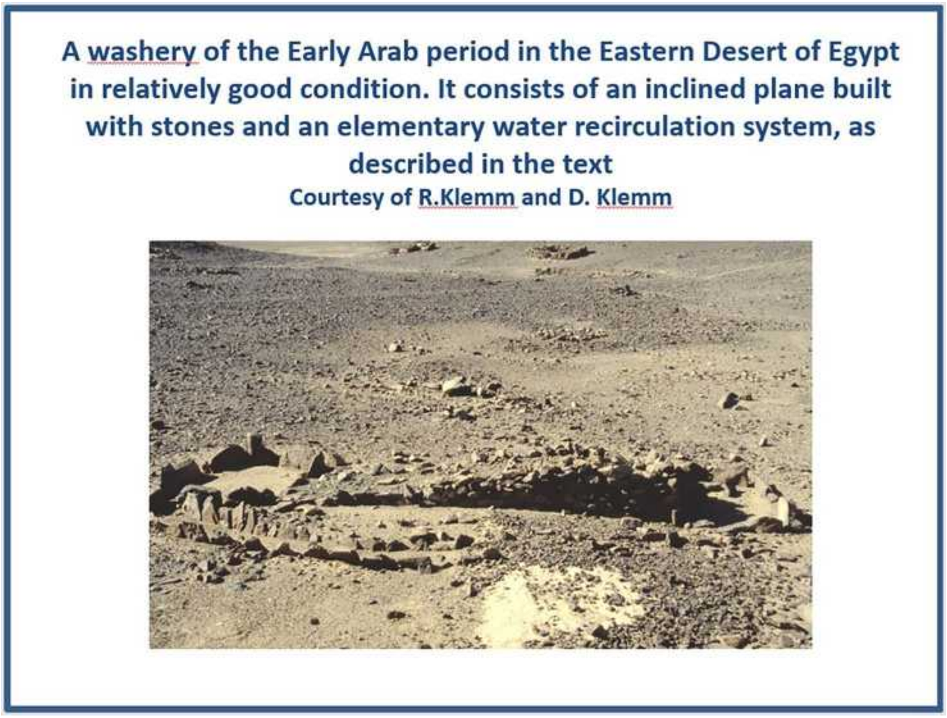

Figure 18. Washery of gold from the Arab times in the Eastern desert of Egypt.

or elsewhere in ancient world through the Classical to Roman times, although the washing of ores in Spain and Portugal is mentioned by Strabo. The Golden Fleece of Colchis belongs to Prehistory and is often supposed to be a primitive sluice for capture of gold grains in rivers. Its myth is well-known, but the history of washeries presents huge gaps so that no assumption can be made at present with regard to their source nor to any eventual technological transfer.

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Processing of Mineral Resources and the Organization of Metal Production in Thasos during the Early Bronze Age

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Abstract: Ancient ore processing and metal production in the minerals-rich north Aegean have been significant aspects of the region's economic character as suggested by combined archaeological, geological and archaeometallurgical research. Archaeological finds from Thasos confirmed that the earliest steps of metallurgical technology on the island date back to the end of the Neolithic period. Excavations at three prehistoric settlements on Thasos, those of Limenaria, Skala Sotiros and Aghios Antonios, revealed evidence for early metallurgical practices that became the subject of recent interdisciplinary study. Attempting to further investigate the technical stages by which minerals were transformed into metals on prehistoric Thasos, this paper is focused on recent mineralogical analysis of ores by means of XRD, the study of stone tools used in ore processing, experimental crushing and grinding of Thasos ores and analysis of metallurgical residues by SEM/EDX. The combined results are useful for reconstructing the *chaîne opératoire* in an attempt to better understand prehistoric copper metallurgy on Thasos and examine its place within the broader Aegean metallurgical tradition of the Early Bronze Age.

KEYWORDS: ORES, STONE TOOLS, CRUSHING, METALLURGY, COPPER, EXPERIMENTATION, THASOS

Introduction

The north Aegean is a region well known for its mineral wealth that became a focus for exploration at an early date. Abundant evidence for mining and metal production spanning over three thousand years could be found at numerous locations. Although previous archaeological research touched upon issues of extraction and circulation of precious metals in this region during antiquity (Koukouli-Chrysanthaki 1990; Picard 2006; Muller 2011), limited studies have been focused on establishing a detailed chronology for the emergence and gradual development of metals production in prehistoric times (Papadopoulos 2008; Bassiakos 2012; Nerantzis and Papadopoulos 2013). While the basic technical characteristics of Aegean Early Bronze Age copper metallurgy are beginning to become clearer for the Cyclades and Crete, with arsenical copper production evidenced at several sites (Bassiakos and Catapotis 2006; Georgakopoulou 2018), similar findings from Thasos have only lately attracted scholarly attention (Nerantzis and Papadopoulos 2013; Nerantzis *et al.* 2016). The current article is focused on the remains of prehistoric ore processing and metallurgical activity on the island of Thasos with its particularly rich mineral resources that were utilized by local communities since the end of the Final Neolithic (*c.*4500-3200 BC) and more prominently by the Early Bronze Age onwards. The methodology applied, comprises an interdisciplinary study of geological and archaeological material including X-ray Diffraction (XRD) analysis of ore samples and Scanning Electron Microscopy coupled by Energy Dispersive X-ray microanalysis (SEM/EDX) of copper slags to approach issues of access to raw materials and smelting technology. Notably the intermediate stage of preparing the ore by crushing, grinding, sorting and handpicking that takes place before smelting is being addressed through a thorough study of lithic tools used in crushing and grinding mineral ores (Nodin 2016; Nodin 2023). Finally, through an experimental simulation of ore crushing it is attempted to better address this crucial step in metallurgy that has received very limited scholarly attention in the past.

Geological information and archaeological evidence for early metallurgical activity on Thasos

Geologically, Thasos is part of the crystalline Rhodope massif and consists of thick metamorphic series of gneiss and marbles lying in succession and in conformity with one another. The complex mineralization of the island comprises lead, zinc, iron and manganese ores and to a lesser extent copper and silver-bearing ores (Higgins and Higgins 1996: 118). The lead-zinc deposits occur in the western part of the island among faulted dolomitic marbles with the most significant occurrences at Vouves, Koumaria, Marlou and Sotiras (Wagner and Weisgerber 1988). They are mainly composed of smithsonite, cerussite and barite belonging to the oxidized zone of the deposits and sphalerite, silver-bearing galena, barite and chalcopyrite of the primary sulphide zone. The iron deposits are substantial and consist of limonite and hematite at places hosting copper carbonates such as malachite and azurite mainly at Makryrachi and Mavrolakas (Figure 1).

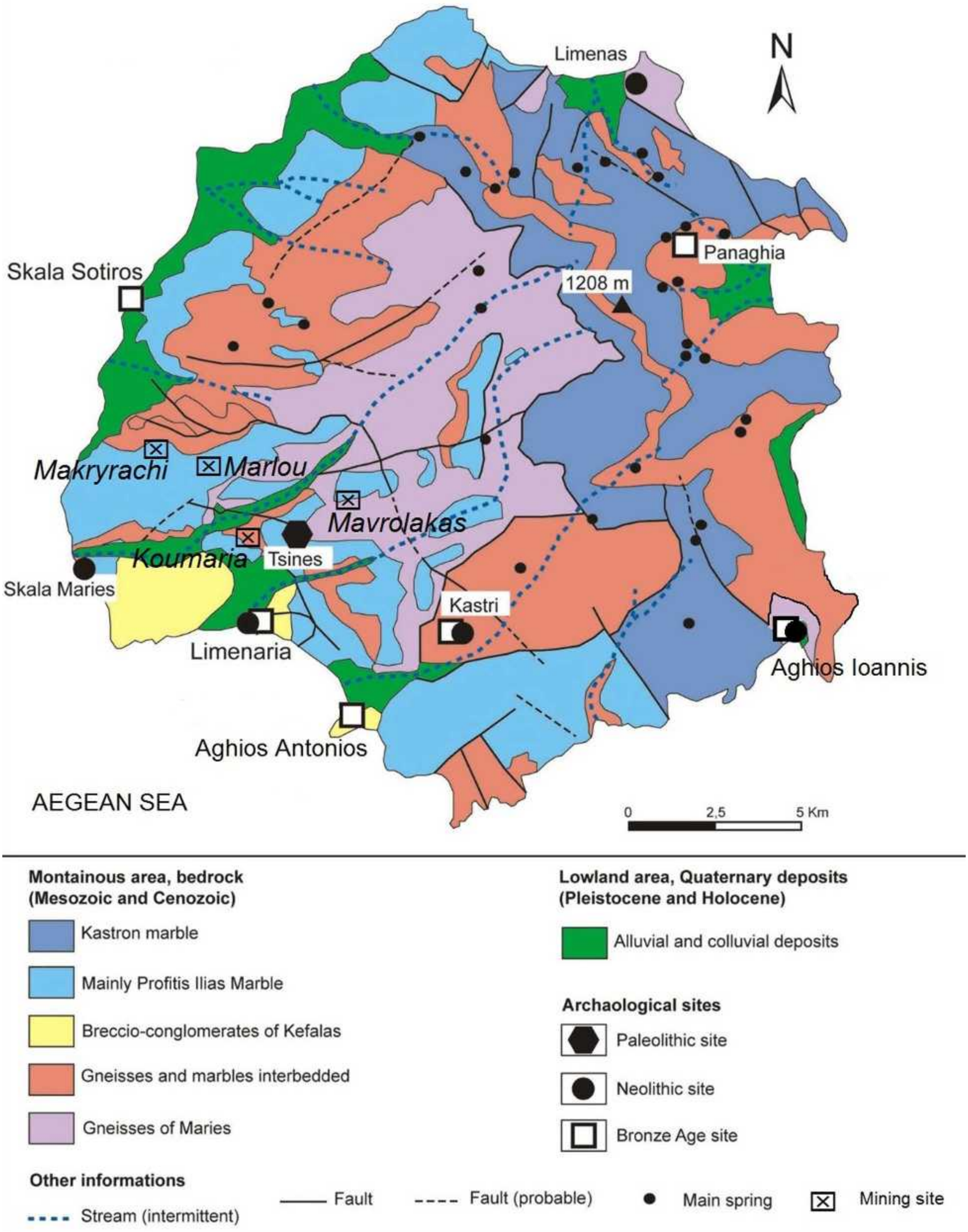

Figure 1. Geological map of Thasos showing major sites mentioned in the text (based on Epitropou 2006 - modified by authors).

Geochemical and mineralogical studies confirmed that limited copper resources were available on the island, which could have potentially supplied the local communities at least since the Early Bronze Age. Large-scale extraction of argentiferous lead ores during antiquity left behind substantial material evidence on the western part of the island such as ancient gallery openings found all over the lead/zinc mineralization and substantial slag heaps (Pernicka *et al.* 1981). Lastly, the primary gold occurrences at Koinyra on the eastern part and the acropolis mine at Limenas were exploited in antiquity by the powerful state of Thasos along with the silver deposits in the western part of the island (Muller 2011).

From the settlement at Limenaria, on the SW part of the island, derive the earliest residues of silver extraction from the entire north Aegean region (Papadopoulos 2008: 69). These important finds have been the subject of interdisciplinary investigation at N.C.S.R. 'Demokritos' and preliminary results have been already published (Bassiakos 2012; Bassiakos *et al.* 2019). The residues related to lead-silver extraction are in form of bowl-shaped litharge fragments coming from a cupellation process and a silver pin, all recovered from a layer of the FN, dating to the early 4th millennium BC (Papadopoulos 2008: 69). The earliest evidence for copper metallurgy derives from the same settlement in form of slag pieces, crucible fragments, and copper alloy objects found in Early Bronze Age (phase I) layers, dating around 3000 BC or slightly later (Papadopoulos 2008: 70). Additional finds related to metallurgy from Limenaria include several ground stone tools such as crushers, pestles, crushing tools and querns used for ore processing and small lumps or fragments of secondary iron ores, hematite and limonite in greater quantity, including some fragments containing cupriferous secondary ores, mainly malachite and azurite (Bassiakos *et al.* 2019, 2744). More findings related to copper production mainly slag pieces, a furnace fragment and a ceramic mould have come to light at the settlement of Aghios Antonios, near Potos (EBA phases II-III) dating between *c.*2800 and 2500 BC (Nerantzis *et al.* 2016; Nerantzis and Papadopoulos 2016). Stone tools for ore processing and metalworking equipment (mould, tuyères) were also found at Skala Sotiros, an EBA (phase II-early 3rd millennium BC) settlement on the NW coast of the island (Koukouli-Chrysanthaki and Papadopoulos 2016).

Materials and method

In order to attempt elucidating the technical processes involved in transforming metalliferous ores into metals, based on the archaeological material from prehistoric Thasos, we focused our investigation on two main stages of the *chaîne opératoire*, that of crushing/grinding and that of smelting such ores. For the first stage, stone tools used in ore processing deriving from the prehistoric settlements of Limenaria and Skala Sotiros were recorded and thoroughly studied to account for their functional usage (Nodin 2016). Traces and residues on their surfaces were also examined to account for the material that was treated. Additionally, an experimental simulation of ore crushing and grinding was conducted in order to better understand the hand movements and other corporeal parameters that affect efficiency in processing such material, broadening in this way our understanding of the potential techniques utilized by the prehistoric metalworker. The ores used in this experimental processing were collected from three mining locations in Thasos, namely Koumaria, Mavrolakas and Elia located in the southwestern part of the island not far from the prehistoric settlements discussed here.

In order to gain further information concerning the efficiency of such a process, ore samples were kept during various intermediate stages of the experiment and were later subjected to mineralogical analysis at the Laboratory of Archaeometry, N.C.S.R. 'Demokritos'. The ground material was subsequently powdered in an agate mortar and was analysed in an X-ray powder diffraction system, Siemens model D500 (CuKα radiation, 40kV, 35mA). The diffractograms obtained were evaluated using EVA software and permitted the identification of the mineralogical composition of the examined material.

For investigating the stage of smelting the ores, remains of copper production mainly slag and related refractories from Limenaria and Aghios Antonios were subjected to SEM/EDX analysis at the same laboratory and the results are summarized in this article. The instrument used is a FEISEM (Quanta Inspec model) with a super ultra-thin window EDS detector. The analytical data were corrected from elements generated by the ZAF software. The samples were mounted in epoxy resin and prepared in polished sections.

Study of stone tools used in ore processing

A recent study (Nodin 2016) of stone tools from the prehistoric settlements of Limenaria and Skala Sotiros, mainly crushing tools, pounders, pestles, lithic anvils and grinding slabs/querns used in the primary processing of mineral ores, has revealed important information on this crucial stage in metal production that is rarely included in archaeometallurgical studies. The terminology that was adopted for classifying tool types is outlined in Wright (1992), Adams (2002) and Hamon (2006) while relevant studies on traces and residues on the surfaces of the stone tools were also considered (Procopiou and Treuil 2002). Based on a

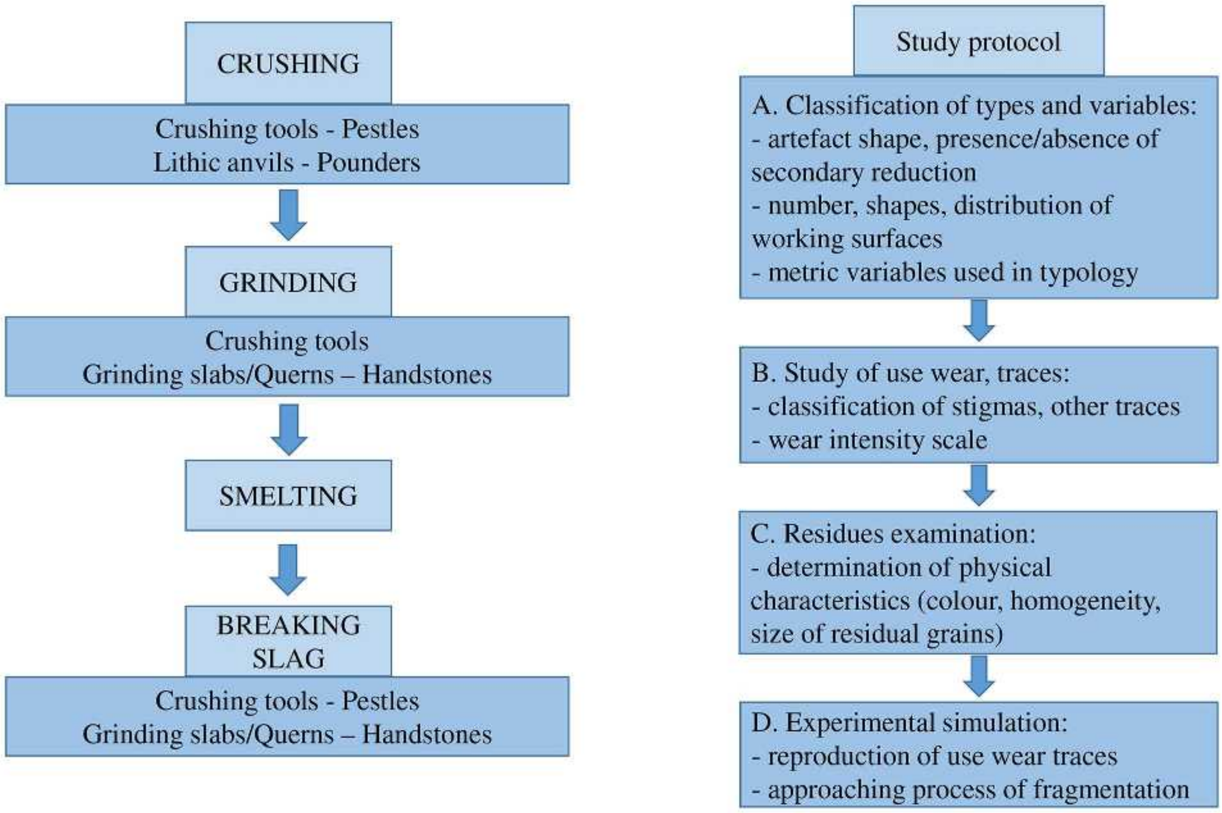

Diagram 1. Flowchart of the *chaîne opératoire* showing the tools involved in each stage (left); flowchart of the study protocol (right).

classification of the major tool types, the functionalities of each object category were explored providing data for an evaluation of the actual practices of crushing and grinding in prehistoric Thasos. Traces of use wear and residues of minerals were examined optically with a microscope camera. Following the functional study an experimental simulation was conducted in order to better understand how ore processing was achieved with the use of stone tools imitating the prehistoric examples and some preliminary results are being presented here for the first time.

The studied archaeological material comprises 97 objects, including four categories of tool types, namely 18 crushing tools (*outils à cupules*),[1] 6 pestles, 3 pounders, 1 lithic anvil, 1 handstone and 68 grinding slabs/querns (Nodin 2016). The steps in the workflow of ore processing and metallurgical production involved the use of certain types of tools as shown in the first flowchart of **diagram 1**. The second flowchart summarizes the study protocol that facilitated the recording of morphological features, metric variables and functional attributes of the stone tools.

For multi-function tools, it was possible to determine a hierarchy of functions and their adaptation towards the desired outcome in each case (Nodin 2016: 9). Additionally, the notion of gripping was taken into account as it bears on the criteria for selecting the raw materials. The prehensile attributes of each tool signify a set of coherent characteristics corresponding to the technical intention of holding the tool both efficiently and comfortably (Nodin 2016: 9). The crushing tools (*outils à cupules*), which will be presented in more detail here due to their multi-functional usage, could be further divided in three main types:

Type 1: The '*galets à cupules*' represented by three examples (LTTh009-012-027). These are quartz pebbles of ovoid shape and ovoid or semi-oval section, whose surfaces bear one or two dimples at the center, not particularly deep due to the hardness of the rock. Their shape reflects polishing due to water action without signs of any further shaping, thus attesting to an exploitation of the alluvial, colluvial and maritime resources around the site (Nodin 2016: 11).

Type 2: The second type is represented by more massive tools of flat or convex profile (concave at the level of the dimple), with an ovoid, semi-circular or semi-oval section. They display a certain asymmetry in terms

[1] The French term *outils à cupules* better describes the multitude of functions that such tools serve. It is translated here as crushing tools although they were used in several applications other than just crushing such as hammering and grinding.

of the distribution of working surfaces. Their main characteristic is the intense pounding inflicted on their extremities suggesting that they were alternatively used as hammers. There are seven examples of this type, four from Limenaria (LTTh010-011-025-036) and three from Skala Sotiros (LTTh028-029-034). Two of these were fashioned from gneiss pebbles (LTTh028-034), one from marble or dolomitic limestone (LTTh025) and four examples were fashioned from blocks of quartz (Nodin 2016: 12).

Type 3: The third type is represented by eight tools of quadrangular shape, half of which derive from Limenaria (LTTh008-023-026-035), the other half from Skala Sotiros (LTTh030-031-032-033). In their majority, they were made of local, schistose gneiss (LTTh026-030-031-032-033-035) with two examples made of marble or dolomitic limestone (LTTh008-023). They are flat, trapezoidal in section, with polished surfaces testifying to actions of abrasion and possibly crushing. They all display a single dimple positioned roughly at the centre. Their edges are angular in shape, with retouched edges (Nodin 2016: 13).

The typological and functional analysis revealed that these tools are largely versatile, having been used alternatively both in a passive and/or a launched position. Taking the example of LTTh031 (Figure 2) examination revealed five broad ranges of use, assuming multiple functions, each leaving behind a particular trace on: the tool's main body, the upper surface, the edges, the sides and extremities (Figure 3). On the main body the tools are characterized mainly by two types of circumscribed impacts on a circular zone. Their edges display signs caused by the application of launched percussion. The interior of the groove testifies partly to crushing blows accompanied by continuous rubbing in a circular manner (Nodin 2016: 80). The upper active surface shows traces of abrasion. Finally, stigmas (marks or scars) on the extremities and sides confirm that these tools were also used as hammers. This 'alternative' use, however, does not seem to depend on a particular variant but rather on specific needs. Their functions are versatile, having served in alternative ways in the passive position but also in a launched percussion mode as has been also confirmed by several other studies focused on similar archaeological material (Hamon *et al.* 2009; Procopiou and Treuil 2002).

Figure 2. Stone crushing tool (LTTh031) used in multiple functions.

The tools selected for macroscopic traceological analysis bear stigmas i.e. marks or scars caused by the fragmentation of soft and/or hard mineral matter. Recent functional studies on ground stone tools were taken into consideration (Adams 2002; 2014; Delgado Raack 2008; Hamon 2006; Hamon *et al.* 2009) in order to formulate a detailed classification of stigmas based on a macroscopic wear intensity scale for which more details

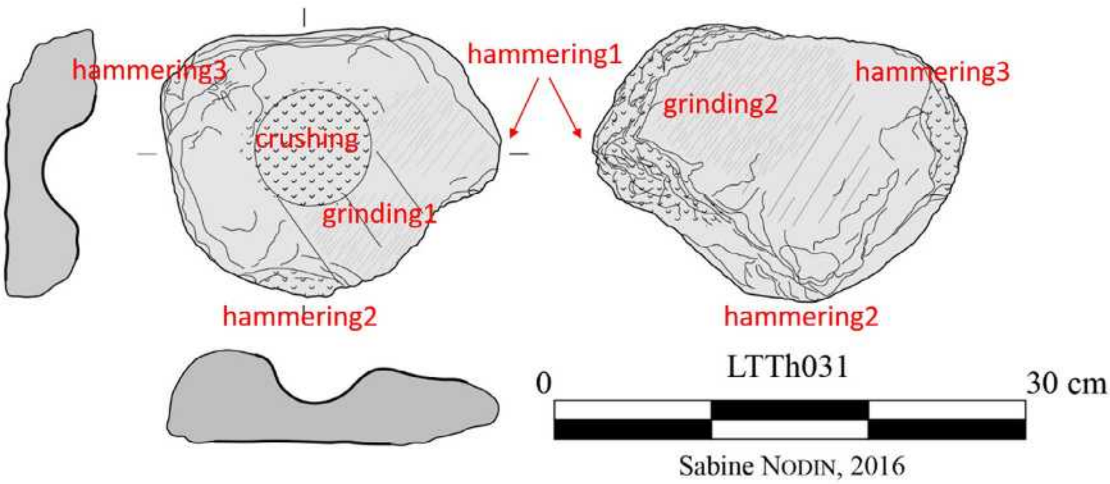

Figure 3. Drawing of the stone crushing tool (LTTh031) used in multiple functions, namely crushing, grinding, hammering (Nodin 2016, 13).

are included in Nodin (2016). Attempting to characterize more precisely the uses of each tool under study, the macroscopic examination focused additionally on the morphology of the rocks as well as the residues present on their active surfaces (Figure 4). It was eventually attempted to determine which physical characteristics (e.g. colour, homogeneity, size of residual grains) could serve as indicators of the nature or degree of processing (Nodin 2016: 83).

Based on the observations from the typological and traceological study, and the residues examination three main functions can be proposed for these crushing tools (*outils à cupules*): firstly crushing of ores, secondly grinding of ores, and thirdly breaking of metallurgical residues (slag). Concerning ore fragmentation, the tools would have been used with an intention of separating the 'economically' useful mineral grains from gangue, thus we presume that the fragmentation process

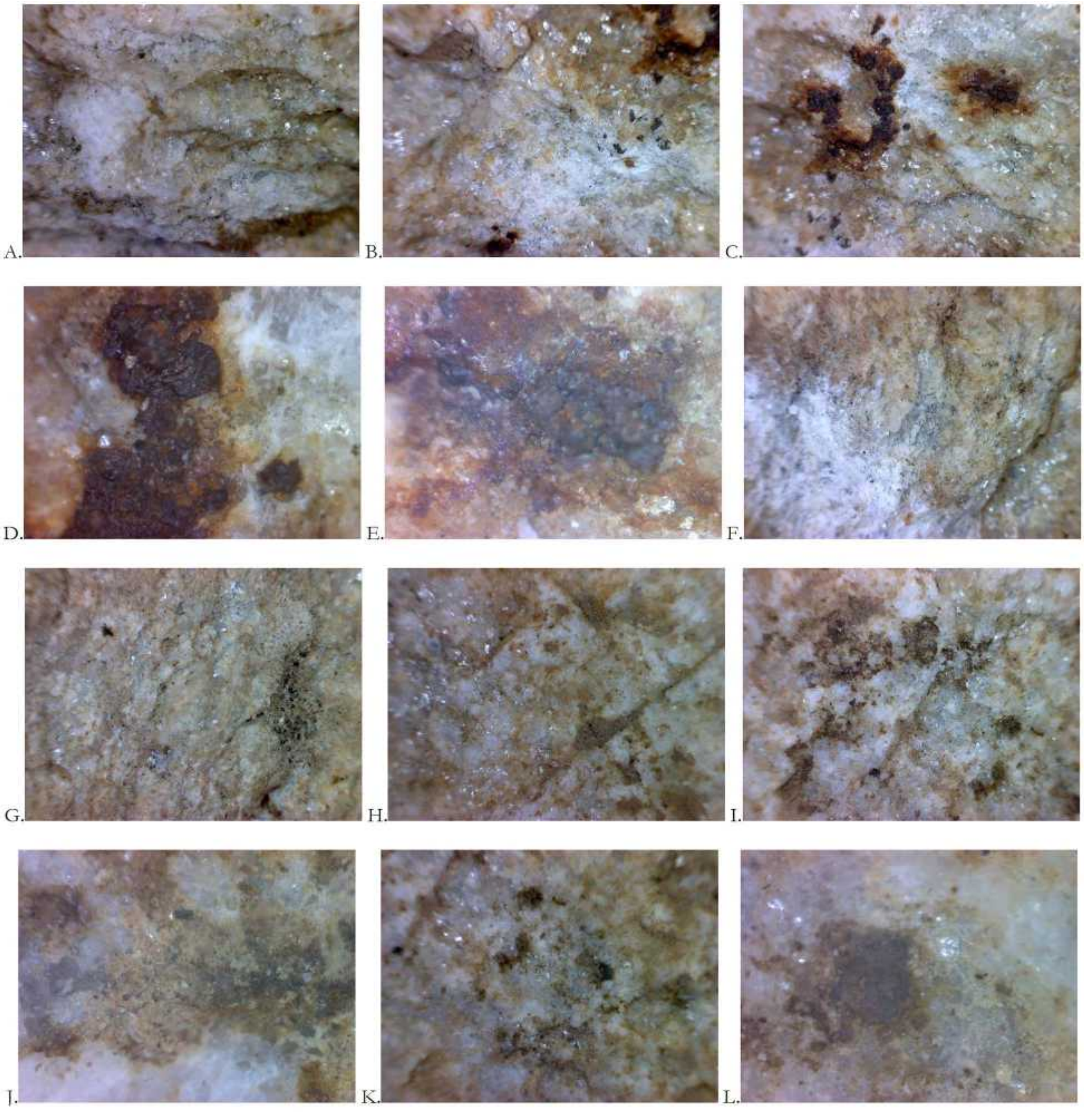

Figure 4. Traces and residues on the surface of crushing tool LTTh026 belonging to type 3. Photos A, B, C, E, G: the edges of the tool attest to a launched percussion, characterized by linear notches related to the hand movement accompanying the formation of transverse grooves. Photos B, C, D, E: scattered traces of punctiform spots and residues of black-reddish to brown, surrounded by orange-yellowish mineral matter, possibly iron oxides and stigmas (scar marks). Photos H, I, K: The grinding surface presents multiple friction streaks riddled by micro-fractures. These propagate a cutting into the stone's thickness, resulting in a progressive levelling of its surface by stripping. Scale: photos A, B, C, F, G, H, I, K were taken under magnification x40 and D, E, J, L under magnification x200 (Nodin 2016, 90).

would be orientated towards an average particle size of about 1 cm. At this size most of the gangue grains would be separated from the visually distinguishable green copper carbonates. After handpicking of the rich in copper grains, further treatment through grinding could lead to finer particle size (possibly down to 0.5 cm). The third possible function concerns fragmentation of slags targeted this time to isolate visible entrapped copper prills (see **diagram 1**). If we consider the variety of impact signs and finer stigmas observed on the surfaces of several tools, in addition to the attached residues, the idea of their successive use in three stages of the *chaîne opératoire* seems a viable hypothesis.

Figure 5. Stone tools used in experimental ore processing: crusher/pestle (15 cm length) and lithic anvil (30 cm length) (photo: Thomas Nicq)

Experimental ore processing

Attempting to evaluate more fully the findings from the functional analysis of the stone tools it was decided to replicate the process of ore crushing/grinding through an experimental approach. The experiment was designed as an attempt to untangle complex issues involving hand movements, bodily posture, duration and pace of the workflow as well as addressing efficiency concerns during ore processing. The simulation aimed at highlighting the mechanical qualities of the lithic material in correlation to a particular type of tool, or even a specific function, according to the definitions described by Sigaut (1991) and the principles for classification of percussion types introduced by Leroi-Gourhan (1971). Similar experimental work carried out by Hamon (2006) for the grinding of plants, soft animal and mineral matter was taken into consideration. Our goal was to test how crushing and handpicking could be effective for concentrating the mineral content in ores by imitating a straightforward process while using tools identical to the archaeological examples.

For the experimental tools, cobbles and flat stone slabs collected from the alluvial valley extending southwest of the settlement of Skala Sotiros were utilized. In particular, we used quartz crushers and pestles to imitate the selection made by the prehistoric inhabitants at both settlements of Limenaria and Skala Sotiros. These were worked against gneiss/schist lithic anvils that were selected on the premise of being as stable as possible with a rather flat top surface (Figure 5). For the pounders/pestles, oval-shaped cobbles were chosen due to their naturally ergonomic curvature, allowing a comfortable and secure application of the palms and a good grip of the last phalanges. The experiment also aimed at approaching the extent to which the choice of a rock is conditioned by its behaviour during use.

Our experimental protocol was thus based on a series of variables aimed at the repeated reproduction of use wear traces performed under controlled parameters in order to evaluate the interaction between the tools and the ores. The emphasis was also placed on the reproduction of the traces of contact between an active and a passive tool in relation to the range of particle size of fragmented ore. The repeated renewal of quartz grains on the surface, the behavior of the rock during strokes and the tendency of the surfaces to become smooth are all technical characteristics that were taken into consideration. The experiment focused on the adaptability of gestures with each type of tool to a given action in order to understand the overall process of ore fragmentation.

The notion of efficiency - in terms of relative yields in the ‘economically’ important mineral - could be quantified by examining the articulation between the two transformation methods, in particular the distinction between the actions of crushing and grinding. The comparison between the traces obtained on the experimental objects and those on the archaeological material would eventually make it possible to compare the method we applied with the methods of the prehistoric craftspeople and appreciate how efficient they could have been in separating ‘useful’ mineral from unwanted gangue.

Each operation was the subject of systematic photographic documentation in order to evaluate hand movements and corporeal positioning. The tools’ macroscopic textures and surface condition, as well as the surfaces and particle size of the crushed ore have been documented through photographs and measurements. Comminution i.e. reduction of the ores particle size progressed during crushing to an average of 1-2 cm, while for the next stage, that of grinding it was attempted to reach a 2-5 mm particle size. Sequences of 30 minutes duration were performed to serve as a basis for calculating the rhythm and speed of execution as well as the regularity of hand movements. The duration of use represents the main reference criterion to compare between use wear on the tools' surface and rate of ore fragmentation. Overall, the duration of work phases ranged from 30 minutes to more than six hours depending on use wear on the tools' surfaces. An evaluation of the yields from each test was achieved through measurement of a) the decrease in tool weight, due to material losses during use and b) the quantities of crushed ore fitting the desired particle size. The values obtained are moderated in accordance to corresponding working times and thus the tools and crushed ore were frequently weighed after each 30 minutes interval. Therefore "relative" efficiency of the tools was evaluated for each intermediate stage within the complete chain of repeated actions. At the same time the traces caused by repeated strokes and residues of ore particles staining the tools' surface provided a reference index readily comparable to the surfaces of the archaeological tools under study.

Stone tools of elliptical or oval morphology seemed to be best adapted to a combination of movements including crushing, stirring or pounding strokes. The tests were carried out with unshaped cobbles, capable of adapting to the majority of gripping modes and uses, developed around two main principles, a) to allow for the double function of the crushers/pestles to be facilitated, i.e. to perform crushing and stirring strokes and b) to determine whether the tenuous aspect of the stigmas on the crushing tools result from specific actions and the nature of the ore being crushed or if this is a direct consequence of the mode of action applied on the tools.

During crushing, the colours of the ores were noted as rough indicators to mineral contents, thus reddish-yellow and brown coloured specimens were crushed without further picking and selecting for grinding. Those with green colour, characteristic of secondary copper minerals, were handpicked and processed further by grinding to an average particle size of 2-5 mm. In terms of duration it should be noted that two persons working for 3.5 hours, divided in 30-minute sessions, managed to crush 60 kg of ore. In terms of enrichment capacity, we should note that 13 kg of gangue was removed from a total of 45.9 kg of Koumaria ore and 3.4 kg of gangue removed from a total of 14 kg of ore from Mavrolakas.

Analytical results on ores and slags

The geological samples that were collected for experimental crushing and analysis are iron-bearing ores in some cases containing visible copper carbonate inclusions. XRD analysis was performed on all samples after crushing while for those that yielded higher contents of copper carbonates a second measurement was taken after handpicking and concentrating the visually recognizable green minerals. Two samples from Koumaria were found to contain dolomite, goethite, quartz and barite. Based on the findings it was decided to process further these particular samples through roasting. This practice is not corroborated by the Bronze Age archaeological finds but the decision was taken in order to test how sufficient this method could be for eliminating sulphur prior to bloomery smelting operations that were common on Thasos from the Early Iron Age onwards. The decision was based on the premise that sulphide (or sulphur-containing) ores were generally roasted before smelting as shown by archaeometallurgical studies in Europe (Benvenuti 2016) and Africa (Humphris and Rehren 2014: 181). A comparison of the XRD spectra between the unroasted (K2) and roasted (K1) samples from Koumaria, shows that maghemite has formed after roasting and calcite became the predominant mineral (Figure 6). Moreover no barite is present in the roasted sample suggesting that this treatment was sufficient for driving off some sulphur contained therein.

Two samples of ore from Mavrolakas (M2, M3) were analysed after crushing while a third sample was analysed initially after crushing (M1) and a second time after handpicking and grinding of the green copper carbonates (M1cop). The analysis has shown that the first sample (M2) contains barite and goethite and the second contains quartz, goethite and hematite (M3). The third sample (M1) was found to contain hematite, malachite, calcite, quartz and goethite while in its ground form (M1cop) it shows clearly increased contents of malachite. As shown by the two spectra of Figure 7, hematite is the predominant mineral in the sample that was only crushed and ground (M1) while malachite becomes predominant in the concentrated sample after handpicking of the green copper carbonates (M1cop). This proves that handpicking and grinding was efficient in concentrating malachite thus increasing the yield of this economically useful mineral. The analysis established that no other green copper mineral was present apart from malachite. Lastly, the minerals identified in the ore samples collected from the mining area of Elia in southern Thasos are mainly goethite, lepidocrocite, barite and less frequently clinoclase.

In order to attempt a reconstruction of the smelting process, several metallurgical finds from Limenaria and Aghios Antonios have been subjected to SEM/EDX analysis. Microscopic examination has shown that most of the copper slags show a glassy matrix filling the voids of crystalline phases, which are mainly composed of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_3) as well as shiny metallic inclusions in form of prills and opaque minerals often green in colour (Nerantzis *et al.*

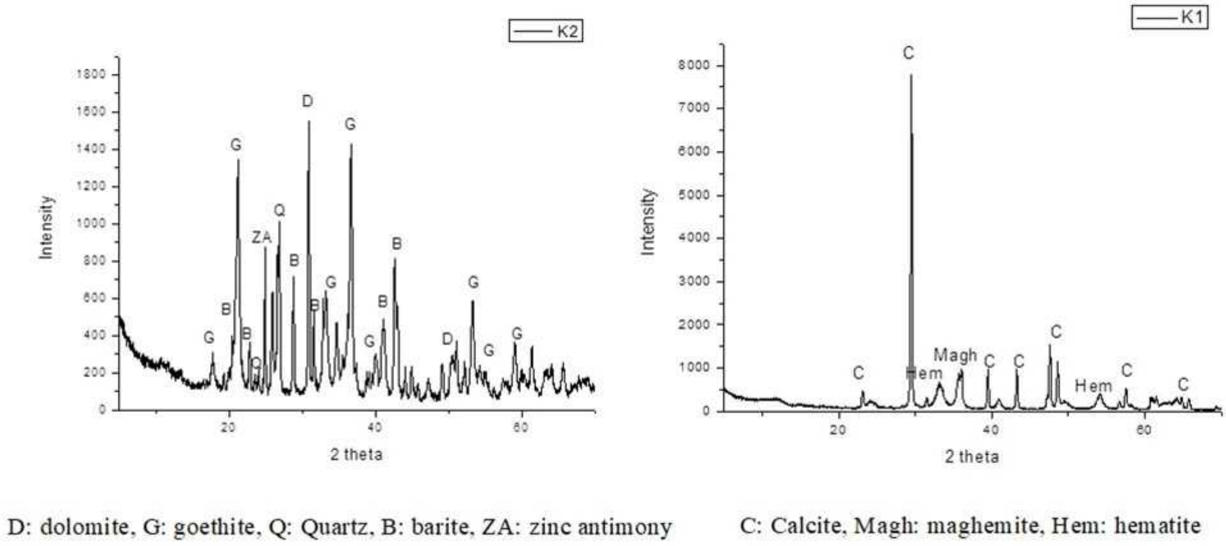

Figure 6. XRD spectra of ore samples from Koumaria. Sample K2 is unroasted while sample K1 is roasted.

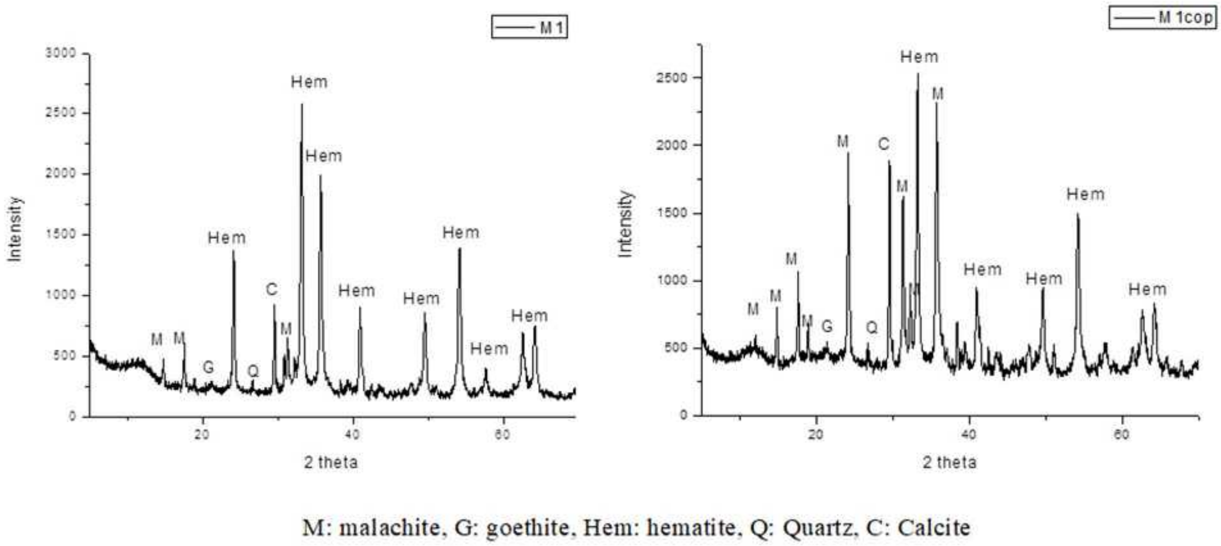

Figure 7. XRD spectra of ore samples from Mavrolakas. Sample M1 was analysed after curshing and grinding, while sample M1cop is an enriched concentrate after crushing, handpicking and beneficiation.

2016: 576). The presence of cuprite (Cu_2O) has also been established in a few instances.

Large spheroid copper prills (50μm to 1mm) as well as matte prills and smaller inclusions were observed in most of the samples (Figure 8). Most analysed matte inclusions contain 65-70% Cu, 20-23% S and around 4% Fe and their presence hints to the possible use of secondary copper minerals, which contain traces of residual sulphides (Nerantzis *et al.* 2016: 578).

All samples were found to contain varying contents of barite ($BaSO_4$) which is a characteristic compound of mineralization on Thasos. The SEM/EDX analysis has shown that barium is present in contents between 2 and 9% in the bulk composition of the analysed samples. Clusters of barite crystals 50μm in size were noted in fissures while a Ca-rich fayalitic phase revealed increased Ba contents (Nerantzis and Papadopoulos 2016: 90). The presence of BaO in increased contents reveals the use of iron ores containing barite that could be the source of increased sulphur contents in these slags. The use of such ores could be further supported by a few instances of angular inclusions of thermally mobilised iron ore within the copper slag as shown in the example of Figure 9. Residual zinc has been detected

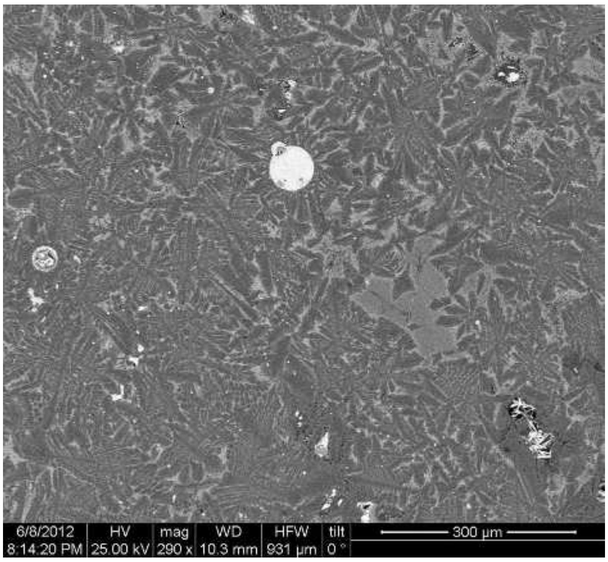

Figure 8. SEM/EDX photomicrograph of slag from Aghios Antonios: laths of fayalite (dark grey), magnetite crystals (mid grey), copper prill (white), matte prill on the left (light grey).

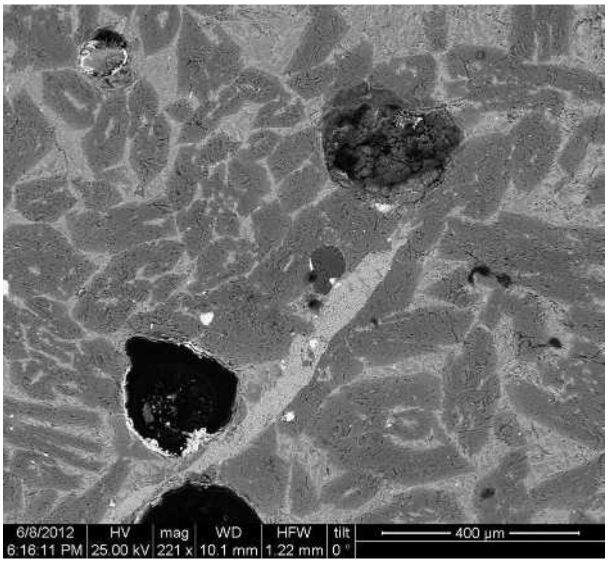

Figure 9. SEM/EDX photomicrograph of slag from Aghios Antonios: laths of fayalite (dark grey), miscrocrytaline fayalitic phase (mid grey), laminated thermally mobilised iron ore (light grey).

in levels between 0.2 and 0.7% with the lowest contents detected in the glassy phase. Zinc is found in most Thasos ore deposits due to the abundant occurrence of the Pb/Zn mineralization on the island (Vavelidis *et al.* 1988).

The heterogeneity of these slags is further corroborated by the chemical analysis of certain inclusions. In particular the iron concentrations in the copper prills show a wide range among the samples at contents between 1.9% and 5.9%. The presence of arsenic within a few copper prills in contents between 2 and 4% might suggest that at least some of the slags derive either from the smelting of copper ores rich in arsenic or the deliberate co-smelting of arsenic-bearing ores along with copper minerals (Nerantzis and Papadopoulos 2016: 91). It should be noted that such contents do not provide indisputable evidence for deliberate alloying since accidentally produced alloys would also produce such concentrations. Further metalworking activities are hinted at Limenaria such as purification of the produced copper, alloying and possibly also recycling. Such information is indicated by the presence of one, unique for Limenaria, crucible fragment the study of which has been published elsewhere (Bassiakos *et al.* 2019).

Discussion

The prehistoric communities of Early Bronze Age Thasos were using a wide range of materials to cover their everyday life needs. Stone, timber and clay were crucial raw materials found in abundance while the scarcer mineral resources containing metals soon attracted their attention (Koukouli-Chrysanthaki and Papadopoulos 2009). Based on the analytical results it has been shown that Bronze Age copper extraction was achieved through smelting of secondary cupriferous ores (malachite and azurite) in which other gangue and metallic minerals co-existed such as iron-ores, calamine, manganese oxides, lead minerals and compounds of silica, calcium, barium and magnesium. A low shaft furnace was most probably utilized, as suggested by the analysis of highly vitrified clay lining that was used to dress the interior of such an installation (Bassiakos *et al.* 2009: 2755). Considering the available data so far it could be suggested that the supply of mineral ores from the upland zone to the coastal settlements was frequent by the Early Bronze Age onwards. The utilization of these local polymetallic ores, confirmed by slag analysis, is proof that the prehistoric prospectors were well accustomed with the different properties of the various ore components. It could be argued that they have prospected the iron ores as indicators for the presence of cupriferous deposits. At this stage iron ores were utilized for their copper contents but in time they may have been recognized as a source of iron, as has been also suggested for the gossans associated with the copper deposits of Cyprus (Kassianidou 1994) and the polymetallic sulphide deposits of western Georgia (Erb-Satullo *et al.* 2014). It appears that in areas with long established copper industries that utilized iron ores it is possible that the transition to iron metallurgy was more straightforward than in areas witnessing a wholesale adoption of the new technology.

Previous analysis on slag from Kastri and Paliokastro, two sites in southern Thasos dating to the Late Bronze Age/Iron Age, revealed similar compositions with Cu contents ranging between 0.6 and 12% with an average of 5% but no arsenic was detected (Photos 1992, 797). These findings suggest that a similar smelting technology was prevalent until the end of the Bronze Age on the island. A comparison of the slags from Kastri and Paliokastro with those from Limenaria and Aghios Antonios, the latter dating to the Early Bronze Age, shows affinities in issues of controlling the smelting process and the use of common mineral resources (Nerantzis *et al.* 2016). Overall, the technology reflected from the currently analysed residues points to a relatively efficient control of the temperatures and redox conditions to allow formation of low viscosity slag that separated from metallic copper. Since these finds derive from the cemeteries around Kastri dating between 1200-900 BC and roughly contemporary surface finds from Paliokastro it could be suggested that copper production on Thasos continued with the use of local resources during this transitional period when iron adoption occurred. The absence of significant As contents in the copper prills signifies a crucial difference from the EBA slag of Limenaria and Aghios Antonios. By the LBA it appears that pure copper was produced in order to become alloyed with tin but this stage of production is not represented by the studied finds. It should be noted that for this early period, the concept of 'experimentation' with different 'ores' should be the prevailing model.

Conclusions

In conclusion, we could suggest that the metallurgists on Thasos during the Bronze Age depended on available local raw materials, namely the secondary, copper oxide minerals hosted in the island's deposits. Our results show that the metalworkers at Limenaria, Skala Sotiros were competent in crushing, sorting and picking the richer fragments, preparing in this way an enriched charge that was introduced to the furnace. Multi-purpose tools, such as crushing tools and pestles were utilized towards that end. The experimental crushing and grinding of ores revealed how the prehistoric metalworkers might have used simple methods for improving the concentration of ore particles aiding in better yields through the smelting stage. Choosing very carefully the tools to use in the experimental simulation proved crucial in terms of their morphological functionality and durability in prolonged and repeated use. Our experiment showed that 30 kg of ore could be efficiently crushed and ground by one person in about 3.5 hours. During this process separation of mineral from gangue and picking the rich particles required careful observation that became more efficient with repeated action. As shown by the XRD results handpicking and grinding of the richer fragments was crucial for enriching the concentrate in malachite content quite substantially.

Overall, the prehistoric metallurgists were competent in copper smelting by achieving to maintain a relatively efficient control of the temperatures and redox conditions prevalent in the furnace interior. Inevitably, they faced some technological inefficiencies observed through losses in the slag of unreduced copper ore and metallic copper in form of prills yet the copper alloy artefacts found in their settlements testify to the successful production of finished objects. Several small piercing tools such as awls and drills, knife blades and jewelry that have been recovered during excavations were made of arsenical copper most probably produced locally (Nerantzis *et al.* 2016). These technological characteristics of copper production prevalent in Early Bronze Age Thasos show parallels to contemporary examples from the Cyclades and Crete where more intensive research has produced substantial results (Bassiakos and Catapotis 2006; Bassiakos and Philaniotou 2007; Georgakopoulou 2007; 2018). Future research and more experimental reconstructions are expected to provide further clues and explore alternative pathways for efficiently processing mineral ores and extracting metals to expand the study of Bronze Age metallurgy in the north Aegean.

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Metalworkers' Workshops at Gonur and the Bactria-Margiana Archaeological Complex (BMAC) Sites

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Abstract: The main purpose of the article is to characterize the metalworkers' workshop at Gonur Depe along with the other excavated workshops within the Bactria-Margiana Archaeological Complex (BMAC) and post BMAC territories.

The well-preserved Bronze Age workshop at Gonur Depe (now part of the Merv oasis, Turkmenistan) with its remains of various industrial rooms, kilns, moulds, and crucibles, is an ideal locale to study the copper and bronze technology of the area. This article will describe in detail not only the BMAC itself but also the industrial technique that flourished in the beginning of the 2nd millennium BC in its territory. In addition, the metallurgical workshop at the Dashli-3 Palace (Afghanistan: Northern Bactria), the settlement Sapalli culture, the metalworkers' workshops at Dzarkutan (Uzbekistan), and the metallurgical and metalworkers' workshop at the Tugai site situated in the Zeravshan cultural province of the Bactria-Margiana Civilization (Uzbekistan, Tajikistan) will also be discussed.

KEYWORDS CENTRAL ASIA · BRONZE AGE · OXUS CIVILIZATION/BMAC METALWORKERS' WORKSHOPS · CRUCIBLES · MOULDS.

Introduction.

The Bronze Age civilizations of the Aegean, like those of Turkmenistan and the Iranian Plateau, were not based on great rivers such as the Nile, the Tigris and Euphrates, or the Indus. The civilizations of Central Asia have been described as "oasis civilization". This, while not strictly accurate, does describe the pattern of intense centres of cultivation and settlement spread out and lying between arid lands of low population density. In the case of the Aegean, the urban or palatial centres were located on islands or near coasts and separated by the sea. So far as the analogy works, the seaways and the desert ways played comparable roles (Renfrew 2006).

At the end of the 20th/beginning of the 19th century BC, Egypt under Amenemhet II of the XIIth Dynasty, shows connections with both Crete and with Mesopotamia and, further, with the Iranian plateau and the Bactria-Margiana Archaeological Complex (BMAC) or "the Oxus Civilization" as demonstrated in the Töd Treasure (Figure 1), which contained among other precious materials, silver vases, raw blocks of lapis, an "oriental" lapis disk and lapis cylinder seals, one of which was engraved with a motif of the divinity of vegetation, similar to others found in Yahya, Shahdad and Gonur (Lyonnet 2005).

The main purpose of this article is to characterize the metalworkers' workshop at Gonur Depe and the workshops at the other excavated sites within the geographical limits of the BMAC and post BMAC territories.

Metalworkers' workshop at Gonur Depe (2300-1500 BC) (Turkmenistan)

According to the most recent interpretation by V. Sarianidi, the "xerothermic crisis" in the last centuries of the 3rd millennium BC forced tribes of agriculturists from the far West to leave their old sites, move in the eastward direction, and settle down along the tributaries of the ancient Murgad delta with its abundance of water. The first settlements of the newcomers were built along the edges of the Murgab delta and very soon small palaces and temples were built. In the northern section of the delta there appeared an independent irrigational oasis now called Kellily. At the same time the main city of the Margush country known as Gonur Depe was founded. Gonur (2300-1500 BC) had a strategically important position on the Murgab River. From here it was most convenient to distribute and control the water supply directed to the numerous northern sites (Figure 2).

The late V. Sarianidi had spent over 40 years of his life excavating this site, studying it thoroughly and trying to preserve it for the future generations (Sarianidi 2005; 2007; 2008).

During the autumn field season of 2005 on the north-western shore of the main southern pool of North Gonur, V.Sarianidi excavated an archaeological complex of 10-12 rooms that in his opinion were most likely used as workshops for producing copper and bronze objects for the needs of the royal palace. The room sizes (20-25 m^2 each) testify to the fact that they were linked to the Royal Palace. The industrial rooms contained a lot

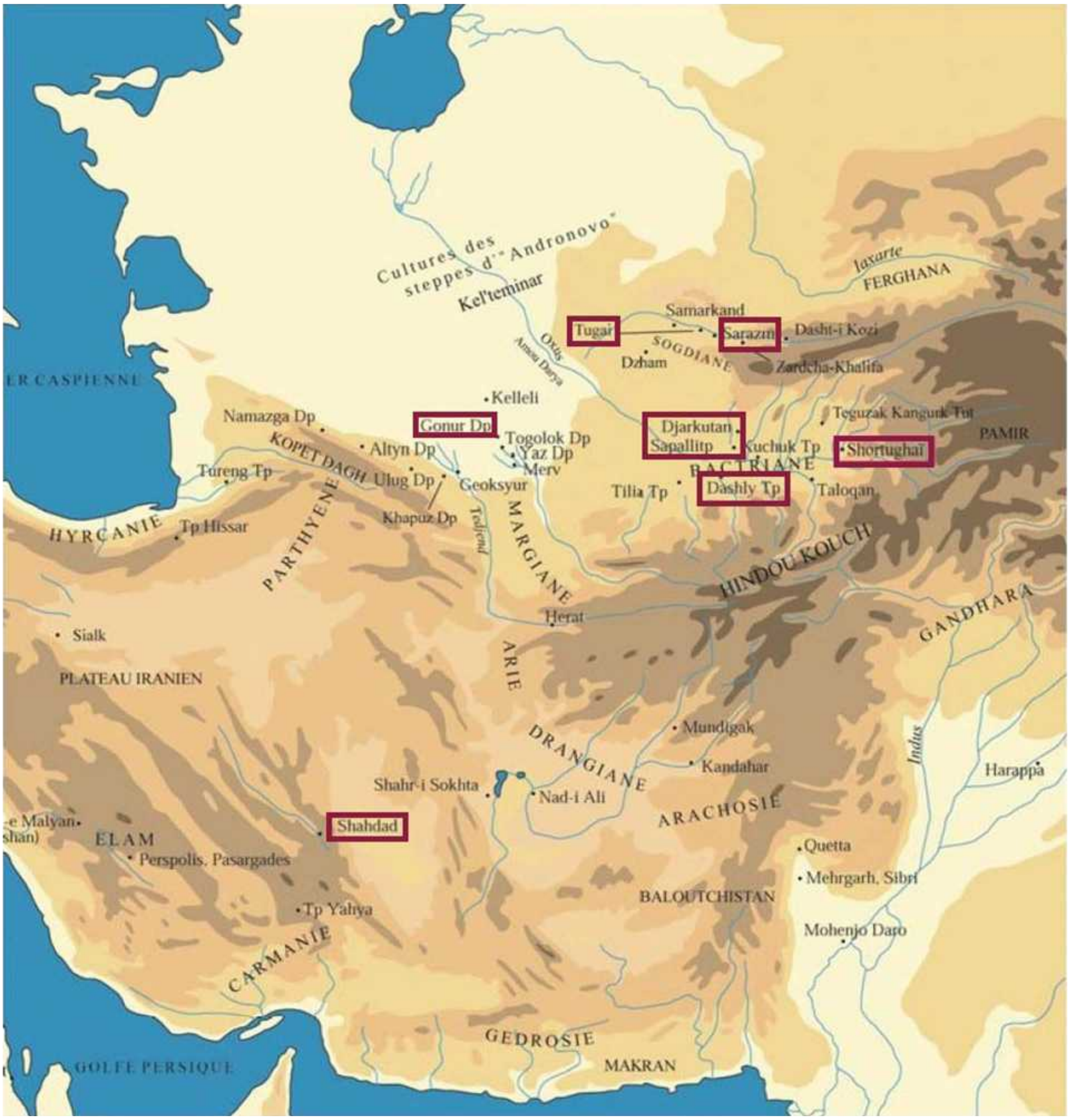

Figure 1. Map of the territories of the Oxus Civilization (from Francfort 2016: 461, Fig. 1a)

of molding forms and fragments from bronze objects (Sarianidi and Dubova 2006).

Radiocarbon analysis of three charcoal samples from rooms 108, 109 and 112 showed a wide range of dates between *c.*2150 and 1430 BC. The last date was corrected by the method of combined version to *c.*1780-1678 BC (Dubova 2008; Zaytseva *et al.* 2008)

In the spring of 2006, the author of this article conducted excavations in this area (Area 9). Alongside the excavations the archaeometallurgical materials from the simultaneously excavated areas (Area 13 and Area15), those of earlier excavated ones, and materials from old field museums, were also investigated.

The earlier excavated rooms 107, 108, 109, 112 and 119 of Area 9 were cleaned again, this time more thoroughly and studied further. It should be noted that by the time of my visit these rooms and the archaeometallurgical constructions inside of them were already considerably washed away. Some finds had been given to museums and I had no chance to see them.

More rooms were found to the south, west and north-west of the industrial rooms that had been excavated

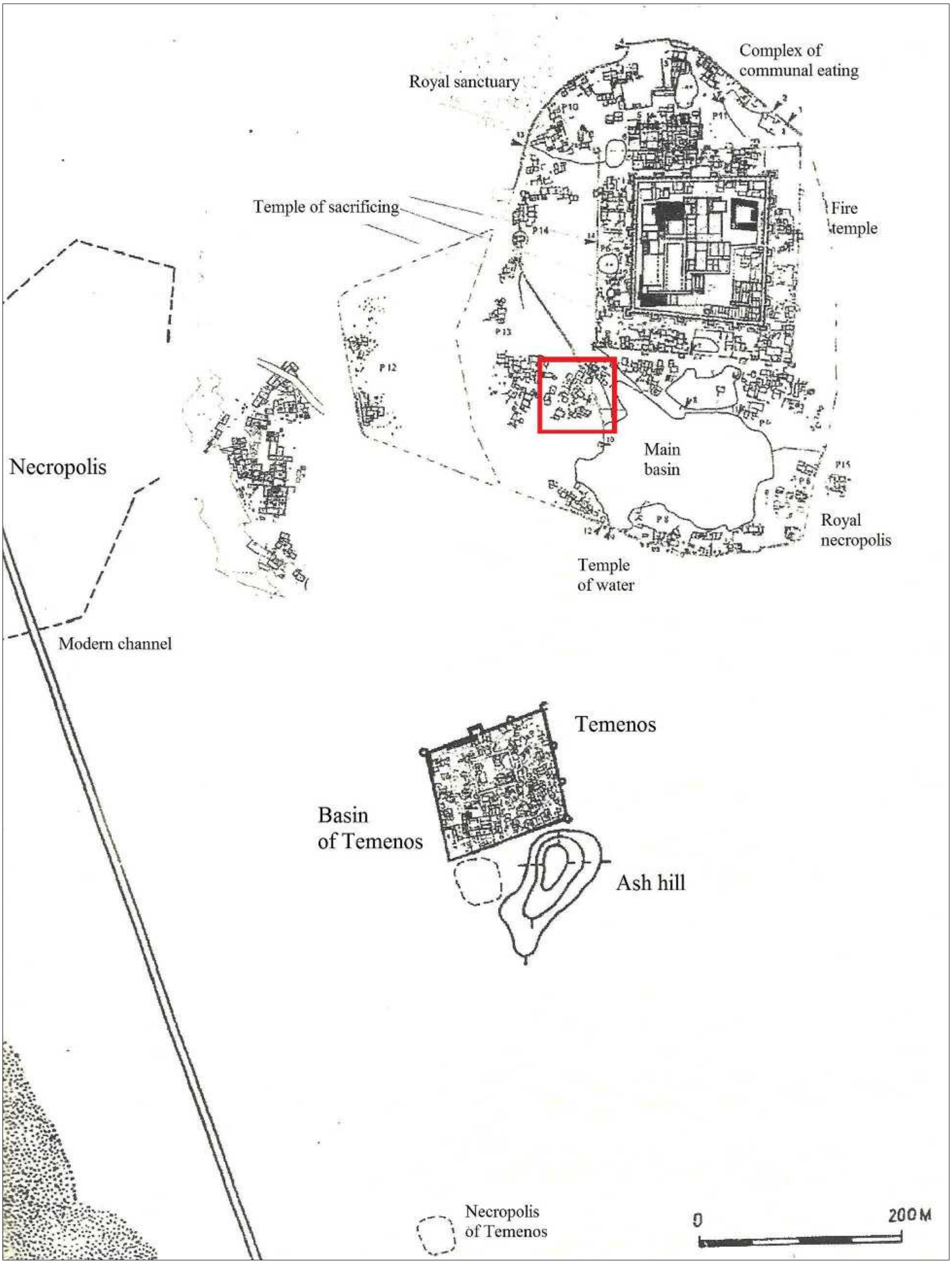

Figure 2. Map of Gonour Depe showing the location of metalworkers' workshop (Area 9)

earlier. The fragments of crucibles and moulds from rooms 111, 117, 118, 121, 122, 123, 126, 130, 131, 132, 141 and 147 make it possible to define their use as industrial.

In general, the architectural complex of Area 9 includes about 150 rooms that are almost sub-square, sub-rectangular, and trapezoid form in plan. The first rooms of this architectural complex were excavated on the northeastern shore of the main pool of North Gonur. The second half of the complex is located on the northwestern shore and it was here where the waste products of metallurgical activity were found in the rooms starting with room 107 and up to 147. Moreover, the waste products were found in all the rooms (Figure 3).

As already been mentioned at the beginning of this article room 147 was most probably the main ritual space of the entire industrial complex. It was not by chance

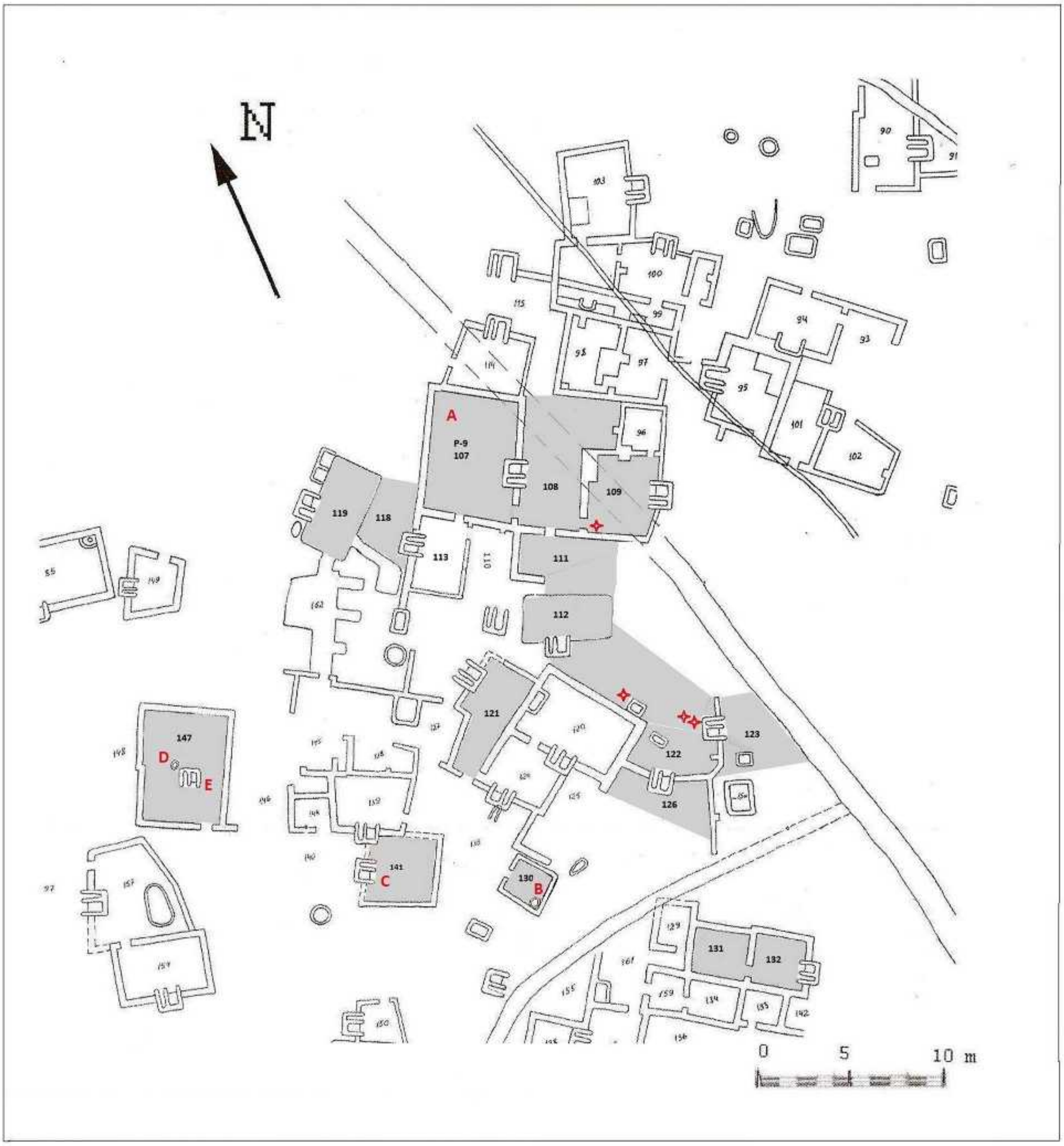

Figure 3. Gonur Depe. The plan of the excavation area 9. Industrial rooms are painted grey:
A - main kiln for secondary melting; B - smith's kiln; C - smith's kiln; D - industrial kiln; E - double-chambered cult furnace/hearth; + the ground kilns for secondary melting in crucibles.

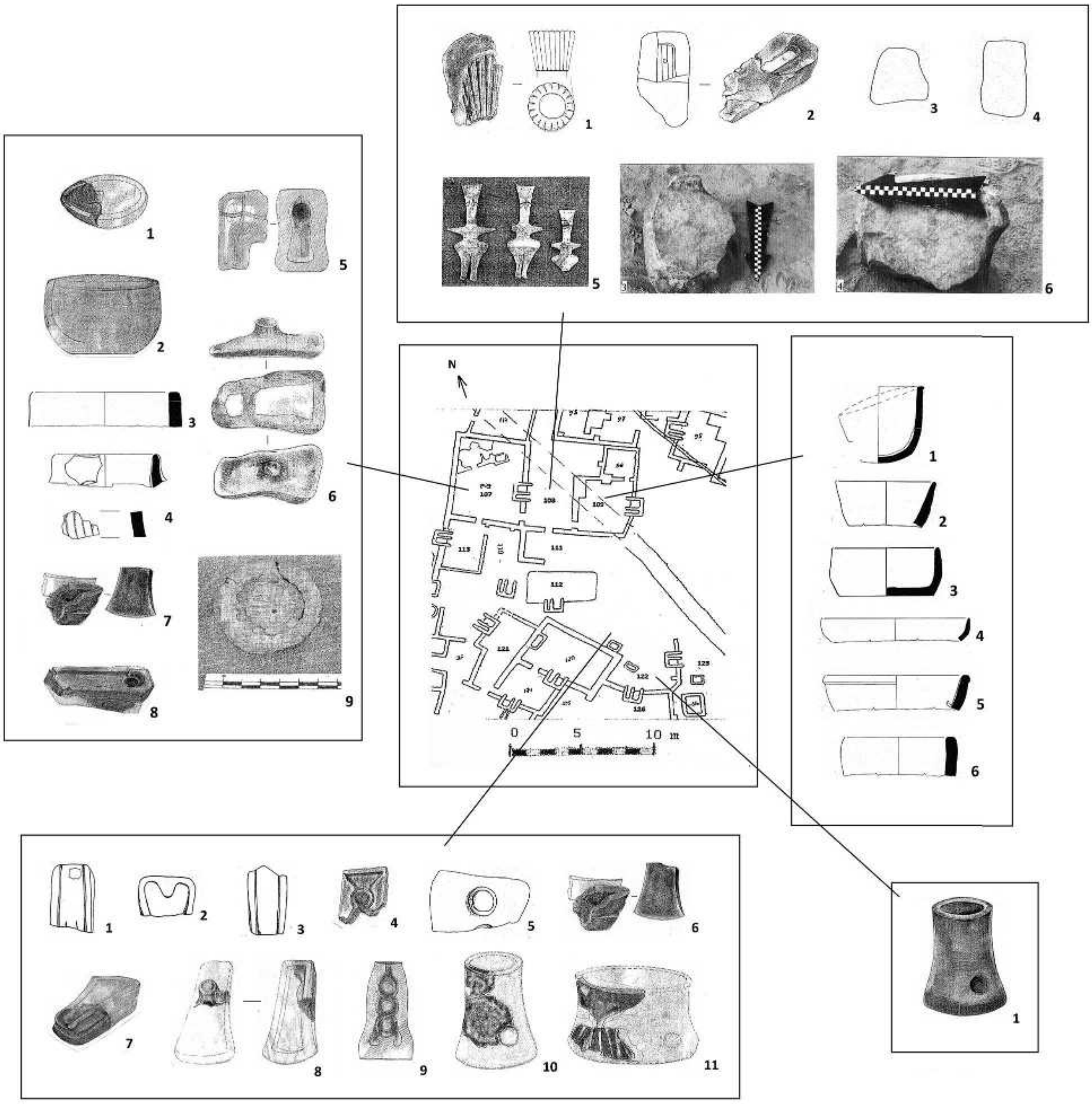

Figure 4. Gonur Depe. The plan of the late metalworkers' workshop and main finds from rooms.

that the industrial kiln was located in the direct vicinity of the ritual hearth. The room was obviously used for magic rituals that were believed to help metalworkers obtain the initial sacred fire for the future good results of the metal process (Papachristou 2016).

In general, the sizes of industrial constructions, the manufacturing inventory, and the industrial wastes in the rooms testify to the fact that initially the workshop was rather large. But later on, it seems that the workshop was diminished, and only rooms 107, 108, 109, 111 and 122 continued to function. This explains why mass finds were excavated *in situ* only in these rooms (Figure 4).

One certainly has to take into consideration the fact that the south-western part of the industrial complex was largely destroyed by the grave pits as well by the later ceramic furnaces and the western outlet of the later canal. Still, based on the difference of paste used for a small crucible from room 147 and the crucibles from rooms 107, 108, 111 and 122; the stone mould from room 131 and the ceramic moulds from rooms 107-122, we get the impression that the stratigraphy of the south-western part of the complex was much more ancient.

When, during the autumn season of 2005, V.Sarianidi and N. Dubova excavated the workshop, they decided that it was most likely a workshop for producing copper and bronze objects for the needs of the Royal Palace. If they are right, then the destruction of the workshop can be logically explained by the fire in the Kremlin, which according to radiocarbon studies occurred in *c.*1995-1744 BC. At the same time, we cannot reconstruct the metalworkers' activity at Gonur Depe since similar data are available at excavation Areas 13, 15, and 16. Recently the same information came from the western area of the "Royal Necropolis" (the so called "accumulation of stones of various sizes including large ones, ceramic shards, crucibles and other objects") but this has not yet been fully investigated (Sarianidi and Dubova 2014). The situation will clear up only when we assemble "all parts of the puzzle".

Workshop at Dashli-3 (3rd quarter of the 2nd millennium BC): Northen Bactria (Afghanistan).

The excavations of the north-eastern wall (façade) in a neglected room (in the secondary use) of the palace showed a burnt layer with traces of spilled metal. According to Sarianidi, the find of a clay half-spherical ladle-crucible with a massive handle-pivot with traces of baked malachite testifies to the fact that a kiln was located here. The clay used for a crucible had a lot of adobe, and metal remains of a kiln charge were found in it. In the courtyard of the same archaeological site, in room 51, was found a kiln consisting of two parts. On the floor of the room were found some remains of spilled metal and a clay mould for casting an axe-chopper (Sarianidi 1977).

Sapalli culture

The Sapalli Culture is the Southern Uzbek variant of the Late Bronze Age Namazga VI complex. It was a culture of sedentary farmers who settled along the tributaries of the Surkhandarya River. In the archaeological literature, this region is also referred to as Northern Bactria. Presently five sites are known, and these have been studied since the 1960s. The eponymous site of Sapallitepe and that of Dzarkutan were investigated by the Archaeological Institute of the Uzbek Academy of Science under the direction of A. Askarov. At the latter site, the German Archaeological Institute was active between 1994 and 2003. The Institute of Art Historical Research worked at Mollalitepe. A large necropolis in Bustan is currently being excavated by N. Avanesova (University of Samarkand). Tilla Bulak is the most recently discovered Sapalli site. Furthermore, surface finds were made near Denau and in the Zerafshan Valley. With regard to Sapalli material culture, it is evident that close relations existed with both Western Tajikistan (Tandyrjul) and Northern Afghanistan (the oasis of Dashly).

Settlement of Sapalli (1700-beginning of 1500 BC) (Uzbekistan)

A square room 52 with an area of 6.5 m2 was excavated at Sapalli. In the south-eastern corner of Quarter III, a metal workshop was found with three small round hearths in a row. One hearth was divided in two parts with a thin brick partition, and the other contained a broken jug. The walls of the hearths were strongly slagged with a dirty-green colour. On their bottoms the regulars with green oxides were found. Seven niches and a hearth-fireplace were excavated in this room also.

The similar small round hearth with a smooth slagged bottom with metal remains was excavated in the south-eastern corner of room 104. Rectangular small hearths for metal melting were found in the north-eastern corner of room 39 and the south-western corner of the room 105. All this indicates the functioning of metallurgical workshops on the settlement.

Metalworkers' workshops at Dzarkutan (14th-9th cc. BC)

Dzarkutan 1 or Dzarkutan is one of the largest monuments in the Bronze Age of the proto-urban civilization of a capital type. Thanks to its considerable sizes it stands out among the other settlements of Central Asia. It is located 60 km to the north of Termez, on the left bank of the Bustansai River, which was once the tributary of the river Amu Darya. Sh.Pidaev and V.Pilipko found it in 1973. This was the same year that the archaeological excavation of the Institute of Archaeology of the Uzbekistan Academy of Sciences (directed by A. Askarov) started. In 1995-2000 the excavations were continued by an Uzbek-German joint team directed by T.Shirinov and D. Huff (Askarov 1975; 1977; Askarov and Shirinov 1993; Shirinov 2000; Huff and Shaydullaev 1999). The archaeological study of the monument is still in process (Mustafakulov at al., 2016; Bendezu-Sarmiento and Lhuillier 2019).

The remains of some separate large settlements, a "citadel", a palace, a temple and other structures, as well as a Necropolis are very well traced on separate hills densely located over the whole site.The temple is situated on the highest south-eastern part of Dzarkutan, whilst the palace is on the opposite side, on the far north-western part of the monuments.

According to archaeological material, the Palace of Dzarkutan was built in the Dzarkutan times (middle of the 2nd millennium BC). It was abandoned in the 10th-9th cc. BC. Long narrow trenches with coating of slagged metal were excavated in the palace courtyard. They were dug into the earth and served as primitive constructions for metal melting (Askarov and Shirinov 1993).

The Dzarkutan's Temple, rectangular in a plan (44.5 x 60 m^2), is oriented in accordance with the parts of the world and encircled by a mighty wall 4.5 m thick. It was built in the early stage of the Dzarkutan era, not earlier than the 14th c. BC. It was presumably abandoned during the Bustan stage of the Molali period (10th c. BC). Archaeological materials from the complex show that during the period of its existence the temple had three chronological stages that left its main planning structure unchanged. Additional excavations revealed nine round bastions on the western, northern, and eastern surfaces of the temple. The western and eastern surfaces were in a mirror-image position, each of them having two bastions located between corner towers.

The metalworkers' workshop was located in one of the temple rooms (Room 8) and functioned during the second and third constructional periods (Figure 5). The excavations brought to light the remains of 8 square metal melting kilns located on a platform ("sufa") made along the eastern wall of the room. The bottoms of the kilns had a half-spherical shape, and in their centre were strongly fired. In one metal melting kiln was a round piece of melted bronze 2 kg of weight and strongly oxidized. In the same room four crucibles for metal melting were found—one of them was intact. On the crucible bottom tiny spots of metal can be seen.

According to V. Ruzanov, these crucibles of a "shoe" type were made by hand of fireproof light colored clay (Ruzanov 2013). Also, according to A. Askarov and T. Shirinov in the central hall of the temple (Room 5) there were found several fragments of thin rods 3-7 cm long as well as a small metal drop.

A. Askarov and T. Shirinov suggest that the eight furnaces for metal melting were not all simultaneously used (Room 8), and that "probably one of them was really used for metal melting whilst most of them served for cooking ritual meals" (1993).

Based on the analysis of the archaeological material from Dzarkutan the scientists came to the conclusion that the discovery of a large number of metal objects and working tools for metallurgy (such as anvils, clappers, small axes, and others) testify to the development of metallurgical trade. The absence of slags or ores at Dzarkutan allows us to speak of metal processing only. It seems likely that metal slags, semi-finished products, and used objects were brought to the settlement for secondary production. At the time, the tradition of burying the dead in the company of metal votive spears (symbols of wealth) and implements of production was spreading more and more widely. All burial rituals including the production of votive objects took place in the temple. Probably, the production of weapons and tools as well as rods and seals was controlled by the palace rulers (Askarov and Shirinov 1993).

Zeravshan cultural province of the Bactria-Margiana Civilization (2nd millennium BC) (Uzbekistan, Tadjikistan)

The territory of the Zeravshan basin was formed under the influence of natural factors and became one of the most important areas of Central Asia in antiquity. Rich copper and multimetal deposits as well as beds of cassiterite and gold contributed significantly the development of metallurgy and metal processing.

In the territory of Zeravshan during the paleometal period several local cultural and chronological groups of monuments of various economic orientations were created, the most dynamic among them being those that combined agriculture and cattle-breeding. The most significant was the Sarazm cultural complex that developed on the basis of a complex agricultural and cattle-breeding economy, which was linked to metallurgy. Also of great interest are the specialized economic complexes of the mining and metallurgical industrial areas (aimed at using local natural resources) with elements of settled cattle-breeding (settlements of Tugai, Medomi, Aktashti and etc.). Here one should also point out the industrial areas directly connected with metal deposits that were used by the Andronovo tribes: Karnab, Aiiakkuduk, Basoichanek, Aauminzatau, Moushiston, and others (Avanesova 2010a, b; 2015).

The proto-Andronovo settlement of Tugai (*c.*2240/1960 BC) found in 1986 on the north-eastern outskirts of the site with the same name, and 18 km to the east of Samarkand, can serve as a good example of a regional metal production centre of the Bronze Age. The settlement belongs to the circle of specialized industrial complexes of miners-metallurgists, and its materials demonstrate the synthesis of several cultural traditions. All structures under investigation are divided into two groups: one of a management and every-day character, and the other of an industrial character with remains of metallurgical production. The slight thickness of the archaeological deposits is certainly evidence that this was a seasonal monument.

To the west of the residential structure a kiln was found with a pit-well. On the same line was a fire conducting canal. Here also were found copper drops and fragments of crucibles with slagged walls (Figure 7, 15). Similar metallurgical structures with industrial traces were found in the Sintashta culture as well (Avanesova 2015).

The materials from the burials of Snab, Zardcha, Khalif, Sazagansai old river, and the Tugai settlement, along with separate finds from the Kyzil Kum desert, enable

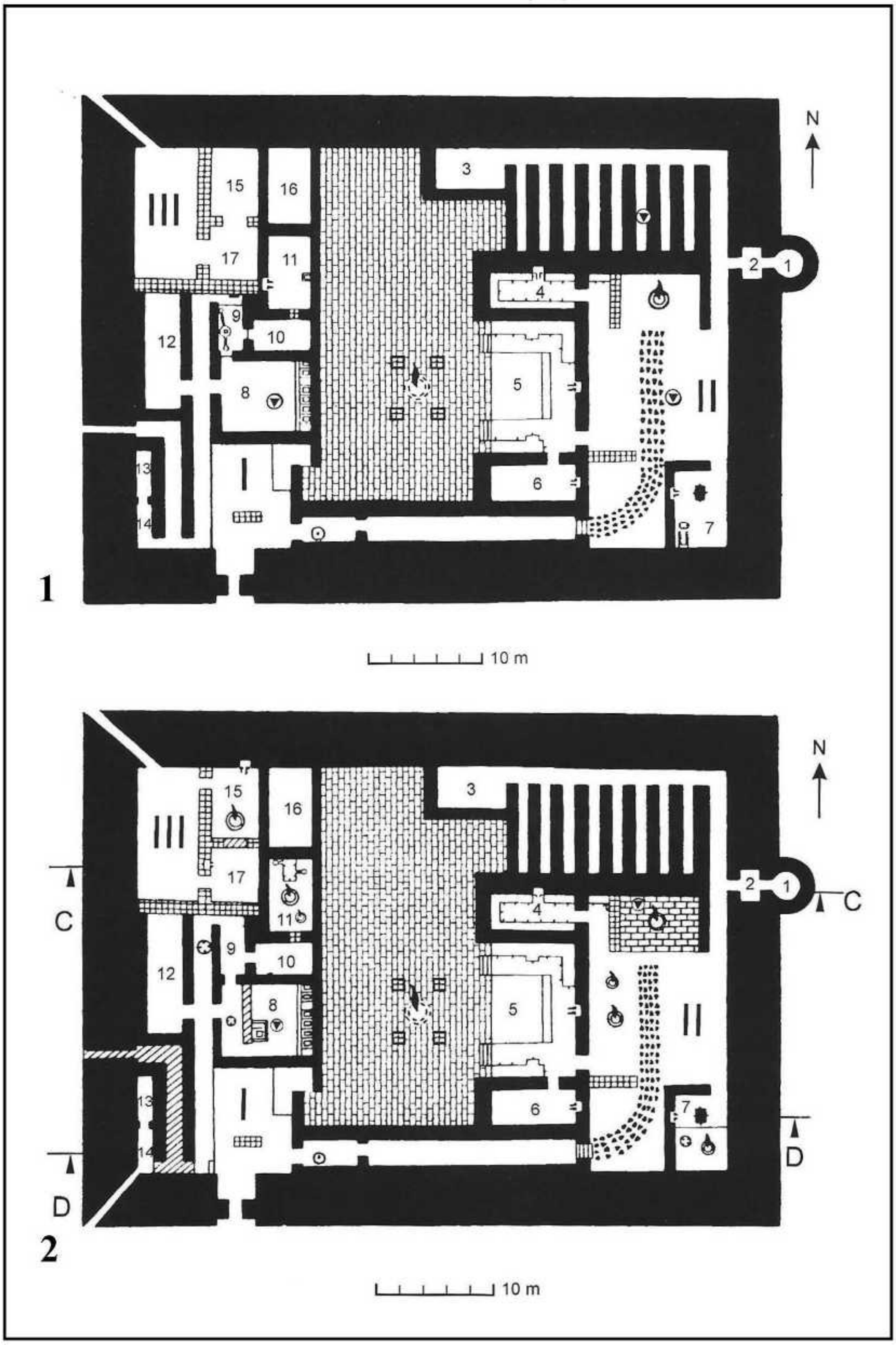

Figure 5. Dzarkutan. The Temple (from Širinov 2003: 36-37):
1- plan of the second constructional period.
2- plan of the third constructional period.

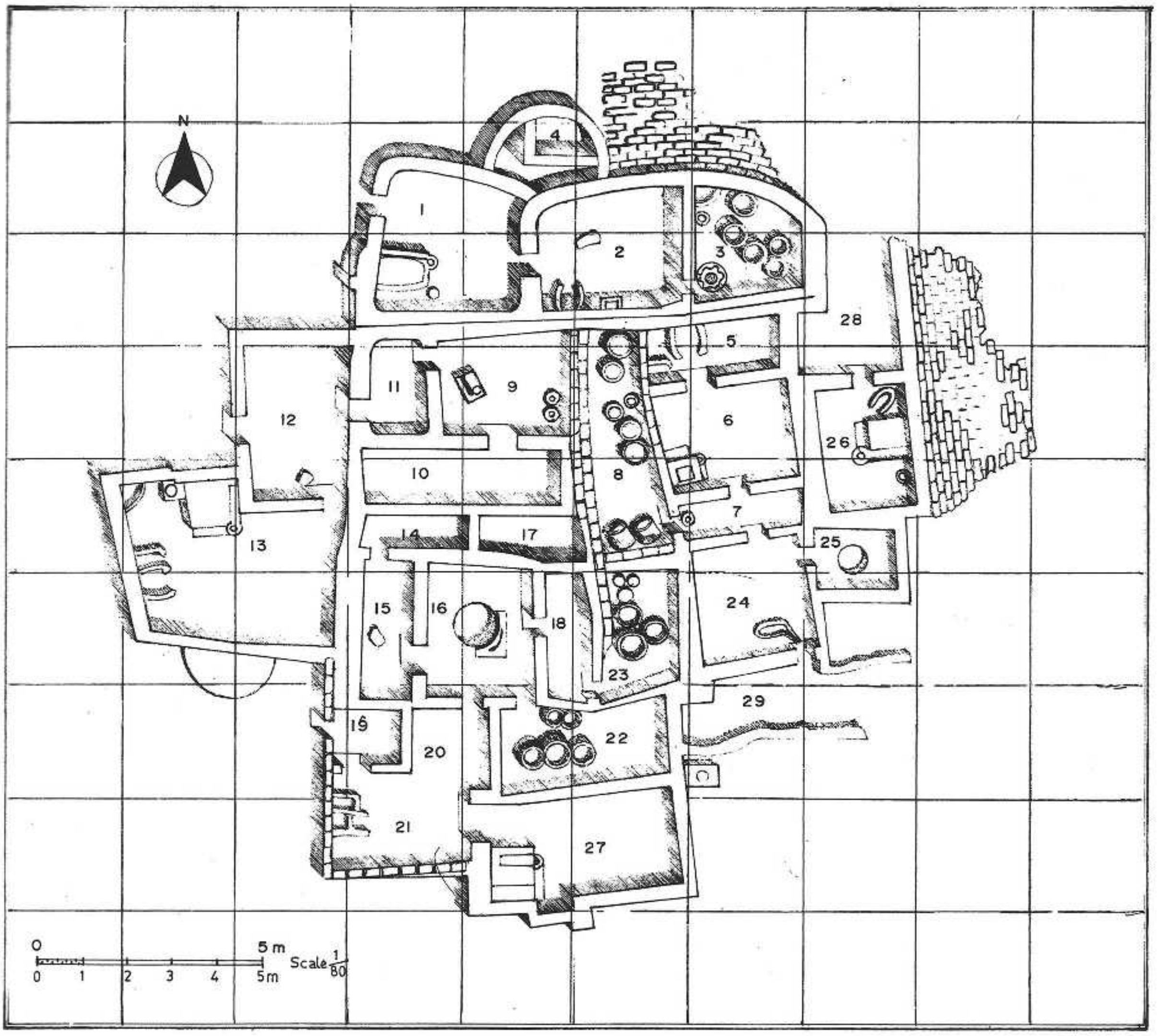

Figure 6. The plan of the Metalworkers' Quarter at Shahdad (Iran) (from Hakemi 1997: 90, fig. 54)

us to state that the Zeravshan basin was part of the zone of the Sintashta-Petrovka expansion in obvious need of metals. This idea becomes more convincing if one thinks that tribes of the Petrovka culture had reached the south of Central Asia, all they way down to the Amu Darya River as testified by the material remains of the early stage of the Sapalli culture (Avanesova 2015).

It is worth mentioning the burial of a woman "metallurgist" (19th-18th cc. BC) in the region of the old river Sazagansai (26 km to the south-west from Samarkand) (Avanesova 2010b).

Discussion

It should be noted that already in the beginning of the 2nd millennium BC large workshops in the territory of the BMAC are found in capitals of proto-urban centers. The capital Gonur is a good example of this. Though archaeological excavations at the settlements are still in progress, even at this stage one is surprised by the quantity of the industrial metal products already found.

The workshop at Gonur Depe has already been compared to the well-known metalworkers' quarter at Shahdad (Papachristou 2016). No doubt, the metalworkers' quarter at Shahdad, located on the south Dasht-i-Lout in Iran, is the best example of industrial metal production in the whole of the Middle East (Hakemi 1997). It dates back to the second half of the 3rd millennium BC. The complex is represented by the remains of 30 small rooms that once made up five large and similar workshops (Figure 6). It has been suggested that the metallurgical industry at Shahdad was based on ore processing. In the territory of the BMAC at large settlements of a capital type no fragments of ore have been found.

In 2006, while investigating the *temenos* ("a sacred area") in the territory of South Gonur, a stone fragment in the shape of a boat with a hole in the centre was found in an old field museum. The stone was initially thought to be a fragment of extremely-rich copper ore (Papachristou 2010). However, the mineralogical investigation of the sample conducted by Dr G. Ikonomou (Director of the Department of "Orictology and Petrography" of the Institute of Geology and Prospecting of minerals [I.G.M.E.] in Athens), showed the presence of crystals of Feldspar, Magnetite, Titanium-Magnetite, Pyroxene, Celadonite, and Quartz (Ikonomou and Papachristou 2019).

Each of the five workshops of Shahdad had one so-called "main kiln" in it. V.Pigott tried to reconstruct the main kilns in Shahdad using a kiln from room 6 as a model. The reconstruction can be described as following: 1) the platform was made only of clay; 2) on the upper part of the kiln was a quadrangular construction-metal smelting firebox (perhaps a tray for charcoal); 3) on the perimeter the kiln was laid with bricks; 4) in the right corner of the construction was an opening that led to sloping trench used for circulation of molten metal; 5) the sloping trench reached the floor of the room and ended in a conical crucible set on the floor; and 6) the trench was covered all along its way from the firebox to the crucible (1999a, b). It should be added that, according to Hakemi, when the crucible set on the floor was full, the trench for metal drainage was closed with a ceramic plug, probably for changing crucibles.

Based on the description of a main kiln from room 107 in the metalworkers' workshop at Gonur Depe made by N.Dubova, we can suggest that at a certain stage of its existence an earthen trapezoid platform was raised in the north-western corner of the room. Along the perimeter of the platform strongly burnt cake-shape raw bricks were placed. On the top of the platform three clay constructions were built, two of which had a quadrangular shape of 30x30 cm and 15-20 cm height. Each of these constructions had a crucible inside with an opening on one side (probably for the drainage of metal). From one of the described crucibles, a trench 70 cm long with small metal drops and balls (copper-bronze) inside of it was coming out (Dubova 2008).

The comparison of kilns shows that, on a whole, they were rather similar (e.g. they all had trenches for metal drainage). But at Gonur Depe we can speak of an improved variant since the kiln there was larger and on its surface two fire boxes instead of one were made. Inside the fireboxes crucibles were placed and the metal from them was supposed to drain down to another crucible that (similar to Shahdad) had to be made in the floor (?). In the workshop of the Temple at Dzakutan there 8 such fireboxes were found, but without a metal drainage trench. At the same time, such trenches filled with metal or slagged metal clining were found in the workshop in the courtyard of the Palace of Dzarkutan.

The finds from the workshop at Gonur Depe contain ceramic artifacts which most probably served as plugs analogous to the finds from the metalworkers' quarter of Shahdad.

From a technical point of view, it is difficult to explain the construction of the main kilns at Shahdad and at Gonur Depe. Their big sizes presuppose the great waste of energy. It would be impossible to achieve in them even heating and uniform atmosphere. The trenches for the metal drainage with crucibles under them are rather long. The metal would have started cooling and thickening already on its way. The metal usually smelts before it is poured it into moulds. It should be heated much above 1083°C so that it would not cool down quickly, would not be too viscous inside the mould, and would fill it up correctly. It is difficult to imagine how metal was drained along the trench from one crucible to another or from a firebox into a crucible. Nevertheless, such fireboxes and trenches with metal lining have been found in three archaeological sites: Shahdad, Gonur Depe and Dzarkutan.

Among constructions excavated at the metalworkers' quarter at Shahdad A. Hakemi points out that in addition to the main kilns, small kilns for secondary production were set up on the floors. The metalworkers' workshop at Gonur Depe (rooms 109, 111 and 122) also contained kilns located right on the floor. Unfortunately, these cannot be reconstructed. Large numbers of crucibles and molds were found next to their remains. In fact, the crucibles in these kilns could have been used for the additional purification of metal, and for adding an alloying component suitable for the specific type of product that they produced

The many variants of crucibles from Gonur Depe can be divided into two main types: 1) Various sizes of cup-shaped crucibles with spouts (Figure 7, 16). This type is characteristic of industrial materials from Shahdad (Figure 7, 12-14). In the BMAC territory they were excavated at the Tugai settlement (Figure 7, 15). According to V.Pigott, their shape better suits the dilution and pouring the diluted metal, not metal smelting (1999a, b).

2) Various forms and sizes of crucibles with a hole in the lower part of a vessel. These types of crucibles were

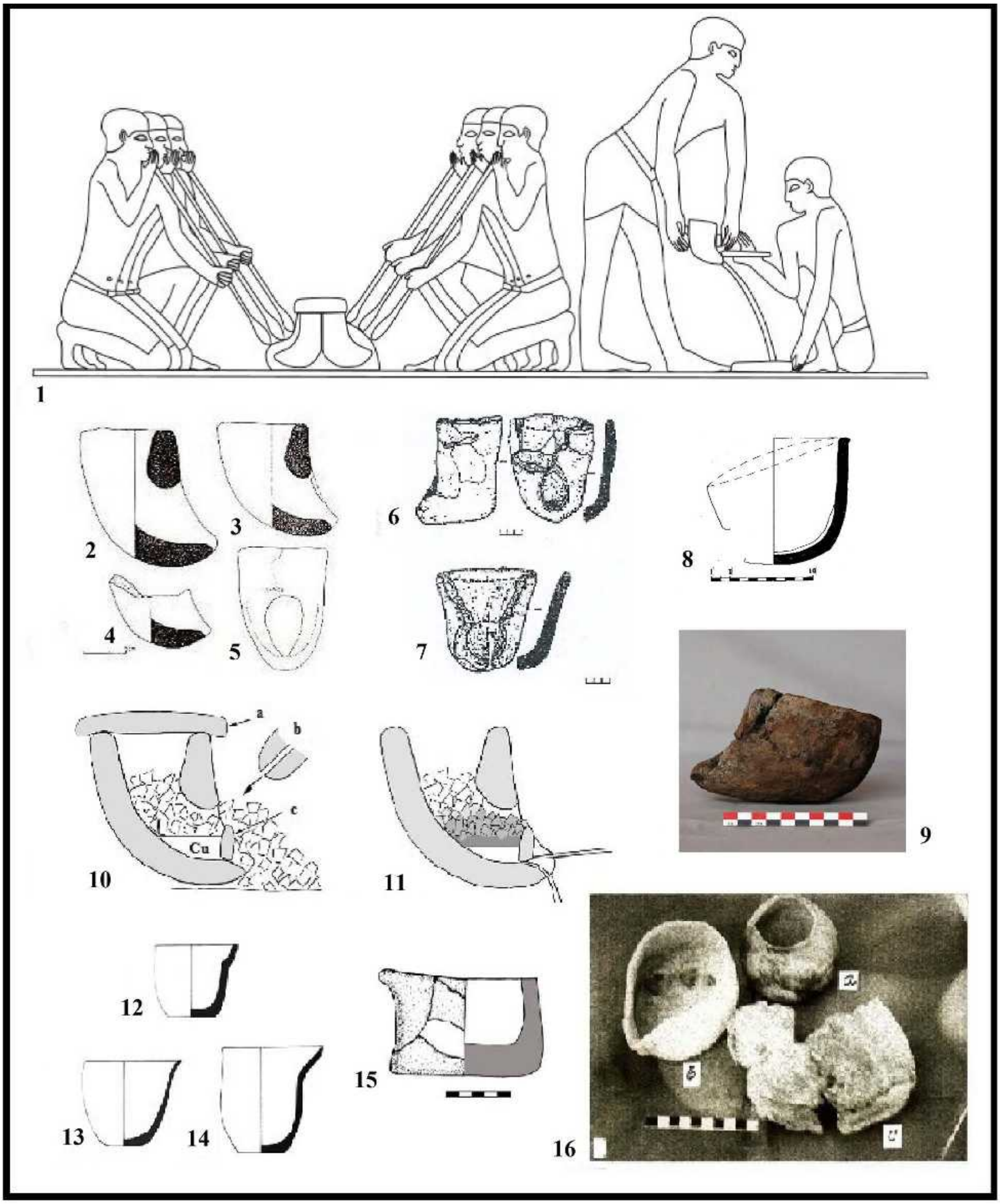

Figure 7. Metalworkers depicted in the reliefs in the tomb of Mereruca,
Saqqara (from Davey 1983: 170, fig. 1); 2-5. Crucibles from Tell edh-Dhiba'i (Irak) (from Davey. 1983: 172, fig. 2); 6-7.Crucibles from Dzarkutan (Uzbekistan) (from Ruzanov 2013: 205, fig. 176, 13-14); 8. Crucible from room 109 of area 9 of Gonour Depe (Turkmenistan) (from Papachristou 2016: 321, fig. 2, 3); 9. Crucible from Elkab (Egypt) (from Clae and Huyge 2016: 41); 10-11. Suggested sections of the crucible during melting and pouring (from Davey 2018: 497, fig. 33.4); 12-14. Crucibles from Shahdad (Iran) (from Hakemi 1997: 707, Vm. 1, Vm. 4, Vm. 3); 15. Crucible from settlement Tugai (Uzbekistan) (from Avanesova, 2015: 54, fig. 6, 5-6); 16. Crucibles from room 114 of area 13 of Gonur Depe (Turkmenistan) (from Papachristou 2010: 277, fig.6, 2).

found among the museum materials and originate from a metalworkers' workshop at Tell edh Dhiba'I (Figure 7, 2-5) that was located at the outskirts of modern Bagdad. The workshop was demolished in the first quarter of the 2nd millennium BC (Davey 1983; 1988). Similar crucibles were excavated at Elkab (Clae and Huyge 2016) in the Nile Valley in Egypt (Figure 7, 9), at Serabit el-Khadim in Synai, and in Tell el-Qitar in northern Syria (Davey and Edwards 2007; Davey 2012; 2018). They are also found among the materials from the Gonur workshop (Figure 7, 8) (Papachristou 2008; 2016) as well as in the workshop of the Dzarkutan Temple (Figures 7, 6-7) (Ruzanov 2013).

Chr. Davey studied the crucibles and other industrial materials from the workshop of Tell edh Dhiba'i and compared them with the images from mastaba of the Mereruka tomb at Saqqara, Sixth Dynasty (*c.*2400 BC) (Figure 7, 1). He argued that the crucibles depicted on the walls of some Egyptian Old Kingdom tombs and others found at the Isin-Larsa period site of Tell edh-Dhiba'i, were originally created to be used as refining vessels (2018). The moulds are best preserved in the metalworkers' workshops of Gonur (Papachristou 2010). The peaceful character of the manufactured products from this workshop is noteworthy (Figure 8).

Within the BMAC and post-BMAC territories metallurgical workshops with all their industrial attributes are better represented in two proto-urban centers: Gonur Depe and Dzarkutan. In both centers, the metalworkers' activities were clearly connected only with metal processing and not with metallurgy and metal processing. The metal processing kilns (melting) were based on some imported semi-products for commercial purposes. In the metalworkers' workshop of the Dzarkutan Temple one of fire boxes contained a fragment of an oxided metal of 2 kg weight (possibly an oxide ingot or "black copper).

Conclusion

The Bactria-Margiana Archaeological Complex or "Oxus Civilization" has unique architecture, an exceptionally

Figure 8. Gonour Depe. The moulds.

rich material culture, and maintained contacts with Mesopotamia, the Indus Valley, and the Iranian Plateau (Lamberg-Karlovsky 2013; Sarianidi and Dubova 2013).

The analysis of the main kilns and crucibles from the metalworkers' workshop at Gonur of the Sapalli culture, shows the presence of two metalworkers' traditions: Iranian and Egyptian-Mesopotamian. Specific objects related to this culture have also been recorded in neighboring areas (Zeravshan valley, Ferghana valley, Indo-Pakistani area, Gorgan plain, Arabianpeninsula, etc.). At that time, along with the long distance trade, the Sapalli experienced increasing proto-urban development, social stratification, task specialization, territorial expansion, and homogenization. Populations lived in mud-bricks or adobe houses in settlements of varying sizes. Monumental architecture, specific burial practices as well as prestigious and luxurious goods reflect a hierarchical society that was possibly organized as proto-state. Numerous aspects linked to the exploitation of natural resources have been intensively studied and others need further research (see: Salvatori 2016; Luneau, 2019; Lyonnet and Dubova 2021).

A very large series of metal artifacts of the Gonur Depe and Sapalli culture were analytically studied (Sarianidi *et al.* 1977; Terekhova 1990; Gibert and Killik 1994; Wertman and Dubova 2014; Kraus 2016; Kaniuth 2006; Ruzanov 2010; 2013). The latest studies show the presence of a rather large quantity of various types of copper-based alloys. This topic is very extensive and will be discussed in another article.

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Early Perforated Aegean Furnaces: Archaeological and Archaeometrical Evidence from the Acropolis (Athens) South Slope

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Abstract: The use of perforated clay vessels of various shapes for pyrotechnological activities was frequent in the early communities of the Aegean as evidenced by archaeological data. Metal production by smelting secondary/oxidized ores in perforated clay furnaces was part of this practice. The related findings from the Final Neolithic sites include mostly body-sherds (constituting the 'cylindrical' walls of these perforated furnaces) that were intentionally broken after their use. These sherds present almost always the same characteristics: intense firing and thickness of the walls *c.*1.0-2.5 cm, perforations with 1.5-2.0 cm diameter, and a distance between the perforations *c.*2.00-4.00 cm. Frequently on their concave interior surfaces a thin vitrification layer is visible. This may host traces or nodules of slag. Metallurgical furnaces with these characteristics were identified for the first time in the Cyclades and Crete at the end of the 1990s, and published a few years later (2005-2007). After systematic analyses of the findings (measurements, clay analyses, and model construction), the reconstruction of a perforated furnace was achieved and demonstrated by experimental simulations under prehistoric conditions. This reconstruction showed that the furnaces were highly efficient in producing copper from secondary ores (malachite etc.).

Until recently, this type of metallurgical furnace was identified in eight sites, one in Attica, six in the Cyclades, and one in Chrysokamino, eastern Crete. This paper presents some new archaeological and archaeometallurgical insights as a result of the study and the archaeometrical analyses of the ceramic material from the southern slope of the Athenian Acropolis. This material came to light during the excavations held by D. Levi and the Italian Archaeological School in Athens in 1922, and provides important evidence for the prehistoric settlement in the area. Recent archaeological research has shown that the findings of the excavation date from the Middle to the Final Neolithic (Dimitriou 2016). Among them stands out a particular group of pottery that seems to have had a different use than the one Levi mentions in his publication. These are perforated sherds with the same dimensions and features as the ones mentioned above. Their technological examination leads to the conclusion that they are also fragments of clay perforated furnace used for metallurgical activities. The analytical studies, still in process, in relation to the results of the archaeometric analyses have shown that the corresponding metallurgical process was related to copper production.

KEYWORDS: COPPER SMELTING, FINAL NEOLITHIC, ACROPOLIS, PERFORATED FURNACES, ARCHAEOMETRIC ANALYSES

Introduction

The intensification of copper production in the Aegean, as shown by archaeological evidence and archaeometric analyses, began from the Final Neolithic period. This evidence comes mostly from sites on the Aegean islands: in the Cyclades, at Kephala (Figure 1),[1] Paoura[2] and Ag. Eirini on Kea;[3] in the Dodecanese at Yali in Nisiros;[4] and on Crete at Kephala Petras.[5] At present, evidence for cooper metallurgical activities during the Final Neolithic on the Greek mainland comes from Sitagroi in Macedonia.[6] From the technological point of view, the process of copper production from the smelting of secondary/oxidized ores' included the use of crucibles or perforated furnaces. The use of perforated furnaces began in the FN (Kephala) and continued (or is encountered) almost until EBA III in the Aegean, and more specifically at the sites of Kephala[7] (Early Cycladic I/EC II) and Avessalos[8] (EC) in Seriphos, Sideri and Palaiopyrgos-Aspra Spitia[9] (EC) in Kythnos, Chrysokamino[10] (Early Minoan III-Middle Minoan IA) in Crete, and at the settlement of Raphina[11] (Early Helladic

[1] Coleman 1977, 113-114
[2] Coleman 1977, 108; 157-158
[3] Caskey 1972, 360; A47
[4] Maxwell-Liritzis *et al.* 2019, 1-30
[5] Papadatos 2007, 155
[6] Muhly 2002, 77-82
[7] Philaniotou *et al.* 2011, 159
[8] Georgakopoulou 2005, 1It
[9] Bassiakos, Philaniotou 2007, 19-56
[10] Betancourt 2006, 109-123
[11] Theocharis 1952, 77-92

II) in Attica. Some fragments from Fournoi (EC I /EC II) on Seriphos and from Skali (EC) on Siphnos do not have perforations. This type of early cylindrical/truncated cone, perforated furnace is not known outside the Aegean.[12]

The perforated furnaces: characteristics and function

At the FN and EBA sites mentioned above findings related to the furnaces consist mostly of body-sherds with perforations (Figures 1, 2, 3). Following their use, the perforated furnaces were intentionally broken. The sherds bear almost always the same characteristics: intense firing and a thickness of the walls *c.*1.0-2.5 cm, perforations with 1.5-2.0 cm diameter, and a distance between the perforations of *c.*2.00-4.00 cm. Frequently on their concave interior surfaces a thin vitrification layer is visible, which may host traces or nodules of metallurgical slag or even green cupriferous stains. Initially, the technological use of these perforated sherds was not clear. For many decades, they were mainly interpreted as 'strainers', without evidence and were included in the same category with real 'strainers'.[13]

Figure 1. Kephala (Kea): Perforated metallurgical furnace fragments and crucibles (Coleman 1977).

During the late 1990s at some sites in the Cyclades (Kythnos)[14] (Figure 3) and on Crete (Chrysokamino)[15] (Figure 2), the systematic study of such archaeological finds demonstrated that the type of sherds bearing perforations were part of metallurgical furnaces. To date, the earliest evidence for such furnaces comes from the Kephala settlement on the island of Kea dated to the FN. [16]

The shaft furnace is a complex structure (Figure 4). Its basic form includes a circular cavity on the ground (or hearth) with a diameter of *c.*40-60 cm often lined with earth or refractory stones, and a clay furnace. The latter was shaped and used as a chimney; it had a cylindrical or truncated cone shape, often with perforations. The chimney usually had a diameter of 30-50 cm with an open top and a base (Figure 5) Important for the smelting procedure were the pot bellows discovered in Chrysokamino; and the nozzles discovered in Sideri/ Kythnos and in Skali /Siphnos. These were usually connected to the furnace by clay pipes, the so-called *tuyères* (Figure 4). Both the bellows and the nozzles were used to drive air into the furnaces. The perforations in the chimney were apparently made to facilitate the entrance of the blowing air into the furnace[17] (Figure 4). This was necessary for the fire to reach the temperature at levels approximately 800° C, whilst the surpassed needed heating (*c.*450-500° C required for activating and keeping forward the composite pyrometallurgical reactions) was attained by introducing air through the bellows or nozzles. The majority of the sites where these kinds of chimneys were found were located on the slopes of hills or on elevated plateaus—ideal places exposed to the medium or slightly strong summer north winds (the latter widely known in the Aegean as "meltemia"). Depending on the part of the chimney where the fragments derive, they preserve or do not preserve traces of metal. If they are fragments from the upper part, not in direct contact with the smelting procedure, they do not usually preserve traces of slag on their internal surface, whereas those fragments with adherent slag traces derive from the lower part of the chimney (Figure 10). The furnaces were demolished after the smelting procedure to take out the final product (Figure 10) in the form of copper nuggets, little globules, or even tinny filaments.

The smelting operation with the use of shaft furnaces with perforated chimneys became clear in its details following the experimental reproduction of the smelting procedure at the Laboratory of Archaeometry in Demokritos National Center for Scientific Research. More specifically a series of laboratory practices simulating Aegean perforated metallurgical furnaces construction and effective operation for metal production (Cu) took place in 2004, 2005, and 2014 (Figure 8)

The steps taken for the reconstruction of the furnace were the following (Figures 5, 6, 7): a) determination of the dimensions of the fragmented clay walls: thickness at 1.0-2.5 cm, width and shape of holes at *c* 1.5-2.0 cm (circular), distance between holes at 2.0 to 3.0 cm, lower and upper diameter of truncated clay cone (calculated from the curved fragments) at *c.*50 cm at the base, *c.*45

[12] Doonan *et al.* 2007, 115
[13] This also occurs with the "cheese-pot" vases. Because of the perforations all around the rim, they were interpreted as cheese-pot strainers, but possibly they had another use. See the next chapter.
[14] Bassiakos, Philaniotou 2007, 19-56
[15] Betancourt 2006, 109-123
[16] Coleman 1977, 113-114
[17] Craddock 2000, 160-162

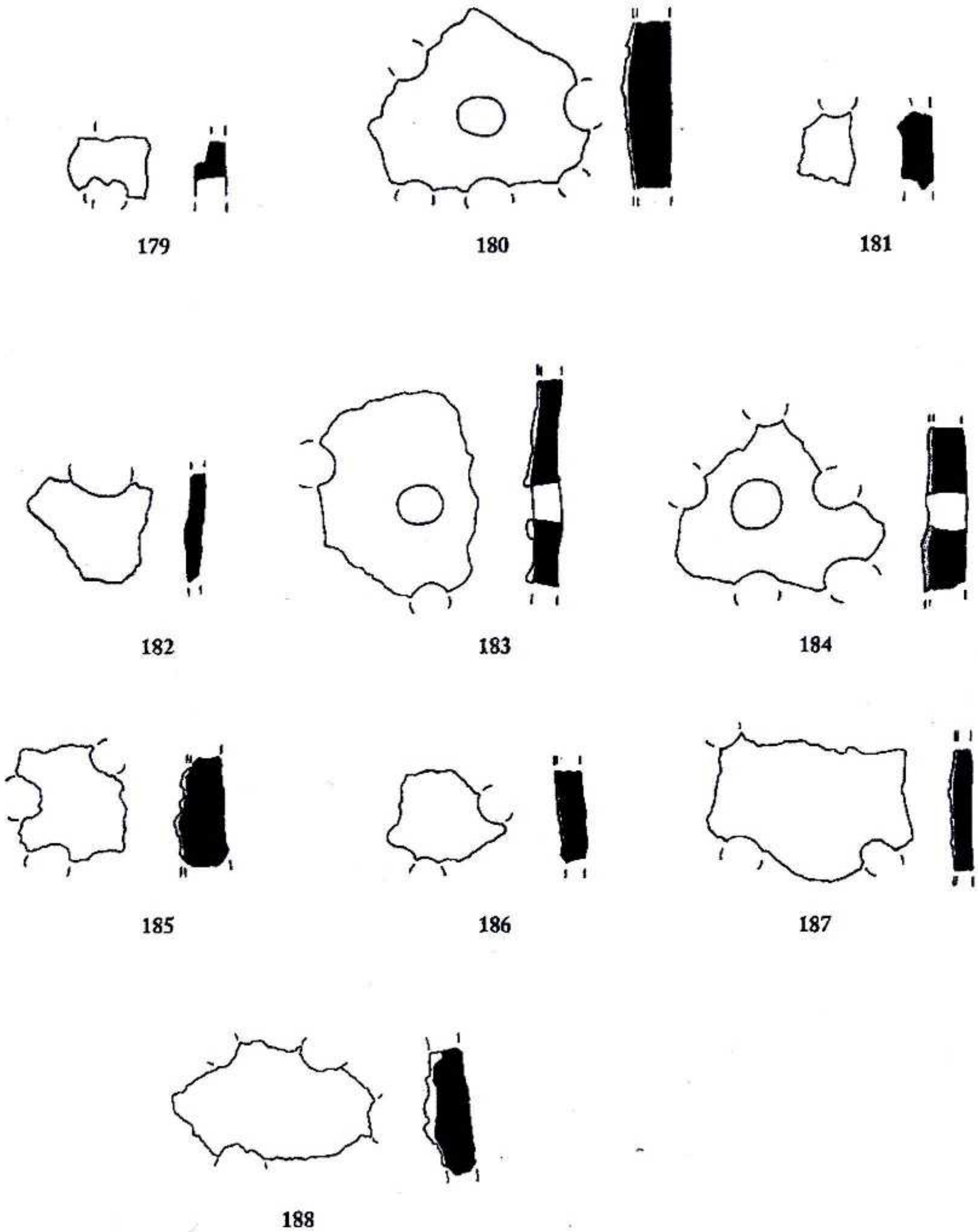

Figure 2. Chrysokamino (Crete): Drawings of furnace fragments (not to scale; Betancourt 2006).

Figure 3. Sideri (Kythnos): Metallurgical furnace fragments with perforations (Bassiakos-Philaniotou 2007).

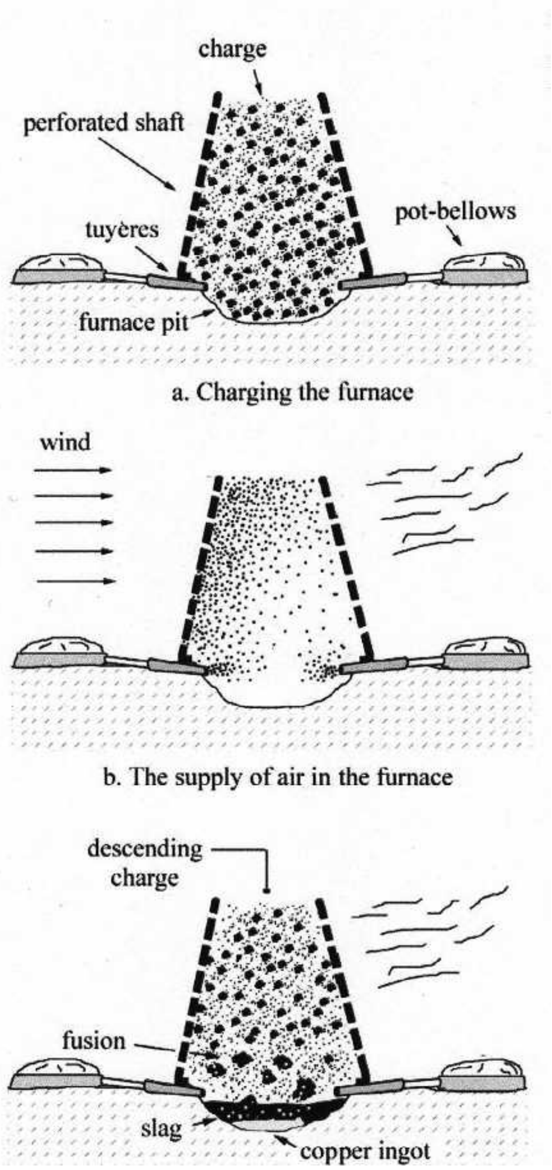

Figure 4. Schematic representation of the smelting process at Chrysokamino (not to scale; Catapotis-Bassiakos 2007).

Figure 6. Tailoring/drawing the furnace by constructing a metallinc pattern (Courtesy Dr Y. Bassiakos).

Figure 7. The perforated furnace shaft reconstructed. Demokritos laboratory of Archaeometry (Courtesy Dr Y. Bassiakos).

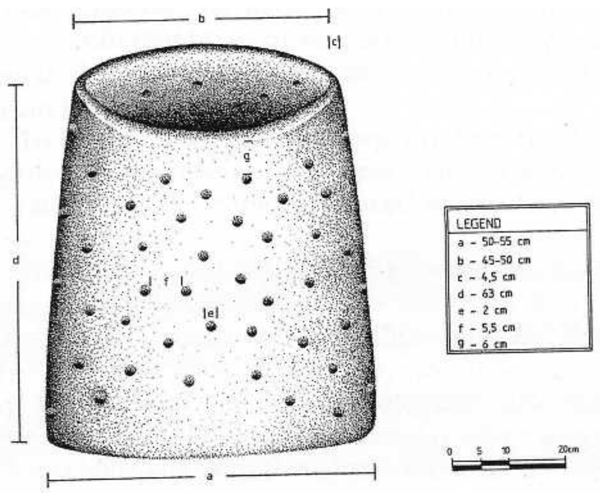

Figure 5. Drawing of the perforated shaft furnace as derived from field and laboratory observations (Kythnos; Bassiakos-Philaniotou 2007).

cm at the top, and a height of *c.*60 cm; b) preparation of the clay consisting of two parts of washed away clay——one part hornblende-sericite schist (0,3-0,6 cm grains sieved), the other part worn straw; and c) tailoring/drawing the furnace, constructing a metallic pattern, and the actual clay furnace (Figures 6–7). The experimental procedure (Figures 8–9) resulted the production of copper "rods"/fibers or nodules of 0,5-2,0 cm and slag, traces of which remained on the inner walls of the furnace (Figure 10). The chemical and metallurgical consistency of the slags was strikingly similar to the prehistoric ones (Figures 11-12). This series of experimental smelts at Demokritos allowed for a deeper understanding of the behavior of the perforated furnaces during smelting and offered the first detailed reconstruction of early Aegean copper-smelting technology.

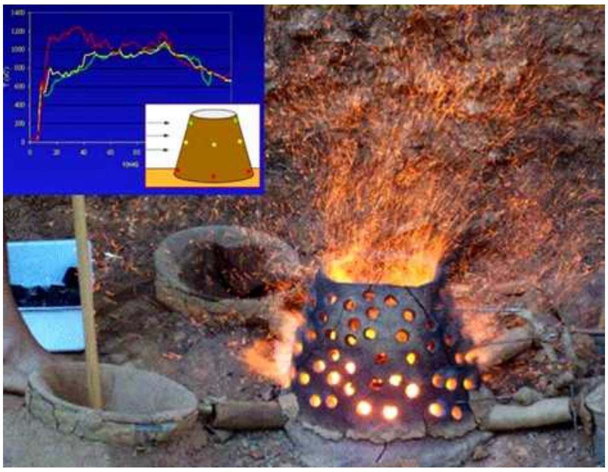

Figure 8. Perforated metallurgical furnace in operation (experiments at 'Demokritos' in 2004, 2005 and 2014) resulted in the production of pure copper of the Aegean type (Courtesy Dr Y. Bassiakos).

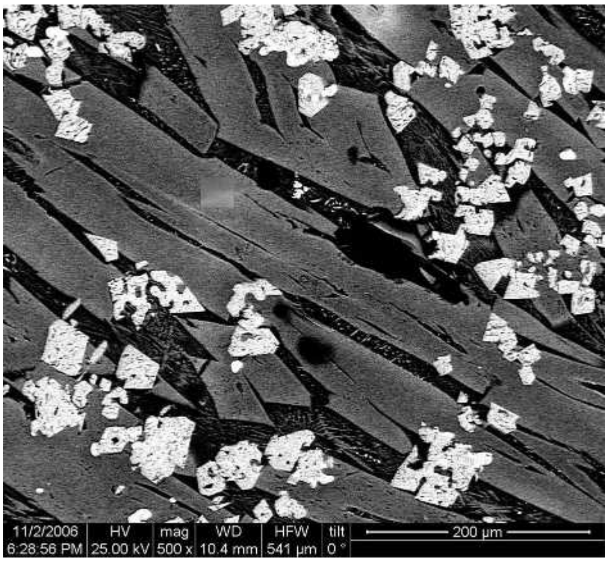

Figure 11. Experimental slag, 'Demokritos' yard, modern (Courtesy Dr Y. Bassiakos).

Figure 9. Smelting slag with low viscosity allowing to flow outside the furnace (Courtesy Dr Y. Bassiakos).

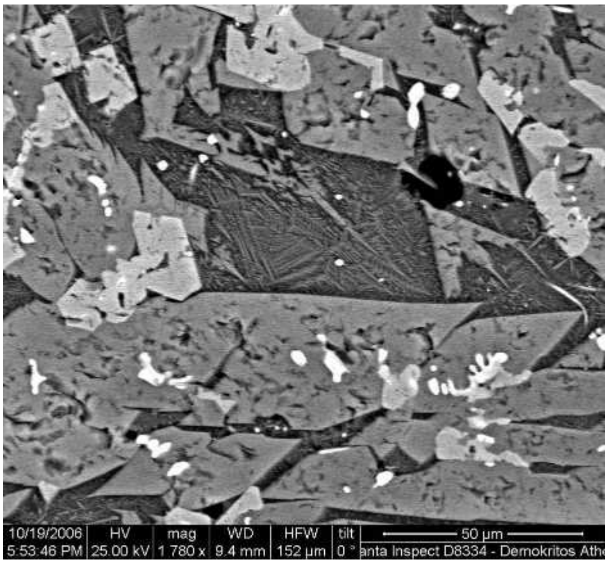

Figure 12. Kythnos, Aegean EBA(EC*II*) or ~4.400 years old (Courtesy Dr Y. Bassiakos).

Figure 10. A large fragment of the conical chimney-shaped furnace with perforations that was demolished so as to retrieve the Cu-containing cake from its interior (2014) (Courtesy Dr Y. Bassiakos).

The Athenian Acropolis south slope research

In 1922-1923 Levi — who subsequently excavated Phaistos — conducted research on the south slope of the Acropolis at Athens on behalf of the Italian Archaeological School. His research proved to be particularly important for the prehistoric occupation of that area as it brought to light unique findings. Some of this material was published several years later (1933) in a brief article at *Annuario*, the journal of the Italian Archaeological School.[18] Since then, the archaeological material from this excavation remained 'forgotten' without being studied as a whole and in base of the

[18] Levi 1933, 411-498

Figure 13. Aerial view of the Athenian Acropolis. 'H' indicates the FN site at the south slope of the hill (with remains of a Neolithic "Hut") where the wall-fragments of a perforated metallurgical furnace were revealed. 'C' indicates a natural chasm (small cave) where other FN sherds were located (Dimitriou 2017).

new archaeological data and archaeometric methods, until recent years when, at the initiative of the first author of this work, study of material was renewed in collaboration with the Italian Archaeological School of Athens and Demokritos,

More specifically in 1922, north of the Stoa of Eumenes, Levi excavated a "Neolithic hut" (Figure 13) as he called it, while one year later, in 1923, he investigated two small caves to the north of the Asclepius temple (Figure 13) dated from the findings to the second period of the Early Bronze Age. From the study of the archaeological material (including pottery, obsidian, stone tools, animal bones, and sea shells) and also from the stratigraphy, Levi formed the opinion that the area he excavated in 1922 between the Odeion of Herodes Atticus and the Asclepius temple was a Neolithic hut. His conclusion was based mainly on the presence of a hearth (Figure 14) and pavement, in addition to the pottery that gave a chronological range from the Middle to the Late Neolithic. The recent study also identified pottery from the Final Neolithic period.[19]

The Neolithic Pottery

Middle and Late Neolithic period

In the strata that expand from the pavement of the "hut" to the virgin soil (lower strata)[20] Neolithic pottery

Figure 14. The bulk left at the south of the Neolithic "Hut", section of the pavement: fill layer with small stones (part of the Lower/Profound Layer) and above the layer of the pavement in yellow clay. In the center, the hearth area not excavated (Fototeca Scuola Archeologica Italiana di Atene).

of the Sesklo culture and sherds of the Dimini culture were found.[21] Sesklo culture sherds have a characteristic painted 'flame pattern' decoration on the exterior surface. This consists of linear motifs reminiscent of a schematic rendering of a flame in red color on a light slipped surface background (Figure 15 above). The latter pottery of the Dimini culture is represented by body sherds with painted decoration that consist of

[19] Dimitriou 2016, 17-19; Dimitriou 2020, 157-159

[20] For more details about the stratigraphy of the Neolithic hut see Dimitriou 2016, 15-17; Dimitriou 2017, 26-29; Dimitriou 2020, 155-157

[21] For Sesklo and Dimini culture see Tsountas 1908

Figure 15. Above: Middle Neolithic pottery (5800-5300 A.C.), Below: Late Neolithic (5300-4500 A.C.) pottery from the Neolithic "Hut" (author photo)

dark colored linear motifs on an off-white surface—a typical decorative pattern of the Late Neolithic II from the site of Dimini in Thessaly (Figure 15 below).

Final Neolithic period

In the strata that extent from the pavement of the "hut" and up to the modern surface, the pottery that came to light belong to the category of red-burnished and black- burnished ware and pattern-burnished ware.

Red burnished and black burnished ware

Several sherds with red-burnished (Figure 16 middle right) and black-burnished surface treatment were present in the Neolithic "hut".[22] As far as the shapes of the vases are concerned, a category that has been recognized is the closed vessel with a high ring-base, a biconical body, and a short, narrow neck (Figure 16 middle left). Usually at both sides of the base, there is a pair of small perforations. This category of vessels is represented at the "hut" by three partially preserved specimens, one of which, though heavily weathered on its outer surface, preserves traces of burnishing in reddish-brown color and pairs of perforations at its base (Figure 16 middle left). Similar vessels were found at the pits of the north slope of the Athenian Acropolis during the excavations of the American School of Classical Studies in Athens.[23]

Pattern-burnished ware

A ceramic category of particular interest is the pattern-burnished ware, represented by one rim and body- sherd fragment found at the western end of the Neolithic "hut" (Figure 16 above). The outer surface of the sherd bears linear decoration, consisting of vertical, parallel lines and belongs to the black pattern-burnished ware category that is typical of the Attica-Kephala *facies*.[24] This ceramic category includes mostly sherds with linear motifs in orange-red color (red pattern-burnished ware), while the sherds with the same linear decoration but in a black-grey color (Black pattern-burnished) are more typical of the islands of North Aegean and Anatolia.[25]

"Cheese-pots"

The so-called "cheese-pots" constitute a ceramic category of the FN repertoire. The name is attributed to open, usually shallow vases (pans) or basins that bear perforations all along the rim. At some point it was believed that because of the perforations these vases were used for making cheese.[26] But one row of perforations and only around the rim probably does not justify this use.[27] Another interpretation is that

[22] Dimitriou 2016, 17-19
[23] Immerwahr 1971, 22-32

[24] Renfrew 1972, 69-70, 77-78, Dimitriou 2016, 17-19
[25] Dimitriou 2020, 158-159
[26] Some, another type of Neolithic vases with perforations all over the body were proved to be cheese-strainers, see Bogucki 1984, 15-30 and Salque *et al.* 2013, 522-525
[27] Probably only perforations all over the body can define a cheese-pot (strainer), used to separate cheese curds from whey, and not only a series of perforations around the rim.

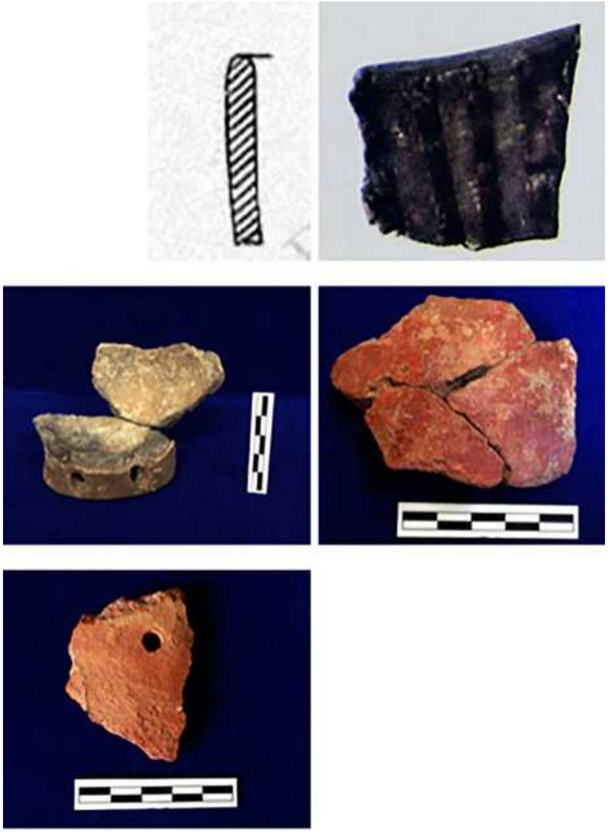

Figure 16. Final Neolithic pottery from the Neolithic "Hut": Above: Pattern-burnished, Middle: Red burnished, Below: Possible "cheese-pot" (author photo).

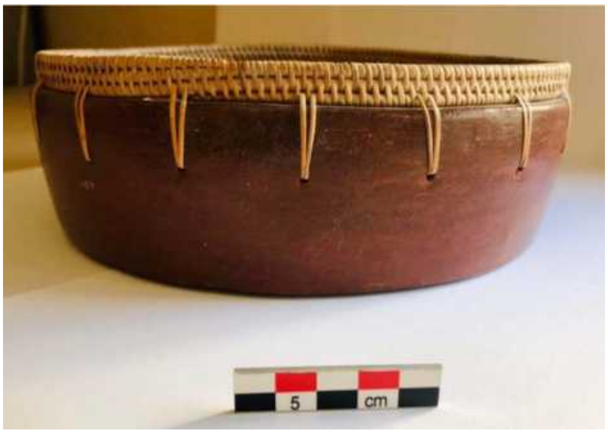

Figure 17. Traditional pottery decoration from Lombok island (Indonesia) (author photo).

the rim perforations possibly made to fix a leather or woven straw construction for functional (lid?) and/or decorative use.[28] This technique finds ethnographic parallels in traditional pottery decorations from Lombok island in Indonesia (Figure 17).[29] Because some of these vases preserve mat-impression on the base and on their external wall surfaces, Sampson proposed that their exterior surface—from the lower part (the base) to the upper part (rim)—was possibly covered by a mat.[30] This can also justify the holes on the rim to fix this mat coverage on the top of the vase (rim). During the Final Neolithic period, there were many categories of perforated sherds, but their use is still unclear.[31] Further research is needed to understand the proper use of the "cheese-pots" and ethnographical parallels can help.

The "cheese-pots" are widespread on the coast and inland Anatolia during the Late Chalcolithic I and II, and in Greece during the Final Neolithic in many sites, from the islands of the north Aegean to the Dodecanese and the Cyclades, and also in many mainland,[32] such as the Neolithic 'hut' on the south slope of the Athenian Acropolis (Figure 16 below).

The Acropolis south slope perforated furnaces: archaeological and archaeometric evidence.

Archaeological evidence

Among the ceramic categories of the FN mentioned above, a particular group of sherds was identified. Their macroscopic study confirmed that they were probably part of another kind of vessel and not "grates" as Levi claimed in his publication. More specifically, a group of six sherds bearing perforations and other common characteristics was identified (Table 1, Figure 18) as follows: a) the perforations were executed while the clay was still fresh and they were straight with no inclination. Their diameter varied between 1.5-2.0 cm, and the thickness of their slightly curved walls was from 1.0 to 1.3 cm; b) the clay was coarse with visible voids, mostly elongated or even pin shaped of burnt out organic remains mainly on the surface of two of them (NK5873, NK 5875) and highly tempered; c) no decoration or slip occurs on any fragment. The clay of the fragments is a light-yellow/slightly pink color, and in some parts is light dark gray or dark red due to fire traces (Table 1). Most of the fragments present traces of burning to various extent on their inner concave surface, while in many cases such traces are visible on the outer surface as well (NK 5871, NK5972, NK5973). In one fragment the inner surface is entirely covered by a kind of black patina, possibly slag deposits (NK5874), and in two cases the fire traces are visible on the outer surface only (NK5875, NK5976). All these elements imply that the object from which the perforated fragments came was used for pyrotechnological activities. Even

[28] Doukaki 2018, 73-74

[29] In Lombok island (Indonesia), in Banyumulek village there is a woven traditional pottery which consists in a straw (*Ketak*) woven decoration fixed with perforations all around the rim. https://gerbanglombok.co.id/2019/07/02/lombok-pottery-handicraft/.

[30] Sampson 2000, 63; Sampson 2018, 6-7, Fig. 7; Doukaki 2018, 73-74

[31] For various categories of perforated sherds mostly with perforations all over the body see Dimitriou 2022.

[32] Dimitriou 2020, 159

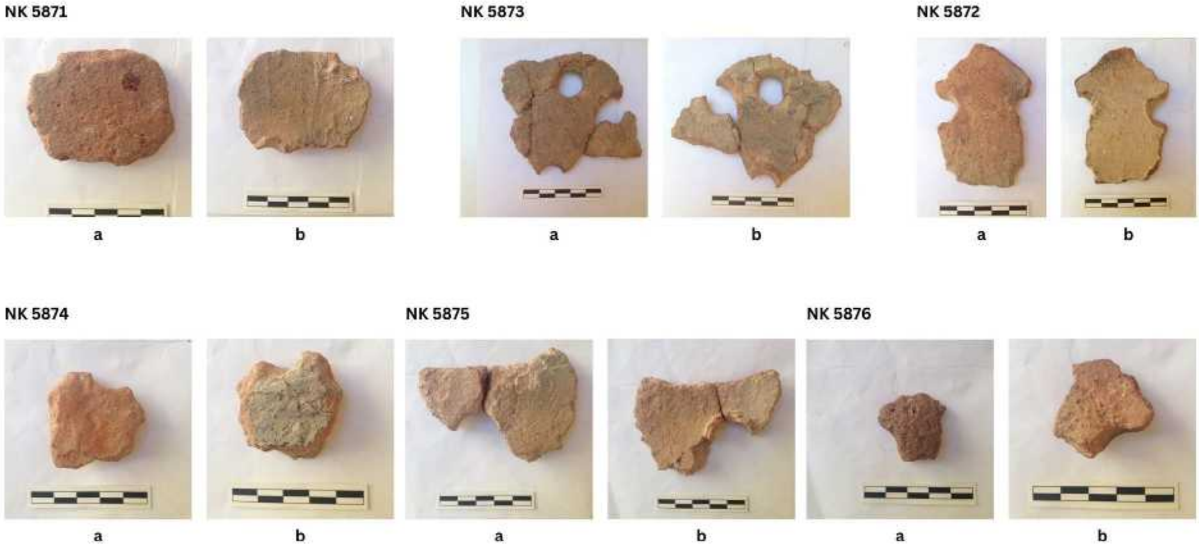

Figure 18. The group of six fragments of the perforated shaft furnace: Inner and outer surfaces (author photo).

Table 1. The group of the furnace fragments from the Acropolis Neolithic "Hut" (south slope)

FRAGMENTS	NUMBER OF HOLES AND THEIR DIAMETERS	DISTANCE BETWEEN THE PERFORATIONS	FRAGMENT THICKNESS	OUTER SURFACE	INNER SURFACE	INCLUSIONS
1 NK 5871	Remains of 2 holes on edge of fragment (Diam. 1.0-1.5 cm)	5.0 cm (Length: 6.0 cm)	1.0 cm	Grey/red color, black in holes, 2 very big red inclusions (Grog)	Yellow clay, light grey in areas, some ribs probably formed during initial construction	Small/Medium red and green/black inclusions. medium-coarse grog inclusions of dark- red color
2 NK 5872	1 (Diam. 2.0 cm), 1 more on edge of fragment (Diam. 1.5 cm), remains of 2 holes on edge of fragment	1.5-3.0 cm (Length max. 8.5 cm)	1.0 cm	Grey/pink color (burnt), voids of burnt out straw	Pink/grey (burnt) color, burnt out straw imprints	Small/Medium red and black inclusions, grog (dark-red) rare inclusions, burnt out straw marks
3 NK 5873	Remains of 4 holes on edge of fragment (Diam. 1.5-2.0 cm)	2.5-3.0 cm (Length max. 10.5 cm)	0.8 -1.0 cm	Grey/red color, black close to holes, burn traces	Yellow color, traces of burn	Small/Medium black, calcite and quartz inclusions. Musc. mica
4 NK 5874	Remains of 3 holes on edge of fragment (Diam. 1.5 cm)	1.0-1.5 cm (Length max. 4.0 cm	1.3 cm	Orange/pink color	Grey (burnt), extensively slag deposit?	Small red and black inclusions, quartz and calcite inclusions. Muscovite mica
5 NK 5875	Remains of 1 hole on edge of fragment (Diam. 2.0 cm)	(Length max. 8.0 cm)	1.0 cm	Yellow/pink color, black in areas, voids of burnt out straw	Yellow/pink, voids of burnt out straw	Small/Medium red and black inclusions, red grog?
6 NK 5876	Remains of 1 hole on edge of fragment (Diam. 1.5 cm)	(Length max. 3.0 cm)	1.0 cm	Dark grey/red color, weathered, black in hole	Yellow/Pink-light grey color	Medium red and black inclusions. some grog inclusions (dark-red)

though these fragments generally preserve the same characteristics, it is not certain if all of them were part of one furnace since they are not joined and there are some small observable differences in the temper and consistency of the clay. If they did not belong to the same furnace, then they probably made up two different ones.

Regarding the context in which these fragments were found inside the hut—comparing what is known from Levi's publication with the recent study of the material in the laboratory—four were in the upper part of the lower layer which corresponds to the pavement of the "hut", one in the lower part of the upper layer (in contact with the pavement of the "hut"), and one without specification. All six fragments derive from the context in which FN pottery was found. In the majority, they were found in the southern sector of the hut (four), while two came to light in the NW Sector (Table 2). These ceramic fragments have very close parallels with other similar perforated sherds with slag remains from some prehistoric sites in the Aegean mentioned in the beginning of this article. Archaeometallurgical analysis of the slag adhering to these pieces indicates that they were metallurgical furnaces, in most cases related to copper production, except for one case from SE Siphnos where they were associated with lead/ silver production.[33] The macroscopic comparison and identification of the Acropolis fragments with the metallurgical furnaces from other Aegean sites led to the need to undergo archaeometric analyses so as to find any metallurgical slag also on the Acropolis fragments.

Table 2. Excavation context of the furnace fragments in the Neolithic "Hut" (south slope)

Fragments	Excavation Context
1 NK 5871	**S Sector**
2 NK 5872	**SW edge of the hut** Stratum under the clay cover Lower layer
3 NK 5873	**SE Sector** Stratum under the red clay Lower Layer
4 NK 5874	**SW Sector** Upper Layer
5 NK 5875	**NW Sector** Lower Layer
6 NK 5876	**NW Sector** Lower Layer

Archaeometallurgical evidence

All of the six ceramic fragments bearing perforations were subjected to multiple analyses using a portable X-ray fluorescence (p-XRF) analysis device of the Laboratory of Palaeoenviroment and Ancient Metal Studies of the NCSR "Demokritos". It took place at the Apotheke of the Eforeia of Athens using a calibrated portable/semi-portable milliprobe XRF (p-mXRF) spectrometer equipped with a Rhodium (Rh) anode X-ray tube, a Si-PiN detector (XR-100CR, Amptek Inc.), and a multichannel analyzer (MCA-8000A, Amptek Inc.). All items were analyzed by an accelerating voltage of 40 kV and a current ranging from 50μA to 200μA, depending on the nature of the analysed item, while each spectrum was collected for 500 seconds. The analysis, both on the outer and the inner side of the fragments, aimed to ascertain the existence of a difference between the chemical composition of the outer and the inner surface. Based on their spectra (Table 3), the outer side of all the fragments was found to consist of K, Ca, Ti, Mn, Fe, Rb, Sr, Zr, the last three in traces (Figure) and all common elements for the chemical consistence of the pottery. Zinc (Zn) was also present in all, pointing to the chemistry of the earthy material used for the ceramic. Arsenic (As) was detected in one of them, namely NK5874.

On the other hand, the analysis on the inner surface of the sherds was targeted on the black patina with which they were covered. In all the elements detected in the inner surface were identical to the elements detected on the outer surface. The only exception was sherd NK5874 in which copper (Cu) was also present (Figure 19). Even though this copper content is limited, one can assume that in combination with the macroscopic analysis these ceramic fragments possibly consist in residue of a metallurgical procedure relating to copper oxides smelting.[34] Given the similarities of sherd NK 5874 with the others in the group analysed above, and taking into account the overall similarities between this group of perforated sherds from the Neolithic "hut" with other sites in the Aegean (Kea, Kythnos, Chrysokamino) (Figures 1, 2, 3), it is almost certain that the other fragments were part of a metallurgical furnace. More detailed analysis using other physicochemical techniques will ascertain this hypothesis in the future.

The reason why not all fragments preserve traces of copper is probably that they are fragments from the middle and upper part of the furnace, that is, they were not in direct contact with the smelting procedure. On the other hand, the lower parts of the furnace (the ones were the smelting procedure was in operation) probably

[33] The site of Kasela near the Akrotiraki settlement at the SE Siphnos (Georgakopoulou 2016, 55, Table 1)

[34] Also three (76*, 174, 175) furnace fragments from Kephala on their inner surface bear slag deposits consisted primarly of iron with smaller quantities of copper, See Coleman 1977, 40;88;113-114

Table 3. XRF analyses of ceramic fragments both on the inner and on the outer side.

Sample	Fe	K	Ca	Ti	Mn	Ni	Cu	Zn	As	Rb	Sr	Zr
NK5872 Inner side	***	*	*	*	n.d.	*	n.d.	*	n.d.	*	*	*
NK5872 Outer side	***	*	*	*	n.d.	*	n.d.	*	n.d.	*	*	*
NK5873 Inner side	***	*	*	*	*	*	n.d.	*	n.d.	*	*	*
NK5873 Outer side	***	*	*	*	*	*	n.d.	*	n.d.	*	*	*
NK5874 Inner side	***	*	*	*	*	*	*	*	*	*	*	*
NK5874 Outer side	***	*	*	*	*	*	n.d.	*	*	*	*	*

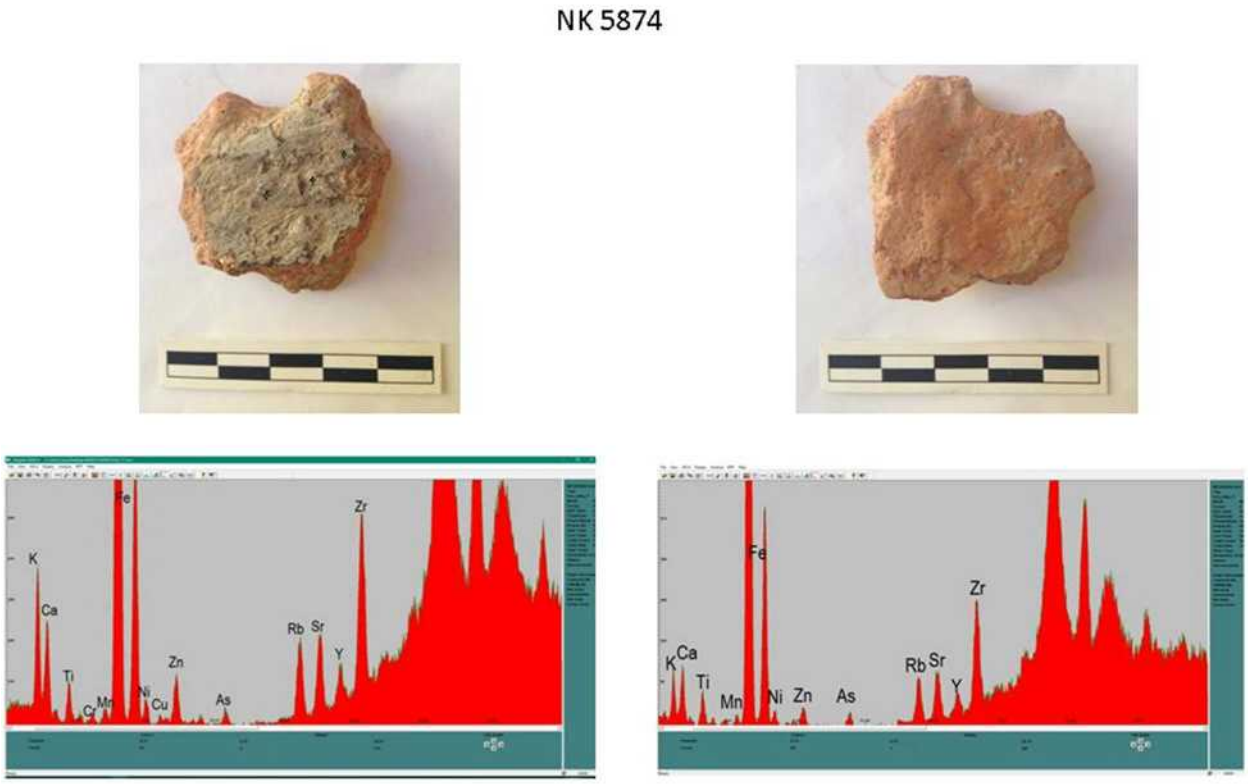

Figure 19. Fragment NK5874: Chemical composition of the outer and inner surface where copper was detected. (author photo.) (Spectrum Images Dr E. Filippaki)

have not survived because after the destruction of the furnace at the end of the smelting procedure these? would have been the parts were some copper slag would have been deposited. To ascertain this hypothesis we should in the future proceed to more detailed analysis using other physicochemical techniques.

Conclusions

As revealed from the macroscopic observations and the archaeometallurgical analysis undertaken in relation with the new study of the pottery, the perforated fragments of metallurgical furnaces from the Athenian

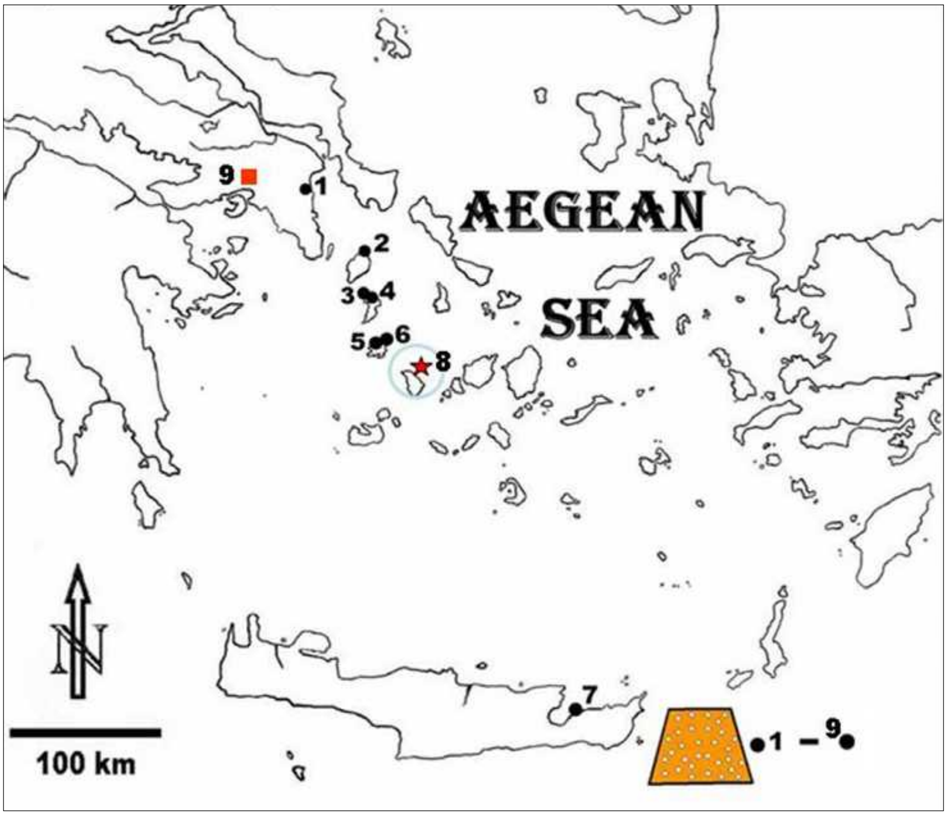

Figure 20. Map of the distribution of the shaft perforated furnaces in the Aegean with the new evidence till now (FN-EBA)

Acropolis south slope is of a great importance for our knowledge of the prehistory of the Acropolis area, and more specifically, the metallurgical achievements during the transition from the Neolithic to the Early Bronze age period.

The presence of perforated metallurgical furnaces at the Athenian Acropolis during the Final Neolithic connects Attica with Kea island, where in the settlement of Kephala perforated fragments of a metallurgical furnace dated in the FN have been found. This not only concerns pottery (pattern-burnished ware)[35], but also—and for the first time—metallurgical technology and expertise. This reinforces the idea of intensive contacts between Attica and the Cyclades much earlier than the *Koine* of the EBA II period. [36] These contacts, as it turns out, were not only limited to the exchange? Of ceramics and obsidian, but also that of raw materials, skills, technological practices, and specialization regarding the emerging metal smelting process of copper ores.[37]

Further systematic study of the findings and the new archaeometric analyses from the area of the Acropolis south slope (the D. Levi excavation project and the *Bothros* at the area of Chalkourgeio) will help to bring to light new important data on pyrotechnological activities in the area. In combination with the study of other archaeological material (except pottery), such a study would help us to understand better the use of the site, i.e. was it really a 'hut' or some other open space for common activities of the prehistoric community, such as the production of metals (copper). All the above would lead to rethinking of the role of the Acropolis in the Neolithic and Early Helladic period, which until today has remained almost forgotten and unknown.

Finally, after identifying the perforated metallurgical furnace in the Acropolis of Athens and confirming its use for copper oxide smelting, we can add this site to the existing Aegean metallurgical map—another site where smelting activities using perforated furnaces is attested (Fig 20). The southern slope of the Acropolis is so far the earliest site out of nine for the use of a copper smelting furnace. New data is expected to emerge in the future that will complete the picture we have formed so far regarding metallurgical technologies in Attica and the prehistory of the Acropolis during this neuralgic period of transition from the Stone Age to the Bronze Age.

35 Renfrew 1972, 77-78
36 Dimitriou 2012, 334-421
37 Dimitriou 2017, 36-37

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Archaeometallurgical Activity in the Two Early Helladic Settlements of Raphina and Askitario, East Attica Greece According to the Excavations of D. Theocharis in the Early 1950s. Preliminary Observations

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Abstract: The Early Helladic settlements of Raphina and Askitario in East Attica (Greece) were excavated by D. Theocharis in the early 1950s. They are related to primary and secondary archaeometallurgical activities connected to copper and silver metallurgical circle as revealed by archaeological data (kiln clay pieces, slags, ores (;), tuyères, moulds, ingot). Among the material, 6 perforated clay pieces out of 14 were identified as pieces of metallurgical kiln in a non-disturbed Early Helladic context of a pit unearthed southwest of the fortified settlement of Raphina. These specific remains connect Raphina with the technological tradition of perforated kilns, well known from other Early Helladic smelting sites in the south Aegean. The questions arising from the current research are: a) the archaeometallurgical character of the activities; b) the similarities and differences of the techniques used in Raphina and in Cycladic sites; c) the origin of the resources (Lavrion or Cyclades); and d) the role of Raphina as a connection point between Central Greece, the Cyclades and Euboea.

Surface analyses employing one semi-portable XRF device (with a Rhodium anode X-ray tube, a Si-PiN detector XR-100CR, Amptek Inc., and a multichannel analyzer (MCA-8000A, Amptek Inc.) were performed on the archaeometallurgical remains. For the finite establishment of the metallurgical operations taking place at Rafina and Askitario, micro analytical and other methods need to be applied in order to complement the preliminary conclusions drawn from the pXRF analyses.

KEYWORDS: PREHISTORIC METALLURGICAL WORKSHOPS, ARCHAEOMETALLURGICAL REMNANTS, PERFORATED METALLURGICAL CLAY FURNACES

The history of excavations

The Early Helladic settlements of Raphina and Askitario in East Attica (Figure 1) were revealed by the excavations of the Archaeologiki Etaeria under the direction of the pioneer excavator of prehistoric Archaeology, D. Theocharis during five excavation periods in the early 1950s (Theocharis 1952, 77–92; Theocharis 1955, 129–151;Theocharis 1956, 105–118; Theocharis 1957, 104–113; Theocharis 1960, 109–117; Theocharis 1961, 59–96).[1] Although the research was not completed, the excavations revealed very interesting information for an extended settlement, an important center of East Attica in the Early Bronze Age. The overall picture of the settlement was not revealed due to its partial destruction as a result of the proximity of the site to the modern town and the use of the area for the installation of military bunkers during the Second War World.

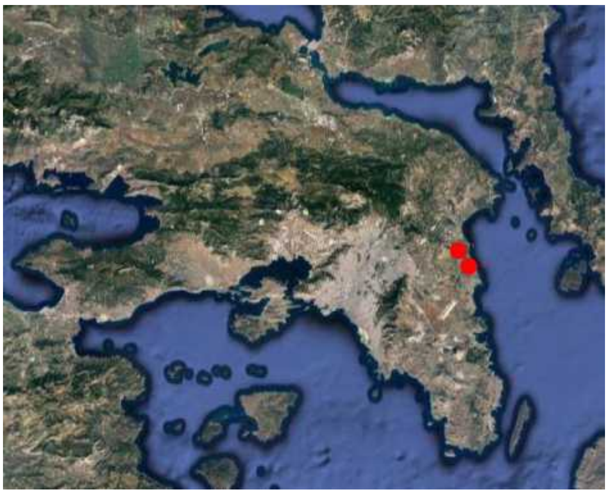

Figure 1. Map of Attika showing sites mentioned in the text : 1. Raphina. 2. Askitario

[1] Excavations were held in Raphina in the years 1951, 1952 and 1953, and in Askitario in 1954 and 1955.

Raphina-The settlement and the archaeometallurgical remains

The Early Helladic settlement of Raphina is situated on a low hill over the modern port**.** The choice of the establishment of the prehistoric settlement was ideal because it was near to the estuary of a river *(Megalo Rema)* (Figure 2), it offered a secure port for maritime communication to the west Cyclades or south Euboea, and it was protected by the strong north-east winds. Habitation of the site began in the Early Bronze Age (Early Helladic II), which constitutes the most representative period, while the Middle and the Late Bronze Age are also represented, probably in less extension in terms of finds according to the archaeological data.

Theocharis' research revealed a settlement with a condense plan that was composed of houses with a megaroid layout containing a main large room with extensions depending on the duration of the use. Between the houses pebbled roads were identified. There were at least six buildings revealed: Οικία A *(House Alpha)*, Οικία B *(House Beta)*, Οικία Γ *(House Gamma)*, Οικία Δ *(House Delta)*, Οικία E *(House Epsilon)*, Οικία Θ *(House Thita)* and a building, Οικία H *(House Heta)* with the oval shaped pit Z *(origma Zeta)* that was probably an installation of a special character**.** Remnants of fortifications (Early Helladic III) were also found in the west part of the settlement. In some cases, the fortifications were used as part of the masonry of the houses, for example, in Οικία Γ *(House Gamma)* (Theocharis 1956, 105–107, fig. 1),Οικία Δ *(House Delta,)* and Οικία Θ *(House Thita)* (Figure 3)**.**

A characteristic dwelling is the fully-excavated Οικία A *(House Alpha)* (Theocharis 1955, 138–140, fig. 5–7), with the main room used for food preparation and storage, and containing an abundance of pottery (at least 50 vessels) (Theocharis 1955, fig. 10). Other findings from the settlement—apart from the pottery—consist of a stone seal (Theocharis 1956, 117–118), whorls, lithic tools, flake and knapped stone tools including obsidian, bone tools, bronze tools, and other metal objects like lead clamps, nails, and hooks which indicate the use, if not the production, of metal objects (Theocharis 1955, 148–149, fig. 14).

Due to the neuralgic site of the settlement with accessibility to the Aegean islands, the pottery found in the settlement shows cultural relations and connections with the Cyclades.

The MH period of the settlement is represented by a few sherds of pottery. The LHIII period is better

Figure 2. View of Raphina coast : **A**: Estuary of *Megalo Rema* **B**: Pits with metallurgical remains C: Early Helladic settlement
(*Φωτογραφία του Νικόλαου Τομπάζη, Ραφήνα, 13 Οκτωβρίου 1952© Μουσείο Μπενάκη / Φωτογραφικά Αρχεία [ΦΑ.10_2863]*

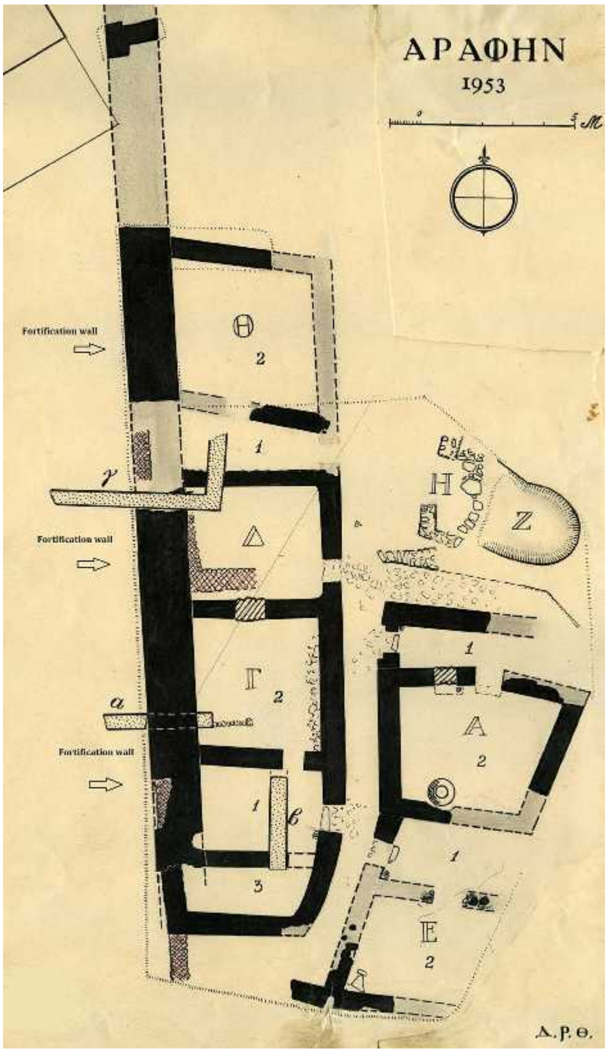

Figure. 3. Plan of the main sector of the excavation of Raphina (Archeion Archaeologikis Etaireias).

represented by pottery and a few movable findings, like an idol of type F, and one zoomorphic idol, both partially preserved (Theocharis 1955, 150, fig. 16). LHIII is also represented by a few architectural remains, such as those in Οικία Γ *(House Gamma)* following the destruction of its Early Helladic phase, but also in an area south of the Early Helladic settlement (Theocharis 1956: 107, 118).

Theocharis' research extended not only to the hill but also to the shore southeast of the fortified settlement where three trenches were excavated (I-III). (Figure 1). In this area, very important archaeometallurgical findings were recovered (Theocharis 1952, 80–81; Theocharis 1955, 130–134).[2] In particular, on the shore near to the estuary of *Megalo Rema,* two pits were revealed: one larger, oval shaped (4,40 X 3,40 m) (Pit A) that was interpreted as *vothros skorion;* and one smaller, of the same shape (Pit B), 15 m south from the larger one and referred to as *spilaiothes origma* as it was dug in the soft rock.[3] A rectangular construction near to these two pits was characterized by the excavator as tomb or as a part of a house (Theocharis 1952, 79–80). (Figure 2)

Apart from the pottery (exclusively of Early Helladic Period), among which parts of spoons *(koxliaria)*, aryter (*arhytires*), pans and four-legged clay supports are included, the larger pit was full of copper slags, pieces of metallurgical clay furnaces, either perforated or not, and four tuyères. In the interior of the smaller pit (with pottery of both Early Helladic and Late Helladic III) copper slags were also found. These archaeometallurgical remnants are connected with primary or secondary metallurgical procedures related to one or more metallurgical installations for copper production. The morphological characteristics of both pits (iregural shape, isomeric slope, and horizontal bottom) and the location of the kiln basement according to the archaeological data, initially lead the excavator to the assumption that these pits had been used as metallurgical furnaces prior their use as pits (Theocharis 1955, 132–134). However, the dimensions of these constructions do not correspond to the dimensions of the known examples from the Early Helladic period. Although the precise sites of the metallurgical furnace/furnaces were not identified with certainty, it is possible that the metallurgical procedure took place in some open-air place near the two pits, which were probably used for both domestic and industrial waste products. The proximity of the probable location of the metallurgical furnace/furnaces to the settlement and the existence of slags among the findings of buildings (Theocharis 1955, 135), associate the inhabitants of the settlement with metallurgical procedures. Additional finds corroborating this aspect are a stone mould, a tuyère, and slags also found in another part of the settlement close to the area of the two pits (Theocharis 1960, 116).

The discovery of Cycladic pottery and a Cycladic idol in this part of the settlement indicates, as in the settlement itself, the great influence of the Early Helladic Cycladic II-III.

Other sites with perforated furnace remnants

It is extremely important to emphasize for the history of Aegean Archaeometallurgy that when D. Theocharis discovered Raphina`s copper slags there were only six slags known from the Early Helladic period and they all came from the area of Cyclades.[4] Later excavations

[2] The archaeometallurgical material was examined in the framework of the authors` phd research.

[3] Unfortunately there was no drawing or picture of Pit B available.

[4] (Tsountas 1898, 175–176). These slags come from Avyssos (Paros)

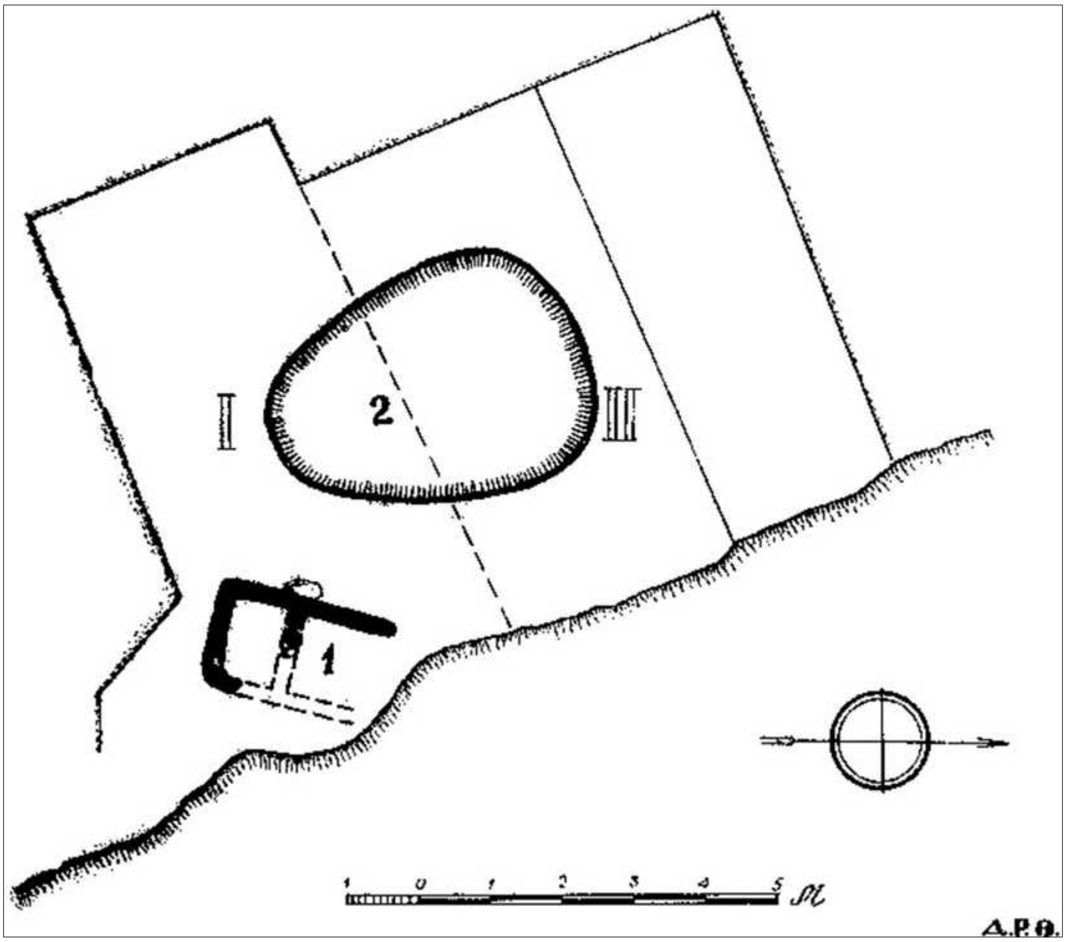

Figure. 4. Plan of the excavated area southwest of the settlement. 1. Rectangular construction. 2. Pit A (Vothros skorion). (Theocharis 1955, fig. 2).

brought to light a large amount of archaeometallurgical remnants that gave very important information about the techniques of metal production used by Aegean prehistoric metallurgists.

As the archaeological data proved, the need for the improvement of metal production methods based on continuous and constant temperatures inside the kiln lead to the discovery of composite permanent equipment (device), consisting of an underground section (hearth) and an above ground section made of clay (kiln), either perforated or not. The use of this complex equipment compiled by bellows and tuyères operated supportively to the natural draughts of the winds as the choice of the metallurgical sites imply. According to experimental simulations, the existence of holes in the clay on upper part of the kiln for the air supply led to the preservation of constantly high temperatures inside the kiln and aimed at producing a more fluid slag with less loss of the metallic product (Catapotis,Pryce and Bassiakos 2008, 113–121). After the completion of the procedure, the clay part was broken so that the metallic product could be taken out. This is the reason why, in the vast majority of cases, kiln fragments are found as waste in reject pits.

The use of perforated metallurgical kiln, although already known in the prehistoric Aegean from the Final Neolithic Kephala on Kea (Coleman 1977: 4, 108, fig. 22) and a final Neolithic layer on the southern slope of the Acropolis in Athens (Dimitriou 2017, 25–38) was an innovative technique attested in Early Helladic sites of eastern Attica and the southern Aegean (western Cyclades and eastern Crete). Bearing in mind the special technological features of this equipment (the dimensions of the hollows, the diameter of the hearth, and the type of tuyères), it seems that this type of metallurgical kiln was produced and widely used in the Early Helladic II period in the southern Aegean. In all cases, this type of kiln was used for smelting copper ores, expect the one case where it was used for smelting silver/lead ores (Kassela,Siphnos) (Papadopoulou 2013, 34–35).

and Kastri (Syros). After the analytical research of the sixth slag from Kastri it was proved to be part of lump of arsenical copper (Stos – Gale, Gale and Gilmore 1984, 31, table 2).

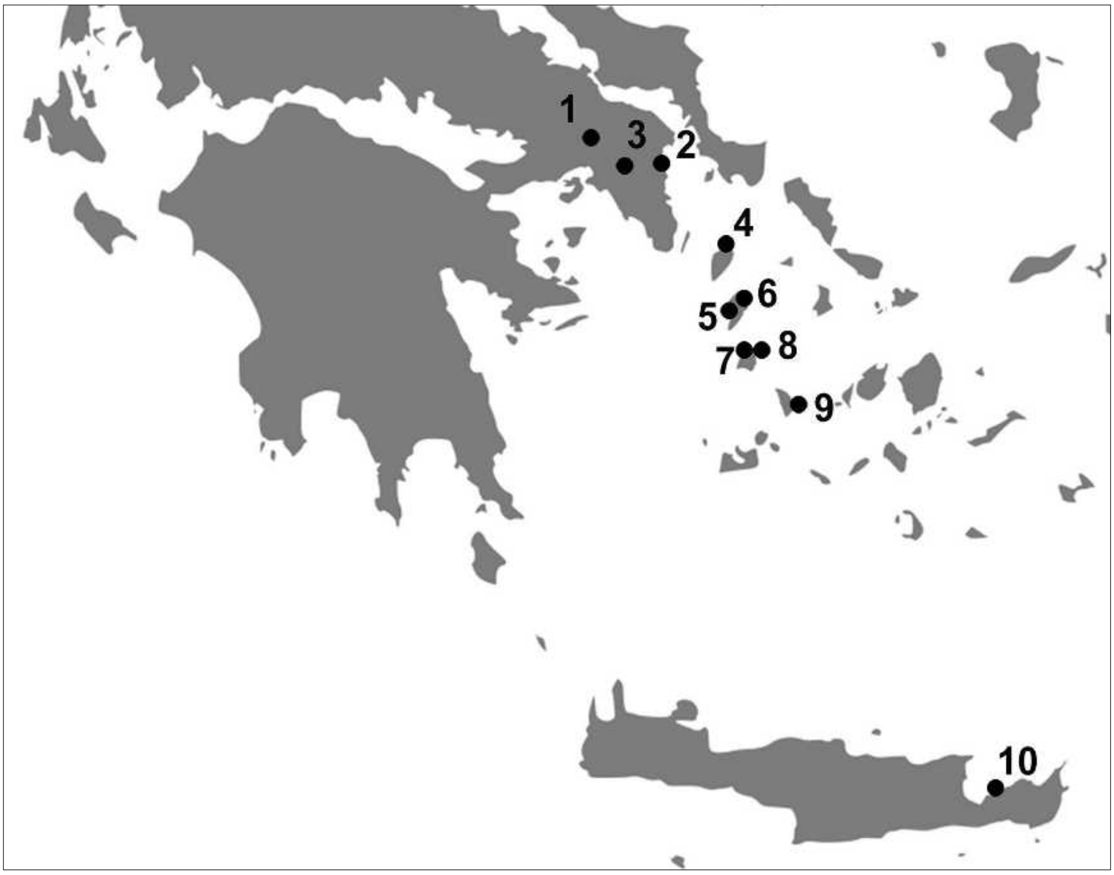

Figure 5. Sites with perforated kilns mentioned in the text : 1. South slope of Acropolis , Attica (FN) 2. Raphina Attica (EHII-III) 3. Gerakas Attica (EH) 4.Kefala Kea (FN) 5.Palaiopirgos /Aspra Spitia Kythnos (EH) 6.Sideri Kythnos (EH) 7.Avessalos, Seriphos (EH) 8.Kefala , Serifos (EH) 9.Kassela , Siphnos (EH) 10.Chrysokamino (EHIII).

Apart from Raphina, the use of perforated kilns seems to be known from another site in eastern Attica: the Early Helladic settlement of Gerakas, where remains were also found in a pit as in the case of Raphina (Plassara 2020). Other important Early Helladic smelting sites with perforated kilns were found in northwestern Kythnos (Sideri and Palaiopyrgos/ Aspra Spitia) (Bassiakos and Philaniotou 2007, 28–30), in western/northwestern Seriphos (Kephala and Avessalos) (Philaniotou, Bassiakos and Georgakopoulou 2011, 159–160), and in eastern Crete (Chrysokamino) (Betancourt 2006, 109–123 ; Betancourt 2008, 105–111). (Figure 5)

Important information concerning copper smelting furnaces come from Early Helladic Skali, a site in the southern part of Siphnos (western Cyclades), which, however, does not belong to the category of perforated furnaces (Papadopoulou 2011, 149–156). Other sites where the use of kilns without perforations was present are Fournoi, Kephala and Avessalos on Seriphos, where the technique of perforated kilns is also evident (Philaniotou, Bassiakos and Georgakopoulou 2011, 158–160).

Askitario – The settlement and the archaeometallurgical remains

A second fortified settlement of the Early Helladic period was also investigated by Theocharis. This was located on the top of Cape Askitario, two km south of Raphina, on a naturally-protected area by cliffs to the north-west and east. The settlement was abandoned or destroyed at the end of the Early Helladic period and was inhabited again in the middle of Late Helladic, as the few finds were revealed especially at the north sector (Theocharis 1957, 104; Theocharis 1960, 113). (Figure 6) The only disruption to the prehistoric backfilling is testified by the installation of military bunkers during the Second War World, as in the case of Raphina.

The settlement was inhabited from EHI through EHIII, and this constitutes its most representative archaeological phase. In this period, the settlement was fortified by a strong fortification wall (the excavation revealed a wall 32 m long, 2.50 m wide, and with an estimated height 3 m) (Theocharis 1957, 106; Theocharis 1960, 113; Theocharis 1961, 63–64), protecting its southwest side. The eastern side of the area was used

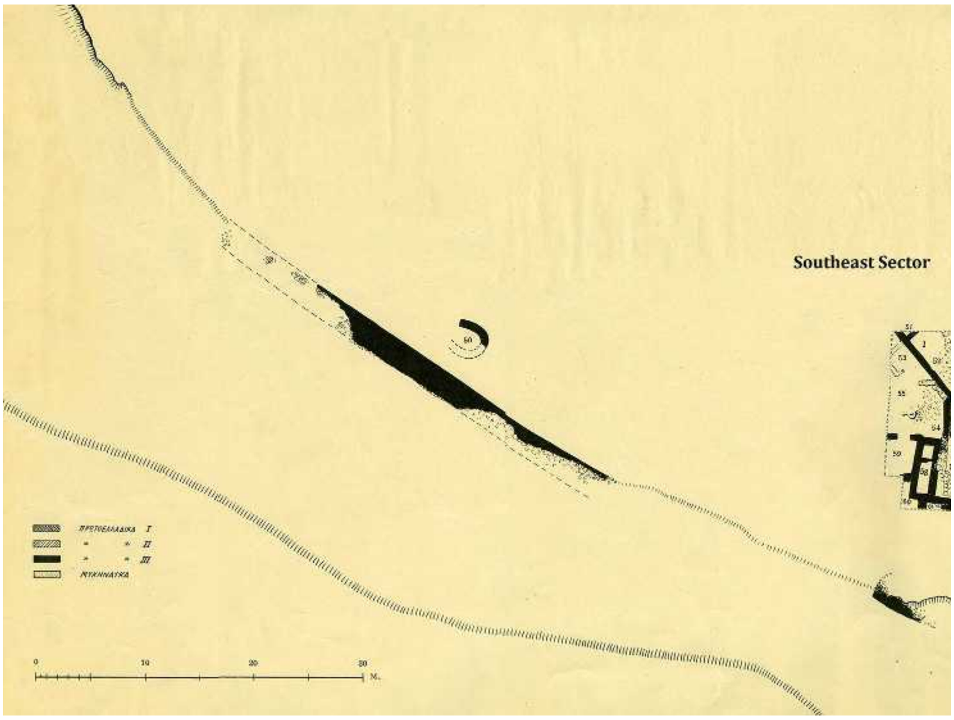

Figure 6. Plan of the acropolis of Askitario by D. P.Theocharis (Archeion Archaeologikis Etaireias).

as a cemetery although children's burials were also discovered within the houses (Theocharis 1960, 115). The excavations revealed two sectors of the settlement, the north sector and the southeast sector. In the north sector eight dwellings were revealed: Οικία Α *(House Alpha),* Οικία Β (*House Beta*), Οικία Γ *(House Gamma)* , Οικία Δ *(House Delta)*, Οικία Ε *(House Epsilon)*, Οικία Ζ (House Zeta), Οικία Θ *(House Thita)*, Οικία Η *(House Heta),* and a pit called *origma Zeta* (Theocharis 1957, 104–107, fig. 1; Theocharis 1961, fig. 3) (Figure 7). Like the case of Raphina, the settlement was organized in a dense plan. It was composed of houses having a megaroid layout, most of which had small dimensions. Between the houses cobbled roads were also identified. The completed excavated Οικία Ε (*House Epsilon*) is a representative example of a megaroid-type house with a main room, an anteroom, an open anteroom, and a roofed yard (Theocharis 1960, 109–112, fig. 2). At the southeast sector a few houses were revealed dated to the Early Helladic II and III (Theocharis 1960, 112–113).

Apart from pottery related to food production or storage with characteristic shapes and decoration of Early Helladic types, the existence of finds of a specific character indicates the involvement of the settlement inhabitants in metallurgical workshop activities, if not *in situ* production. Specifically, a stone mould (Figure 8) was found in EH III Οικία Α *(House Alpha)* (Karaindrou 2019) while in the nearby EH III Οικία Β *(House Beta)* a lead ingot (Karaindrou 2019) (Figure 9) was discovered**.** Apart from these two objects related to bronze and silver metallurgical circle, a slag (Figure 10) was found in Οικία Ε *(House Epsilon)* of the settlement (Karaindrou 2019). The stone mould made by grey steatite is of a close type, partially preserved in the one of its two parts, while on the back side one stripped groove had been engraved for the better adjustment of the joint of its two parts.

The mould is 12 cm long, 7 cm wide, and 3.5 cm high, and it was used for casting a spear head. Although used, there were no signs of burning or staining of the molten metal in the mould macroscopically or detected by pXRF analysis. Similar moulds are known from Sesklo (Tsountas 1908, 333–334, fig. 265) and Agios Mammas (Olynthos) (Hänsel 2003, 475–481, figs 1–2), while a few later examples come from Kastanas (Hochstetter 1987, 20–21, fig. 5, 3; 28, 7), Chalandritsa (Soura 2014, 60–69; Soura 2017, 483–495, fig. CXCIV-CXCV) and Aigeira in Achaea (Alram Stern 2004, 16–17 , fig. 1:18, 2:6). The spear-shaped lead ingot ("*leaf laurel shape*" according to the excavator`s description) is nearly totally preserved: 19 cm in length, 2.8 cm wide, and 1.4 cm thick with a weight of 417.24 gr. A quite similar ingot of later chronology was found in Lazarides, Aigina (Polychronakou Sgouritsa 2012, fig. 4). In another house of the settlement (House E), the use of lead is attested by the discovery of a lead clamp. This metallic object with a copper nail is one of the few metal objects unearthed in the settlement (Theocharis 1961, 75). The copper slag, almost cubic shaped, is 9.3

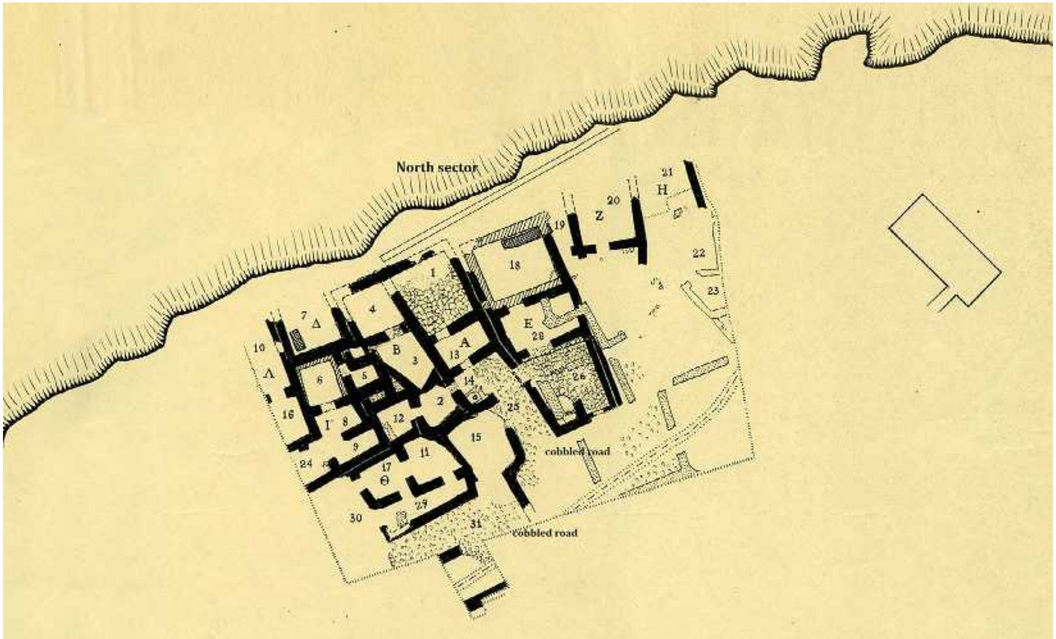

Figure 7. North sector of the excavation of Askitario (Archeion Archaeologikis Etaireias).

Figure 8. Stone mould from Askitario (Building A) (photograph by the author).

Figure 10. Slag from Building E (photograph by the author).

Figure 9. Lead Ingot from Askitario (Building B) (photograph by the author).

cm long, 6.5 cm wide, and 7.8 cm thick. Macroscopically a prill of copper was attested on its surface.

The existence of these isolated findings in separated buildings does not indicate the existence of metal workshop although the involvement of the inhabitants of the settlement with metalworking is certain. It is very probable that these kinds of workshop activities, which are related to secondary archaeometallurgical processes, are associated with the ones unearthed at Raphina.

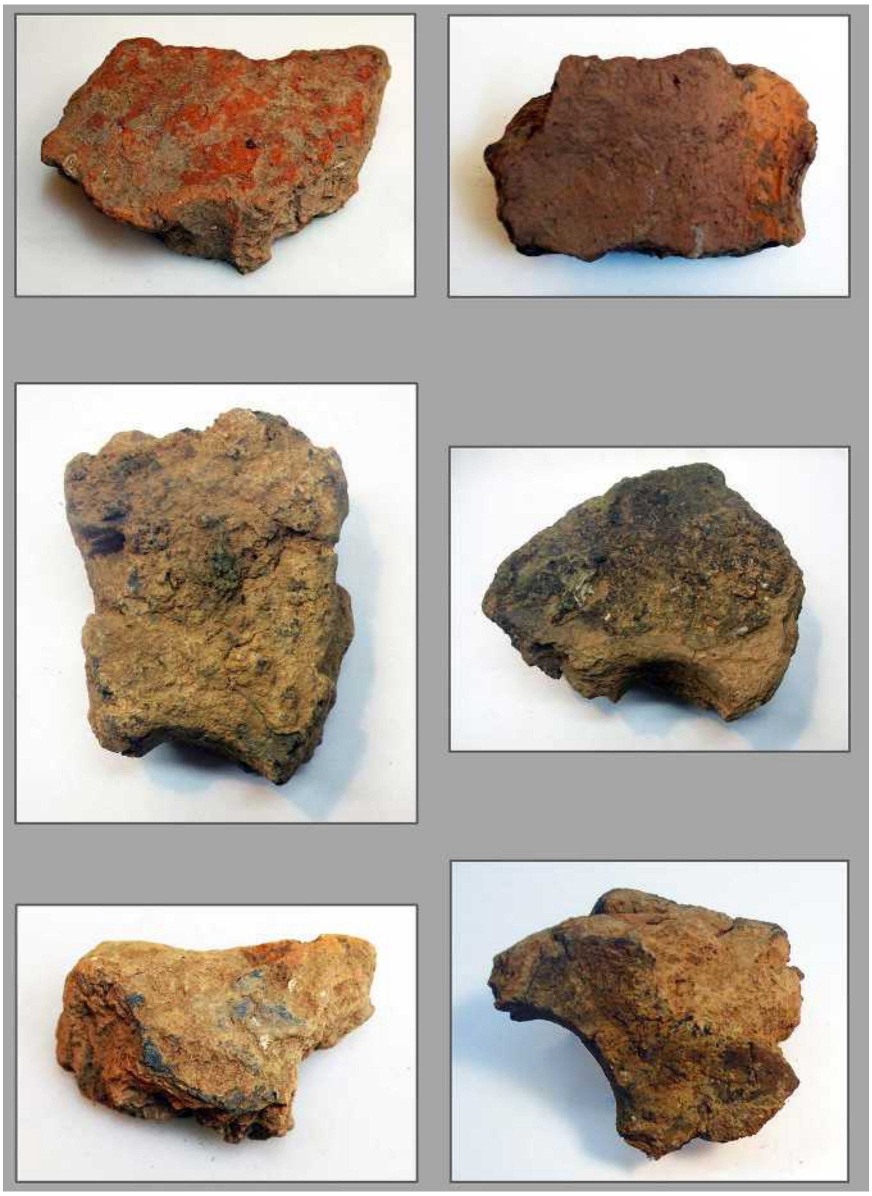

Figure 11. Perforated furnace fragments from Raphina, East Attica (photograph by the author).

The importance of Raphina's archaeometallurgical remains:

Early Helladic Raphina with its archaeometallurgical remains belongs to the few prehistoric sites on the Greek mainland (only three, all them in Attica) where early metallurgical practices employing the peculiar types of perforated furnace are attested though material evidence. Comparatively more sites with perforated metallurgical furnaces used for early metal production have been studied in the Cyclades (Kythnos, Siphnos, and more) and in eastern Crete (Chrysokamino). Although to date no scientific evidence connects the metallurgical remains of Raphina with the metalliferous deposits of Lavrion, this cannot be excluded. On the other hand, the location of both settlements, Raphina and Askitario, on coastal sites and physically protected, certainly played an important role in the development of a communication network between Central Greece, the Cyclades, and Euboea and their copper deposits.

Raphina's archaeometallurgical remains provide evidence for initial metallurgical procedures, and thus render it an early archaeometallurgical site. Since Raphina is located on a coastal site of eastern Attica facing the Cyclades, we can surmise the existence of contacts between the Greek mainland and Aegean islands and archaeometallurgical links from as early as the EBA period.

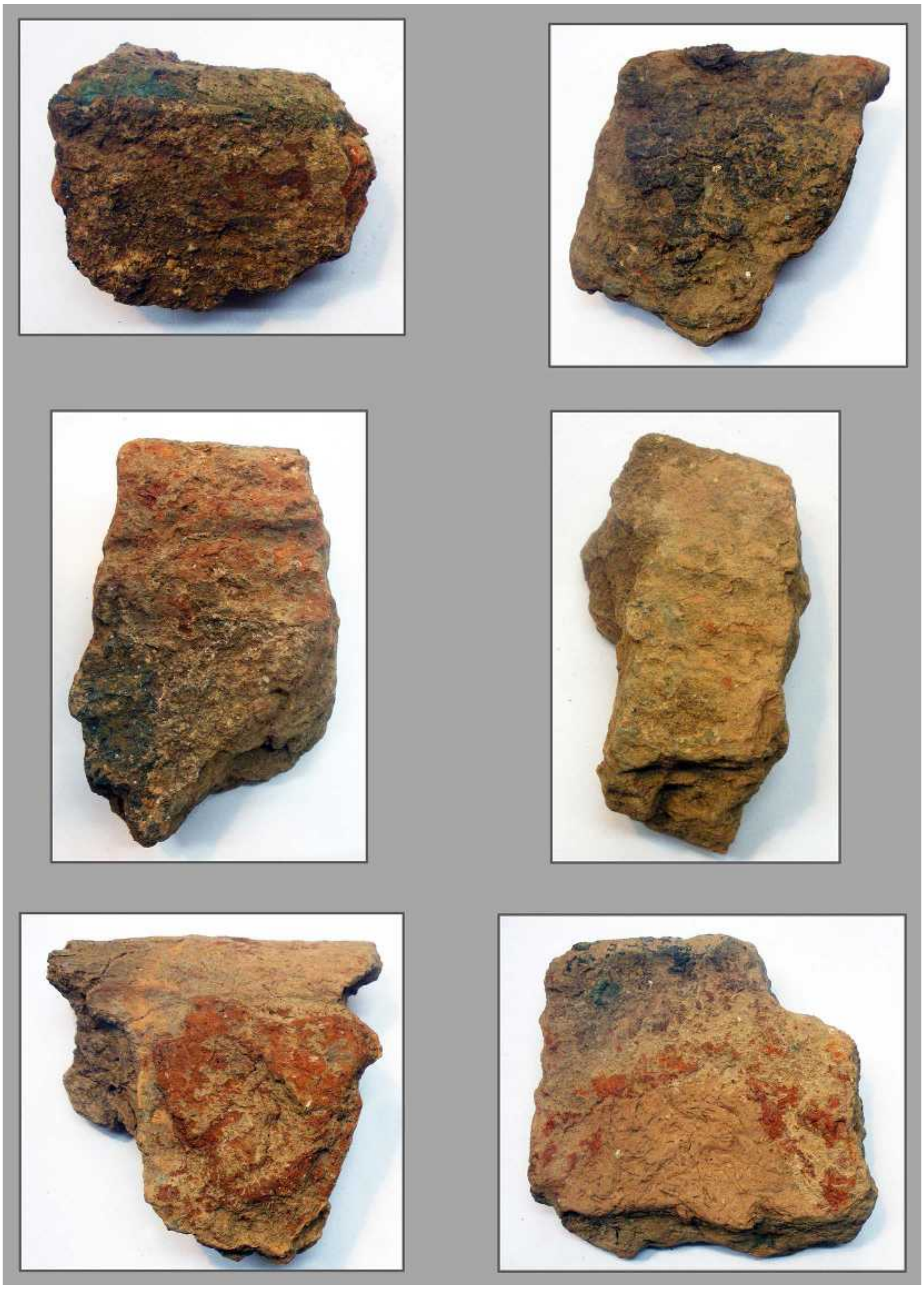

Figure 12. Not Perforated furnace fragments from Raphina, East Attica (photograph by the author).

Previous relevant research

In spite of the high archaeometallurgical importance of the above sites, only three copper slags from Pit A (*vothros skorion)* in Raphina have been studied (chemically and microscopically) by N. Gale and Z. Stos-Gale, whose work was presented in the International Symposium "Aegean Metallurgy in the Bronze Age" at Rethymno in 2004 (Gale, Kayafa and Stos-Gale 2008, 87–104).Their analytical research proved that the slags examined were metallurgical slags, probably connected to the fragments of kilns. This strengthened the assertion of the excavator of D. Theocharis regarding metal production in Early Helladic Raphina.

Sample	Description	Elements identified (presenting by their peak intensity)	Excavation
RAPH1	Slag	Fe, Cu, Pb, Mn, Ca	Raphina, Pit A
RAPH2	Slag	Fe, Cu, Pb, Ca	Raphina, Pit A
RAPH3	Slag or ore	Cu, Fe, Pb, Mn, Ca	Raphina, Pit A
RAPH4	Slag or ore	Cu, Fe, Ca	Raphina, Pit A
RAPH5	Slag	Pb	Raphina, Pit A
RAPH6	Slag	Fe, Cu, Mn, Pb	Raphina, Pit A
RAPH7	Slag	Fe, Cu, Pb, Mn, Ca,Ti	Raphina, Pit B
RAPH8	Slag or ore	Cu, Fe, Mn, Ca	Raphina, Pit B
RAPH9	Slag or ore	Cu, Fe	Raphina, Pit B
RAPH10	Perforated furnace	Fe, Cu, Pb, Mn, Ca, Ti	Raphina, Pit A
RAPH11	Perforated furnace	Cu, Fe, Mn, Ca, Pb	Raphina, Pit A
RAPH12	Perforated furnace	Cu, Fe, Zn, Pb, Ca	Raphina, Pit A
RAPH13	Perforated furnace	Cu, Fe, Mn, Ca	Raphina, Pit A
RAPH14	Perforated furnace	Cu, Fe, Mn, Pb, Ca	Raphina, Pit A
RAPH15	Furnace	Cu, Fe, Pb, Ca	Raphina, Pit A
RAPH16	Furnace	Fe, Cu, Zn,Pb, Ca	Raphina, Pit A
RAPH17	Furnace	Fe, Cu, Ca, Zn, Pb, Mn	Raphina, Pit A
RAPH18	Furnace	Cu, Fe, Mn, Ca, Pb	Raphina, Pit A
ASK.1	Slag	Fe, Cu, Pb, Mn, Ca	Askitario, Building E
ASK.2	Ingot	Pb	Askitario, Building B

Table 1 P-xrf analysis of archaeometallurgical remains from Early Helladic settlements Raphina and Askitario, East Attica .

Furthermore, the analytical data of lead clamps from Raphina (Liritzis 1996: 164–5, Figures 4.5, 1.2) (and the slags themselves (Gale, Kayafa and Stos-Gale 2008, 99–101, 96 (Table 6)) confirm the providence of copper and lead from Lavrion, thus supporting the theory of early silver, lead, and copper ore exploitation in this area.

The new project

Preliminary archaeological and technological studies began on about 20 fragments or intact archaeological objects from both Raphina and Askitario after obtaining the appropriate permits from the National Archaeological Museum, where the material is kept.

The main aims of the project are to: 1) investigate the archaeometallurgical character of the finds; 2) examine whether the primitive smelters were engaged with solely copper or lead/silver production; 3) search for the origin of the ores smelted there (Lavrion or Cyclades); and 4) look for similarities or differences in the employed practices on these sites with technological parallels from the Cyclades and Crete (Katsambas and Chrysokamino).

According to first archaeological studies, Group A contains six clay furnace fragments (out of 14) that bear perforations (Figure 11). They are all made of coarse fabric clay, of a red-orange color fired in high temperatures. The inner concave surface often exhibits vitrification layers bearing slag traces. The thickness of the pieces vary from 4 to 5.3 cm while the diameter of the perforations are all 3 cm. They seem to belong to more than one furnace bearing in mind the differences in the consistency of the clay and the impact of temperature. Group B consists of eight pieces without perforations and with a slightly finer thickness (varies 3–4,5 cm). (Figure 12)

Surface analyses by employing one semi-portable XRF device (with a Rhodium anode X-ray tube, a Si-PiN detector XR-100CR, Amptek Inc., and a multichannel analyzer (MCA-8000A, Amptek Inc.) were performed on clay fragments, slags, the mould fragment, and the lead ingot.

Preliminary results

The XRF analyses performed on the inner surfaces of the furnaces' fragments demonstrate the presence of metallurgical residues. The results of the pXRF (Table 1), indicate that the metallurgical ceramics of Raphina were used for the processing of copper (Cu), though minor concentrations of lead (Pb) and zinc (Zn) were also detected. The presence of Cu as a main component in the Raphina slags indicates the smelting of Cu in the area. The results of the analysis of the slag from Askitario are similar to the aforementioned results from Raphina. The presence of Pb and Zn raise the question of whether they are indicative of the raw materials used during the smelting process.

Future examination

For the finite establishment of metallurgical operations at Rafina and Askitario, micro analytical and other methods need to be applied so as to complement the preliminary conclusions drawn from the pXRF analyses.

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Non-Destructive p-XRF Investigation of Prehistoric Metal Artifacts from Sites in the Karystos Area (South Euboea, Greece)

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Abstract: Archaeological excavations and surveys in Karystos/South Euboean prehistoric sites have revealed the important role of this area between the Aegean Islands and mainland Greece in the exchange and social networks of the prehistoric Aegean. In the context of an attempt to further our knowledge of the production, circulation, and utilization of metal items in the prehistoric Aegean, a series of artifacts from the area were analyzed by means of portable X-ray fluorescence spectroscopy (p-XRF). The corpus of analyzed items includes a Late Neolithic II awl and three Early Bronze Age II items from Agia Triada cave, a Late Neolithic II– Early Bronze Age I axe from the site of Gourimadi, a likely fragment of a copper ingot and various artifacts from the Agios Nikolaos site (Middle to Late Bronze Age), and metallurgical ceramic fragments of an uncertain date from a recently discovered site in the Katsaronio plain. Our preliminary qualitative analytical data revealed that the Agia Triada artifacts, the Gourimadi axe, and the Agios Nikolaos ingot are made of copper, occasionally containing arsenic and lead. Similarly, remnants of copper on the Katsaronio metallurgical ceramics show enhanced arsenic. On the contrary, a tweezers' part and a metal sheet from Agios Nikolaos are made of copper-tin alloys, thus revealing the use of bronze. The reported preliminary analytical data correlate with the archaeological interpretation (i.e. dating) of the Agia Triada and Gourimadi finds and confirm their Late Neolithic/Early Bronze Age dates. Moreover, the simultaneous use of arsenical and tin bronzes in the Agios Nikolaos site indicates a later date (first half of the second millennium BC?).

KEYWORDS: ARSENIC, TIN, INGOT, LATE NEOLITHIC, EARLY BRONZE AGE, METALLURGICAL FURNACE, KARYSTIA.

Introduction

Archaeological surveys and excavations indicate that the area of Karystos ("Karystia") was a part of the wider Aegean world of interactions. Known settlements such as Akri Rozos, Kalamos, Agia Pelagia, and others have yielded materials indicating external contacts (Cullen *et al.* 2013, 59). The degree, frequency, and character of the connections with the Cyclades, the mainland, and other regions is not, however, entirely clear yet. Euboea does not belong to the Cycladic islands, but lies in close proximity to them (Tankosić 2011, 4-5, 2017; Mavridis and Tankosić 2016a, 214). Euboea's southern part, which is separated from the rest of the island by mountains, can even be considered as the northernmost Cycladic island, based on both the features of the landscape and the archaeological evidence from the area (Tankosić 2017; Tankosić and Katsianis 2018, 243). Connections with the Cyclades are present already from the Late Neolithic period (Mavridis and Tankosić 2016b; Mavridis 2017). It is well documented that the Euboean Gulf functioned as an important maritime thoroughfare in prehistory, evidenced by the Cycladic contacts attested at several archaeological sites along its shores (Tankosić 2011, 283-295; 2017, 102). This position of the Karystos area provides an opportunity to investigate issues related to the connection between material culture and social identity as well as the overall character of connections among Euboea, the Cyclades, and other regions. In this respect, the presentation of the metal artifacts discovered from excavations and surveys in the area of Karystos and their dating—ranging from the Neolithic to the Middle Bronze Age—presents a unique opportunity to explore the role of the area in the production and consumption strategies of metals in the Aegean.

In the framework of the current study, metal items discovered at various sites on the area of Karystos were analytically investigated by means of non-destructive portable X-ray fluorescence analysis (p-XRF). The corpus of analyzed items includes a Late Neolithic awl

Figure 1. A map showing the sites mentioned in the text; insert shows South Euboea with the area of interest marked in rectangle. Maps are adapted from scihub.copernicus.eu.

and three Early Bronze Age items recovered from a burial context in the Agia Triada cave excavated between 2007-2010 by the Ephoreia of Palaleoanthropology and Speleology (Mavridis and Tankosić 2016a, b; Mavridis 2017) (a pair of tweezers, a dagger and a cylindrical lead object); a Late Neolithic II– Early Bronze Age I axe found on the surface of the Gourimadi site during the Norwegian Archaeological Survey in the Karystia project (NASK, Tankosić *et al.* 2021), and a fragment of a copper ingot, partial tweezers, a piece of wire, and a lead mass collected during a surface survey at the Agios Nikolaos site (Middle to Late Bronze Age) (Figure 1). We also tested two fragments of metallurgical ceramics from a recently discovered site in the Katsaronio plain that is currently of uncertain dating (Tankosić *et al.* 2021) (Figure 1 and 2). Despite its preliminary character, the current research project is of importance as there is a notable literature gap in data pertaining to early metallic artifacts from south Euboea. In addition, the results reported herein hint towards a rather early appearance of metals in the area, and strongly indicate local processing of relevant materials.

Methodology

All items were analyzed at the facilities where they are stored, the Karystos Archaeological Museum and the conservation laboratory of the Ephorate of Palaeoanthropology and Speleology using a portable X-ray Fluorescence spectroscopy device. The employed setup comprised of an Rh-anode X-ray tube (50W, 50kV, 75μm Be window), a Si-PiN X-ray detector (XR-100CR, Amptek Inc.), and a multichannel analyzer (MCA-8000A, Amptek Inc.). Collected spectra were qualitatively processed using the ADMCA software (Amptek Inc.). Wherever possible, soil contamination was gently removed from the surfaces of the items prior to XRF investigation in order to avoid interference in the spectra. However, further treatment of the surface (e.g. corrosion removal) was currently impossible, so the collected XRF spectra were treated in a qualitative basis. Through employment of long collection times (generally in the range of 300 to 600 seconds) and adequate acquisition parameters, spectra of optimized elemental peak intensities to background ratios were collected. In the case of certain items, spectra from more than a single spot were collected (see Table 1). Due to a series of experimental restrictions (analysis conducted on severely corroded items and often on curved/non flat areas, and the like), it was not deemed possible to proceed with the quantification of the analytical data. Therefore, the relative intensities of the various elements detected are represented in a merely qualitative manner: three stars (***) mark the major element; two (**) the main ones; and one star (*) denotes minor elements (Table 1).

Results and discussion

Indicative p-XRF spectra are shown in Figure 3; the qualitative XRF analysis data are summarized in Table 1.

Figure 2. (a) Axe from Gourimadi; (b) Partial tweezers and (c) Ingot fragment (?) from Agios Nikolaos; (d) *Top*: awl from Agia Triada/ *Bottom*: metallurgical ceramic, Katsaronio plain; arrow indicates metal remnants.

Agia Triada cave items

Analytical data reveal that the Agia Triada cave items were either made of pure copper (Late Neolithic awl) or of copper containing arsenic and occasionally lead (Figure 3, Table 1). The cylindrical object of lead was found to contain only minor traces of iron, most probably related to soil contamination. The fact that none of the copper items bears tin is consistent with the early copper metallurgy practices in the Aegean and neighboring areas (see e.g. Craddock 1976; Mangou and Ioannou 1997, 1998, 1999; Papadimitriou 2001; Nerantzis *et al.* 2016; Georgakopoulou 2018). Therefore, it may be stated that the elemental profiles of the Agia Triada cave metal items correspond with the archaeological interpretation of the site (Mavridis and Tankosić 2016a; Mavridis and Tankosić 2016b; Mavridis 2017).

Agios Nikolaos items

Three spot analysis conducted on the Agios Nikolaos copper ingot revealed that it contains arsenic. This fact indicates: a) an early date (arsenical bronze employment); and b) that the copper was already alloyed and therefore ready to be used in secondary metallurgical processes such as casting or/and hammering (Tylecote 1976; Georgakopoulou 2018). In contrast, the partial tweezers and the wire were made of bronze (copper alloyed with tin) containing minor quantities of arsenic and lead. The detection of arsenic traces may reflect experimentation on the newly-introduced tin-alloyed bronzes or/and recycling of older arsenical bronze items. The detection of lead most probably pertains to either intentional (e.g. for facilitating casting) or accidental (impurity) addition (Papadimitriou 2001). Though Bronze items are occasionally unearthed in 3rd millennium BC Aegean contexts, it is generally accepted that tin was not introduced in western Aegean metallurgy before the first half of the 2nd millennium BC (Craddock 1978; Mangou and Ioannou 1997, 1998, 1999; Papadimitriou 2008). In this context, our preliminary analytical data highlight an important—and possibly long-lasting—activity at the site of Agios Nikolaos.

Gourimadi axe

The Gourimadi axe was found to consist of copper. A minor iron peak that appears in the pertinent spectra (see Figure 3b) pertains to either surface soil contamination or impurities introduced during the

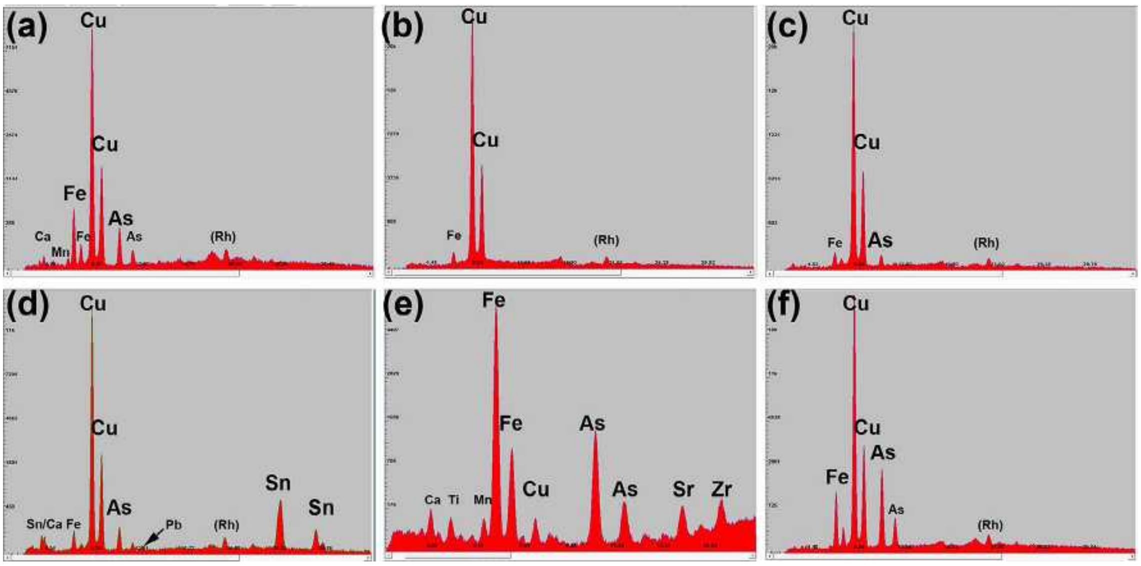

Figure 3. Indicative XRF spectra. **(a)** Dagger, Agia Triada **(b)** Axe, Gourimadi **(c)** Ingot, Agios Nikolaos (AN) **(d)** Tweezers (AN) **(e)** Metallurgical ceramic fragment, inner/vitrified surface, Katsaronio (K) **(f)** Metallurgical ceramic, remnants of metal (K). Rh peaks (appearing in most of the spectra) pertain to the X-ray source.

Table 1. Qualitative p-XRF analyses results. The minor, main, and major elements are denoted by one, two and three stars respectively. Abbreviations: tr: traces.

Findspot	Item	Analyses	Detected elements										
			Ca	Ti	Mn	Fe	Cu	Zn	As	Pb	Sr	Zr	Sn
Agia Triada	Awl	1				*	***						
		2				*	***						
	Lead mass					*				***			
	Tweezers					*	***		*	*			
	Dagger	1	tr	tr	tr	**	***		*				
		2	tr	tr		**	***		*				
Gourimadi	Axe	1				tr	***						
		2				tr	***						
Agios Nikolaos	Ingot	1				*	***		tr				
		2				*	***		*				
		3				tr	***		tr				
	Tweezers	1				*	***		*	tr			**
		2				*	***		*	tr			**
	Lead mass					tr				***			
	Wire					*	***		*	*			tr
Katsaronio plain	Furnace fragment	1-inside	*	tr	*	***	**			tr	*	tr	
	(A)	2-outside	*	*	tr	***	*		**	tr	*	*	
		3-metal remnants	tr	tr	tr	*	***		**				
	Furnace fragment	1-inside			*	**	***		tr				
	(B)	2-outside	*	*	tr	***	*	tr	**			*	

smelting of the raw materials. Objects such as axes were commonly made of harder materials in order to withstand the loads introduced during their use; hence the use of unalloyed copper in case of the Gourimadi item seems odd. In addition, a close inspection of the axe reveals that its surface is notably uneven and retains various casting defects (Figure 2a), indicating that the item did not undergo hammering. It thus appears that this particular object was probably not manufactured for the purpose of being used as an axe. On the contrary, its shape and elemental composition[1] imply employment of an axe mould for casting purposes. Similar practices are known to have been adopted by Bronze Age societies in various European sites where axe moulds were frequently used for ingot casting purposes (Kuijpers 2015; Needham 2018; Gandoix *et al.* 2019). Another possibility is that the axe comes from the yet-undiscovered funerary contexts, since the item was a surface find and its original deposition context is impossible to pinpoint.

Katsaronio plain metallurgical ceramics

The Katsaronio metallurgical ceramic comes from findspot 12-18, and was discovered during the NASK project (Tankosić *et al.* 2021). The ceramic fragments probably correspond to a metallurgical furnace and were made of reddish clay tempered with plant material (probably straw) and coarse grains of unidentified mineral(s) (Figure 2c/bottom). Such materials were often added to clay pastes to improve the behavior of metallurgical ceramics upon their use (Martinòn-Torres and Rehren 2015). These fragments are non-homogeneous in terms of texture. For this reason, various spots on the ceramics were subjected to p-XRF analysis. Specifically, spectra were collected from the inner (vitrified) and external (non-vitrified) surfaces of the fragments, as well as from the remnants of oxidized metal still preserved on the edges of a fragment and presumably corresponding to the smelting product (Figure 2c/bottom and Table 1). Analytical data show that both the inner and outer parts of the ceramics contain various (typical for clayey materials) elements (Ca, Ti, Mn, Fe, Rb, Sr) along with copper and arsenic. On the other hand, the metal remnants on the rim consist of copper, arsenic, and a bit of iron (Figure 3f). The fact that arsenic is detected on both the furnace ceramic body and the metal remnants constitutes strong evidence of arsenical bronze production. This in, turn, suggest a rather early date for the findspot 12-18. Finally, it is worth noting that in terms of typology, the Katsaronio metallurgical fragments seem to stem from an "unperforated" furnace. This deviates from Early Bronze Age practices in the Aegean islands, which commonly employed perforated furnaces (Pryce *et al.* 2007; Bassiakos and Philaniotou 2007; Philaniotou *et al.* 2011).

Conclusions

The qualitative p-XRF data stand in agreement with the archaeological interpretation of the metal artifacts under discussion. Items made of tin bronze (with traces of arsenic) and an arsenical bronze ingot were unearthed from the Agios Nikolaos site. The coexistence of the two typical copper alloys of the Bronze Age at a single site suggests an early 2nd millennium BC dating. The two Late Neolithic II items from Gourimadi and Agia Triada sites were made of unalloyed copper, while the Early Bronze Age items from Agia Triada were made of arsenical bronzes. The Gourimadi LN II item is of special interest as it indicates the use of an axe mould for casting purposes, possibly indicating that at least some kind of secondary metal processing took place at the site itself. At the moment, it is difficult to show that primary (extractive) metallurgical processes were also practiced in the area of Karystos at this early date. Nevertheless, preliminary results from the Katsaronio plain metallurgical ceramic XRF analysis seem to favor this hypothesis. The analytical data presented herein indicate a presumably important (and to date unexplored) role of the area of Karystos in the development of early Aegean metallurgy. Therefore, it is important to continue and expand the current project by enhancing the toolkit of available analytical techniques and including more items. Our preliminary qualitative data already highlight the need for quantitative elemental analysis which, in combination with microstructural investigation, will reveal important technical aspects of early metallurgical practices—such as raw materials procurement/provenance and processing—in the Karystos area.

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[1] The smelting of As-bearing copper ores was not a universal practice in early Aegean metallurgy, and thus the use of unalloyed copper was not uncommon (Katapotis *et al.* 2011).

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Τεχνικές εξέτασης (pXRF / SEM-EDS) σε χάλκινα ευρήματα από το Μινωικό Ιερό Κορυφής των Κυθήρων

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Abstract: At the location of Ayios Georgios sto Vouno on Kythera island, is the Minoan Peak Sanctuary, the only one that has been found outside Crete. Based on archaeological data, it was founded in the MMIB period and remained in use until the YMIB. The sanctuary was excavated in two periods, a) 1992-1994 by the unforgettable archaeologist G. Sakellarakis and b) 2011-2015 by the University of the Peloponnese under the direction of the Assistant Prof. Emilia Banou. Main characteristic of the sanctuary's location is the diversity and the variety (113 bronze statuettes of Minoans adorants and bronze offerings: human limbs, a figurine of a scorpion, a small votive double axe, cut-out figurines as well as various miniature blade cut-outs) of bronze offerings.

The aim of the present study is to examine issues related to technology, manufacture and potential origins of metal findings from the Kythera peak sanctuary, through a preliminary examination of 19 of the bronze objects. Chemical analysis of these objects was carried out at the Archaeometry Laboratory of the University of the Peloponnese using a portable X-ray fluorescence (pXRF) device and a Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) system.

Both analytical techniques have shown that the objects are made of copper-based alloys containing both arsenic and tin, except one which is manufactured by a silver-copper alloy, containing amounts of arsenic and tin as well. Elements detected in almost all of the objects examined are lead, iron, zinc, silver, nickel and antimony, while elements such as calcium, aluminum, silicon, magnesium and chlorine may be due to corrosion, or may be related to the smelting procedure or to the presence of soil remains, entrapped to corrosion encrustations. Sulfur was also detected in some of the objects. Objects containing high levels of zinc are probably from later periods as the deliberate addition of zinc to copper alloys appears after Roman times.

The results of the research showed that the analyzed objects varied in their elemental composition, and indicate the existence of different sources of ore origin, the use of metal from recycling as well as the use of different alloys depending on the type of object that would be manufactured. The low concentration in the tested alloys of elements such as iron in combination with the high concentration of elements such as lead may lead to the assumption that the melting point of the produced alloy could was controlled. Possible conditions for the selection of alloys could be: the manufacturing techniques, the concentration of other non-pure elements and the mechanical properties of the produced object. In addition, some amorphous metal lumps may be fragments of ingots since their composition indicates pure bronze with a detected high copper content, while, another bronze waste may be a bronze prills residue indicating manufacture *in situ*. It is noteworthy that in a period when tin bronze was already used, significant tin concentrations have not been detected, while, a high copper content has been documented by the analyses. Thus, the objects were probably made by pure copper with a low amount of impurities. From the recorded distribution of tin and arsenic we could conclude that in the examined objects the only cases where a deliberate alloying occurs are the arsenical coper of the figurine base and two cases of tin bronzes.

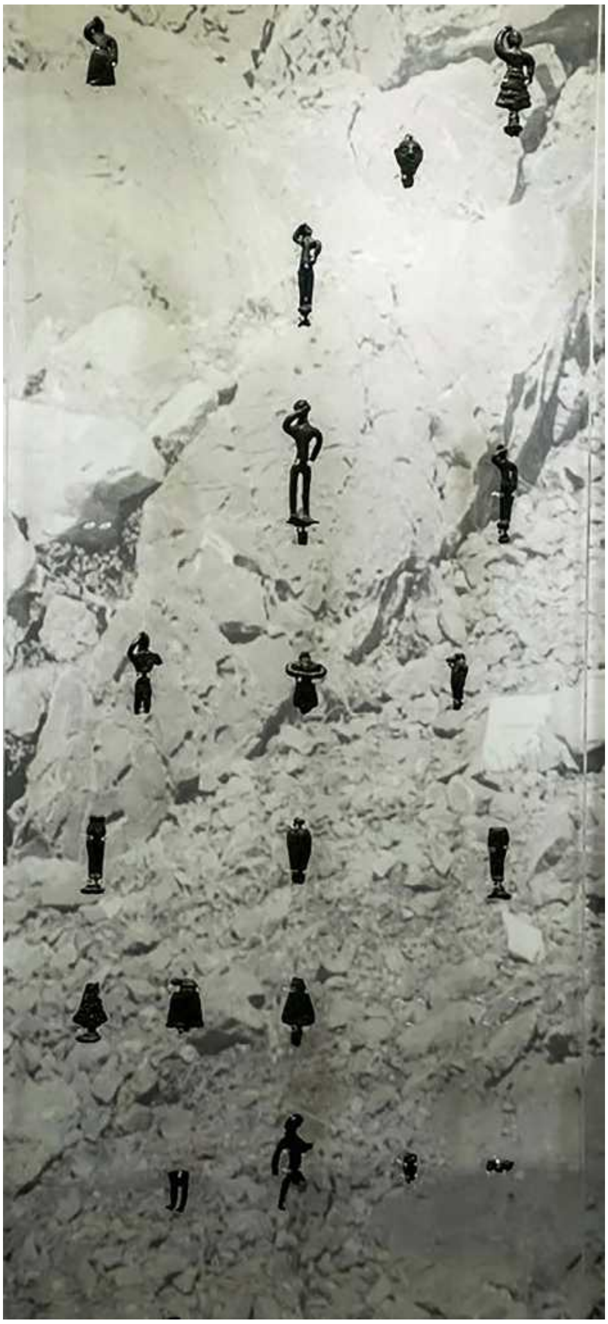
Research on the technology, manufacturing and possible provenance of the metal in the middle of the 2nd millennium BC, based on the analytical techniques of the bronze votives from the Minoan peak sanctuary at Ayios Yeorgios sto Vouno on Kythera continues in the context of a doctoral study running by the author.

KEYWORDS: CHEMICAL ANALYSES, XRF ANALYSIS, SEM-EDS ANALYSIS, COPPER ALLOYS, COPPER MANUFACTURE

Αρχαιολογικά δεδομένα

Στη θέση Άγιος Γεώργιος στο Βουνό Κυθήρων βρίσκεται Μινωικό Ιερό Κορυφής, το μόνο που έχει εντοπιστεί εκτός Κρήτης μέχρι σήμερα. Με βάση τα αρχαιολογικά δεδομένα, ιδρύθηκε στη ΜΜΙΒ περίοδο και παρέμεινε σε χρήση έως την ΥΜΙΒ. Το ιερό ανασκάφτηκε σε δύο περιόδους η πρώτη το 1992-1994 από τον αείμνηστο αρχαιολόγο Γιάννη Σακελλαράκη και η δεύτερη το 2011-2015 από το Πανεπιστήμιο Πελοποννήσου υπό την διεύθυνση της Αναπληρώτριας Καθηγήτριας κ. Αιμιλίας Μπάνου (Banou 2012, Sakellarakis 2011).

Χαρακτηριστικά γνωρίσματα της θέσης του ιερού είναι η πληθώρα και η ποικιλία των χάλκινων αφιερωμάτων μεταξύ των οποίων 110 χάλκινα ειδώλια λατρευτών και χάλκινα αναθήματα ανθρώπινων μελών, ειδώλιο σκορπιού, διπλός πέλεκυς, περίτμητα ειδώλια και λεπίδια (Εικόνα 1.4) (Banou 2012, Banou 2014).



Εικόνα 1. Νέο Αρχαιολογικό Μουσείο Κυθήρων: Χάλκινα ειδώλια λατρευτών, ανθρώπινα μέλη και περίτμητα από το Μινωικό Ιερό Κορυφής στον Άγιο Γεώργιο στο Βουνό Κυθήρων.

Εικόνα 2. Αρχαιολογικό Μουσείο Πειραιά: Χάλκινα ειδώλια λατρευτών, ειδώλιο σκορπιού, διπλός πέλεκυς, περίτμητα από το Μινωικό Ιερό Κορυφής στον Άγιο Γεώργιο στο Βουνό Κυθήρων.

Τεχνολογική έρευνα

Με σκοπό την εξέταση θεμάτων που αφορούν την τεχνολογία, την κατεργασία και την πιθανή προέλευση των μεταλλικών ευρημάτων από το ιερό κορυφής των Κυθήρων, εξετάστηκαν προκαταρκτικά 19 από τα χάλκινα αντικείμενα της ανασκαφικής περιόδου 2011-2012. Μέσω των τεχνικών ανάλυσης έγινε προσπάθεια να αποσαφηνιστούν θέματα σχετικά με τη χημική τους σύνθεση καθώς και με τεχνολογικά χαρακτηριστικά τους, να προσδιοριστεί ο τύπος του κράματος που χρησιμοποιήθηκε και να διερευνηθεί ο συσχετισμός των ευρημάτων με άλλα παρόμοια καθώς και με πηγές μεταλλευμάτων. Η χημική ανάλυση των αντικειμένων πραγματοποιήθηκε στο εργαστήριο Αρχαιομετρίας του Πανεπιστημίου Πελοποννήσου, χρησιμοποιώντας φορητή συσκευή Φθορισμού Ακτίνων Χ (pXRF) και Ηλεκτρονικό Μικροσκόπιο Σάρωσης εφοδιασμένο με Φασματόμετρο Ενεργειακής Διασποράς Ακτίνων Χ (SEM-EDS). Η έρευνα βρίσκεται σε εξέλιξη στο πλαίσιο διδακτορικής διατριβής από την γράφουσα.

Η επιλογή των ευρημάτων που εξετάστηκαν έγινε λαμβάνοντας υπόψη ότι: α) διαφορετικά κράματα έχουν χρησιμοποιηθεί στην κατασκευή αντικειμένων που προορίζονται για διαφορετικές χρήσεις, β) ο χώρος χρησιμοποιήθηκε όχι μόνο κατά τη διάρκεια των προϊστορικών αλλά και κατά τη διάρκεια των βυζαντινών και μεταβυζαντινών χρόνων, περιλαμβανομένων των σπάνιων ευρημάτων της κλασσικής και ρωμαϊκής

Εικόνα 3. Αρχαιολογικό Μουσείο Πειραιά: Χάλκινα αναθηματικά λεπίδια και ειδώλια λατρευτών από το Μινωικό Ιερό Κορυφής στον Άγιο Γεώργιο στο Βουνό Κυθήρων.

Εικόνα 4. Αρχαιολογικό Μουσείο Πειραιά: Χάλκινο ειδώλιο σκορπιού, ειδώλια λατρευτών και ανθρώπινα μέλη από το Μινωικό Ιερό Κορυφής στον Άγιο Γεώργιο στο Βουνό Κυθήρων.

Πίνακας 1. Περιγραφή του χάλκινου ελάσματος KYT_AYV_BS_19 **και συναφείς πληροφορίες**.

Table 1. The Bronze Sheet KYT_AYV_BS_19

<table>
<tr><td rowspan="2"></td><td>Weight: 2.1gr</td><td>Dimensions (max.)
Length:5.3cm
Width: 3.2cm
Thickness: 0.1cm</td><td>Excavation date: 21/07/2011</td></tr>
<tr><td colspan="3">Excavation data:
From rubble of retaining wall</td></tr>
<tr><td colspan="4">Macroscopic description:
Rectangular copper-based sheet with a probable incised leg at the centre; on the perimeter repoussé dot decoration; suspension hole in the middle of upper edge; yellowish color on the front - silver appearance on the back; greenish and gray-black corrosion products appear locally in very thin layers; black spots unevenly distributed mainly on the back.</td></tr>
</table>

εποχής, οπότε και χρησιμοποιήθηκαν διαφορετικοί τύποι κραμάτων χαλκού και γ) παρουσιάζει ενδιαφέρον η αναζήτηση αντικειμένων που σχετίζονται με μεταλλικές διαρροές

Τα επιλεγμένα αντικείμενα κατανεμήθηκαν σε τέσσερις κατηγορίες ανάλογα με την τυπολογία τους και συγκεκριμένα αναλύθηκαν επτά ελάσματα, επτά κατάλοιπα χύτευσης, ένα τμήμα από βάση ειδωλίου και τέσσερα θραύσματα από μεταλλικά αγγεία. Στην κατηγορία των ελασμάτων περιλαμβάνονται περίτμητα αναθηματικά λεπίδια και τμήματα ελασμάτινων αντικειμένων, ενώ στην κατηγορία των καταλοίπων χύτευσης περιλαμβάνονται μικρού μεγέθους άμορφες μάζες από κράμα χαλκού που πιθανόν αποτελούν μεταλλικές διαρροές ή δηλώνουν υλικό από/για κατεργασία μετάλλου, (Panagopoulou 2016).

Στην κατηγορία των χάλκινων ελασμάτων το αντικείμενο KYT_AYV_BS_19 παρουσιάζει διαφορετική εμφάνιση καθώς πρόκειται για ένα ορθογώνιο έλασμα με εγχάρακτη διακόσμηση, πιθανόν ποδιού, στο κέντρο, διάστικτη διακόσμηση στην περίμετρο και οπή ανάρτησης στο κέντρο. Το αντικείμενο έχει κιτρινωπό χρώμα στην εμπρόσθια όψη και ασημίζουσα εμφάνιση στην πίσω όψη, ενώ κατά τόπους διακρίνονται πρασινωπά και γκρι έως μαύρα περιορισμένου πάχους στρώματα διάβρωσης στις δύο όψεις του και μαύρα στίγματα στην πίσω όψη (Πίνακας 1).

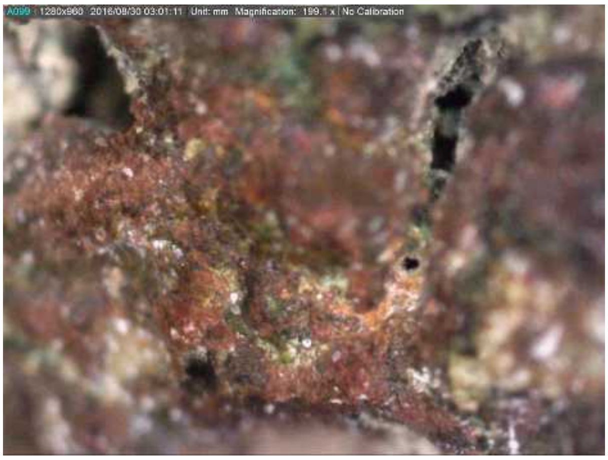
Οπτική Μικροσκοπία

Μέσω ενός οπτικού ψηφιακού μικροσκοπίου και σε μεγέθυνση έως 200X παρατηρήθηκαν, στην κατηγορία των καταλοίπων χύτευσης, χαρακτηριστικά που επιβεβαιώνουν την ύπαρξη στερεοποιημένου τηγμένου μετάλλου. Επιβεβαιώθηκε η ύπαρξη σφαιριδίων χαλκού που σε κάποιες περιπτώσεις περιβάλλονται από οξείδια του χαλκού και του σιδήρου. Εντοπίστηκαν επίσης ασβεστιτικά συσσωματώματα τα οποία μπορεί να προέρχονται από το μετάλλευμα ή να υπάρχουν ως διαβρωμένα υλικά εκκαμίνευσης, από τη χρήση ασβεστίου κατά τη διάρκεια της τήξης. Παρατηρήθηκε η ύπαρξη πορώδους που σχηματίστηκε κατά τη ροή και την ψύξη του μετάλλου, διαγνωστικό χαρακτηριστικό του πορώδους που προκαλείται από αέρια και σχηματίζει οπές εξαιτίας της εξαγωγής ατμού κατά τη διαδικασία της τήξης (Panagopoulou 2016). Ο ατμός θα μπορούσε να παραχθεί ως αέριο ανάφλεξης (combustion gas) από την καύση του ξύλου που χρησιμοποιήθηκε και οι κενοί χώροι (οι πόροι) θα μπορούσαν να έχουν προκληθεί από τον αέρα και τον ατμό που παγιδεύτηκαν κατά τη χύτευση του τηγμένου μετάλλου (για παράδειγμα στις περιπτώσεις των KYT_AYV_BW_04, BW_05, BW_14 και BW_17). Τα ευρεία και σε βάθος κενά υποδεικνύουν ότι δεν έχει γίνει περαιτέρω επεξεργασία από την εκκαμίνευση του μεταλλεύματος (smelting) (Mangou and Ioannou 2000). Σε ορισμένες περιπτώσεις εντοπίζονται υπολείμματα άνθρακα που προκαλούνται από την καύση (Εικόνα 5-10).

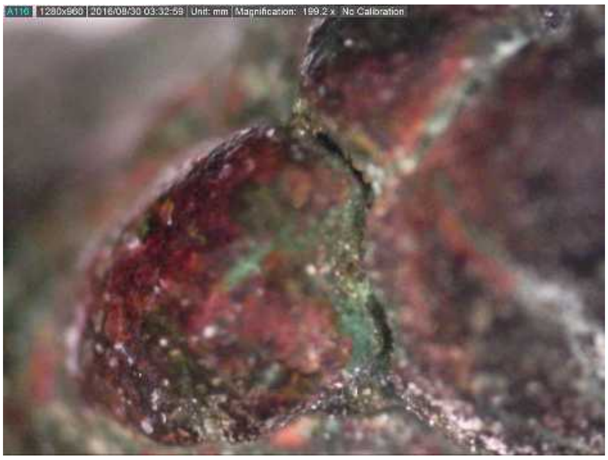
Χημικές Αναλύσεις: pXRF και SEM-EDS

Η εξέταση των αντικειμένων έγινε αρχικά με φορητή συσκευή ακτίνων Χ (pXRF) για τον προσδιορισμό της χημικής σύστασης των επιλεγμένων ευρημάτων. Πρόκειται για μη καταστρεπτική τεχνική που δίνει γρήγορα αποτελέσματα όσον αφορά στον ποιοτικό και

Εικόνα 5. Ασβεστιτικά συσσωματώματα παγιδευμένα σε μεγάλες οπές (κατάλοιπο χύτευσης KYT_AYV_BW_17).



Εικόνα 6. Πορώδες που σχηματίζεται κατά τη ροή και την ψύξη του μετάλλου (κατάλοιπο χύτευσης KYT_AYV_BW _17).



Εικόνα 7. Στερεοποιημένο τηγμένο μέταλλο που υποδεικνύει ροή μετάλλου (κατάλοιπο χύτευσης KYT_AYV_BW _05).

Εικόνα 8. Υπολείμματα ασβεστίου και εμφάνιση χαρακτηριστικού πορώδους που προκαλείται από αέρια κατά την διαδικασία της τήξης (κατάλοιπο χύτευσης KYT_AYV_BW _04).

Εικόνα 9. Οξείδια του χαλκού και διαβρωμένα σφαιρίδια χαλκού (κατάλοιπο χύτευσης KYT_AYV_BW _ 04).

Εικόνα 10. Σφαιρίδια χαλκού και μαύρο στρώμα πιθανόν από οξείδια σιδήρου και υπολείμματα άνθρακα (κατάλοιπο χύτευσης KYT_AYV_BW _14).

ποσοτικό προσδιορισμό των στοιχείων που εξετάζονται. Η τεχνική επιτρέπει την ανίχνευση βαρέων στοιχείων, όπως το αντιμόνιο (Sb) και ο μόλυβδος (Pb), στοιχείων που παρουσιάζουν ενδιαφέρον στη μελέτη των κραμάτων του χαλκού, σε ποσότητες ιχνοστοιχείων (Liritzis and Zacharias 2011). Οι ρυθμίσεις που χρησιμοποιήθηκαν ήταν: κίτρινο φίλτρο αργιλίου – τιτανίου, τάση επιτάχυνσης 40 kV, ρεύμα 12 μA, διάμετρος δέσμης ακτίνων X 3X3 mm και χρόνος μέτρησης για κάθε σημειακή ανάλυση 60 δευτερόλεπτα.

Στη συνέχεια, για τη στοιχειακή ανάλυση του κράματος με αναλύσεις μάζας χρησιμοποιήθηκε συσκευή SEM-EDS, εξέταση που έγινε υπό κενό, με δευτερεύοντα ηλεκτρόνια και με την οποία πραγματοποιήθηκαν μικρού μεγέθους σημειακές αναλύσεις σε μεγεθύνσεις 200X και 1400X. Οι ρυθμίσεις που χρησιμοποιήθηκαν ήταν: τάση επιτάχυνσης 20 kV, απόσταση εργασίας 15 mm και χρόνος συλλογής 90 δευτερόλεπτα. Στοιχεία όπως το θείο (S) και ο φώσφορος (P) μπόρεσαν να ανιχνευτούν με αυτή την τεχνική.

Λόγω της ανομοιογένειας που παρουσιάζουν τα κράματα και εφόσον δεν έγινε λήψη δείγματος, ελήφθησαν πολλαπλές μετρήσεις από κάθε αντικείμενο, ανάλογα με το μέγεθος και τη γεωμετρία της επιφάνειας του. Όλες οι μετρήσεις καταγράφονται σε ποσοστό επί τοις εκατό κατά βάρος και τα δεδομένα κανονικοποιούνται στο 100% από τα όργανα. Η ακρίβεια των μεθόδων ελέγχθηκε με χρήση πιστοποιημένων κραμάτων αναφοράς.

Οι διακυμάνσεις στις μετρήσεις μεταξύ των δύο μεθόδων είναι αναμενόμενες λόγω της ανομοιογένειας των κραμάτων και της λήψης των μετρήσεων από διαφορετικές περιοχές με το κάθε όργανο εξέτασης, καθώς και της δυσχέρειας στην ποσοτικοποίηση στοιχείων σημαντικών για τα κράματα χαλκού, όπως το αρσενικό και ο μόλυβδος, λόγω της επικάλυψης των κορυφών τους. Το διαφορετικό βάθος διείσδυσης των δύο τεχνικών εξέτασης, δεδομένου ότι οι ακτίνες X διεισδύουν σε μεγαλύτερο βάθος από τη δέσμη ηλεκτρονίων, μπορεί επίσης να οδηγήσει στη λήψη διαφορετικών μετρήσεων από το κάθε όργανο (Georgakopoulou and Bassiakos 2015). Επιπλέον, στην περίπτωση της εξέτασης με pXRF, η χρήση φίλτρου αργιλίου – τιτανίου έχει αποκλείσει τα ελαφρύτερα στοιχεία και μπορεί να οδηγήσει έτσι στην υπερεκτίμηση κάποιων αλλά και στην καταγραφή στοιχείων με μικρότερες συγκεντρώσεις.

Οι πίνακες 2, 3 και 4 παρουσιάζουν τη χημική σύνθεση των αντικειμένων που αναλύθηκαν χρησιμοποιώντας pXRF. Οι πίνακες 5, 6 και 7 παρουσιάζουν τη χημική σύνθεση των ίδιων αντικειμένων χρησιμοποιώντας SEM-EDS. Στους πίνακες καταγράφεται η μέση τιμή όλων των μετρήσεων που έγιναν σε κάθε αντικείμενο. Οι δύο μέθοδοι ανάλυσης (pXRF και SEM-EDS) έδειξαν ότι τα αντικείμενα είναι κατασκευασμένα από κράματα χαλκού που περιέχουν τόσο αρσενικό όσο και κασσίτερο, εκτός από το έλασμα BS_19 (Πίνακας 1) που είναι κατασκευασμένο από κράμα αργύρου –

Πίνακας 2. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο XRF στην ομάδα των χάλκινων ελασμάτων (n.d.: μη ανιχνεύσιμο).

Bronze Sheets

Table 2. Concentration of the elements (mean values) detected with XRF method expressed in % wt. (n.d.: non detected).

ΚΥΤ_ΑΥV	BS_01	BS_02	BS_06	BS_07	BS_08	BS_10	BS_19
CuO	86,10	93,35	79,04	79,43	98,83	82,84	31,33
As_2O_3	0,63	0,32	0,05	0,00	0,13	0,01	1,14
SnO_x	1,38	1,93	0,27	0,06	0,24	0,21	9,35
PbO	2,81	1,72	0,26	0,04	n.d.	0,21	0,13
Fe_2O_3	0,82	0,74	1,16	0,04	0,18	1,21	0,33
ZnO	7,74	1,31	15,88	26,01	0,48	12,72	4,49
Ni	0,03	0,20	0,55	n.d.	0,05	0,64	1,79
Sb_2O_5	0,11	0,11	0,26	0,02	0,04	0,18	0,17
Ag	0,10	0,06	0,31	0,01	0,04	0,25	50,47
MnO	0,06	0,05	0,20	n.d.	n.d.	0,17	0,04
Co_3O_4	0,04	0,04	0,27	n.d.	n.d.	0,22	n.d.
ZrO_2	0,09	0,12	0,87	0,02	n.d.	0,69	0,20
Nb_xO_x	0,07	0,07	0,72	0,10	n.d.	0,52	n.d.
Bi_2O_3	n.d.	0,02	0,16	n.d.	0,02	0,12	0,56

Πίνακας 3. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο XRF στην ομάδα των καταλοίπων χύτευσης (n.d.: μη ανιχνεύσιμο).

Bronze Wastes

Table 3. Concentration of the elements (mean values) detected with XRF method expressed in % wt. (n.d.: non detected).

KYT_AYV	BW_04	BW_05	BW_15	BW_16	BW_17	BW_18
CuO	77,88	72,25	73,35	85,94	83,82	87,57
As_2O_3	0,01	0,20	1,15	0,33	0,17	0,08
SnO_x	0,30	0,73	0,54	0,12	0,16	0,16
PbO	0,28	0,09	5,85	3,68	n.d.	0,10
Fe_2O_3	0,80	5,04	2,44	0,39	3,68	0,10
ZnO	17,05	17,87	13,50	6,92	9,89	10,88
Ni	0,68	0,24	0,35	0,27	0,73	0,63
Sb_2O_5	0,29	0,55	0,48	0,31	0,14	0,11
Ag	0,34	0,64	0,54	0,17	0,06	0,06
MnO	0,22	0,32	0,25	0,10	0,18	0,12
Co_3O_4	0,28	0,62	0,35	0,12	0,08	n.d.
ZrO_2	0,93	0,75	0,61	0,46	n.d.	0,06
Nb_xO_x	0,76	0,39	0,37	0,40	n.d.	n.d.
Bi_2O_3	0,17	0,32	0,21	0,79	0,23	0,13

Πίνακας 4. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο XRF στη βάση ειδωλίου και στην ομάδα των θραυσμάτων χάλκινων αγγείων (n.d.: μη ανιχνεύσιμο).

Figurine Base and Vessel Fragments

Table 4. Concentration of the elements (mean values) detected with XRF method expressed in % wt. (n.d.: non detected).

KYT_AYV_	FB_03	KYT_AYV_	VF_09	VF_11	VF_12	VF_13
CuO	76,05	CuO	79,10	71,54	67,35	83,92
As_2O_3	1,20	As_2O_3	0,08	0,93	1,68	0,02
SnOx	0,62	SnO_x	0,23	0,52	0,59	0,13
PbO	6,33	PbO	0,93	5,75	4,75	0,33
Fe_2O_3	3,47	Fe_2O_3	1,04	1,73	3,02	0,42
ZnO	8,91	ZnO	16,23	16,03	19,83	13,70
Ni	0,45	Ni	0,75	1,24	0,87	0,41
Sb_2O_5	0,29	Sb_2O_5	0,22	1,17	0,45	0,12
Ag	0,56	Ag	0,21	0,26	0,28	0,08
MnO	0,28	MnO	0,19	0,15	0,21	0,01
Co_3O_4	0,38	Co_3O_4	0,13	0,22	0,37	0,09
ZrO_2	0,65	ZrO_2	0,43	0,25	0,33	0,38
Nb_xO_x	0,30	Nb_xO_x	0,29	0,18	0,26	0,41
Bi_2O_3	0,12	Bi_2O_3	0,17	0,03	0,01	0,01

Πίνακας 5. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο SEM-EDS στην ομάδα των χάλκινων ελασμάτων (n.d.: μη ανιχνεύσιμο).

Bronze Sheets

Table 5. Concentration of the elements (mean values) detected with SEM-EDS method expressed in % wt. (n.d.: non detected).

KYT_AYV_	BS_01	BS_02	BS_06	BS_07	BS_08	BS_10	BS_19
CuO	81,00	96,21	87,68	55,60	89,42	58,70	8,64
As_2O_3	0,60	0,40	0,76	2,21	0,42	1,50	0,51
SnO_x	2,92	0,64	0,67	2,88	0,55	0,30	0,83
PbO	2,49	0,31	0,90	1,86	0,62	0,79	0,84
FeO	0,79	0,48	0,43	0,87	0,59	1,49	0,66
ZnO	6,41	0,39	0,80	25,13	0,44	1,10	1,42
Ni	0,44	0,55	n.d.	5,29	n.d.	n.d.	1,43
Sb_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ag	0,24	0,17	0,86	2,24	0,29	1,77	78,80
S	n.d.	n.d.	1,75	n.d.	n.d.	n.d.	0,69
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1,02
Al_2O_3	2,14	1,31	n.d.	6,32	2,13	12,00	2,95
SiO_2	5,32	1,73	n.d.	13,20	5,72	33,46	3,24
P_2O_5	2,14	1,70	n.d.	n.d.	1,03	n.d.	n.d.
Cl	2,00	n.d.	8,70	10,06	2,85	4,11	n.d.
K_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	3,81	n.d.	n.d.	10,76	2,27	7,36	3,33

Πίνακας 6. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο SEM-EDS στην ομάδα των καταλοίπων χύτευσης (n.d.: μη ανιχνεύσιμο).

Bronze Wastes

Table 6. Concentration of the elements (mean values) detected with SEM-EDS method expressed in % wt. (n.d.: non detected).

KYT_AYV	BW_04	BW_05	BW_14	BW_15	BW_16	BW_17	BW_18
CuO	84,75	64,03	47,12	73,49	88,98	83,74	93,57
As_2O_3	0,50	0,61	1,60	0,36	0,94	0,84	0,57
SnO_x	0,29	5,70	0,81	1,53	0,25	0,78	0,60
PbO	0,23	n.d.	0,35	5,40	0,37	0,96	1,08
FeO	0,50	3,89	28,82	1,59	0,34	6,61	0,40
ZnO	0,17	1,29	0,53	1,19	2,45	0,38	0,46
Ni	0,46	n.d.	0,97	n.d.	n.d.	n.d.	n.d.
Sb_2O5	n.d.	n.d.	1,86	n.d.	0,53	n.d.	n.d.
Ag	0,22	n.d.	n.d.	n.d.	0,14	0,30	0,59
S	n.d.	0,85	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	n.d.	2,45	n.d.	n.d.	n.d.	n.d.	n.d.
Al_2O_3	3,57	8,04	4,99	4,90	1,79	n.d.	n.d.
SiO_2	10,80	18,33	11,32	14,92	9,63	2,80	n.d.
P_2O_5	n.d.	n.d.	n.d.	2,59	n.d.	n.d.	n.d.
Cl	2,14	4,12	n.d.	0,65	1,04	6,07	3,80
K_2O	n.d.	n.d.	n.d.	1,62	n.d.	n.d.	n.d.
CaO	2,06	11,73	12,51	3,58	1,79	n.d.	n.d.

Πίνακας 7. Συγκεντρώσεις % κ.β. (μέση τιμή) των στοιχείων που ανιχνεύτηκαν με την μέθοδο SEM-EDS στη βάση ειδωλίου και στην ομάδα των θραυσμάτων χάλκινων αγγείων (n.d.: μη ανιχνεύσιμο). **Figurine Base and Vessel Fragments** Table 7. Concentration of the elements (mean values) detected with SEM-EDS method expressed in % wt. (n.d.: non detected).						
KYT_AYV	FB_03	KYT_AYV_	VF_09	VF_11	VF_12	VF_13
CuO	64,13	CuO	54,87	58,27	55,16	94,63
As_2O_3	2,43	As_2O_3	0,89	1,19	1,17	0,28
SnO_x	0,58	SnO_x	1,39	14,17	5,90	0,15
PbO	14,18	PbO	1,22	4,23	6,89	0,46
FeO	n.d.	FeO	0,64	0,65	2,95	0,29
ZnO	0,22	ZnO	1,07	12,47	10,68	4,33
Ni	n.d.	Ni	0,92	0,72	0,86	n.d.
Sb_2O_5	0,75	Sb_2O_5	n.d.	7,66	4,08	n.d.
Ag	n.d.	Ag	0,43	0,13	0,27	0,26
S	n.d.	S	1,77	n.d.	n.d.	n.d.
MgO	n.d.	MgO	n.d.	n.d.	n.d.	n.d.
Al_2O_3	1,37	Al_2O_3	11,11	1,98	4,11	n.d.
SiO_2	16,53	SiO_2	34,08	5,40	6,74	n.d.
P_2O_5	1,91	P_2O_5	n.d.	n.d.	2,89	n.d.
Cl	4,81	Cl	3,00	1,43	1,65	n.d.
K_2O	n.d.	K_2O	1,76	n.d.	n.d.	n.d.
CaO	3,25	CaO	3,95	4,77	9,30	n.d.

χαλκού. Η υψηλή περιεκτικότητα σε χαλκό δείχνει ότι στις περισσότερες περιπτώσεις πρόκειται για καθαρό μέταλλο (Panagopoulou 2016).

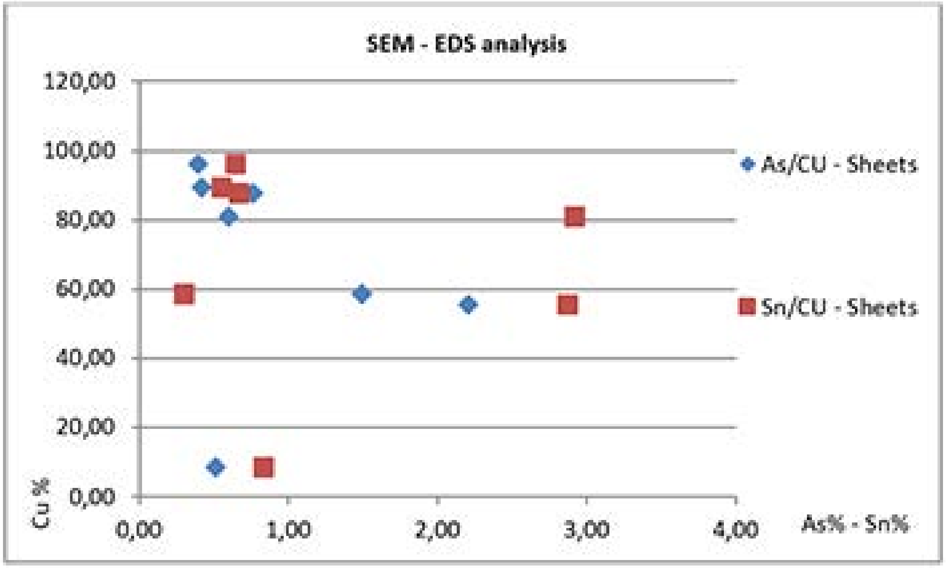
Στα κράματα εντοπίζεται περιεκτικότητα αρσενικού και κασσίτερου (Γραφήματα 1-4) σε χαμηλές συγκεντρώσεις, με την ποσότητα του χαλκού να καταγράφεται σε υψηλά επίπεδα. Ο συνδυασμός αρσενικού και κασσίτερου παρατηρείται και σε άλλες περιπτώσεις στο Αιγαίο, όπως στο Καστρί της Σύρου, όπου η μεταλλουργία περιελάμβανε προσθήκη κασσίτερου σε αρσενικούχο χαλκό, και σε περιοχές της Ανατολίας όπου ανάλογοι συνδυασμοί χρησιμοποιούνται στην κατασκευή κοσμημάτων και γενικότερα στην κατεργασία του χαλκού (Muhly 2006). Στις Κυκλάδες, ορυκτά του χαλκού είναι αναμεμιγμένα με αρσενικούχα μεταλλεύματα, ενώ αρσενικούχα ορυκτά υπάρχουν στο Λαύριο και στην Κύπρο (Mangou and Ioannou 1997, Stos-Gale 2000, Webb *et al.* 2006). Αντίθετα, ο κασσίτερος εισάγεται, κυρίως από περιοχές της κεντρικής Ασίας, του Αφγανιστάν και της Ανατολίας και μεταφέρεται στο Αιγαίο μέσω θαλασσίων οδών από τη Συρία (Gillis and Clayton 2008, Muhly2006). Αρσενικούχος χαλκός και μπρούντζος συνυπάρχουν για αρκετά χρόνια είτε λόγω της ανακύκλωσης παλαιών μετάλλων είτε ως αιτία τοπικής παραγωγής που βασίζει τη χρήση αρσενικούχου χαλκού σε μεταλλουργική παράδοση και στη διαθεσιμότητα ορυκτών πηγών από το Αιγαίο (Papadimitriou 2008).

Άλλα στοιχεία που έχουν ανιχνευτεί σε όλα σχεδόν τα αντικείμενα είναι ο μόλυβδος, ο σίδηρος, ο ψευδάργυρος και ο άργυρος, ενώ σε μικρότερες συγκεντρώσεις ανιχνεύτηκαν τα στοιχεία νικέλιο, αντιμόνιο, ασβέστιο, αργίλιο, πυρίτιο, μαγνήσιο και χλώριο. Θείο καταγράφηκε σε λίγες περιπτώσεις με SEM-EDS.

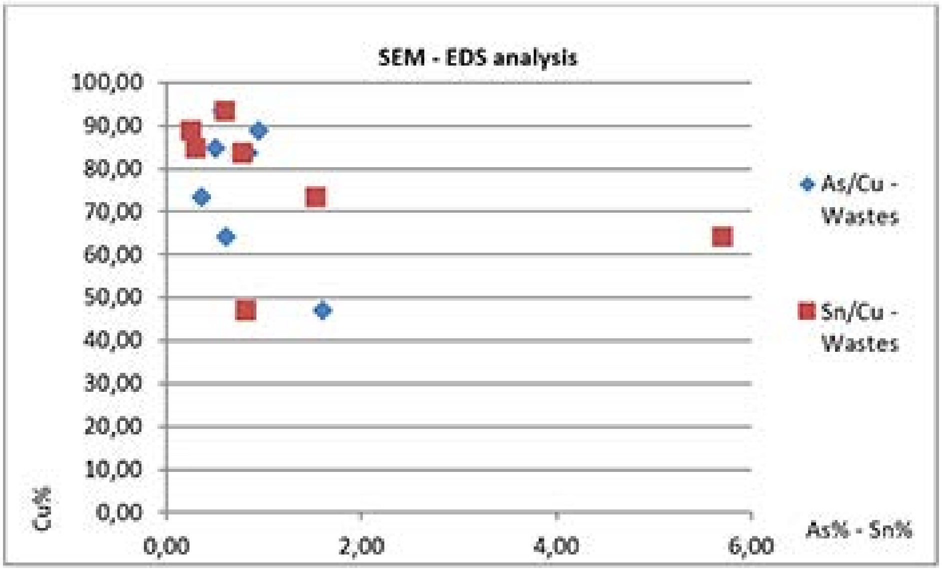
Σχετικά με τα στοιχεία που ανιχνεύτηκαν σημειώνονται τα εξής:

α) Μόλυβδος και σίδηρος μπορεί να υπάρχουν στο μετάλλευμα ή να έχουν προστεθεί.

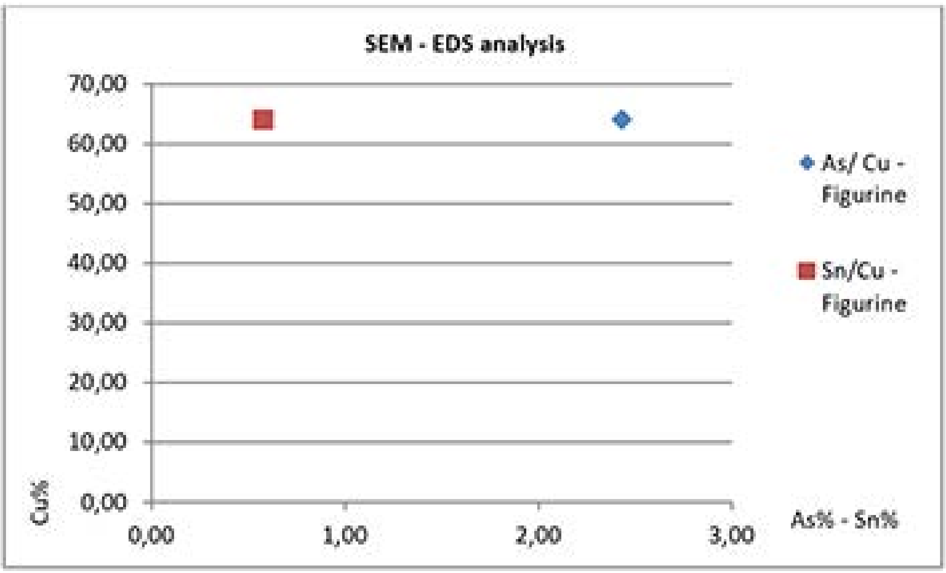
Όσον αφορά στον μόλυβδο, συγκέντρωση πάνω από 2%, που διευκολύνει την χύτευση και οδηγεί σε πιθανότητα κατ' επιλογίν προσθήκης, καταγράφηκε στη βάση ειδωλίου αλλά και σε αντικείμενα από τις άλλες κατηγορίες που εξετάστηκαν. Η ύπαρξη μολύβδου σε σφυρήλατα αντικείμενα είναι επιβλαβής και θεωρείται ότι περιέχεται ως ακαθαρσία στο μετάλλευμα ενώ σε χυτά αντικείμενα βελτιώνει το σημείο τήξης του παραγόμενου κράματος και την ρευστότητά του (Papadimitriou 2008). Ωστόσο, η συγκέντρωση του μολύβδου σε ορισμένες περιοχές όταν το κράμα βρίσκεται ακόμα σε υγρή μορφή, λόγω της βαρύτητας, μπορεί να οδηγήσει σε υπερεκτίμηση της περιεκτικότητας του, ανάλογα με το σημείο που εξετάζεται (Georgakopoulou and Bassiakos 2015,



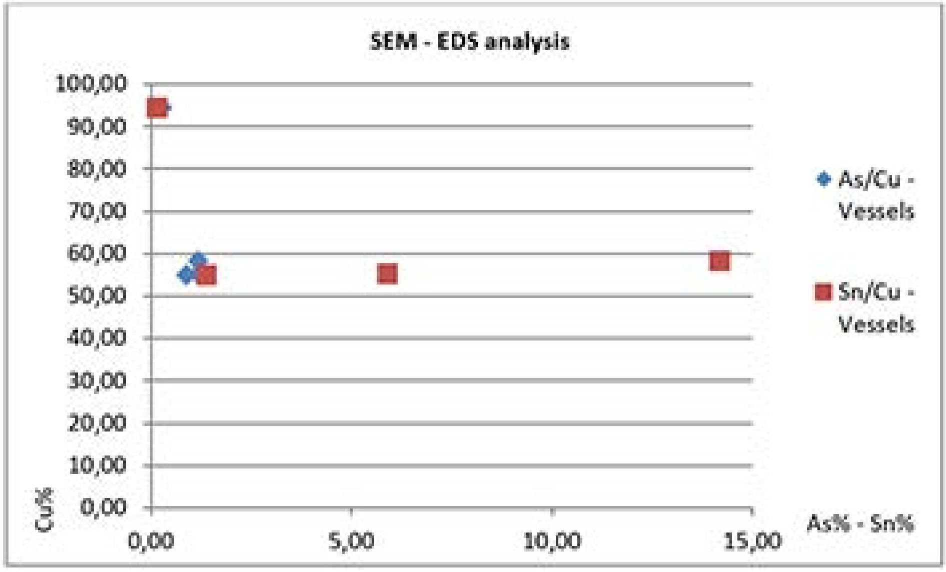
Γράφημα 1. Κατανομή αρσενικού και κασσίτερου έναντι του χαλκού στην κατηγορία των χάλκινων ελασμάτων με ανάλυση SEM-EDS.



Γράφημα 2. Κατανομή αρσενικού και κασσίτερου έναντι του χαλκού στην κατηγορία των καταλοίπων χύτευσης με ανάλυση SEM-EDS.



Γράφημα 3. Κατανομή αρσενικού και κασσίτερου έναντι του χαλκού στην βάση ειδωλίου με ανάλυση SEM-EDS.



Γράφημα 4. Κατανομή αρσενικού και κασσίτερου έναντι του χαλκού στην κατηγορία των θραυσμάτων μεταλλικών αγγείων με ανάλυση SEM-EDS.

Papadimitriou 2008). Συγκεντρώσεις μολύβδου έως και 4% θεωρείται ότι μπορεί να προέρχονται από το μετάλλευμα καθώς ανάλογα ποσοστά έχουν καταγραφεί σε σκωρίες χαλκού από εκκαμίνευση (Georgakopoulou 2004, Mangou and Ioannou 1997).

Η παρουσία σιδήρου στα κράματα χαλκού μπορεί να οφείλεται στα μεταλλεύματα που έχουν χρησιμοποιηθεί ή στην κατ' επιλογήν χρήση ορυκτών σιδήρου ως συλλίπασμα κατά την εκκαμίνευση (Mangou and Ioannou 2000).

β) Μόλυβδος, Άργυρος και Σίδηρος εμφανίζονται σε μεταλλεύματα στις Κυκλάδες.

Ορυκτά αργύρου και μολύβδου εξορύσσονταν σε νησιά των Κυκλάδων όπως στην Κέα, την Κύθνο και τη Σίφνο (Gale *et al.*1985, Katapotis and Bassiakos 2007, Muhly 2006, Stos-Gale 2000, Webb *et al.* 2006), ενώ γνωστές περιοχές εκκαμίνευσης χαλκού είναι οι Σκουριές στην Κύθνο και το Δασκαλειό στην Κέρο όπου τα μεταλλουργικά κατάλοιπα περιλαμβάνουν χαλκό, μόλυβδο, ορυκτά σιδήρου και λιθάργυρο (Gale *et al.* 1985, Georgakopoulou 2004).

γ) Στις πολύ-μεταλλικές αποθέσεις στο Λαύριο εμφανίζονται ορυκτά χαλκού που περιέχουν μόλυβδο και αρσενικό ή αντιμόνιο, σίδηρο, άργυρο καθώς και αρσενικό και ψευδάργυρο (Gale *et al.* 2008, 2009). Στο Λαύριο υπάρχουν επίσης και ορυκτά του χαλκού που περιέχουν θείο (Bassiakos and Tselios 2012, Charalambous *et al.* 2015).

δ) Το αντιμόνιο είναι σύνηθες ιχνοστοιχείο σε κράματα χαλκού και προέρχεται από το μετάλλευμα (Mangou and Ioannou 1997, Papadimitriou 2008).

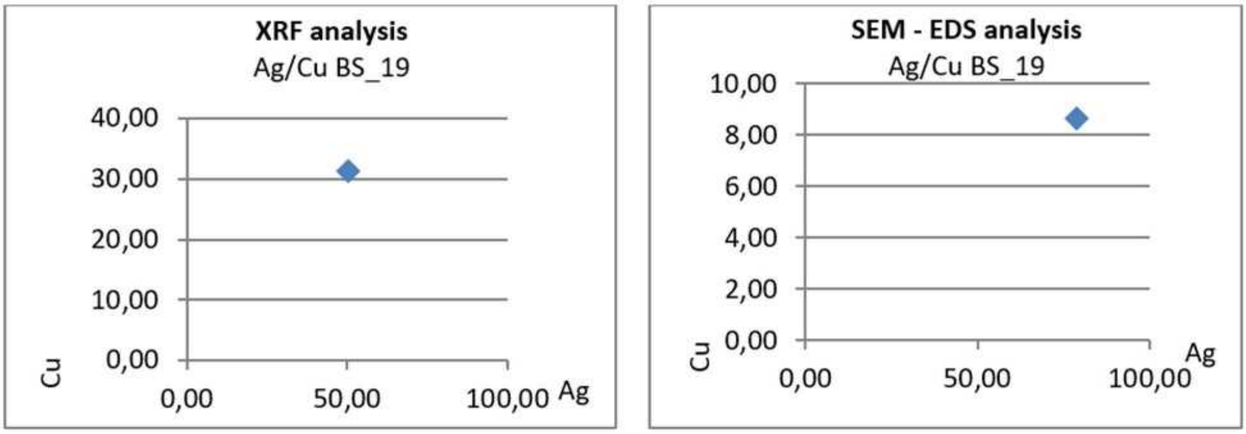
ε) Σε τάλαντα από την Κρήτη συχνά περιέχονται σε μικρές συγκεντρώσεις, ως δευτερεύοντα στοιχεία, σίδηρος, ψευδάργυρος και νικέλιο (Charalambous *et al.* 2015, Doonan *et al.* 2007, Mangou and Ioannou 2000).

στ) Σε μεταλλεύματα θειούχου χαλκού στην Κύπρο εμφανίζεται ψευδάργυρος και ορυκτά χαλκού που περιέχουν σίδηρο (Charalambous *et al.* 2015, Gale and Stos-Gale 2012, Mangou and Ioannou 2000).

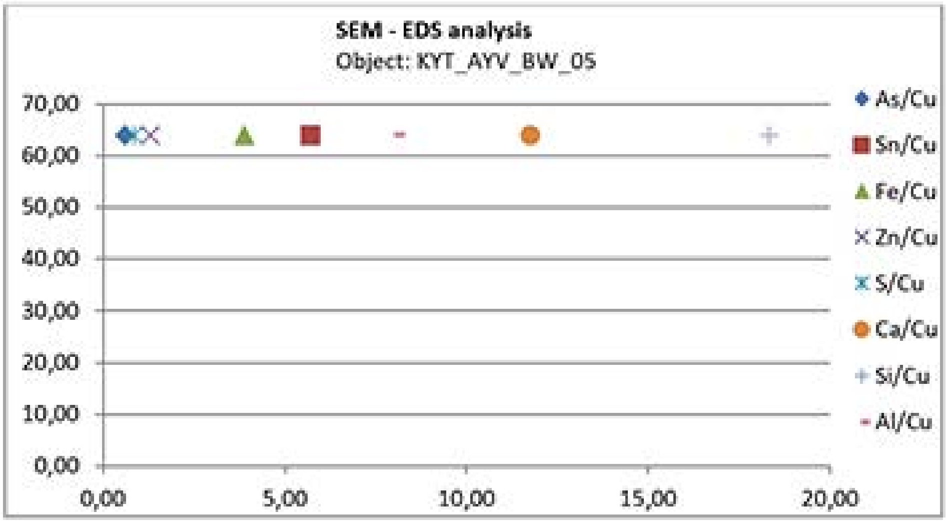
ζ) Σίδηρος, ασβέστιο, αργίλιο, πυρίτιο και μαγνήσιο μπορεί να σχετίζονται με τη διαδικασία της εκκαμίνευσης (Gale *et al.* 1985, Mangou and Ioannou 2000, Stos-Gale and Gale2006). Η ύπαρξη αργιλοπυριτικών συστατικών επηρεάζει το σημείο τήξης της σκωρίας, τη θερμοκρασία του κλιβάνου καθώς και τον διαχωρισμό του μετάλλου από την σκωρία στον κλίβανο. Ιδιαίτερα η ύπαρξη χαλαζία (SiO_2) στις σκωρίες χαλκού υποδηλώνει ότι ο χαλκός πιθανότατα εισήχθη προς επεξεργασία ως ορυκτό παρά στη μεταλλική μορφή του (Georgakopoulou 2004).

η) Ψευδάργυρος, ασβέστιο, αργίλιο, πυρίτιο, μαγνήσιο και χλώριο μπορεί να οφείλονται σε προϊόντα διάβρωσης και σε υπολείμματα ασβεστιτικών συσσωματωμάτων χώματος. Η συγκέντρωση του σιδήρου μπορεί επίσης να καταγράφεται αυξημένη λόγω της διάβρωσης.

Το κράμα αργύρου με χαλκό από το οποίο έχει κατασκευαστεί το έλασμα BS_19 συναντάται σπάνια στην Ελλάδα (Γράφημα 5). Εκτός από τη προσθήκη χαλκού στον άργυρο ώστε να παραχθεί ένα αντικείμενο κίβδηλο, κράματα αργύρου – χαλκού, μπορεί να έχουν χρησιμοποιηθεί λόγω της διαφορετικής εμφάνισης και ιδιοτήτων που προσδίδουν στα αντικείμενα. Τέχνεργο από παρόμοιο κράμα αργύρου – χαλκού έχει βρεθεί στο Μόχλο της Κρήτης με περιεκτικότητα αργύρου 35% κ.β.



Γράφημα 5. Κατανομή χαλκού και αργύρου στο έλασμα KYT_AYV_BS_19 με τις δύο μεθόδους ανάλυσης.



Γράφημα 6. Αναλογίες των στοιχείων που περιέχονται στο κατάλοιπο χύτευσης KYT_AYV_BW_05 έναντι του χαλκού καταγεγραμμένες με SEM-EDS (μέσος όρος των μετρήσεων).

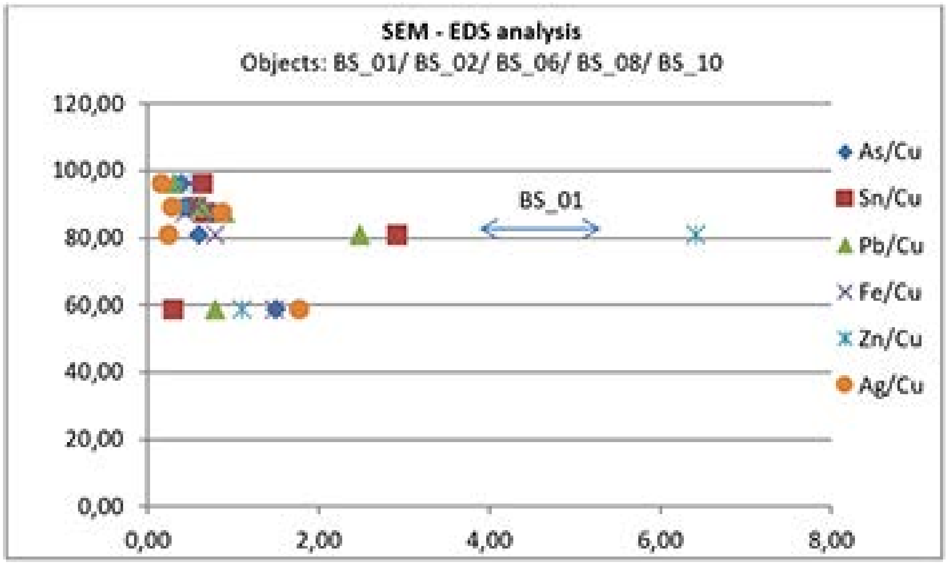
ενώ αντίστοιχα κράματα με περιεκτικότητα αργύρου που κυμαίνεται μεταξύ 16% και 70% κ.β. έχουν βρεθεί στην Ανατολία (Muhly 2006, Hauptmann *et al.* 2002, Tselios 2008). Η Κύπρος επίσης διατηρούσε εμπορικές σχέσεις με την Ανατολία εισάγοντας και εξάγοντας πρώτες ύλες αλλά και κατασκευασμένα αντικείμενα, ενώ μεταλλουργοί από την Ανατολία πήγαιναν στην Κύπρο προς αναζήτηση μετάλλων (Webb *et al.* 2006).

Περιεκτικότητα θείου ανιχνεύτηκε με SEM-EDS μόνο σε τρία αντικείμενα. Μεταλλεύματα θειούχου χαλκού που περιέχουν σίδηρο αλλά είναι απαλλαγμένα από μόλυβδο απαντώνται στην Κύπρο, ενώ και στο Λαύριο υπάρχουν αποθέσεις χαλκοπυρίτη, ορυκτών του χαλκού με θείο (Bassiakos and Tselios 2012, Charalambous *et al.* 2015). Ενδιαφέρον παρουσιάζουν οι αναλογίες των στοιχείων στην περίπτωση του κατάλοιπου χύτευσης BW_05 (Γράφημα 6), ένα από τα τρία αντικείμενα στα οποία ανιχνεύτηκε θείο και το οποίο περιέχει σίδηρο αλλά όχι μόλυβδο, γεγονός που οδηγεί σε πιθανή προέλευση από την Κύπρο.

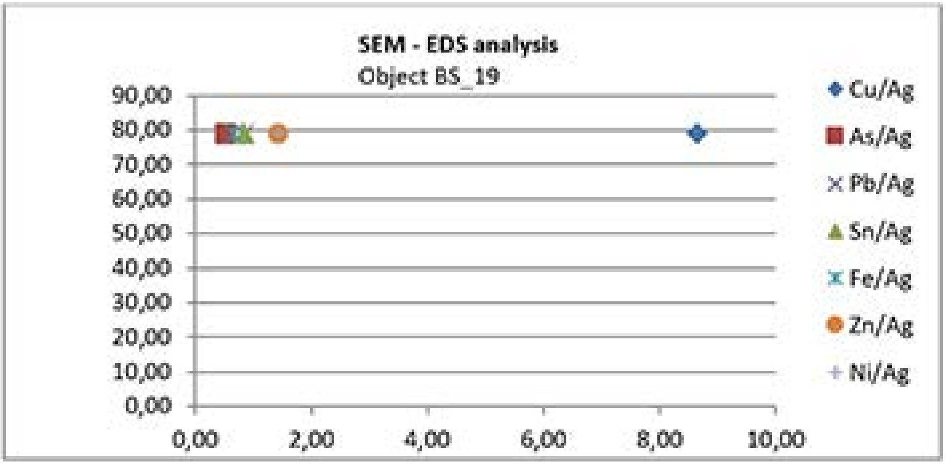
Στην ομάδα των χάλκινων ελασμάτων παρατηρείται υψηλή καθαρότητα χαλκού και καταγράφονται πολύ χαμηλές περιεκτικότητες άλλων μεταλλικών στοιχείων, διαδικασία που βελτιώνει την ικανότητα του μετάλλου να σφυρηλατείται χωρίς να ρηγματώνεται (Papadimitriou 2008). Η προσθήκη κασσίτερου αυξάνει τη σκληρότητα του κράματος αλλά μόνο στο έλασμα BS_01 σημειώνεται σημαντική περιεκτικότητα κασσιτέρου, όπου όμως περιλαμβάνεται και υψηλό ποσοστό μολύβδου, επομένως το παραγόμενο κράμα δεν είναι ισχυρό. Επιπλέον στην ομάδα αυτή καταγράφεται χαμηλή περιεκτικότητα σιδήρου, καθώς όταν μορφοποιούνται αντικείμενα με σφυρηλάτηση, η παρουσία σιδήρου είναι επιβλαβής (Γράφημα 7).

Δεδομένου ότι η σκόπιμη προσθήκη ψευδαργύρου στα κράματα χαλκού ήταν άγνωστη στην προϊστορική περίοδο, το έλασμα BS_07 πιθανόν ανήκει σε μετέπειτα χρονικές περιόδους.

Οι αναλογίες των στοιχείων στο έλασμα BS_19 παρουσιάζονται ξεχωριστά στο Γράφημα 8 λόγω της



Γράφημα 7. Κατανομή των στοιχείων αρσενικό, κασσίτερος, μόλυβδος, σίδηρος, ψευδάργυρος και άργυρος έναντι του χαλκού καταγεγραμμένες με SEM-EDS.



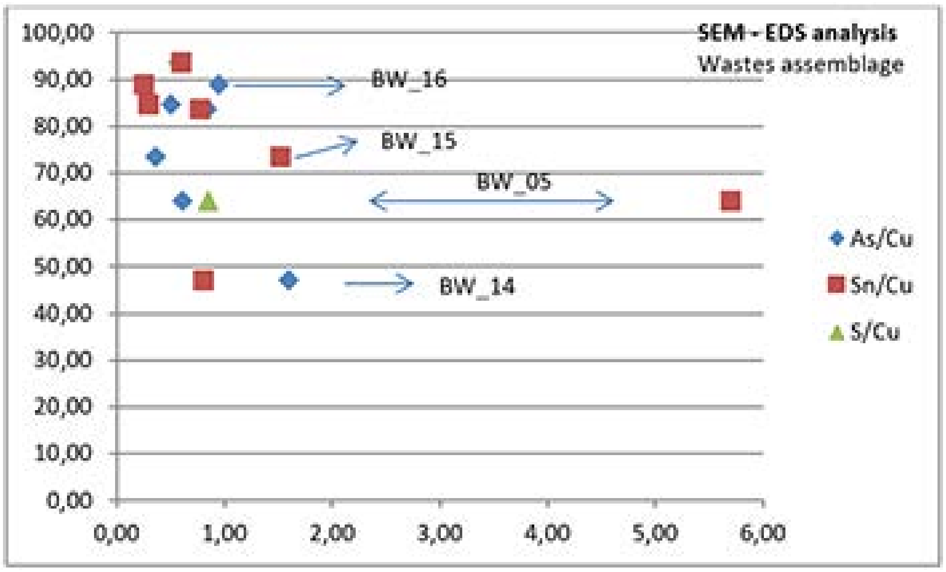
Γράφημα 8. Κατανομή των στοιχείων χαλκός, αρσενικό, κασσίτερος, μόλυβδος, σίδηρος, ψευδάργυρος έναντι του αργύρου στο έλασμα ΚΥΤ_AYV_BS_19 καταγεγραμμένες με SEM-EDS.

διαφορετικής σύνθεσης του κράματος. Στο κράμα, εκτός του χαλκού και του αργύρου, κατεγράφησαν περιεκτικότητες έως 2% στα στοιχεία αρσενικό, μόλυβδος, κασσίτερος, σίδηρος, ψευδάργυρος και νικέλιο και παρουσιάζει ομοιότητες με κράματα αργύρου – χαλκού, η κατεργασία των οποίων αποσκοπούσε στην παραγωγή αντικειμένων με ασημίζουσα και λαμπερή εμφάνιση.

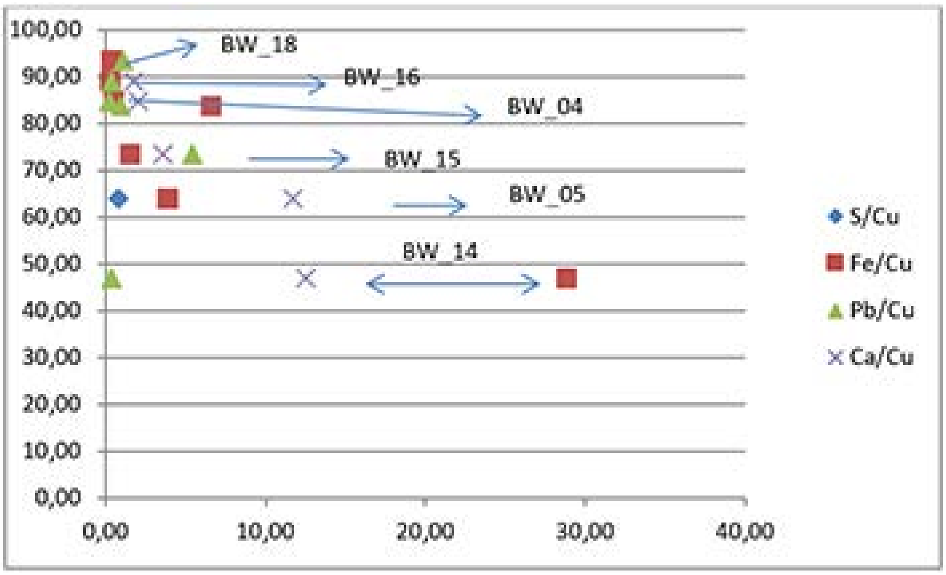
Λαμβάνοντας υπόψη τις δυσκολίες - περιορισμούς των μεθόδων σχετικά με τον υπολογισμό της συγκέντρωσης του αρσενικού αλλά και την εξάτμισή του κατά τη διαδικασία της τήξης (Papadimitriou 2008, Tselios 2008) θα μπορούσαμε να πούμε ότι στα κατάλοιπα χύτευσης BW_14 και BW_16 η περιεκτικότητα αρσενικού δείχνει ότι μπορεί να προέρχονται από ανακύκλωση. Διαφορετική σύνθεση παρουσιάζει το κατάλοιπο χύτευσης BW_05 το οποίο περιέχει το υψηλότερο ποσοστό κασσίτερου που ανιχνεύτηκε, πιθανόν από τήξη χαλκού – κασσίτερου (Γράφημα 9).

Συνεπώς, διάφοροι τύποι κραμάτων ενδέχεται να χρησιμοποιούνται ανάλογα με τα παραγόμενα αντικείμενα και τις προσδοκώμενες ιδιότητές τους. Επίσης, η υψηλή συγκέντρωση χαλκού στην κατηγορία αυτή ενδέχεται να υποδεικνύει ότι πρόκειται για καθαρό μέταλλο που προοριζόταν για την κατασκευή αντικειμένων. Δεδομένου ότι ο κασσίτερος ήταν σπάνιο και πιθανώς ακριβό υλικό, σε σύγκριση με το αρσενικό που θα μπορούσε να προέρχεται από ανακύκλωση παλαιών μετάλλων, θα μπορούσαν να χρησιμοποιούνται διαφορετικά είδη κραμάτων. Επιπλέον η επιλογή του κράματος θα μπορούσε να γίνεται ανάλογα με τις διαθέσιμες πηγές. Το κατάλοιπο χύτευσης BW_05 είναι από τις λίγες περιπτώσεις όπου ανιχνεύτηκε θείο και φαίνεται να έχει διαφορετική πηγή προέλευσης, πιθανών, όπως προαναφέρθηκε, την Κύπρο (Panagopoulou 2016).

Οι υψηλές συγκεντρώσεις σιδήρου και ασβεστίου στο κατάλοιπο χύτευσης BW_14 πιθανόν οφείλονται σε



Γράφημα 9. Κατανομή των στοιχείων αρσενικό, κασσίτερος και θείο έναντι του χαλκού στην κατηγορία των καταλοίπων χύτευσης καταγεγραμμένες με SEM-EDS.

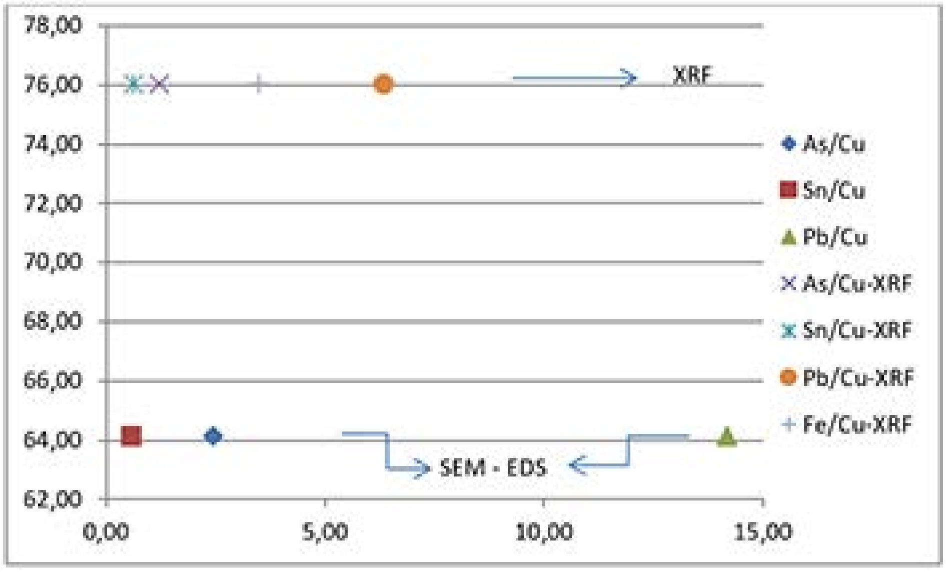


Γράφημα 10. Κατανομή των στοιχείων θείο, μόλυβδος, σίδηρος, και ασβέστιο έναντι του χαλκού στην κατηγορία των καταλοίπων χύτευσης καταγεγραμμένες με SEM-EDS.

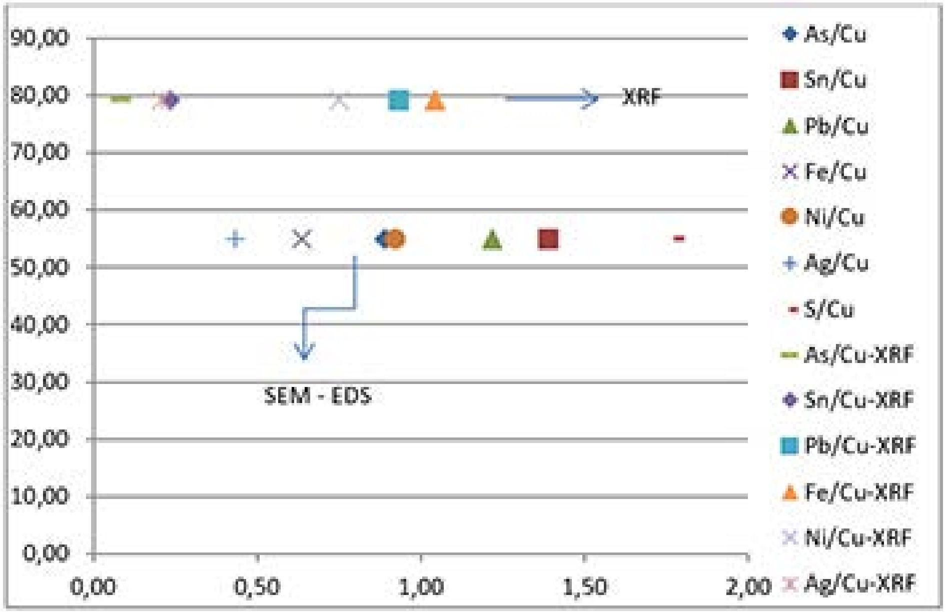
συσσωματώματα προϊόντων διάβρωσης και χώματος. Η σημαντική ποσότητα πυριτίου που ανιχνεύτηκε σε περιπτώσεις καταλοίπων χύτευσης μπορεί να οφείλεται στα μεταλλεύματα χαλκού που έχουν χρησιμοποιηθεί, δεδομένου ότι στην προαναφερθείσα μικροσκοπική εξέταση έχουν παρατηρηθεί ασβεστιτικά συσσωματώματα παγιδευμένα μεταξύ των οξειδίων του χαλκού (Panagopoulou 2016).

Καθαρός μολυβδούχος χαλκός, για χύτευση αντικειμένων, φαίνεται να είναι το κατάλοιπο χύτευσης BW_15 καθώς καταγράφεται σημαντική ποσότητα μολύβδου και υψηλή καθαρότητα χαλκού. Η χαμηλή συγκέντρωση σιδήρου στα κατάλοιπα χύτευσης BW_04, BW_16 και BW_18 σε συνδυασμό με την υψηλή καθαρότητα χαλκού μπορεί να υποδηλώνει τάλαντο οξειδίων δευτερογενούς ανάμιξης (Γράφημα 10) (Panagopoulou 2016).

Η περιεκτικότητα αρσενικού που έχει καταγραφεί και με τις δύο τεχνικές εξέτασης στο τμήμα του χάλκινου ειδωλίου θα μπορούσε να οδηγήσει στο συμπέρασμα ότι πρόκειται ίσως για τη μοναδική περίπτωση προσθήκης αρσενικού κατ' επιλογήν (Γράφημα 11). Δεν αποκλείεται βέβαια και η χρήση μετάλλου από ανακύκλωση αφού οι επωφελείς ιδιότητες του αρσενικούχου χαλκού δεν είναι απαραίτητες στην κατασκευή ειδωλίων ενώ αρσενικούχος χαλκός και χαλκός έχουν σχεδόν την ίδια σκληρότητα στη χύτευση και μόνο μετά από επεξεργασία σφυρηλάτησης ο αρσενικούχος χαλκός αποκτά καλύτερες ιδιότητες. Ο μόλυβδος προστέθηκε για βελτίωση της χύτευσης ενώ το αρσενικό δρα ως αντιοξειδωτικό στη χύτευση, καταστέλλοντας την ευθραυστότητα λόγω της παρουσίας εγκλεισμάτων οξειδίων του χαλκού στο μέταλλο (Papadimitriou 2008). Η προσθήκη αρσενικού στο κράμα, όμως, δίδει στο παραγόμενο αντικείμενο μια ασημίζουσα εμφάνιση



Γράφημα 11. Κατανομή των στοιχείων αρσενικό, κασσίτερος, μόλυβδος και σίδηρος έναντι του χαλκού στη βάση του ειδωλίου καταγεγραμμένες με τις δύο τεχνικές εξέτασης.

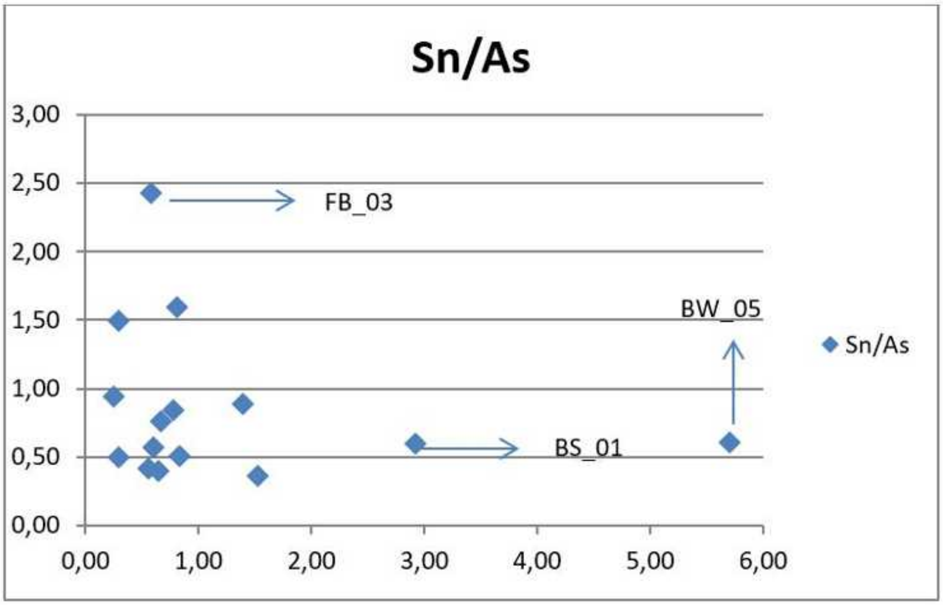


Γράφημα 12. Κατανομή των στοιχείων αρσενικό, κασσίτερος, μόλυβδος, σίδηρος, νικέλιο, άργυρος και θείο έναντι του χαλκού στο θραύσμα KYT_AYV_VF_09 καταγεγραμμένες με τις δύο τεχνικές εξέτασης.

την οποία οι μεταλλοτεχνίτες υπό προϋποθέσεις επιζητούσαν. Η παρουσία σιδήρου στη χύτευση δεν αποτελεί καθοριστικό παράγοντα, ωστόσο, σε υψηλές περιεκτικότητες, μπορεί να αυξήσει το σημείο τήξης του κράματος (Papadimitriou2008). Η χαμηλή συγκέντρωση σιδήρου σε συνδυασμό με την υψηλή συγκέντρωση μολύβδου μπορεί να οδηγήσει στην υπόθεση ότι υπήρχε δυνατότητα ελέγχου του σημείου τήξης στο παραγόμενο κράμα. Πιθανές προϋποθέσεις επιλογής κραμάτων μπορεί να λογιστούν: οι τεχνικές κατασκευής, η συγκέντρωση των ξένων – μη καθαρών στοιχείων και οι μηχανικές ιδιότητες του παραγόμενου αντικειμένου (Panagopoulou 2016).

Τα θραύσματα αγγείων που περιέχουν υψηλά ποσοστά ψευδαργύρου προέρχονται πιθανότατα από μεταγενέστερες περιόδους καθώς η σκόπιμη προσθήκη ψευδαργύρου σε κράματα χαλκού εμφανίζεται μετά τους ρωμαϊκούς χρόνους (Papadimitriou2008). Η μικρότερη ποσότητα ψευδαργύρου σε συνδυασμό με το καθαρό μέταλλο χαλκού στο θραύσμα λαβής συνιστά κοινή σύνθεση για ανάλογα τμήματα αγγείων μεταγενέστερων περιόδων.

Η σύνθεση του θραύσματος FV_09 με ποσότητα κασσίτερου και μολύβδου πιθανόν υποδηλώνει προϊστορικό κράμα (ανάλογη περιεκτικότητα με αυτή του ελάσματος BS_01). Η περιεκτικότητα θείου που ανιχνεύτηκε σε συνδυασμό με τον εντοπισμό μολύβδου και αργύρου δείχνει πιθανή προέλευση του μετάλλου από το Λαύριο ενώ η υψηλή συγκέντρωση μολύβδου μπορεί να οφείλεται σε προσθήκη κατ' επιλογήν (Γράφημα 12).



Γράφημα 13. Κατανομή κασσιτέρου έναντι του αρσενικού καταγεγραμμένη με SEM-EDS.

Συμπεράσματα

Συνοψίζοντας, από την χημική εξέταση των ευρημάτων του Μινωικού Ιερού Κορυφής στον Άγιο Γεώργιο στο Βουνό Κυθήρων μπορούμε να πούμε ότι τα αντικείμενα που αναλύθηκαν ποικίλουν ως προς τη στοιχειακή τους σύνθεση. Ενδέχεται λοιπόν να μην προέρχονται από μία μόνο πηγή ή από την ίδια παραγωγική διαδικασία. Η πλειοψηφία των αντικειμένων που εξετάστηκαν έχουν κατασκευαστεί από καθαρό χαλκό ενώ ανιχνεύτηκαν μικρές συγκεντρώσεις κασσίτερου. Η χαμηλή περιεκτικότητα σε αρσενικό που καταγράφηκε μπορεί να οφείλεται είτε στο μετάλλευμα είτε στη χρήση μετάλλου από ανακύκλωση (scrap). Οι μικρές ποσότητες διαφόρων εγκλεισμάτων μετάλλων σε συνδυασμό με τις χαμηλές ποσότητες αρσενικού και κασσίτερου, ενισχύουν την πιθανότητα χρήσης μετάλλων από ανακύκλωση. Δεν μπορεί να αποκλειστεί όμως και η παραγωγή ενός κράματος κατ' επιλογίν με αρσενικό και κασσίτερο (Panagopoulou 2016).

Διαφορετικά κράματα χρησιμοποιούνται ανάλογα με το είδος του αντικειμένου που πρόκειται να κατασκευαστεί. Από τις συγκεντρώσεις κασσίτερου και αρσενικού στο θραύσμα ειδωλίου, στο έλασμα BS_01 και στα κατάλοιπα χύτευσης BW_05 και BW_14 διακρίνεται προσθήκη αρσενικού στα χυτά αντικείμενα έναντι προσθήκης κασσίτερου σε σφυρήλατα αντικείμενα, ενώ αναγνωρίζονται περιπτώσεις καταλοίπων χύτευσης από κράματα τόσο με κασσίτερο όσο και με αρσενικό. Σε μια εποχή που ο μπρούντζος ήδη χρησιμοποιείται δεν ανιχνεύθηκαν σημαντικές συγκεντρώσεις κασσίτερου, ενώ εντοπίστηκαν υψηλά ποσοστά χαλκού με μικρή ποσότητα ξένων στοιχείων. Από την κατανομή του κασσίτερου και του αρσενικού (Γράφημα 10) μπορούμε να πούμε ότι οι μόνες περιπτώσεις κραματοποίησης κατ' επιλογίν είναι ο αρσενικούχος χαλκός του θραύσματος ειδωλίου FF_03 και ο μπρούντζος στις περιπτώσεις του ελάσματος BS_01 και του καταλοίπου χύτευσης BW_05 (Panagopoulou 2016).

Η υψηλή περιεκτικότητα χαλκού στα κράματα σε συνδυασμό με την ανίχνευση στοιχείων όπως ο μόλυβδος, ο άργυρος, ο ψευδάργυρος και ο σίδηρος θα μπορούσε να αποτελέσει ένδειξη για πιθανή προέλευση μεταλλευμάτων από το Λαύριο, από όπου η διαδικασία εξόρυξης μπορεί να αποφέρει ορυκτά με περιεκτικότητα σε χαλκό έως 90% κ.β. Με πιθανή προέλευση από την Κύπρο θα μπορούσε να συνδεθεί ένα κατάλοιπο χύτευσης (BW_05) στο οποίο ανιχνεύτηκαν στοιχεία που περιέχονται στα θειούχα μεταλλεύματα του νησιού, ενώ το χάλκινο έλασμα BS_19 θα μπορούσε να σχετίζεται με την Ανατολία είτε ως αντικείμενο που έχει εισαχθεί είτε ως τεχνική κατασκευής (Panagopoulou 2016).Υψηλές συγκεντρώσεις χαλκού έχουν επίσης καταγραφεί σε αντικείμενα από την Κρήτη, ενώ χημικές αναλύσεις ταλάντων από μεταλλεύματα οξειδίων του χαλκού της Ύστερης Εποχής του Χαλκού που βρέθηκαν στην Κρήτη έχουν δείξει καθαρό χαλκό (99% και περισσότερο) με πολύ μικρή περιεκτικότητα αρσενικού (περίπου 0,3%) (Gale and Stos-Gale 1986, Papadimitriou 2008). Συνεπώς, τα άμορφα τμήματα καταλοίπων χύτευσης των οποίων η σύνθεση δείχνει καθαρό χαλκό και συγκεκριμένα τα KYT_AYV_BW_04, KYT_AYV_BW_16, and KYT_AYV_BW_18, μπορεί να αποτελούν θραύσματα ταλάντων, κυρίως από δευτερογενή τάλαντα μεταλλευμάτων οξειδίων του χαλκού, που προορίζονταν για την κατασκευή νέων αντικειμένων ή να έχουν προσφερθεί ως αφιερώματα στο ιερό (Panagopoulou 2016).

Η έρευνα για την τεχνολογία, την κατεργασία και την πιθανή προέλευση του χαλκού στα μέσα της 2ης χιλιετίας π.Χ. με βάση τις τεχνικές ανάλυσης των χάλκινων αφιερωμάτων από το Μινωικό Ιερό Κορυφής των

Κυθήρων συνεχίζεται στο πλαίσιο εκπόνησης σχετικής διδακτορικής διατριβής από την γράφουσα.

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Non-Destructive Physicochemical Analysis on Islamic Metallic Objects: A Preliminary Study on Construction Materials

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Abstract: The Museum of Islamic Art (Benaki Museum in Athens) has a wide variety of Islamic objects. A part of its collection was studied through physicochemical analysis. The objects included are sixteen metallic artifacts: three candlesticks, six basins, a cup, an ewer, two compasses, two pen boxes and an incense burner. These artifacts are dated from the 13th to the 15th centuries, they derive from Iran, Syria, Turkey and Egypt, and were constructed with complex manufacturing alloys as determined by the non-destructive physicochemical analysis conducted. The main construction materials were copper, zinc, iron, lead and tin, as detected by X-Ray Fluorescence Analysis.

KEYWORDS; ISLAMIC ART, METALWORK, 13TH–15TH CENTURY, X-RAY FLUORESCENCE ANALYSIS

Introduction

This report studies a part of the collection of the Museum of Islamic Art (Benaki Museum). This part of the collection consists of sixteen metallic Islamic artifacts that vary in their use: three candlesticks, six basins, a cup, an ewer, two compasses, two pen boxes, and an incense burner and are dated from the 13th to 15th centuries and originate from Iran, Syria, Turkey and Egypt. Islamic metalwork and its remarkable tradition is an important chapter in the history of Islamic Art, with each region displaying its own characteristics.

The main source of the construction metals of the studied artifacts are minerals and ores. Because metals and alloys vary, metalworkers typically used a wide range of raw materials. The alloys were not always manufactured on purpose. Because of the impurity of some minerals numerous metals in their core are common. Therefore traces of uncommon metals can be found in a metallic object (Forbes 1971).

This study's main objective is to identify the construction materials of the artifacts through physicochemical analysis. This will allow us to document the raw materials that were available at the time and region, as well as identify the metalworking techniques used by craftsmen not only in construction, but also in decoration and alloy production. X- Ray Fluorescence Analysis was used in all the studied artifacts and its results allow us to categorize them as a part of classic Islamic metalworking.

Islamic metalworking

Islamic art is not defined by religion of Islam or the craftsmen's religion. Islamic art is a term used for the categorization of all artistic works created in the Islamic region, including all the areas that were under Islamic influence, such as North Africa, Eastern Europe, Russia, India, China etc. (Blair *et al.* 2003; Ettinghausen *et al.* 2001).

The repertoire of Islamic art includes metallic objects of great aesthetic value and unique metalworking techniques. Despite a common Islamic cultural identity, each region tended to have its own characteristics. Craftsmen usually mastered only one metalworking art in order to create objects of high quality though there were many categories of artifacts and utensils, for instance, tools, scientific instruments, kitchen utensils, lighting devices, furniture, weapons such as swords, blades, armors, etc. (Ward 1993; Allan 1896; Bloom 2009).

Figure 1. Basins inscribed with the representation of horsemen or arabesque patterns (Museum of Islamic Art, Benaki Museum, Athens)

Islamic temples were decorated with various metallic objects although the lack of objects for purposes of worship is noticeable, especially when contrasted with other religions. Ornaments, silver doors with gold doorknobs, luxurious furniture, and silver plaques engraved with the names of donors are the most common metal artifacts (Bloom 2009).

There were various metalworking techniques and metalworkers progressed through time in tools and materials. The most commonly used metals were gold, silver, and alloys of copper such as brass and bronze, tin, lead, and iron. An alloy of copper and nickel ("white copper") was used as a replacement for silver, since there could be a significant lack of this precious metal for many years at a time. Each technique had multiple methods and each metal was treated according to its properties (Baer 1983; Hodges 1989).

Casting was a common method using different kind of moulds or the lost wax method. A large number of objects were made from multiple moulded parts, which the metalworkers attached with the soldering method. This involved using a soft metal as a "glue" or other techniques such as metallic nails, running on, burning on, and welding (where the metal parts were heated and hammered together). Medium sized objects were manufactured from single metal sheets. Cold metalworking was used mostly on copper alloys. Annealing, hammering, sinking, striking and raising were some of the cold working methods (Hodges 1989; Baer 1983; Mattusch 1988).

Decoration was an important part of a metallic object. Gold, silver, or copper inlays such as niello on silver were the most common. The objects were carved, pierced, or incised with sharp tools, creating unique perforated patterns. Gilding and silvering, known as the method of plating, were used in order to give a more luxurious form to an artifact. Designs were often embossed or intaglio, using the repousse technique (hammered metallic sheet from the back) or hammered in a pre-carved pattern, known as Damascene decoration. Metallic pellets or wires from soft metals were easy to manufacture, and were attached through hammering or soldering. The surfaces were then usually smoothed with acid (Hodges 1989, 1992; Mattusch 1988; Maryon 1971; Todd *et al.* 1994; Untracht 1986; Baer 1983; Lasseter – Clare *et al.* 2008; La Niece 2009; Shen 2017; Thompson 1998).

Studied metallic artifacts

The studied metallic artifacts are a part of the Islamic collection in the permanent exhibition of the Museum of Islamic Art, Benaki Museum (Figures 1, 2 and 3). The artifacts are derived from Iran, Syria, Turkey and Egypt, and are dated from the 13th to the 15th centuries. These type of objects made of brass with gold, with silver and copper inlays, were massively produced around the 12th century in Iran. There were numerous metalworking centers from the 13th century onwards, such as Mosul, Syria, Damascus and later on Cairo. Decorations reflected everyday life (e.g. illustrations of utensils) until they were replaced with inscriptions in the Mameluk era.[1]

Basins were manufactured by a single metal sheet through hammering. The ewer and the candlesticks were probably made piece by piece in moulds and then soldered together. The cup and the compasses seem to have been crafted in single moulds, in item 13166 the lid is missing. Pen box (1174) was made from thin metal sheets with silver-colored pellets as decoration. Pen box (13175) has a thick metallic core that was

[1] The information, descriptions, and the photographs of the objects were provided by the Museum of Islamic Art of the Benaki Museum, Athens, Greece.

Figure 2. Candlesticks and pen boxes with inlays and black substance (Museum of Islamic Art, Benaki Museum, Athens)

Figure 3. Compasses, cup, ewer (with inlays and black substance) and incense burner (Museum of Islamic Art, Benaki Museum, Athens)

probably made in moulds. The incense burner has a unique pierced body with a repeating cross pattern. The inlays are characterized by color (gold or silver) in order to differentiate them. All have an unknown black bituminous substance on their surface.

Experimental method

The physicochemical analysis was applied *in situ* and strictly non-destructive. It was important to collect quantitative and qualitative results, hence the use of X-Ray Fluorescence Analysis with the portable XRF THERMO SCIENTIFIC NITON XL3+ GOLDD. Additionally, a comparative study was conducted based on the study by Orfanou *et al.* (2018) that categorized the types of alloys that were used and the amount of metals added to the main mixture.

Results

The main construction materials as revealed through X-Ray Fluorescence Analysis were: copper (Cu), zinc (Zn), iron (Fe), lead (Pb), tin (Sn) and nickel (Ni), athough traces of multiple elements were also found; titanium (Ti), calcium (Ca), manganese (Mn), vanadium (V), chromium (Cr), cobalt (Co), arsenic (As), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb) (Figure 4-6). The only precious metal found was gold (Au) in the inlays of the basin (13074) and candlestick (13038). A unique copper alloy with a high percentage of tin and lead was detected. High tin copper alloys are not uncommon in these kinds of artifacts. In fact, high lead copper alloys are a unique specimen of the different alloying techniques metalworkers used at the time.

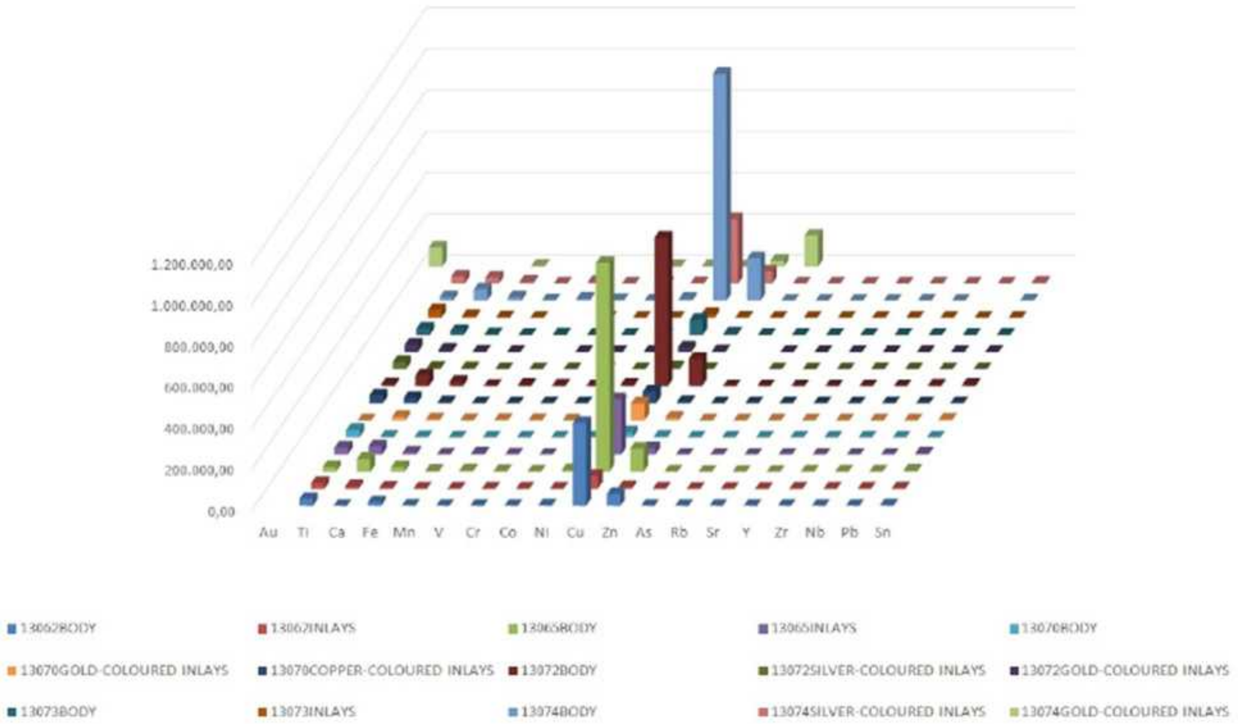

Figure 4. X-Ray Fluorescence Analysis (Results in ppm) – Basins

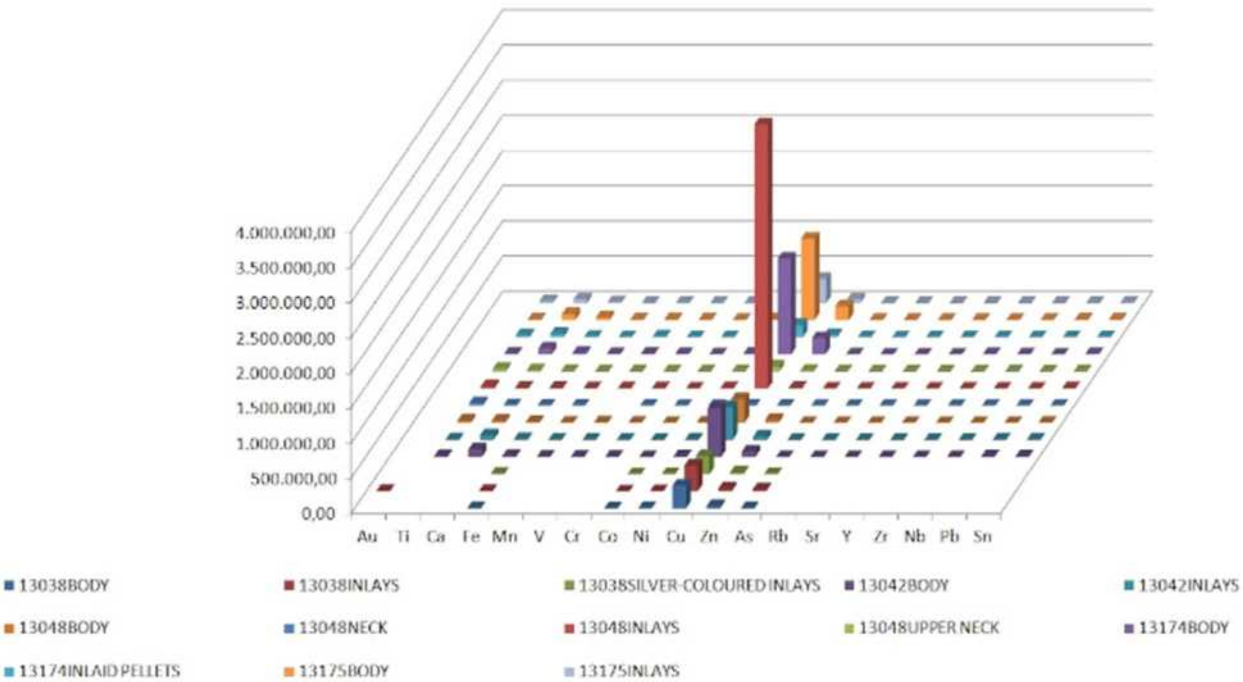

Figure 5. X-Ray Fluorescence Analysis (Results in ppm) - Candlesticks, Pen Boxes

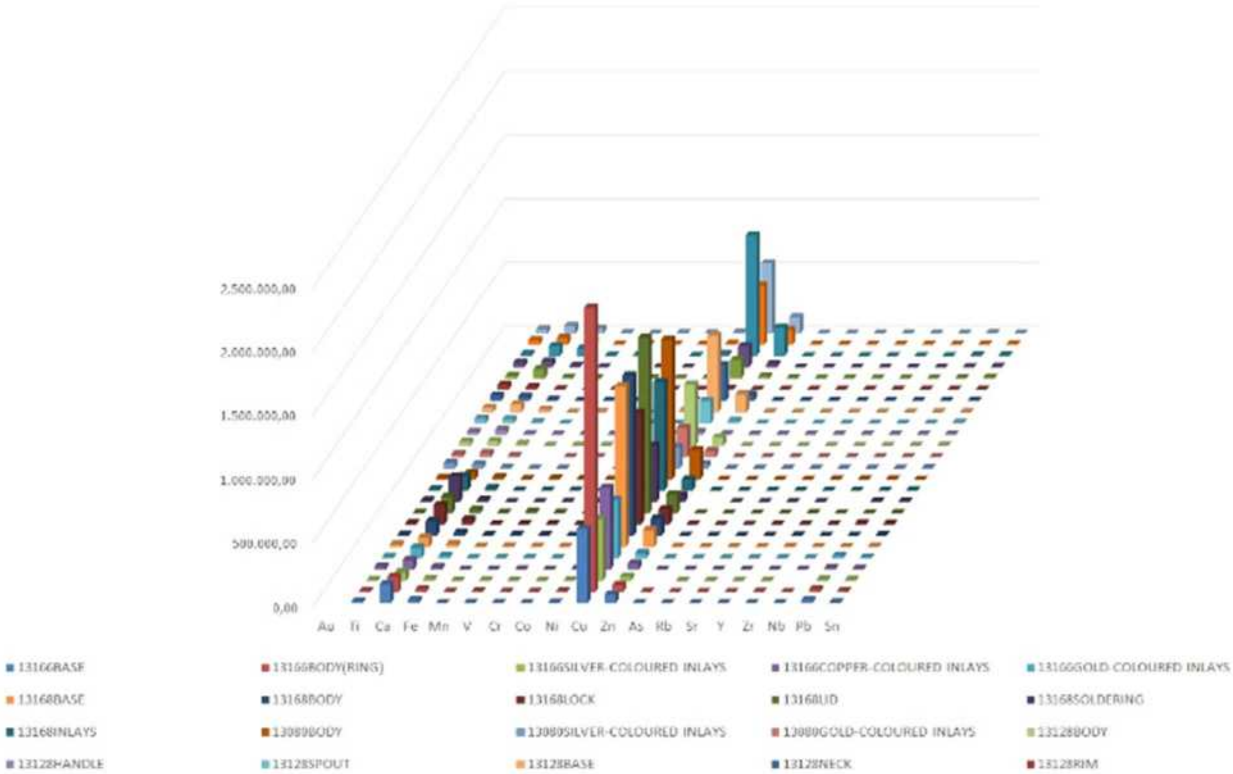

Figure 6. X-Ray Fluorescence Analysis (Results in ppm) - Compasses, Cup, Ewer, Incense Burner

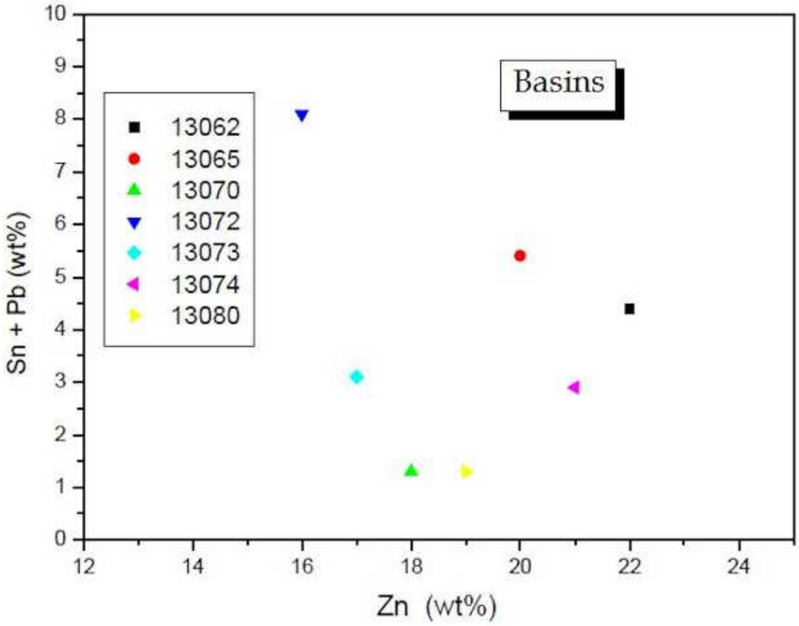

Figure 7. Comparative results Sn+Pb (wt%) to Zn (wt%) – Basins

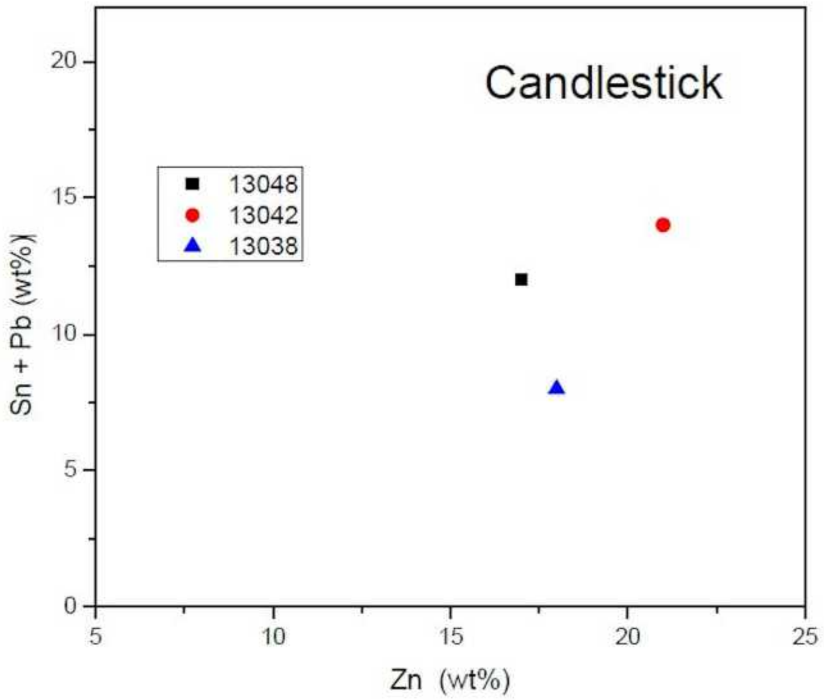

Figure 8. Comparative results Sn+Pb (wt%) to Zn (wt%) – Candlesticks

Using X-Ray Fluorescence Analysis the alloys were categorized in accordance with their added metals, and were based on the study by Orfanou *et al.* (2018);

- A copper alloy with high amounts of lead in percentages of 2 to 8wt %
- A copper alloy with tin 1 to 7wt % without added lead
- A regular copper alloy of brass (copper and zinc alloy) brass
- A brass with high amounts of lead 9 to 15wt %

Having a comparative study on groups of artifacts such as basins and candlesticks so to identify the sum of tin and lead (%) in comparison with the amount of zinc (%), provided the research with information on the availability of these metals and their usage. Figures 7 and 8 show the differences between the objects in each group. These display a fluctuated course because they derived from different metalwork centers and metalworkers. The lack of precious metals in the composition of the alloys is remarkable—not only in these two particular groups of objects but in all the artifacts of the collection— and indicates a possible deficiency of gold and silver at the time (Bloom *et al.* 2009; Komaroff 1994; Porter 2012).

Conclusions

The characteristics of the collection's construction techniques, metals, and inlaid decorations can place them in the metalworking centers of Herat in Khorasan and Fars and render them similar to the work of the fifteenth-century artist Mahmud Al Kurdi in Iran. The construction techniques were diverse. The candlesticks, for instance, were crafted piece by piece and then attached together, while basins were worked as one metal sheet that was rounded and curved. Decorations vary: the artifacts were incised, carved, embossed, and inlaid with silver, gold, or other metals, such as copper. These kinds of metallic objects, constructed by copper alloys, belong to the category of classical Islamic Art metalwork without the extensive use of precious metals. Similar objects are found in collections around the world (Museum of Islamic Art in Doha-Qatar, Lyon Museum of Fine Arts, Victoria and Albert Museum in London) (Baer 1983; Hodges 1989; Untracht 1986; Ward 1993).

This preliminary study could be a stepping stone for further research since Islamic metallic artifacts have a wide range of construction materials due to the fact that the area of Islamic metalworking is broad.

Acknowledgements

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Physicochemical Analysis of Mortars: A Case Study of Mortars from the Macedonian Tomb of the Aghia Varvara Site, in Veroia, Greece

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Abstract: Macedonian tombs are numerous in the region of Macedonia in Northern Greece. The Macedonian tomb located at the Aghia Varvara site in Veroia (Greece) is placed chronologically in the second quarter of the 4th to the mid-2nd century BC. It is a one-chamber vaulted tomb carved in limestone creating a temple-like facade. The entire surface of the facade is coated with white mortar. This study aims to analyze the chemical composition of the mortars used in the tomb, and for this purpose thirteen samples were processed through physiochemical analysis. Optical Microscopy (OM), Stereoscopy, X-Ray Fluorescence Analysis (XRF) and Scanning Electron Microscopy (SEM) were used in order to study the stratigraphy, the chemical composition, the manufacturing technology and any influences from related structures. Optical Microscopy and Stereoscopy confirmed the uniformity of colour and layering— two layers, a whitish upper layer and a lower grey in all the samples. The main materials in all samples as detected through Scanning Electron Microscopy are Si, Al, Ca, Mg and K as main compounds. X-Ray Fluorescence Analysis further detected (Pb), (Sr), (Zn), (Ti) and (Fe) in small amounts. Physicochemical analysis determined that the type of mortars used on the tomb in the Aghia Varvara site were common in the region of Macedonia. Since the stratigraphy and composition of the mortars is similar to that found in other sites, this information could be an important step for further research.

KEYWORDS: MACEDONIAN TOMBS, SAINT VARVARA SITE – VERIA, GREECE, FOURTH TO MID-SECOND CENTURY BC, MORTARS, OPTICAL MICROSCOPY (OM), STEREOSCOPY, X-RAY FLUORESCENCE ANALYSIS (XRF), SCANNING ELECTRON MICROSCOPY (SEM)

Introduction

The thirteen studied samples are from the Macedonian tomb located at the Aghia Varvara site in Veroia and dated in the second quarter of the fourth to the mid- second century BC. This Macedonian tomb is a one-chamber vaulted tomb carved in limestone that created a temple-like façade coated with white mortar. The rectangular entrance was sealed with porous stone blocks. The tomb chamber from the floor of the corridor to the top of the room was completely covered with white lime mortar, as were the corridor and the three beds of the burial chamber (Figure 1).

Figure 1. Aghia Varvara Tomb, Façade

Mortars are complex materials combining hydraulic or aerial binding components, aggregates, additives, and admixtures. The chemical and mineralogical analysis of ancient mortars can provide us with information regarding the origin of the materials and the construction methods employed. They can also assist us in determining the compatibility of the original materials with those used in the restoration of monuments (Middendorf 2005; Szczepaniak *et al.* 2006).

The thirteen samples were studied through multiple physicochemical analysis methods: Optical Microscopy, Stereoscopy, X-Ray Fluorescence Analysis, and Scanning Electron Microscopy. It was determined that the materials used on the tomb are common in the region of Macedonia.

Ancient Macedonia

The history of Macedonia begins in ancient times and is a subject of ongoing research with interesting findings. The names "Macedonia" and "Macedonian" are etymologically derived from the root "mak" meaning "long, tall" and referring to Macedonians as "tall men" or "highlanders". According to Herodotus, the Macedonians were a Greek tribe that derived from the Dorians (Harper 2019; Sverkos 2013).

The concept of Macedonia as a geographical region was introduced during the classical period. Ancient Macedonia expanded to the region of the southern Balkan Peninsula. The original Macedonian tribes inhabited the eastern slopes of Mount Olympus and the Pierian mountain plateau. Later on, they spread to the plains below Mount Paiko across the Axius River and to the slopes of Bermion. The population was included into the Macedonian kingdom, thus becoming "Makedones". Although Alexander I, son of Amyntas, king of Macedonia (495-452 BC), was the one who laid the foundation for the development of the kingdom, it was during the reigns of Phillip II and Alexander III, the Great that it flourished and became known worldwide (Sverkos 2013; Gandeto 2002; Nawotka 2010).

Macedonian tombs

Macedonian tombs are defined as large complexes of burial monuments intended for the burial of members of the upper classes of the Macedonian kingdom. The majority of these monuments were found in Macedonia and date from the middle of the 4th to the end of the 2nd century BC (Gossel 1980).

One of the most detailed descriptions of Macedonian tombs is given in Plato's "Laws". Plato describes the structure of the tomb of the "Euthynai", that is, the tomb of the divinely-appointed masters of the leaders, in 947d-947e: "*Their tomb shall be constructed underground, in the form of an oblong vault of spongy stone, as long-lasting as possible, and fitted with couches of stone set side by side; in this when they have laid him who is gone to his rest, they shall make a mound in a circle round it and plant thereon a grove of trees, save only at one extremity, so that at that point the tomb may for all time admit of enlargement, in case there be need of additional mounds for the buried...*"

The structure of the tombs consisted of the burial chamber, which sometimes had a painted interior, a square or a rectangular shape, and a barrel-vaulted roof. The exterior had monumental facades that imitated houses, temples, or gateways, and was mostly plastered. The impression given by the architecture was of a luxurious residence. The entire structure was covered by an earthen tumulus after the burial was completed. These types of tombs were common from the fourth through the second century BC and over seventy have been so far excavated (Smith and Plantzos 2018; Roisman and Worthington 2011).

Ancient aigai - Saint Varvara site, Veria

Under the Pierian mountain plateau, on the south side of the Aliakmonas River, lay Aigai, the ancient capital of the Kingdom of Macedonia, consisting of many small settlements. The prosperity of Aigai was reached under Philip II, when the city was transformed into a cradle of culture and a locale for elegant architecture. After his assassination in 336 BC Philip was buried there. After Alexander the Great died, Macedonia gradually fell into the hands of the Romans. Aigai was destroyed following the defeat of the Macedonians by the Romans in 168 BC. The site was forgotten until 1977 when an excavation was undertaken by Manolis Andronikos (Freeman 2014; Errigton 1990).

Four tombs were uncovered during the excavations of 1977, one of them being the tomb of Philip II. In 1980 three more tombs were found. Excavations continued throughout the 1980s and 1990s. In March 2014, five more royal tombs were discovered in Vergina. The identification of the other bone remains is of great interest as theories vary among researchers (Roisman and Yardley 2011; Borza 1990; Carney 2015).

During the widening of the road in Aghia Varvara, in the Municipality of Veroia, a carved chamber tomb was discovered and excavated. It is a single-chamber barrel-vaulted tomb, rock cut in limestone bedrock. The pediment of the tomb's monumental entrance—carved out of the limestone—was partially damaged by a bulldozer. The entrance's entire outer surface was covered by white plaster. Similarly plastered was the entire surface of the chamber's walls, while the chamber itself, along with the hallway leading to the entrance of the tomb, had a maximum length of 3x2.95 m and a maximum height of 1.85 m.

The tomb's hallway also had walls covered with a white plaster. Plastered in the same way were three funerary beds located in the main chamber. An architectural peculiarity of the rock-cut tomb of Aghia Varvara is the three-levelled staircase carved from the limestone in the northern side of the tomb—precisely between the entrance and the northern funerary bed (Figure 2) (Stefani 2001-2004).

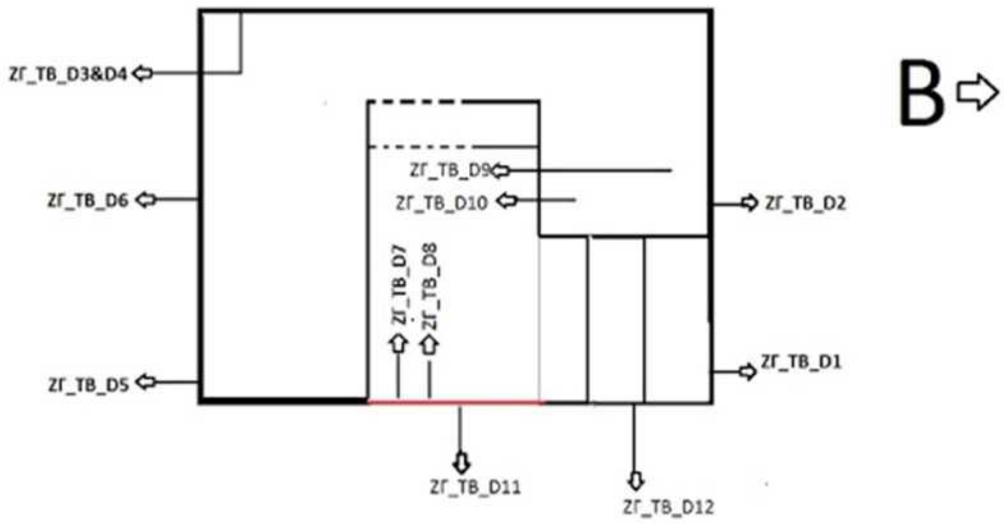

Figure 2. Aghia Varvara Tomb, Ground Plan

Numerous findings were discovered in the tomb, such as vessels, a perfume bottle dated in the end of the third century BC, a copper coin from Cassander's reign (*c*.306 BC), iron nails, and various objects that were located in the hallway. Twenty three ceramic vessels were found, fifteen of which were located just in front of the staircase (some may have fallen from it) while others were probably positioned right in front of it. Eight more vessels were found on the floor of the corridor. They are dated to the second quarter of the 4th to the middle of the 2nd century BC, which corresponds to the period in which the tomb was used (Stefani 2001-2004).

Experimental method

This study aims to analyze the chemical composition of the mortars of the tomb in order to identify the materials that were used at the time and to properly categorize the tomb among similar sites. The mortar samples were extracted with the aid of a scalpel and tweezers from already damaged areas. The hardness of the samples was notable despite the high levels of humidity, and thus extra caution was taken during the procedure.

The thirteen samples were placed on microscope slides for all the physicochemical analysis performed: Optical Microscopy, Stereoscopy, X-Ray Fluorescence Analysis, and Scanning Electron Microscopy. A comparative study was conducted based on studies from similar sites.

Optical Microscopy and Stereoscopy were used to provide information about the stratigraphy and were conducted with an Optical Microscope - LEICA DM 2500 M and a Stereoscope - LEICA M205 FA. The X-Ray Fluorescence Analysis (XRF) and Scanning Electron Microscopy were carried out to analyze the composition of the mortars with the portable XRF THERMO SCIENTIFIC NITON XL3+ GOLDD and Scanning Electron Microscope - JEOL JMS-840^A (Liritzis 2006; Elsen 2006; Injuk 2006; Froh 2004; Cowley 1993).

Results

The detailed observation of the samples via Stereoscope and Optical Microscope provided information about their colour and stratigraphy. The uniformity of the samples—all consisting of two layers with white and grey hues—is remarkable. More specifically, each has a white external (upper) layer and a grey internal (lower) layer. The morphology was simple to determine as it was visible to the naked eye, that the upper layer was finely grained in comparison with the coarse-grained lower layer (Figure 3).

Quantitative analysis carried out with the energy-dispersive X-ray spectrometer (EDS), coupled with the SEM confirmed the main compounds of the mortars Si (10%-40%), Al (10%-50%), Ca (30%-50%), Mg (0.5%-1.8%) and K (0.2%-4%). Furthermore, X-Ray Fluorescence

Figure 3. Sample's stratigraphy

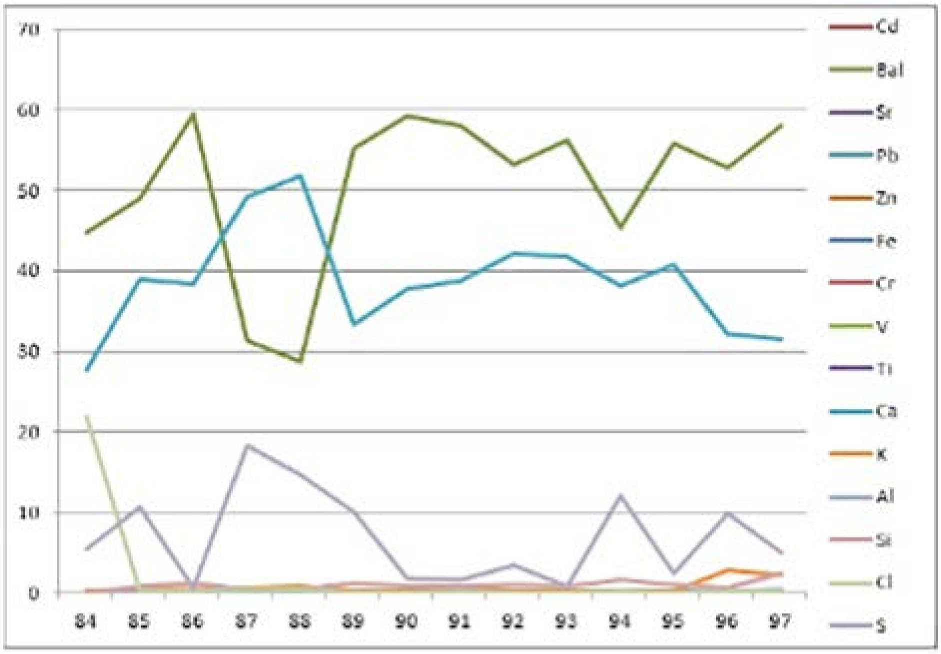

Figure 4. X-Ray Fluorescence Analysis Results

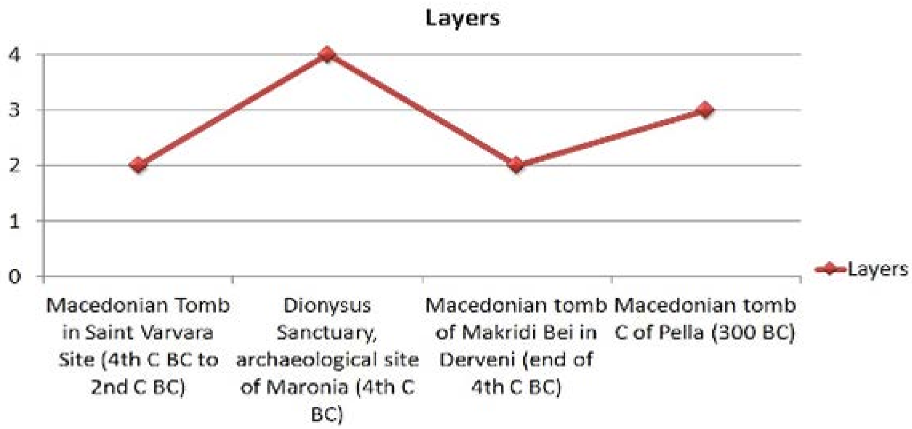

Figure 5. Comparative results of samples' stratigraphy of multiple sites

Analysis detected (Pb), (Sr), (Zn) and (Ti) in small amounts in the samples. Fe is observed at 0.1-0.2% apart from sample ΖΓ_TB_D4 that contained higher amount (about 0.5%). Finally, the upper layer contained a higher percentage of calcium 5-10%.

Figure 4 shows the variations in the composition of the materials among the samples. In descending order, the elements detected are calcium (Ca), potassium (K), iron (Fe), strontium (Sr), titanium (Ti), aluminum (Al) and zinc (Zn). Potassium, iron, strontium titanium, aluminum, zinc, and barium have steadily low percentages in all the samples.

Comparative study

Having obtained information on the construction materials, we tried to understand the complexion of the compounds and the methods used in that period of time. Thus, a comparative study was conducted based on the study by Papayianni *et al.* (2013) in which samples were extracted from three different archaeological sites in Macedonia. The main materials of the mortars from all three sites are hydrated lime and pozzolan ($SiO_2 + Al_2O_3 + Fe_2O_3$), with a four to two-layer stratigraphy, as shown in Figure 5.

Comparing the results with the Aghia Varvara Site in Veroia, we note the following similarities in the main materials of the mortars. First of all, they are all lime based. In stratigraphy the tomb at the Aghia Varvara site has similarities with the Macedonian Tomb of Makridi Bei in Derveni: both sites have a two layer mortar sample though they differ in colour. Another site in which a similar type of mortar was used is Aiani's archaeological site in Northern Greece dated from fifth to the third century BC and studied by Iordanidis *et al.* (2013). Here, a masonry mortar sample from "tomb A" of the cemetery, has similarities in colour, (cream-coloured sample from Aiani) and composition.

Conclusions

Physicochemical analysis determined that the type of mortars used in the Saint Varvara site is common in the region of Macedonia as their stratigraphy and composition is similar to other sites. Macedonian tombs are a subject of unique importance due to their complicated construction and the multiple methods and materials that were used. The site of Aigai is an exceptional example of Macedonian history and culture since it is not limited to burial sites as architectural samples of the period, but also testifies to the technological knowledge that was needed to manufacture these types of mortars.

The information provided by this study could be an important step for further research. This should not be confined to the region of Northern Greece, but be expanded in all the known lands that were included in the Macedonian kingdom in order to contribute to the ongoing study of Macedonian history.

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Non-Destructive Analysis and Experimental Replication of 5th Millennium BC 'Crusted' and Pattern Painted Pottery from West Macedonia, Greece

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Abstract: The early Final Neolithic (*c*.4700-4450 BC) ceramic production in W. Macedonia, Greece is characterised by a variety of materials, shapes, sizes and practices of surface treatment. As part of the study of the Neolithic pottery excavated from Megalo Nisi Galanis in the Kitrini Limni/Sarigiol basin (1987-1989, 1993), 13 early Final Neolithic 'crusted' and pattern painted sherds were analysed with non-destructive near-infrared (NIR) and X-ray fluorescence (XRF) techniques. The aim was: (a) to identify the chemical and mineralogical compositions of the paint layers and (b) to test the hypothesis that 'crusts' were a post-firing application and to differentiate them from paints applied before firing. The results showed that eight of the 13 sherds bear raw pigments applied after firing, four before firing and one sherd both before and after. Based on the NIR, and not on the traditionally used mid-infrared (MIR) spectra, it was also possible to estimate the samples' firing temperatures. Experimental replication of 'crusted' and pattern painted Neolithic pottery types at THETIS, a ceramics studio specialising in ancient technology, complemented the analytical results and enhanced our understanding of the ceramic production process, from vessel formation to decorative surface treatment and firing.

KEYWORDS: Final Neolithic pottery, West Macedonia, Greece, crusted pottery, pattern painted, non-destructive analysis, XRF, NIR, clay minerals, experimental replication.

Introduction

The analytical data presented here for the first time were obtained in the context of a multi-faceted archaeological project that took shape in the late 1980s but evolved with intervals in the course of three decades. The project comprised systematic surface survey of the Kitrini Limni (Sarigiol) basin in West Macedonia, near the town of Kozani, small-scale excavation at Megalo Nisi Galanis (MNG), one of the prehistoric sites in Kitrini Limni, study of the environment and geology of Kitrini Limni and its surrounding area, as well as in-depth studies of various categories of excavated artefacts (see Fotiadis *et al.* 2019 for the most recent synthesis).

The early Final Neolithic (FN) pottery from MNG

MNG was excavated in 1987-1989 and again in 1993. The excavated deposits in the northern part of the site cover the period from the advanced Middle Neolithic to the early FN in Greece, but traces and 'pockets' of pottery from both earlier and later phases are also present.

The early FN deposits (*c*.4700-4450 BC) represent settlement debris and waste. The pottery found in them is characterised by a considerable variety of shapes, sizes, clay bodies and surface treatments and differs markedly from what has preceded it. Open shapes, in particular bowls of various profiles and sizes, are the most common shapes. Most of them are undecorated although their surfaces may be slipped and burnished. There are, however, few small size bowls with elaborate incised decoration and medium size bowls with painted decoration.

The early FN ceramic inventory at MNG also comprises several large basins and jars, perforated pots ('strainers'), grooved bowls with a bulging upper part, 'scoops', miniature and asymmetrical pots, as well as angular or quadrangular containers and sherds recycled as tools (Fotiadis *et al.* 2019: 23-25; Kalogirou 1994: 107-180). Potters exploited mostly local sources of raw materials, including non-calcareous and calcareous clays, as indicated by macroscopic observations and field surveys, as well as petrographic analysis of 41 sherds (Kalogirou 1994: 197-210).

'Crusted' pottery

At MNG, 'crusted' pottery is a distinct feature of the early FN ceramic production, as it is the case in many other Neolithic sites in Greece. 'Crusted' refers to pots with a thick coating of white, cream or bright coloured pigment on their surface (red, pink, orange)[1] that is friable and impermanent (Kalogirou 1994: 110). Two kinds of white and light-coloured crust were distinguished macroscopically: a yellowish or cream-coloured one that does not dissolve in water or cold

[1] The colour of the pink/red crusts falls primarily in the Munsell 5R hue.

hydrochloric acid and a powdery one that dissolves readily in water.[2]

'Crusts' were identified on plain, incised and pedestalled bowls ('fruitstands') and possibly on ladles (see Fotiadis *et al.* 2019: figs SM3.7 and SM3.8 for examples of 'crusted' pottery).

'Crusts' were applied on the finished exterior and/or interior of early FN pots to form linear and solid patterns, as well as to fill incisions in order to make the pattern stand out. A combination of two or more crusts on a single pot also occurs, even though such examples are few and their state of preservation rather poor. Interestingly, on a couple of sherds the red crust covered the fractures, suggesting that crusts were applied to broken pieces of pottery as well.

'Crusts' were for long assumed to be post-firing applications, but few related physicochemical analyses had been carried out until the late 1980s (see, for instance, Coleman 1977; Jones 1986) when the study of the pottery excavated at MNG began. In the field, the following criteria were used to designate a sherd as 'crusted': a) the existence of a glossy, burnished surface preserved under the 'crust', considering that, if the crust had been applied before firing, it would have removed the gloss; b) the presence of small pits and voids on the surface of the pot, created from burned vegetal matter in the clay body during firing, filled with white or coloured pigment; c) the presence of a thick red, pink or orange layer of pigment clearly distinguishable from the dark gray or black surface of the fired pot (Kalogirou 1994: 119-120).

Pattern painted pottery

In addition to 'crusted' pottery, medium size bowls decorated with painted patterns, assumed to have been applied before firing, also occur among the early FN pottery at MNG, albeit in small numbers. Two main variations have been distinguished: a) "cream-on-red" (being more common) and b) "red-on-white".

The pots with "cream-on-red" decoration (see Fotiadis *et al.* 2019: figs 16 and SM3.6) have a monochrome burnished interior. The bowls were modeled, scraped, and then coated on the exterior with a pigment that was applied uniformly from rim to bottom. A second pigment was subsequently used to paint the patterns on the solid background. The light-colored slip on the exterior of the bowls is, in general, very friable. After the pots were painted and left to dry, they were burnished. The bowls in this group were largely made from a non-calcareous clay body.

The "red-on-white" pattern painted pots have a dark monochrome, burnished interior (Kalogirou 1994: figs 68-69). Their clay body is also non-calcareous and contains microscopic flakes of silver mica, tiny white subangular grains of quartz and perhaps feldspar, and occasional specks of dark red iron oxide. The best-preserved example, a bowl with a diameter of 21 cm and a height of 10 cm, was mended from 42 sherds (Kalogirou 1994: fig. 68). One horizontally perforated round lug is found just below the rim; a second lug can be securely reconstructed diametrically opposite. The exterior is uniformly coated with a pigment that has fired to a white color. On top of it, horizontal bands of parallel zigzag lines were painted with a different material that has fired to a pinkish red color (Munsell 5R 5/4). It is possible that a third pigment was also used on the exterior to outline the painted patterns. After it was painted, the bowl was uniformly burnished to a high gloss.

Materials and Methods

For the analyses carried out in 2003, 13 'crusted' and pattern painted sherds were selected from well documented archaeological contexts at MNG. Based on the macroscopic examination in the field, all types of 'crusts' were sampled. Pattern painted sherds were purposefully added in the sample to contrast and compare them with the 'crusted' sherds. For 7 of the selected sherds petrographic data were also available (Kalogirou 1994: 197-210).

Non-destructive near-infrared (NIR) and X-ray fluorescence (XRF) techniques were used with the aim to obtain the mineralogical and chemical characterisation of the paint layers of the pattern painted and 'crusted' examples and to test the hypothesis of post-firing decoration in the case of the latter.

Description of the samples

Sample **NGAL-1** *(passa3 M27γδ.1) - Figure 1f*

Large body sherd from a bowl with a globular profile. The curvilinear red and brown patterns on the exterior were painted on a whitish solid background. The interior is dark grey monochrome and highly burnished (Fotiadis *et al.* 2019: fig. SM3.6, bottom row, 1st from left; Kalogirou 1994: fig. 69d).

Sample **NGAL-2** *(passa M27γδ.1) - Figure 1a*

Base fragment from a pattern painted "red-on-white" bowl. The interior surface is light brown burnished (Kalogirou 1994: 149-153, fig. 69a; 2002: fig. 5, bottom left).

[2] The colour variation may, in fact, be due to differential preservation.

[3] *Passa* (in Greek) designates the MNG excavation unit.

Sample **NGAL-3** *(passa M27δ.8.1) - Figure 1c*

Rim from a "red-on-white" pattern painted bowl, with dark brown-coloured pigment outlining the red pattern. The interior is dark grey burnished but worn and scratched. The clay body is fine gritty with tiny white inclusions. It probably contained organic matter, deduced from the voids visible against the dark brown core (Kalogirou 1994: 149-153, fig. 69a). This sample was also analysed by petrography (petrographic sample B4; Kalogirou 1994: 197-210).

Sample **NGAL-4** *(passa M27γδ.4)*

Fragment from a cylindrical pedestal with two cutouts, possibly belonging to a 'fruit stand'. The pedestal has a spalling scar on the exterior and a base diameter of 15 cm. The exterior surface has fired to a nearly black colour and bears a red crust. The interior is very dark gray with traces of red crust. The clay body is fine gritty with tiny whitish inclusions. This sample was also analysed by petrography (petrographic sample 3; Kalogirou 1994: 197-210).

Sample **NGAL-5** *(passa M26β.7)*

Body fragment from a crusted bowl. A part of the rim with an elongated lug was also found, but the two pieces do not join. The exterior surface is dark grey with pink/red crust that forms a solid band. Red crust was found on the interior as well, but it has fired to a lighter colour (Kalogirou 1994: 119-124).

Sample **NGAL-6** *(passa M26β.6.1)*

Rim fragment, most likely from a crusted 'fruit stand' with a maximum diameter of 30 cm and wall thickness 7mm. The edge of the rim is worn. The exterior surface has red crust (Munsell 10R 4/6, 8) (Kalogirou 1994: 119-124). This sample was also analysed by petrography (petrographic sample B5; Kalogirou 1994: 197-210).

Sample **NGAL-7** *(passa M26β.10) - Figure 1e*

Rim from a "cream-on-red" pattern painted bowl with a diameter of *c.*22 cm and wall thickness 7.5 mm (Kalogirou 1994: 141-149, fig. 64e). The exterior is evenly burnished, while the interior is burnished in a streaky manner and fired to a brown-grey colour. The clay body contains moderate amounts of small red grits and mica, but no calcite. The core is oxidized reddish brown. This sample was also analysed by petrography (petrographic sample A1; Kalogirou 1994: 197-210).

Sample **NGAL-8** *(passa M26αγ.1)*

Rim from a pattern painted "cream-on-red" bowl with a rim diameter of 28 cm and wall thickness 5 mm. A small rise on the exterior surface may indicate the beginning of a lug (Kalogirou 1994: 141-149, fig. 65e and 2002: fig. 4). The interior has been fired to a brown colour. The red pigment (Munsell 5R 4/6 or 5R 5/4) on the exterior surface is rather friable, perhaps indicating that it was applied before firing, but when the pot was quite dry, therefore, it did not bond well with the surface. The colour of the light-coloured pigment is Munsell 10YR 7/3. The clay body is fine with scattered, sparse, white grains of quartz. The core is light brown oxidized but gray in the middle. This sample was also analysed by petrography (petrographic sample 10; Kalogirou 1994: 197-210).

Sample **NGAL-9** *(passa M26β.6)*

Rim fragment from an open shallow bowl with a whitish crust on its exterior and interior, and with traces of red crust on top of the whitish one on the exterior (Kalogirou 1994: 119-124).

Sample **NGAL-10** *(passa M26β.6) - Figure 1d*

Fragment from the flat bottom and part of the wall from a bowl. The bottom diameter is 9 cm and its thickness 5 mm. The exterior surface, including the underside of the bottom, bears a pale-yellow crust (Munsell 2.5Y 7/3), probably discoloured that flakes off easily (Kalogirou 1994: 119-124 and 2002: fig. 1, bottom row, 1st from left). The interior surface is dark grey and worn. The clay body is fine with occasional grains of quartz up to 2mm long and mica. This sample was also analysed by petrography (Kalogirou 1994: 197-210; petrographic sample 9).

Sample **NGAL-11** *(passa M26βδ.13)*

Body sherd from a slightly carinated bowl with white crust on the exterior surface. The crust is distinguished against the light brown background of the body. The sherd is possibly worked. The clay body is fine with mica and tiny voids, while the core is a brown/reddish brown colour. This sample was also analysed by petrography (petrographic sample A7; Kalogirou 1994: 197-210).

Sample **NGAL-12** *(passa M36αγ.5)*

Small rim fragment from a bowl with a red painted band on the exterior from which begins a pattern painted decoration done with a thick application of white crust. The white crust forms patterns on the interior as well (Fotiadis *et al.* 2019: fig. SM3.8, upper row, 4th from left; Kalogirou 1994: 122, fig. 46d).

Sample **NGAL-13** *(passa M36αγ.5)*

Small rim fragment from a bowl. A thick white crust, better preserved on the interior, was applied over

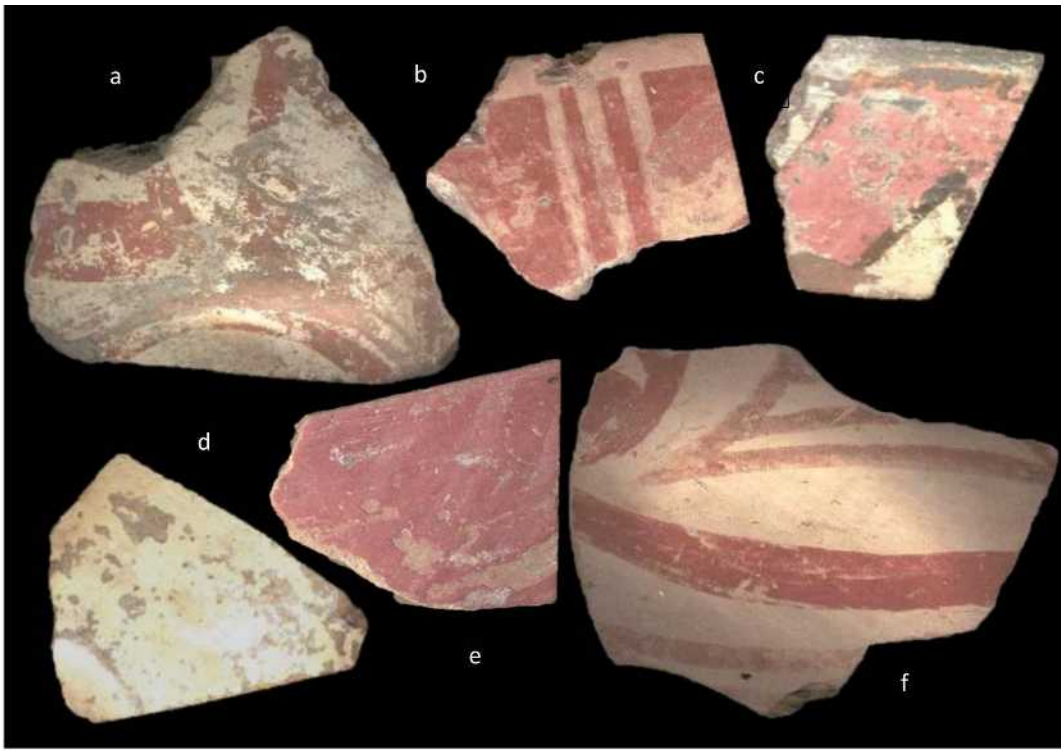


Figure 1. Decorated sherds from Megalo Nisi Galanis bearing crusted or painted decoration, early FN ; (a) NGAL- 2, (b) NGAL- 8, (c) NGAL- 3, (d) NGAL- 10, (e) NGAL- 7, (f) NGAL- 1

the dark grey surface of the body (Fotiadis *et al.* 2019: fig. SM3.8, upper row, 2nd from left; Kalogirou 1994: 122).

Analytical Techniques

The sherds were first examined under the stereomicroscope (Olympus SZX9, Highlight 3100, CCD Sony Exwave HAD, magnification 10-150x). Following an exploratory analysis of both surfaces of the sherds by near-IR technique in order to test the different paint layers and the ceramic body, we proceeded with non-destructive chemical analysis of the surface coatings and pigments with the X-ray fluorescence technique (XRF: Rh anode X-ray tub, 50 kV 1mA, PIN Peltier cooled X-ray detector, conditions 40kV filtered excitation, 15kV unfiltered, spot area 3mm^2). For each point analysed, two spectra were obtained, at low and high energy (15KV and 40KV) for the determination of the major and minor elements (Si, S, Cl, K, Ca, Ti, Fe) and the trace elements (Cr, Mn, Ni, Cu, Zn, Rb, Sr) respectively. The processing of the spectra led in principle to the semi-quantitative analysis of the materials involved. In a third phase, a detailed 7-12 point analysis by near-IR technique was performed on each sample (FT-NIR 4000-12.000 cm^{-}1, Vector 22N, Bruker Optics). A total of 150 spectra were obtained which were grouped and listed for each sample separately. For the estimation of the firing temperature by NIR, small samples of three sherds, NGAL-2, NGAL-10 and NGAL-12, were refired in the laboratory at 600°C under oxidising conditions (200°C/h rate, 1h final temperature) and were analysed for comparison.

Results and Discussion

Chemical Analysis - X-ray Fluorescence Technique

The nd-XRF analysis led to a first classification with respect to Ca, Fe and K normalised to Si. As shown in Table 1, most of the materials used for the coatings and pigments are characterized by low calcium (Ca) content and differentiate in the Fe content; the red pigments are highly ferruginous, which attests to the use of Fe-oxides. Samples NGAL-3, NGAL-12 and NGAL-13 are an exception showing higher Ca. The same samples differ from the others in Ca/Fe vs K/Si ratios (Figure 2). We note that most of the samples are distributed in two areas, A and B, the former characterising non-calcareous (white and red pigment) or ferruginous (red pigment) materials with low content of illite/mica. The second area is characterized by non-calcareous or ferruginous materials, with a high content of illite/mica; the light-coloured coatings of the NGAL-1, NGAL-2, NGAL-8 samples belong to this category. The same applies for the light-coloured coating of NGAL-3 which is characterized by higher Ca. Examination of the specimens in the stereomicroscope showed that

Table 1. Classification of the 'crusts' and pigments according to the nd-XRF analysis (see also Figure 2)

	white-cream	red	brown-black
A : low Ca/Fe, low K/Si			
Non-calcareous or ferruginous material, does not contain mica/illite	NGAL-9, 10, 11	NGAL-1, 3, 5, 6, 7,8	
B : low Ca/Fe, high K/Si			
non-calcareous or ferruginous material, contains mica/illite	NGAL-1, 2, 8	NGAL-2, 4	NGAL-1
high Ca/Fe, low K/Si			
calcareous material, does not contain mica/illite	NGAL- 13, 12	NGAL-12	
high Ca/Fe, high K/Si			
calcareous material, contains mica/illite	NGAL-3		NGAL-3

all samples with high K/Si values contained fine mica platelets. The white pigments of NGAL-12 and NGAL-13 are characterized by high Ca and do not contain mica.

In Figures 3a and 3b, we note a positive correlation of the Fe content to Ni and Cr. The red pigments are characterized by higher concentrations of both trace elements. The increased Cr content is expected to relate to the presence of chromite, known industrial product of the Ptolemais Basin (to the N of Kitrini Limni), whereas Ni to 'garnierite' $(Ni, Mg)_6Si_4O_{10}(OH)_8$, a phyllo-silicate mineral of the serpentine group, characteristic of the geology around the Kitrini Limni Basin (IGME 1980). The light-coloured coating of NGAL-1, NGAL-2, NGAL-3 and the white pigment of NGAL-11 and NGAL-12 are characterised by lower amounts of Ni and Cr.

An interesting result of the analysis is that the brown-black pigments in the NGAL-1 and NGAL-3 samples (Figure 1f, 1c) do not directly relate to the use of Mn minerals, as it was expected from both the microscopic examination of the material and the abundance of manganese minerals in the area (IGME 1980). The analysis of the brown pigment for NGAL-1, showing a slight relative increase in Mn relative to the background is very low (MnO_2 <0.5%) when compared to the usual MnO_2 content in natural umbers (2-13%). In the sample NGAL-3 (Figure 1c), the texture of the black pigment is identical to that of the light background. The colour refers rather to the use of a carbon-based (soot or other organic) material for the NGAL-3 and possibly for NGAL-1 as well.

Infrared Spectroscopy

The results of the near-IR are summarised in Table 2. The mineralogical phases presented in Table 2 allow us to characterise both the raw materials used and the firing conditions involved. The mineralogical phases identified are given separately for the light-coloured or white pigments and for the red pigments. For the unspecified organic materials, the characteristic absorption peaks are given as notes.

Mineralogical Analysis

a) 'Serpentine signature'

The peak at 7239 cm^{-1} is an indicative signature of serpentine (the graph in pink in Figure 4 corresponds to a standard reference serpentine spectrum) contained in sherds NGAL-3, NGAL-4, NGAL-7, NGAL-8, NGAL-9, NGAL-10, NGAL-12, NGAL-13, as a component of the material that has been used for the light coating and the red and white pigments.

b) 'Talc vs. saponite' signature

Initially, the peak at 7185cm^{-1} was attributed to the presence of trioctahedral smectite, probably saponite. Detailed comparisons with standard talc samples, presenting also a sharp and narrow peak at 7185cm^{-1}, verified its presence in the 'crusts' and the ceramic body. The intense talc signal in the material overcomes the saponite signal in the second derivative of the spectra. However, as shown in the primary NIR absorption spectra, almost all spectra have a component of trioctahedral smectite in the mixture that corresponds to saponite.

Firing temperatures

In order to estimate the temperature ranges to which the Neolithic pots have been exposed, we made use of the ubiquitous kaolinite content of almost all clays to which the infrared spectroscopy is particularly sensitive. The peak at 7069 cm^{-1} in the red spectra in Figure 5 is indicative of the kaolinite in the ceramic body of sample NGAL-7. Also, a diagnostic peak of kaolinite appears at lower frequencies (4527 cm^{-1}). Typical kaolinite spectra are given in the two images of Figure 5 in dark green. As shown from a series of measurements on commercial clays containing a mixture of clay

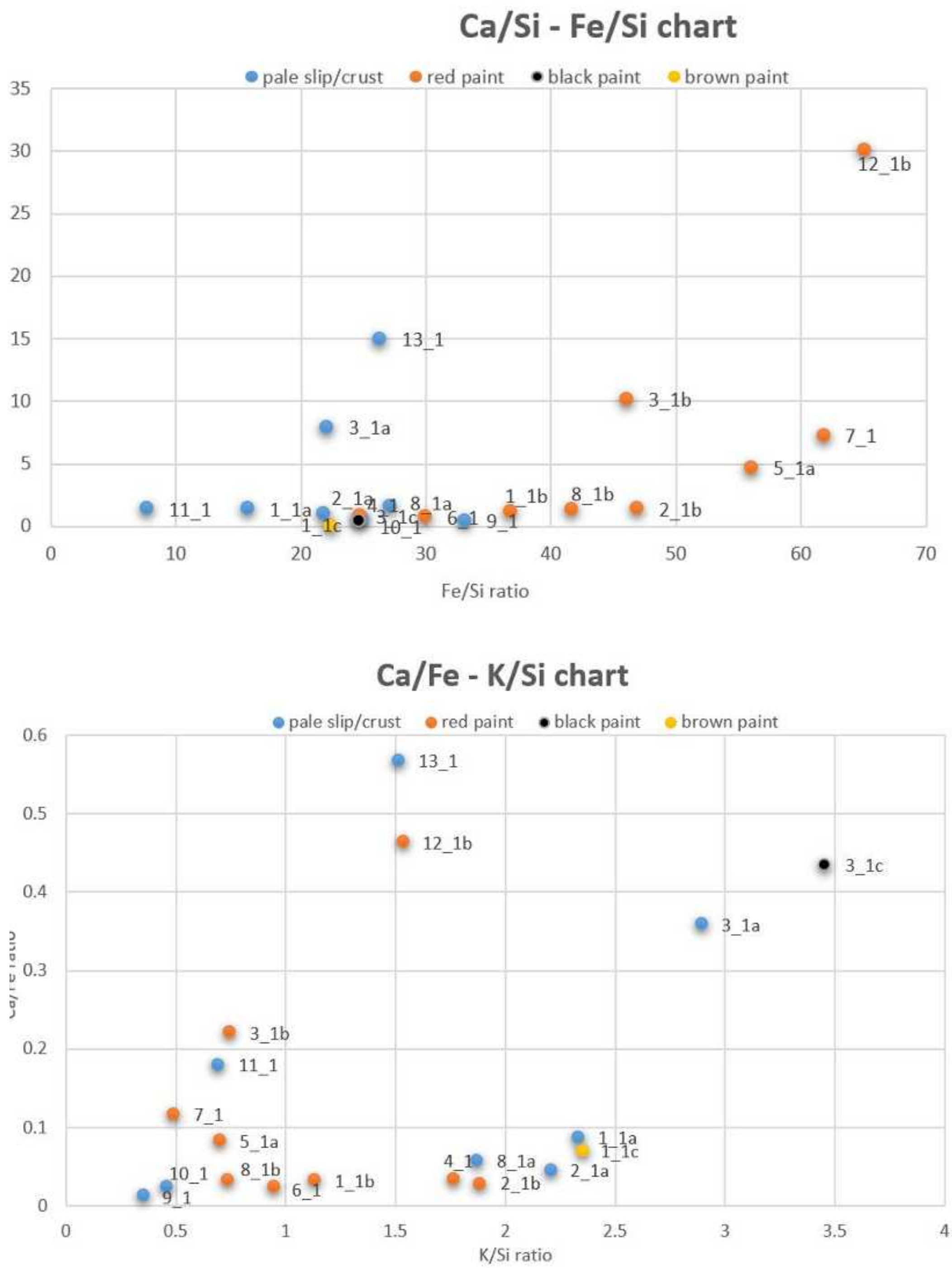
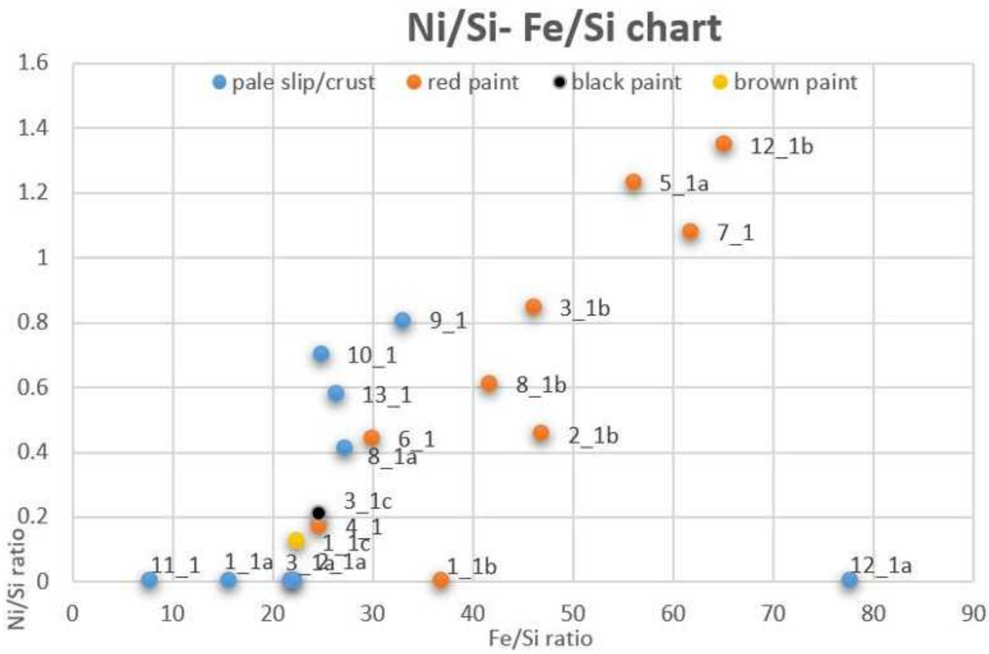


Figure 2. (a) Scatter diagram of Ca-Fe normalised to Si for all areas analysed. The red pigments are characterised by higher Fe content, (b) the Ca/Fe ratio vs K/Si, express the mica/illite in the material (see also Table 1).

minerals, the kaolinite component exhibits specific absorption changes with thermal treatment in the range of 350-800°C, allowing the firing temperature estimation in low fired archaeological samples. In Figure 5, NGAL-7, which has a thickness of 0.8-1 cm, has been exposed to temperatures not exceeding 600-650°C (blue lines in the spectra), while at the core of the break that is dark grey, the firing temperature is lower by 200°C (red spectra). This variation in the temperature can be explained by a rapid-firing of the pot (45min-1h) in an open fire.

An interesting feature is observed on the NGAL-10 sherd (blue spectra in Figure 6) and the refired specimen at 600°C in an oxidising atmosphere (red spectra in Figure 6). In the layer of the white coating,



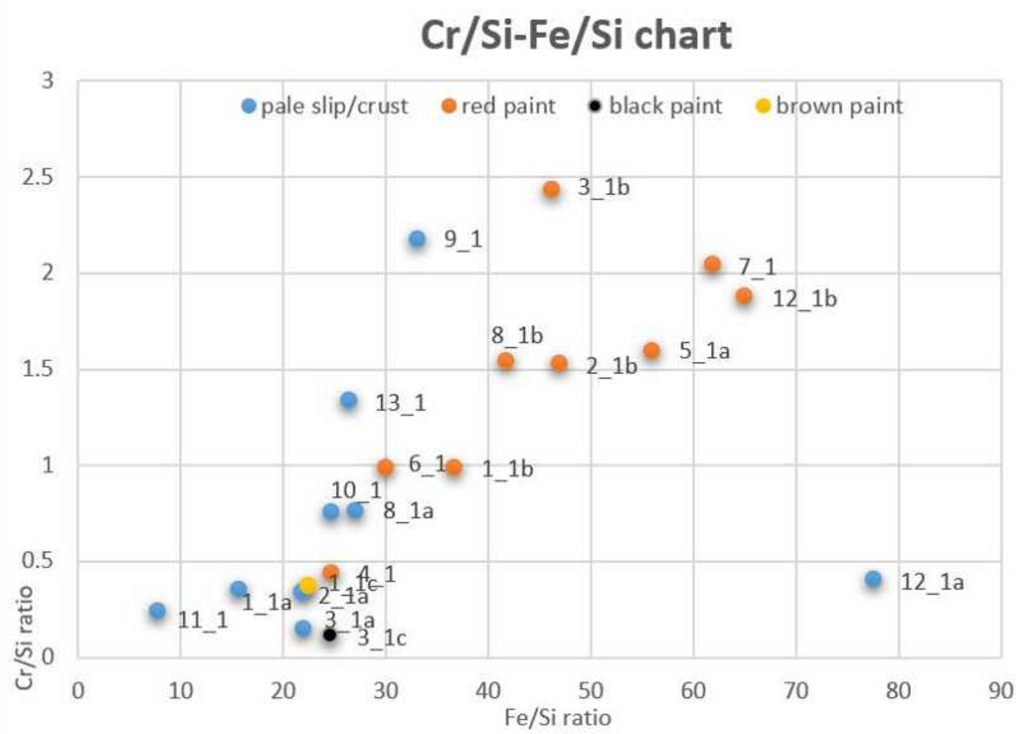


Figure 3 a, b. scatter diagrams of Ni, Cr and Fe normalised to Si. We note the increased concentrations of Cr and Ni trace elements in most red and some white pigments, as well as in the ceramic background of some samples, compatible with minerals in the Ptolemais-Kozani basin.

a significant decrease in the serpentine component is noted after refiring, while in the ceramic body, the talc signal becomes sharper and exhibits a relative increase. By using the 'talc' signature as an indicator, we assume that the ceramic body was originally exposed to temperatures not exceeding T≤ 600°. Conversely, the white pigment bearing the 'serpentine' signature was not thermally treated and, therefore, we assume that it was applied on the surface of the pot raw, that is, after the firing.

Organic materials

The samples NGAL-4, NGAL-6, NGAL-8, NGAL-9, NGAL-10, NGAL-12, NGAL-13 are rich in organic materials as shown by the corresponding spectra in the range 5500-6000cm^{-1} (Figure 7). Two types of organic compounds are distinguished: the first corresponding to peaks 5774-5665 cm^{-1} and the second, detected only at NGAL-12 and NGAL-13, with characteristic peaks at 5955-5910 cm^{-1}. The light blue spectra with no evidence of organic material correspond to the ceramic body. Organic compounds appear to be associated with the pigment layer. Except for NGAL-6, in all the other samples mentioned above, the pigments have been applied on the surface of the vessels after firing as shown in Table 2. Therefore, it is reasonable to assume that the organic materials detected are either pre-existing substances in the natural raw materials or represent a binder used to stabilize the pigments on the surface of the vessels.

In sum, the analytical results show that:

a. four sherds (NGAL-1, NGAL-2, NGAL-5, NGAL-6) were decorated **before** firing - Figure 1a,1f,
b. eight sherds (NGAL-4, NGAL-7, NGAL-8, NGAL-9, NGAL-10, NGAL-13) were decorated **after** firing - Figure 1b, 1d, 1e,
c. one sherd (NGAL-3) was decorated both **before** and **after** firing, as it bears a raw, red inorganic pigment and a brown organic pigment on top of a light-coloured coating applied before firing - Figure 1c.

Table 2. Mineralogical phases identified by NIR spectroscopy. The pigments that were exposed to temperatures ≥ 600oC are marked as fired, F. (*) subs stands for substances.

Sample	Red pigment/crust	White-Light coloured pigment/crust	Ceramic body	additional
NGAL-1	hematite talc-saponite F	talc-saponite F	talc-saponite	
NGAL-2	hematite talc-saponite F	talc-saponite F	talc-saponite	
NGAL-3	hematite talc-saponite serpentine	talc-saponite F	talc-saponite	
NGAL-4	hematite talc-saponite serpentine		talc-saponite	Organic subs* 5774-5665cm^{-1}
NGAL-5	hematite talc-saponite F		talc-saponite	
NGAL-6	hematite talc-saponite F		talc-saponite	Organic subs 5774-5665cm^{-1}
NGAL-7	hematite talc-saponite serpentine		talc-saponite kaolinite	
NGAL-8	hematite talc-saponite serpentine	talc-saponite serpentine hematite	talc-saponite	Organic subs 5774-5665cm^{-1}
NGAL-9	-	talc-saponite serpentine	talc-saponite	Organic subs 5774-5665cm^{-1}
NGAL-10	-	talc-saponite serpentine	talc-saponite	Organic subs 5774-5665cm^{-1}
NGAL-11	-	unspecified material	dioctahedral smectite/ bentonite	
NGAL-12	hematite talc-saponite serpentine	unspecified material	talc-saponite	Organic subs 5774-5665cm^{-1} +5995-5910cm^{-1}
NGAL-13	-	talc-saponite serpentine + unspecified material	talc-saponite	Organic subs 5774-5665cm^{-1} +5995-5910cm^{-1}

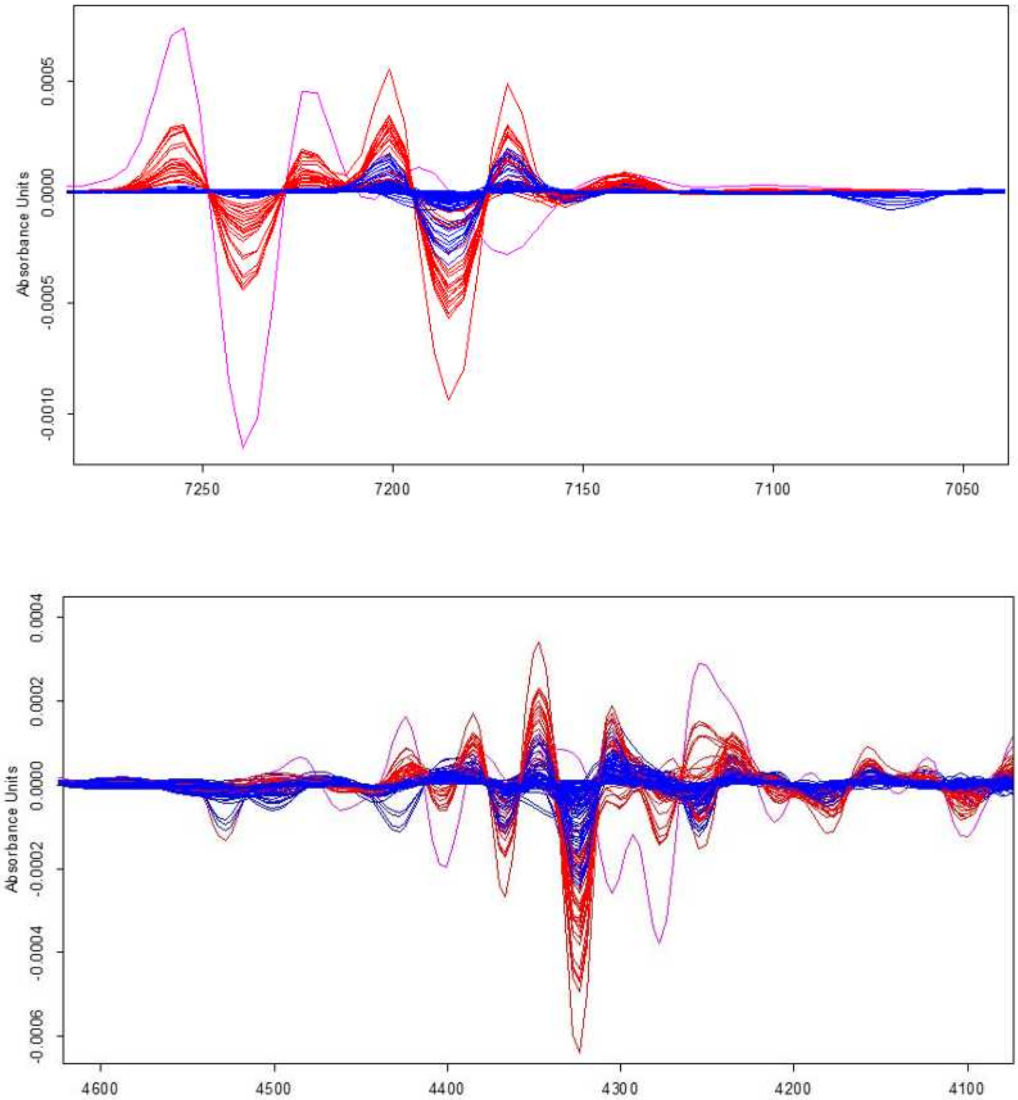


Figure 4. The peak at 7239 cm-1 is indicative of the presence of serpentine in the NIR spectra of all spots analysed. The graphs in red correspond to the spectra containing the phase of serpentine. The NIR spectrum of standard reference serpentine is given for comparison (pink graph).

Data consolidation

The white non-calcareous and the red ferruginous pigments identified are rich in clay minerals of the talc-saponite series, which are weathering products of the disintegration of mafic rocks (e.g., serpentinites, gabbros). These findings are compatible with the geology of the Kitrini Limni and the Ptolemais-Kozani basins (IGME 1980). The increased traces of Ni and Cr proportional to Fe detected with the XRF in almost all the pigments as well as in the ceramic body, combined with the more specialised analysis of the clay minerals (talc-saponite vs. smectite) provided strong discriminating tools to support the use of the local clay materials and mineral pigments by the Neolithic potters.

Moreover, the findings of the present study corroborate the results obtained from the petrographic analysis of 41 early FN sherds from MNG, as well as a preliminary analysis of selected clay materials from Kitrini Limni by X-Ray Diffraction (XRD) and petrography carried out in the '90s. More specifically, the petrographic analysis of the early FN sherds, including samples NGAL-3, NGAL-6, NGAL-7, NGAL-8, NGAL-10, and NGAL-11 of our study, had already pointed to the use of local raw materials for pottery-making (Kalogirou 1994: 205-210). Besides, the analysis of the clays indicated the presence of kaolinite, together with illite and smectite in different proportions. Other minerals identified were calcite, quartz, serpentine and some muscovite or biotite mica (see Kalogirou 1994: 185-188 for a short discussion).

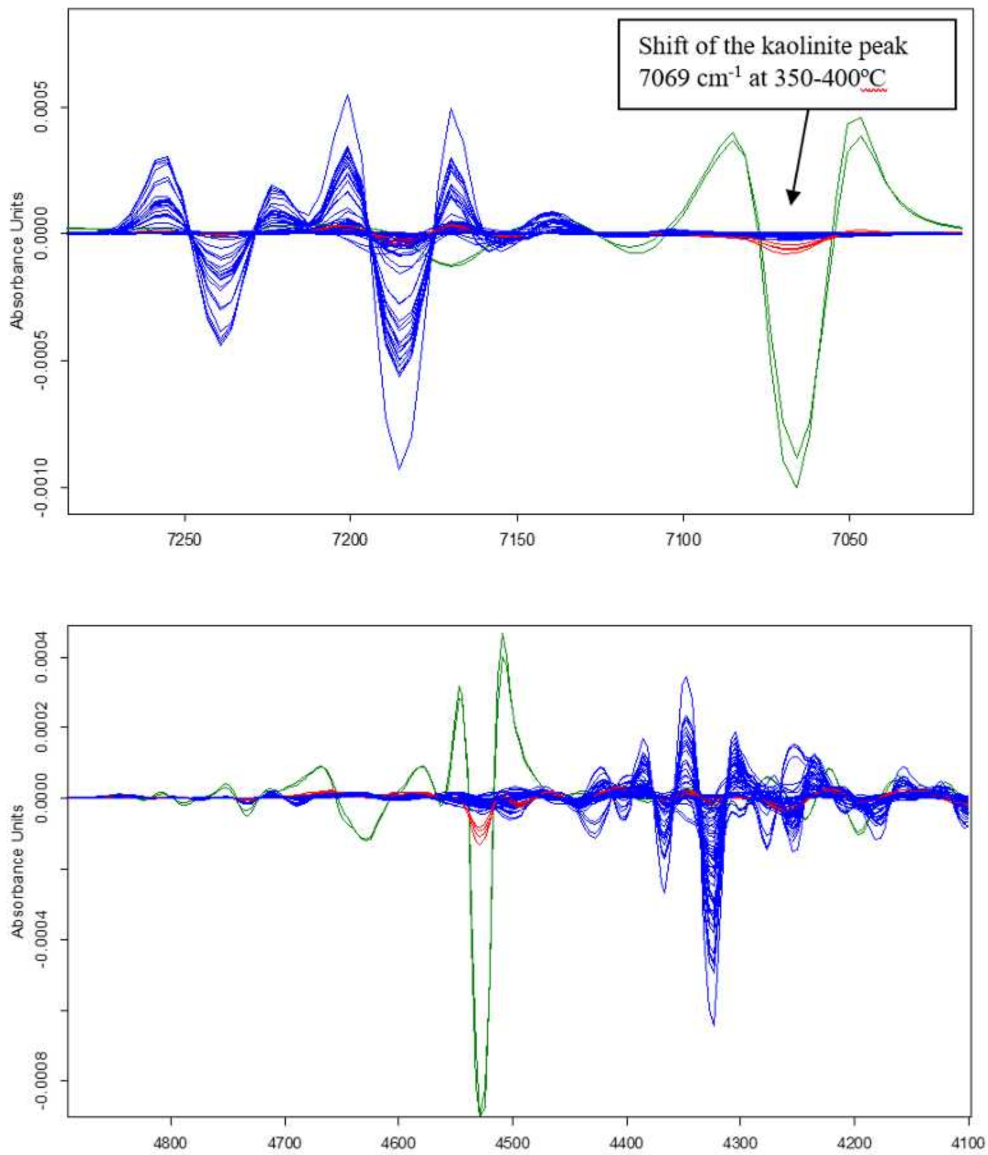


Figure 5. NGAL-7 sherd (Figure 1e), NIR spectra in a cut section; the blue spectra are from spots of the ceramic body near the surface, the red from the interior, the green spectra from raw kaolinite. We note the presence of the shifted 7069 cm-1 peak of kaolinite occurring at 350-400oC that indicates a low firing temperature.

It is worth noting that the analytical results from MNG are largely comparable to those obtained from the analysis of FN 'crusted' pottery from the settlement of Ftelia in Mykonos (Aloupi 2002), where the indicative trace element for the locality of raw materials used by the potters was Ba. In Ftelia, the white and red crusts were identified as raw talc and ochres applied after firing.

The MNG samples analysed in the context of the present study belonged to pots fired in open fires, with a short firing process and at temperatures not exceeding 600-700°C. This is confirmed by the NIR spectra, but also by the presence of a grey-black core in the break of the sherds indicating incomplete combustion of the organic matter in the clay. The very good retention of the gloss due to polishing/burnishing of the pot's surface, and of the coating on the sherds bearing fired painted decoration (NGAL-1 and NGAL-2 in Table 1) corroborates the temperature determination.[4]

[4] The surface gloss due to polishing disappears with firing over 750oC.

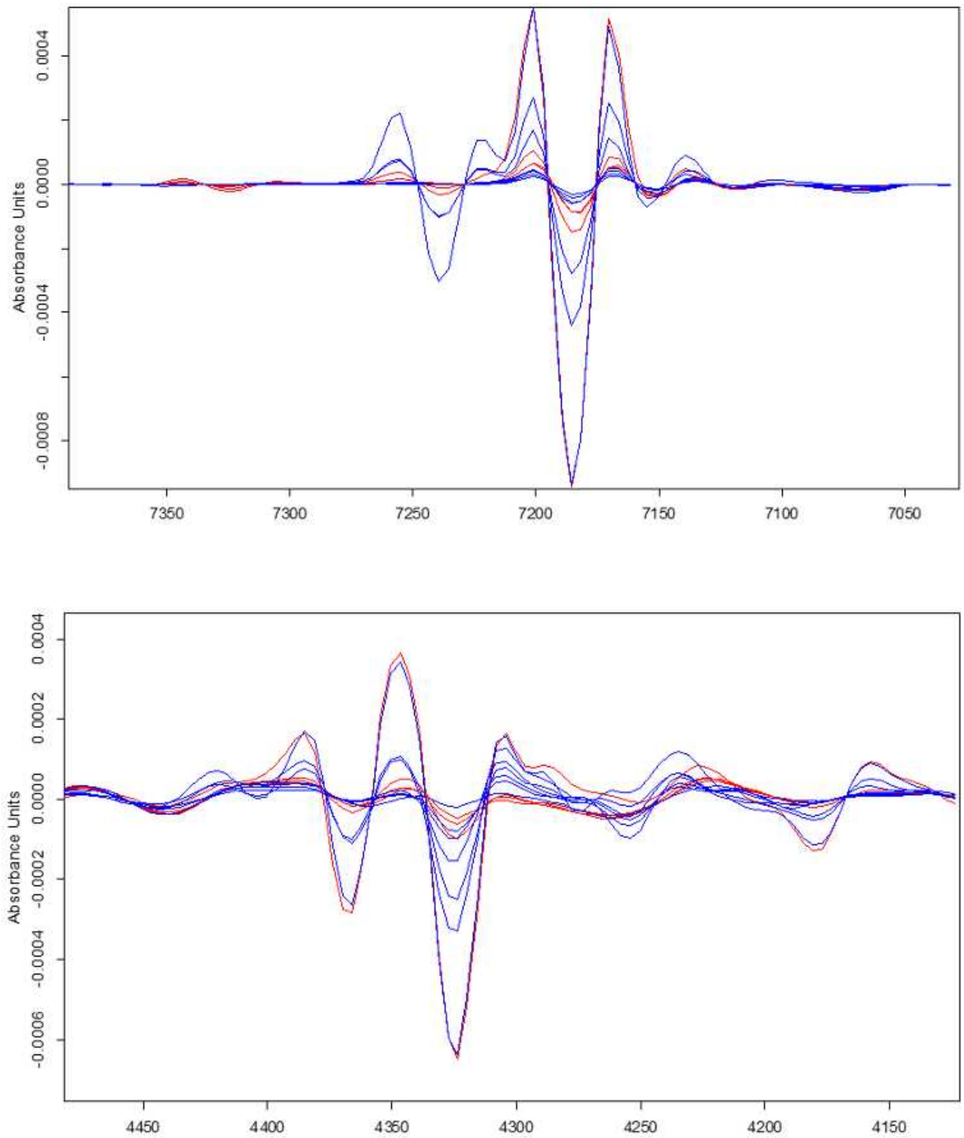


Figure 6. NIR spectra for NGAL-10 sherd – Figure 1d (blue spectra) and the refired specimen at 600oC - ox (red spectra). In the layer of the white coating, a significant decrease in the serpentine component is observed while in the ceramic body the talc signal becomes sharper and shows a relative increase. The ceramic body has been exposed originally to temperatures that do not exceed T≤ 600°C, while the white pigment is not thermally treated and had been therefore applied on the surface after the firing.

The colour of the exterior surface, which is often dark grey or brown, is due to the reducing firing conditions commonly found in open fires and at low temperatures in the range of 400-650°C. The successful colour contrast and aesthetic effect of NGAL-1 and NGAL-2 (Figure 1a, 1f) which were exposed to mostly oxidising conditions and to possibly higher temperatures at the end of the firing, could not be easily achieved under the conditions explained above. Thus, it is reasonable to assume that the inability of the potters to control adequately the firing conditions may explain, at least in part, why fired pots were painted over with raw pigments to achieve the desired colour effect.

Experimental replication

In order to update and complement the results of the analytical techniques performed in 2003, especially regarding the firing conditions, and to further explore the functional aspects of low-fired pots, we replicated three characteristic bowl shapes.

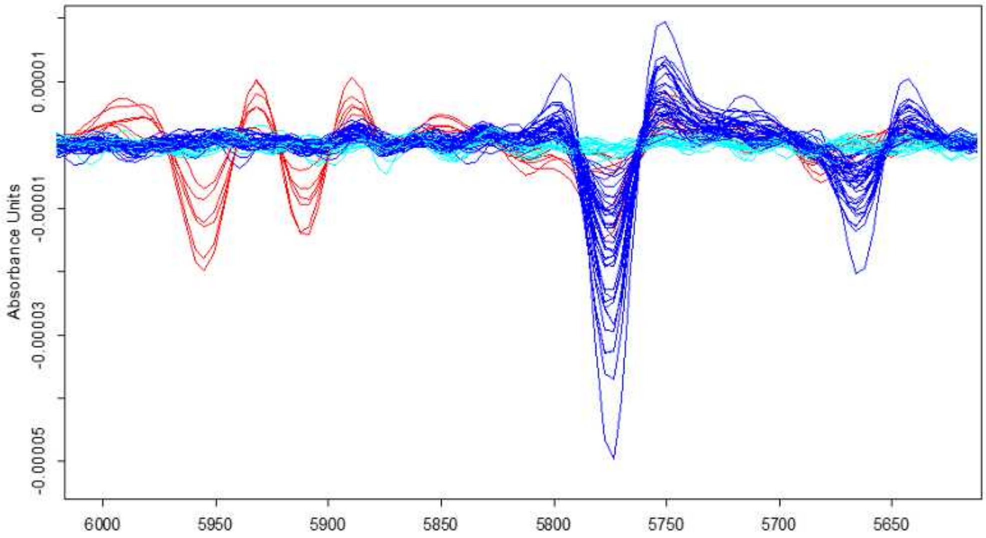


Figure 7. The samples NGAL-4, 6, 8, 9, 10, 12, 13 are rich in organic materials; two types of organic compounds are distinguished, the first corresponding to peaks 5774-5665 cm-1 (blue spectra) and the second detected only at NGAL-12 &13 with characteristic peaks at 5955-5910 cm-1 (red spectra). The light blue spectra, with no evidence of organic material, correspond to the ceramic body. The organic compounds appear to be associated with the pigment layer.

As depicted in Figure 8a, the replicated shapes represent typical early FN bowls with 'crusted' or pattern painted decoration. For the laboratory experiments, we utilised commercially available materials compatible with the raw materials found in the Kitrini Limni basin and its surroundings.

The bowls were formed with the coiling technique using a fine-grained sedimentary clay from Crete containing moderate CaO and Fe_2O_3 (6.5-7.5%). To emulate the mineralogical composition of the light-coloured crust, a clay slip was produced using a mixture of two different clays in a 1:1 ratio: an English ball-clay containing kaolinite, smectite, mica and quartz and the Cretan clay used for the body containing bentonite/smectite, illite and kaolinite. Each bowl was burnished on the interior and exterior with the smooth curved part of a wooden tool until polishing was obtained (Figure 8a). One bowl was further decorated with two different ochres, following the pattern seen on sample NGAL-2. Five different pigments, based on commercial ochres varying in colour from yellow to brownish red, were applied on a slip-coated clay tablet used as a reference colour chart.

The bowls and the pigment tablet were first fired at 600°C under intense reducing conditions with a fast firing involving a total duration of 1 hour 30 minutes. In order to emulate the firing in an open or pit fire, the pots were placed inside a larger ceramic container with shredded newspaper and charcoal between them and covered with a lid. The firing was performed in an electrical kiln with continuous increase of the temperature until Tmax 600°C and was left at this temperature for 10 minutes. After documenting the results (Figure 8b), the pots were placed again in the ceramic container in the same arrangement and were refired as above at Tmax 700°C. As shown in Figure 8c the conditions were mostly oxidising at the end of the second firing. The bowl with the painted red decoration on the light-coloured surface coating, replicating NGAL-2 sherd (Figure 1a), was reproduced successfully. Two bowls that were placed towards the bottom of the container turned black on the interior, one with a 'cloudy' appearance and the other with an attractive bichrome effect, black inside and almost uniformly light coloured on the outside.

The two experimental firings showed that the red pigments, containing mostly hematite, did not change colour in oxidising conditions (compare Figures 8a and 8c), whereas in reducing conditions (Figure 8b), they turned dark or grey due to carbon soot that settled on the surface. The same is true for white pigments and coatings, which in oxidising conditions acquire light colours, whereas in reduction they turn grey. These colour changes were further demonstrated by the colouration of the painted tablet that was used as a colour reference chart for the painting materials used for the experiment.

The application of red pigments combined with light coloured clay or carbon black resulted in the replication of the more vivid styles of NGAL-3 sherd (Figure 1c and Figure 8d2, 8d3). It is worth noting that the use of a water-soluble glue as an organic binder produced a rather shiny and smooth surface on the crusts, while the Neolithic sherds exhibit a fine-grained, smooth but powdery appearance, likely attributed to wear and preservation conditions.

An attempt to fill the replicated pots with a liquid (water and milk) was unsuccessful, as they were not water-tight and immediately started forming cracks. This failure is understandable since the pots were exposed to low firing temperatures, when either sintering or initiation of the vitrification process had not yet occurred (lack of ceramization). Consequently, the application of a thick 'crust' on the surface of a container that came out of the potter's fire fragile and permeable could make it functional, especially if the organic binding compound played the role of liquid repellent, protecting the walls of the pot.

In sum, the replication experiments verified our assumptions on FN firing practices and strengthened the conclusion that post-firing 'crusting' was probably an attempt to improve the appearance of pots fired

Figure 8. (a) Hand built and polished bowls before firing. The two bowls on top middle and right are coated with a light coloured slip, while one of them bears a painted decoration with Fe-oxides; (b) the same bowls after reducing firing at 600oC; (c) refiring at 700oC in mixed/oxidising atmosphere led to clear colours - see d1, case of the sherd NGAL-2 in Figure 1a - or to cloudy appearance depending on the placing of the pots; (d) application of red 'crust' with a light coloured clay using an organic binder (case of sherd NGAL-8 in Figure 1b), and application of red and black pigments on a fired light coloured slip (case of the sherd NGAL-3 in Figure 1c).

to a dull colour or with clouds on their surface and to enhance their usability.

Towards a new non-destructive methodology for determining firing temperatures of ancient ceramics

The usual analysis of clay soils and low fired archaeological ceramics with infrared spectroscopy relies on the mid Infrared domain (4000-1000 cm^{-1}), where changes concerning dehydroxylation of most clay minerals take place. Maniatis *et al.* (2002), placed special emphasis in the 3700-3600 cm^{-1} spectral absorption region in order to estimate the firing temperatures of low fired clay structures, focusing on the two characteristic sharp peaks at 3621 and 3697 cm^{-1} which according to Frost and Vassalo (1996) correspond to kaolinite hydroxyls.[5]

Recent publications in clay mineralogy, present typical mid-IR (MIR) and near-IR (NIR) spectra of different clay mineral families and discuss how basic information on crystal chemistry can be derived. Though MIR spectroscopy has been applied to clay minerals studies since the early 1960s (Grim 1968; Farmer 1975), during the last decades NIR spectroscopy has become more commonly applied to the study of clay minerals. The dominant clay minerals in mixed clay soils show diagnostic absorptions in the NIR also referred to as Short-wave infrared light (SWIR domain). These absorption bands are caused by vibrational transitions and commonly display sharp and narrow features. The diagnostic bands are mainly on ~1400 nm (~7140cm^{-1}, overtones caused by OH), ~1900 nm (~5260 cm^{-1}, overtones caused by molecular water), and ~2200 nm (4540 cm^{-1}, combination tones caused by Al-OH). Some weak absorption bands in the 2300–2500 nm (4350-4000 cm^{-1}) region are attributed to the presence of Fe-OH and/or Mg-OH in the clay minerals (Fang *et al.* 2018). More specifically, kaolinite is featured by two spectral doublets: one is near 1400 nm at 1395 and 1414 nm (7168 and 7069 cm^{-1}) attributed to OH and the other is near 2200 nm at 2163 and 2208 nm (4623 and 4528 cm^{-1}) and is connected with molecular vibration of Al-OH bonds.

In the first phase of this study, we mostly made use of the 7069 cm^{-1} peak shift occurring at 350-400ºC, which disappears at 600ºC. The above more recent bibliographic data allow us to re-evaluate specific features of the NIR spectra. For the interpretation of the spectra of the Neolithic samples containing serpentine, talc-saponite and kaolinite we relied on the analysis of Martian phyllosilicates by NIR spectroscopy (Daly *et al.* 2011; Gavin *et al.* 2012). As the NIR spectra of phyllosilicates evolve characteristically with temperature, they allow a mineral's NIR spectra to be used as a proxy thermometer for maximum alteration temperature. At temperatures above 800ºC however, NIR spectra become featureless for most phyllosilicates.

Our laboratory refirings at 600ºC showed serious decreases in the serpentine spectra in all bands referred to above. In the characteristic talc-saponite component in the clay bodies that had been fired to T≤600ºC, the talc peak at 7185cm^{-1} becomes sharper at 600ºC and increases, while the saponite features remain unaltered and this is compatible to bibliography (Daly *et al.* 2011; Akai 1992). Since the 1400 nm (~7140cm^{-1}) hydration feature for saponite disappears at 800°C and this peak is present in all ceramic bodies examined, we can safely assume that the firing didn't exceed this temperature. The kaolinite component, which is common in almost all clay-soils used for pottery-making, appears to be very useful for the determination of firing temperature of archaeological ceramics with this non-destructive technique. According to Daly *et al.* (2011), at 500°C the doublet near 1400nm becomes a single absorption feature, which decreases in depth before disappearing at 800°C. The doublet near 2200 nm, a combination of 2Al-OH vibrations, becomes a single band at 500°C. Its depth decreases until 1000°C and then slightly increases at 1100°C. A series of laboratory experiments with a documented set of clay-soils treated at different firing conditions (temperatures, oxidising-reducing atmosphere) with NIR spectroscopy may allow the establishment of a fast, non-destructive methodology for the estimation of firing temperature of ancient ceramics.

Conclusions

Archaeological inferences

The results of our study point to a degree of freedom in the way Neolithic potters of the early FN period at MNG used the available range of raw materials and techniques to cope with their lack of control over firing. Unlike the MNG potters who produced the Late Neolithic black-topped pots with remarkable success and consistency, potters of the early FN period could not apparently achieve desired colours by firing alone.

Decoration designated in the field as "pattern painted", in all but one case was applied before firing, whereas in the case of pottery designated as 'crusted', various pigments and paints were used in their raw state after firing. It is likely that in the early FN phase at MNG raw pigments were used to either improve the pots' appearance after a less successful firing—as in the case of pots that looked "dull" or had firing clouds, or to drastically change the colour of a pot by painting it over with bright colours. As Vitelli has aptly remarked

[5] Maniatis *et al.* (2002) have attributed the two peaks to Al-OH bonds of kaolinite based on Grim (1968).

about crusted pottery from Franchthi Cave in the Peloponnese, "the potters were fascinated with colour" (1999: 92).

The case of sample NGAL-3, which was painted both before and after firing, is intriguing because it implies that Neolithic potters used paints and painting techniques in more complex ways than we had previously thought. Further investigation of this occurrence with a larger sample—an occurrence that as far as we know is documented for the first time in a Neolithic context in Greece, could be rewarding.

The estimation of firing temperatures resulting from our analyses showed that both 'crusted' and pattern painted pots were low fired. This implies that they were less durable, and their life cycle was rather short. With the exception of pedestal bowls ('fruitstands'), the pots on which post-firing crusts or pre-firing painted decoration were applied are not fancy shapes. For sure, they were not appropriate containers to hold water or other liquids, not even for drinking since they could easily fall apart.

We conclude that the potters did not aim for pots made to last and to sustain frequent, daily handling and use. Unlike in earlier phases at MNG (for example in the Late Neolithic), in the early FN contexts few attempts of pot mending can be documented. When pots broke, they were discarded or, in some cases, their broken pieces were recycled into handy tools (Kalogirou 1994: 173-177).

Archaeometric inferences

In terms of the analytical methodology, the study relied exclusively on the application of non-destructive techniques and made the most of them for the characterisation of the materials involved for the production of 'crusted' and pattern-painted pottery at MNG, the estimation of firing temperatures, as well as the manufacturing practices. The experimental replication complemented the analytical results and became a useful tool for testing and understanding the Neolithic potters' practices using modern, but compatible materials, as far as their composition.

The combination of different approaches and sets of data from the various phases of the overall project's life cycle examined under a contemporary lens has allowed us to go beyond standard archaeometric interpretations. Moreover, the use of Short-wave domain in the n-IR spectra (SWIR) for the evaluation of the clay minerals' composition and the changes they undergo with firing, may soon lead to the development of a new, non-destructive, fast, and reliable technique for the determination of firing temperatures in technological studies of prehistoric pottery.

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The excavations at MNG reported here were conducted by the Greek Archaeological Service in 1987-1989 and again in 1993 under the directorship of Prof. M. Fotiadis (University of Ioannina) and Dr. A. Hondroyanni-Metoki (Head of the Ephorate of Antiquities of Kozani). AK gratefully acknowledges Indiana University, the Institute for Aegean Prehistory, the Dr. M. Aylwin Cotton Foundation and the Mediterranean Archaeological Trust for providing funding to support her archaeological research and study of the pottery from MNG. The laboratory analyses were carried out in 2003 with the participation of I. Aslani (Chemical Engineer, THETIS) and M. Gika (Chemical Engineer, Institute of Theoretical and Physical Chemistry – NHRF) in the framework of the CERAMED Research Programme (2003-2006), funded by the 5th Framework Programme for Research, Technological Development and Demonstration with the coordination of the National Research Foundation in Greece. Drs I. Giannopoulos, G. Chrysikos, V. Gionis (Institute of Theoretical and Physical Chemistry – NHRF) and A. Karydas (INP- NCSR Demokritos) collaborated on the data processing at the time. The replicated Neolithic pots were produced in 2019 by I. Nalbani, a ceramist at the THETIS workshop. The authors would like to express their warm thanks and gratitude to all the individuals mentioned above.

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Microscopic and Analytical Studies of Late Classical and Hellenistic Pottery from Ancient Messene, Greece

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Abstract: A large assemblage of late Classical and Hellenistic pottery from a deposit in the south terrace of the temple of Asclepius in Ancient Messene (Area XVI/2), Greece, was analyzed using micro-invasive analytical techniques in order to study technological and provenance issues. The samples were dated based on their typological characteristics between the second half of the 4th and the 3rd centuries BC. The assemblage includes coarse wares, such as cooking pots and tableware, transport amphorae and fine wares, primarily drinking vessels. Moreover, these deposits yielded a large number of miniature cups (*skyphoi*) of a votive character, a common find in several sanctuaries in the Greek world. Both visual and analytical characteristics of the samples were examined using the following techniques: a) LED-OM documentation; b) SEM-EDS analysis for the technological and chemical characterization of the clay fabric; and c) p-XRF to assist the chemical fingerprinting. So far, few archaeometric analyses have been conducted on Late Classical and Hellenistic pottery from Ancient Messene. Therefore, the results of the study presented here can provide vital technological information for Late Classical and Early Hellenistic pottery from this site.

KEYWORDS: CLASSICAL-HELLENISTIC POTTERY, PROVENANCE, FIRING TEMPERATURE, ANCIENT MESSENE

Introduction

The site of ancient Messene (Figure1) has been excavated since the 19th century by the Archaeological Society at Athens. Yet, extensive and systematic excavations commenced in 1987, under the direction of Professor Petros Themelis (Themelis, *PAE* 1986-2015). These revealed numerous public buildings of the city, such as the Agora, the Theatre, the Ecclesiasterion, the Stadium, the Gymnasium, and the Palaistra as well as temples and sanctuaries. Published pottery assemblages of the Hellenistic period from the site include those from monument K3 (Rogl 2005; Themelis 2000) Furthermore, Hellenistic pottery from the wider region of Messenia has so far only sporadically been published in the proceedings of the Hellenistic pottery conferences in Greece between 1976 and 2016 (e.g. for the pottery from the 'Tsopani Rachi' near Pylos, see Danali 2011). Similarly, studies on Messenian clay fabrics of pottery, of any period, appear only occasionally (e.g. Matson 1972; Giannopoulou 2002). As a result, the definition of 'Messenian', in both pottery typology and clay fabrics, requires further exploration and study.

This paper is based on the study of clay samples from Hellenistic pottery assemblages excavated in the south terrace of the Asclepius temple in Messene (for excavation preliminary reports, see Themelis, *PAE* 1987, 1990, 1993-1996). It focuses on the application of different analytical techniques and advanced statistical analysis on selective pots of the late 4th-3rd centuries BC in order to understand and evaluate their likely provenance. Additionally, technological parameters will be explored, and emphasis will be given in the examination of visual parameters of the clay fabric so as to investigate how the chemical composition and the firing conditions affected the final product.

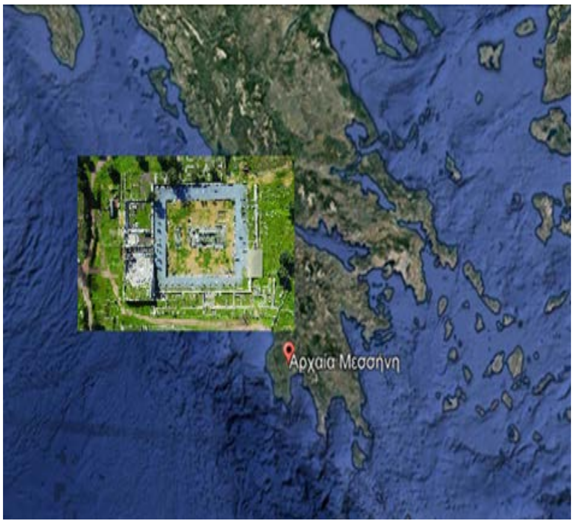


Figure 1. The location of Messene is noted on the map with a red circle; image created by Google Earth); the inset image shows the excavated area of the sanctuary of Asclepius (after Themelis 2014, 78,)

Samples and Methodology

The corpus consists of 283 pottery samples taken from fine wares, such as drinking vessels and tableware, from coarse wares, such as cooking pots, *lekanai* and jugs, transport amphorae and miniature vessels (primarily *skyphoi*) from the deposits on the south terrace of the Asklepieion (Area XVI/2). This area was excavated in the 1990s; the finds included pottery (primarily Classical and Hellenistic, but also a few Archaic fragments), coins, clay figurines, and terracotta relief plaques. A *terminus ante quem* at the end of the 3rd century for the constructions in the south terrace of the Asclepieion was suggested by the excavator (Themelis 1987a, 1990b, 1994c, 1995d; the study of the pottery from this assemblage has been undertaken by Eleni Zimi and is currently in progress).

Macroscopically, several technological characteristics of this pottery assemblage suggest a local provenance. These are: a) the fugitive, easily-flaking off the surface dark slip (Douglas *et al.* 2021; Rogl 2005); b) the limited presence of decoration; and c) the emulation of forms produced in big centers like Athens and Corinth or in regional workshops found in the immediate vicinity of Messenia, such as in Elis, Achaia, Arcadia or more distant ones, like in Argos. This is an indication of a socially closed and economically self-sufficient society (Themelis 2005).

From this large assemblage of 283 pottery samples, 26 were selected to be chemically analysed; the selection was based on the preliminary microscopic examination and aimed to be representative of the different fabric groups from the assemblage. The parameters that were taken into account were: (1) colour of clay fabric; (2) colour of inclusions; (3) frequency of inclusions; (4) size and shape of inclusions; (5) coarseness; and (6) porosity. The colour of the clay fabric was described based on the Munsell Soil Colour Chart along with the colour of inclusions. The frequency of inclusions was described based on charts for estimating proportions of mottles and coarse fragments included in the Munsell Soil Colour Chart. The size and shape of inclusions were described according to the specifications of the Munsell Soil Colour Chart. Coarseness and porosity were estimated empirically.

Based on the above categorization, 8 basic fabric groups were identified. Additionally, 3 geological clay samples were collected from Valyra, a village in the immediate vicinity of the site of Ancient Messene, with natural clay soils and a long-standing pottery tradition. These were chemically analysed for comparative purposes and in relation to the provenance of the pottery.

The ceramic body of all samples was first examined via Optical Microscopy, using a LED I-SCOPE by Moritex, in combination with Munsell Soil, Colour Chart of 2000. The composition of the major oxides of the clay was determined by a Scanning Electron Microscope (SEM) by JEOL (JSM-6510LV) coupled with EDS (Oxford Systems). The analytical data were obtained by INCA software. The analyses were conducted at 20 kV accelerating voltage, under a magnification of ×200 and with a count time of 180 s. At least 3 measurements were taken for each sample on different areas of polished fresh cuts from micro-samples embedded in resin. SEM/EDS was also used to obtain information about the manufacturing technology (Maniatis and Tite 1981; Tite and Maniatis 1975). The chemical composition of the major elements of the samples, estimated by SEM/EDS, is presented in Table A-1 of the Appendix.

For the examination of the likely provenance of the sources, the minor and trace elements were estimated using a portable XRF (p-XRF), (Liritzis and Zacharias 2011). The device used was Bruker Tracer III SD with a beam diameter of 3mm. Data quantification was made using S1PXRF software and the built-in calibration curve for soil and clays. In order to optimize the analytical range, two settings were used: (1) an unfiltered low-energy excitation mode (high voltage set at 15 kV and current of 24 μA, analyses carried out under vacuum) was used for the analysis of major and minor elements with an atomic number, Z, between 11 and 29; and (2) an Al/Ti filtered (0.012 inches Al plus 0.001 inches Ti) high-energy excitation mode (high voltage set at 40 kV and current of 12 μA) was used for the analysis of minor and trace elements with an atomic number Z>29. At least 3 measurements were taken for each sample.

The precision of the two devices, SEM/EDS and p-XRF in relation to the clay samples was determined with the use of clay IAEA standard Soil 7 (Palamara *et al.* 2016). According to Table 1, the precision is good, with the exception of SiO_2 which is underestimated by p-XRF while CaO is overestimated. More information about the evaluation of p-XRF is given by Palamara *et al.* (2016).

The field research for the selection of clay soils

As mentioned above, the geological clay samples were collected from the area of Valyra, which is very close to ancient Messene. Between the 1920s and 1990s this area, along with neighboring villages, had a flourishing

Table 1. Concentration of major elements (in wt%) of the standard Soil 7, estimated by SEM/EDS and p-XRF.

		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Soil 7	**XRF**	0.83	1.43	12.44	46.68	1.82	31.44	0.68	4.69
	SEM	0.38	2.40	14.03	48.02	2.14	27.69	0.62	4.72
	Real, values (IAEA)	0.42	2.40	11.38	49.35	1.87	29.23	0.64	4.71

ceramics production. Unfortunately, there is nothing left today in the landscape to indicate this long-standing tradition in pottery manufacture. Fragments of half-destroyed kilns, still visible in the area a few decades ago, were noticed by locals.

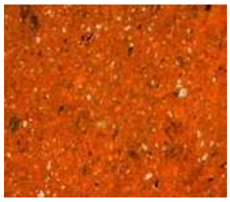
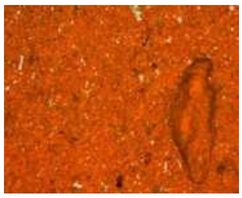
The geological clay samples were gathered from two sites. The first sample, C1, came from the site 'Goubes'. Its name refers to the "big holes" (*c*.3 m in diameter) that were dug in the area by potters in order to collect clay supplies for their blooming ceramic workshops. The colour of this clay is reddish and had more plasticity due to moisture. The second sample, C2, came from the site 'Palaiolkamina'. The colour of the clay is gray and has a very fine and sandy texture (Table 2). The clay samples were then refined at the laboratory by sieving. For the purification a fine sieve with a diameter of 0.466 mm was used. Following the removal of all the impurities, the clays were mixed with water for the manufacture of small clay briquettes. Two additional briquettes, C3 and C4, were prepared, mixing C1 and C2 in different ratios, because the gray clay was too sandy to be used on its own. The different ratios of the two clays are shown in Table 2.

Table 2. Clay samples C1 and C2 prior to treatment

Name of clay samples	Photo after the purification
C1	
C2	

The C2, due to its sandy texture, did not have the plasticity required to produce a clay tile (Table 3). For this reason, this sample was excluded from the chemical analysis; only the C1, C3, and C4 geological clay samples were selected for further examination. The

Table 3. Mixing quantities of the clay pastes used in this study.

Name of clay tiles	Contents of clay powder	Photo after firing	LED image (magnification x50)
C1	30 gr red clay powder		
C2	30 gr gray clay powder	No tile was produced due to the sandy texture of the soil.	
C3	30 gr red clay powder(C1) 20 gr of gray clay powder (C2)		
C4	15 gr red clay powder (C1) 15 gr gray clay powder (C2)		

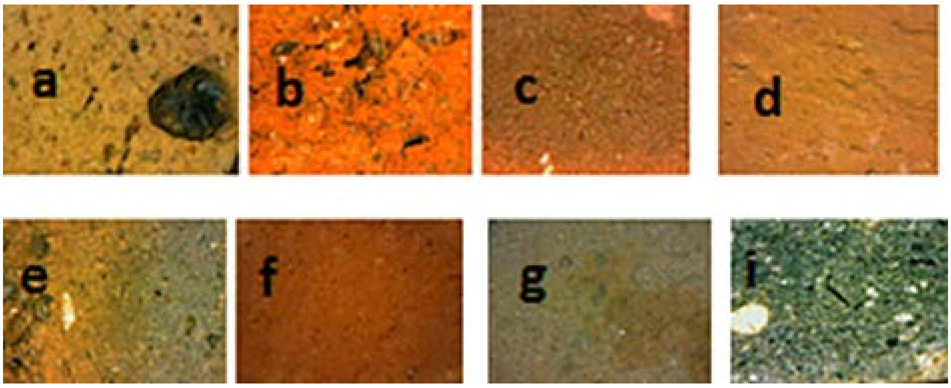


Figure 2. Representative LED images of the 8 fabric groups (a: Fabric I-CW; b: Fabric IV-CW; c: Fabric III- FW; d: Fabric II-FW; e: Fabric V-CW; f: Fabric VI-FW; g: Fabric VII-FW; i: Fabric VIII-CW)

Table 4. Visual characteristics examined from the assemblage in the 8 fabric groups (FW: fine wares; CW: coarse wares)

Fabric	Munsell Soil Colour Chart	Percentage of samples	Type of pot	Frequency of inclusions	Colour of inclusions	Size and shape of inclusions	Coarseness	Porosity
Fabric I	5YR7/3 Pink	2%	Open vessels Drinking cups *Skyphoi*	Low	White Red Black	Very fine granular	FW	High
Fabric II	5YR 7/4 Pink	1%	Bowls *Lekanai* Plates	Low	White Red Black	Very fine granular	FW	Low
Fabric III	2.5YR 5/8 Red	1%	Open vessels Drinking cups *Kantharos*	High	White Red Black	Very fine to medium granular, angular	CW	High
Fabric IV	2.5YR (6/6, 6/8, 7/8) Light red	79%	Bowls *Lekanai,* Drinking cups *Skyphoi,* Cooking pots Lopas Amphorae Plates *Pithoi*	Low	White Red	Very fine granular	FW	Low
Fabric V	5YR (5/6,7/6) Reddish yellow	1%	Cooking pots Lopas, Bowls *Lekanai*	High	White Red Black	Fine, medium to coarse granular, angular	CW	High
Fabric VI	2.5YR 5/4 Reddish brown	11%	Open vessels, Bowls *Lekanai,* Plates Drinking cups *Skyphoi*	High	White Red Black	Fine to medium granular, angular	FW	Very compact (with big inclusions)
Fabric VII	5YR 6/1 Reddish gray	3%	Open vessels, Drinking cups *Skyphoi*	High	White Red	Very fine to fine granular	FW	Low
Fabric VIII	2.5YR 5/1 Reddish black	2%	Bowls *Lekanai* Cooking pots Lopas Lid	High	White Red	Fine to coarse granular angular	CW	High

clay tiles were shaped, put aside to dry, and then fired in an electrical furnace at a temperature of 960 C°, in oxidizing atmosphere for 10 hours The manufacturing and firing process of the clay tiles took place in a local pottery workshop in the historical center of Kalamata.

Ceramic body

Visual characteristics

Multiple visual characteristics were analyzed by macroscopic and microscopic examination. As has been previously discussed in the Samples and Methodology section, 8 different fabric groups were identified, as described in Figure 2 and Table 2. Drinking cups and plates of various kinds present a fine clay matrix with few inclusions (Figure 2 c, d, f, g), while *chytrai* and *lekanai* appear coarser (Figure 2 a, b, e, i). In addition, most of the samples are porous. High porosity reduces heat transfer, thus improving the mechanical properties of vessels by reducing the crack propagation (Rice 1987; Kilikoglou *et al.* 1998; Hein *et al.* 2008). The big white inclusions are chemically identified as calcite while the grey as quartz, commonly used as temper (Shepard 1985).

Chemical composition

The concentration of the major elements of the ceramic bodies was determined by SEM/EDS (Table A-1). As aforementioned, the microscopic examination led to the identification of 8 fabrics, whereas five chemically diverse groups (A, B, C, D and E) were determined based on chemical examination. It is worth mentioning that the fabrics and the groups could generally not be correlated.

Group A consists of five samples with the highest CaO content (>14 wt%). Two samples, M1 and M17, also present microscopic similarities, as they both belong to Fabric I. The light colour of their fabric is affected by their high calcium content (close to 18 wt%), as the combination of high calcium content along with proper fire conditions can lead to whiter clay pastes (Molera *et al.* 1985).

Group B is characterized as calcareous (CaO>6 wt%) (Table A-1) and includes most of the samples that belong to Fabric IV, with the exception of the M15 sample which belongs to Fabric III. Group C has only two samples, M8 and M22, and is also characterized as calcareous, with a CaO content between 9wt% and 10 wt%. The high calcium content that the samples from A, B, and C group present, correlates with the improvement of the mechanical properties of the pots (Rice,1987).

Group D is characterized as non-calcareous (CaO<6 wt%) (Table A-1). From Group E two samples, M24 and M25, present both microscopical and chemical homogeneity as they belong to the same Fabric VIII and are non-calcareous (CaO<6 wt%). It is also microscopically testified that, these samples present high coarseness with high frequency of inclusions.

The colour of ceramics is generally affected by a number of parameters, such as the chemical composition of the clay, or the firing conditions, or a combination of these (Rice 1987). Regarding the effects of the chemical composition, iron is generally considered as the element with the strongest correlation to the fabric hue (Molera *et al.* 1998). This cannot be verified in the present assemblage, as shown from the FeO versus Al_2O_3/SiO_2 bi-plot (Figure 3b): for example, samples M1, M16, M17, which are the most pale, present a high amount of FeO content (from 8 to 12 (wt%). The red hue can also be associated with inclusions rich in silicate and lower development in reaction rims around grains

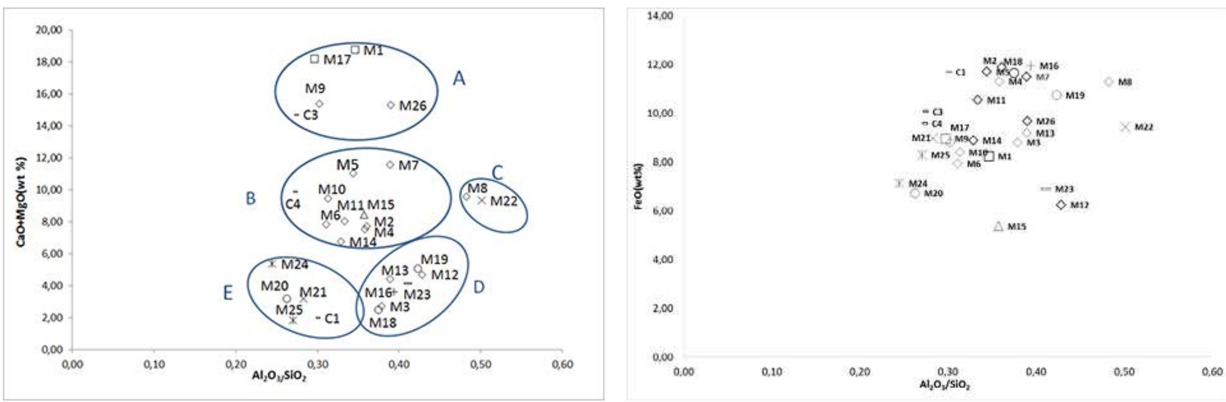


Figure 3. Concentrations of Al_2O_3/SiO_2versus CaO+MgO (left) and FeO versus Al_2O_3/SiO_2 ratio (right) (square: M1, M17, rhombus: M2-M14,M26, triangle:**M**15, cross:**M**16, circle: **M**18, **M**19, **M2O**, **Xsymbol**:M21, **M**22, big line: **M**23, **Ж**symbol:M24,**M**25, small line: C1, C3, C4)

(Pérez-Monserrat *et al.* 2021). This is also something that cannot be verified from the bi-plot, as for example samples M15, M22 and M23, which microscopically present a darker clay body, show great fluctuation of the Al_2O_3/SiO_2 ratio (from 0.35 to 0.50 (wt%). In plot of Figure 3 (right) a noteworthy positive correlation is seen, that is, increased amounts of FeO as the clay becomes finer. This is something that can be verified from the SEM/EDS, as the finest grained samples tend to present a more compact and less porous clay matrix in comparison with the coarser ones, under the same firing temperature (Rathossi *et al.* 2010). In total, for the studied samples, a straightforward correlation between color and composition was not verified.

Provenance study

In order to explore the provenance of the pottery groups under study a comparison of the following samples was undertaken: a) the 3 geological clay samples; b) 26 archeological samples; and c) relevant bibliographic data from contemporary pottery assemblages with similar forms in the areas of Corinth (MacPhee, *et al.* 2010), Athens (MacPhee, *et al.* 2010), Patras (Rathossi, *et al.* 2004), Sicily (Aquilia, *et al.* 2015) and Apulia (Magnone, *et al.* 2008).

From this combined information, the Ni versus TiO_2 biplot was created (Figure 4). This particular bi-plot was chosen because the concentrations of these elements were commonly provided both in the reference data and in the understudy pottery. Moreover, Ni and TiO_2 are the most determined elements (more than 50%) with high discrimination frequency (Kuleff and Djingova 1996). According to this bi-plot the archaeological samples can be divided into two main clusters. The 3 geological clay samples (C1, C3, C4) do not correlate chemically with the archaeological samples, as according to the Ni-TiO_2, bi-plot used for the provenance studies, the samples were outliers (Figure 4).This means that the possibility for determining the ancient clay sources should be excluded. Thus, a more detailed geological research needs to be done for revealing ancient Messenian clay sources. Bibliographic data from Attica and Corinth were extensively used as references, based on the strong network of economic and social exchange that developed with ancient Messene during the Late Classical and Early Hellenistic period (Themelis 2005).

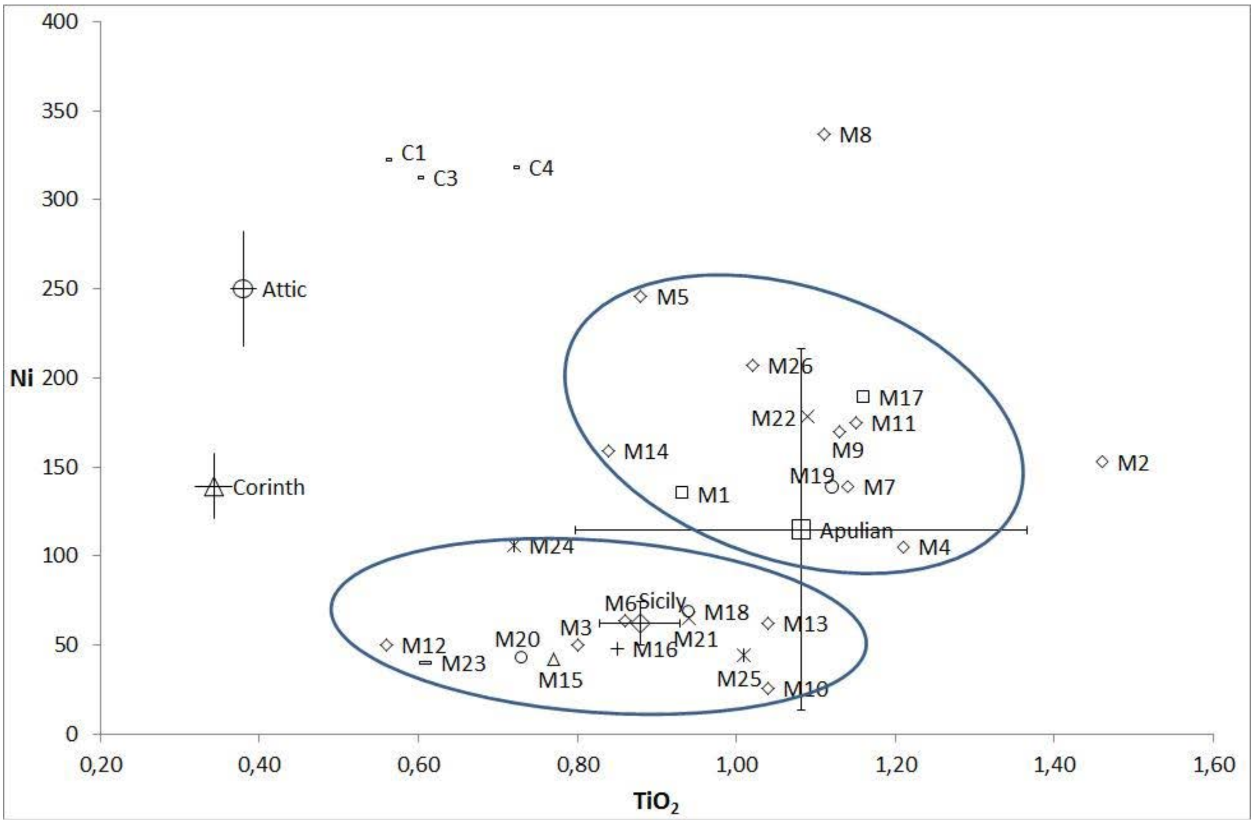


Figure 4. Concentration of Ni versus TiO_2 (square: M1, M17, rhombus: M2-M14,M26, triangle:**M**15, cross:**M**16, circle: **M**18, **M**19, **M**2O, **Xsymbol:** **M**21, **M**22, big line: **M**23, **Ж**symbol: M24, **M**25, small line: 1 clay, 3 clay, 4 clay, big square: Apulian, big rhombus: Sicily, big triangle: Corinth, big circle: Attic)

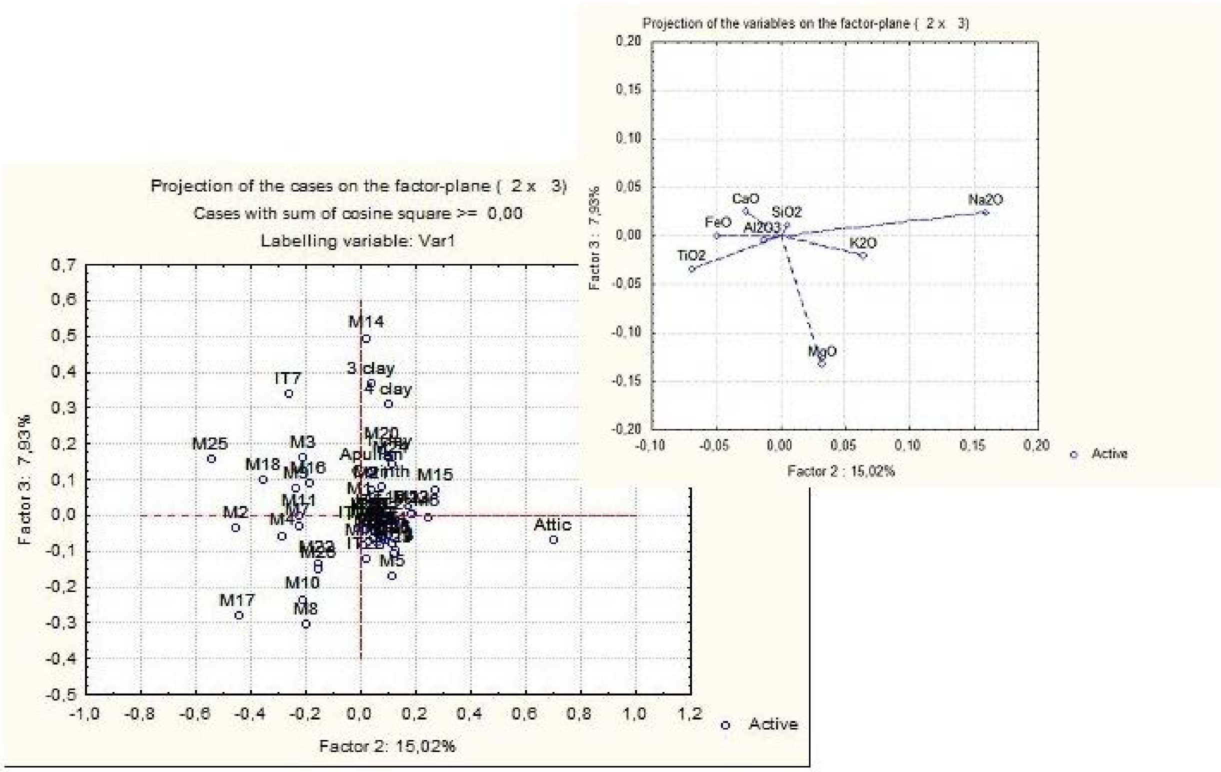


Figure 5. PCA plot (inlay plot: PCA vectors plot) showing the fluctuation between the archaeological, geological and bibliographic data

Finally, the understudy samples provided evidence of a local origin as revealed by the comparison with the reference samples from Attica and Corinth.

In contrast, some of the archaeological samples seem to be correlated chemically with the Apulian and Sicilian ones. The M8 and M2 samples are outliers with distinct chemical composition from all reference samples. The Patras data are not included in this bi-plot since the Ni concentration was not provided by Rathossi, *et al.* (2004).

For a more detailed investigation of the likely provenance sources, Principal Component Analysis was carried out using all major elements determined by SEM/EDS and p-XRF. Trace elements were excluded because they had no available bibliographic data (Figure 5). The PCA plot highlights the heterogeneity of the pottery under study. The Na_2O content, which primarily affects the samples according to the vectors plot, could reveal that the chemical variation and the heterogeneity of the samples is related to a different clay source. The significant differences noted among the samples regarding the concentration of both the CaO and the MgO could be correlated to the use of a different calcium source. According to the PCA chart (Figure 5), Attic is clearly rejected as a likely source, while Corinth, Patras, Apulia and Sicily present similar traits. Based on the available data, the provenance cannot be clearly determined. A more detailed geological research and the use of petrographic techniques could determine the issue of provenance.

Firing conditions

The microstructure of the pottery samples was examined in detail in order to study the firing temperature and firing conditions. From the 29 samples, 9 samples were selected for examination, 6 archaeological and 3 geological clay samples. The selection of the samples was based on: a) the colour of the core (sandwich or biocoloured); b) the calcium content; and c) the shape of vessels (open or close forms).The SEM examination showed that all samples were fired in a mixing firing temperature (oxidizing-reducing-oxidizing) at a temperature close to 900-950 °C (Figure 6a), and that their microstructure presents an extensive vitrification state. The only exception is sample M13 which was fired at a higher firing temperature ranging from 1050 to 1100 °C (Figure 6b) as suggested by its continuous vitrification state with medium bloating pores (Maniatis and Tite,1981). This textural re-arrangement is common in non-calcareous samples, but only when the temperature is above 1100 °C (Recardi *et al.* 1999). The high firing temperature of M13 was macroscopically imprinted in a three-coloured

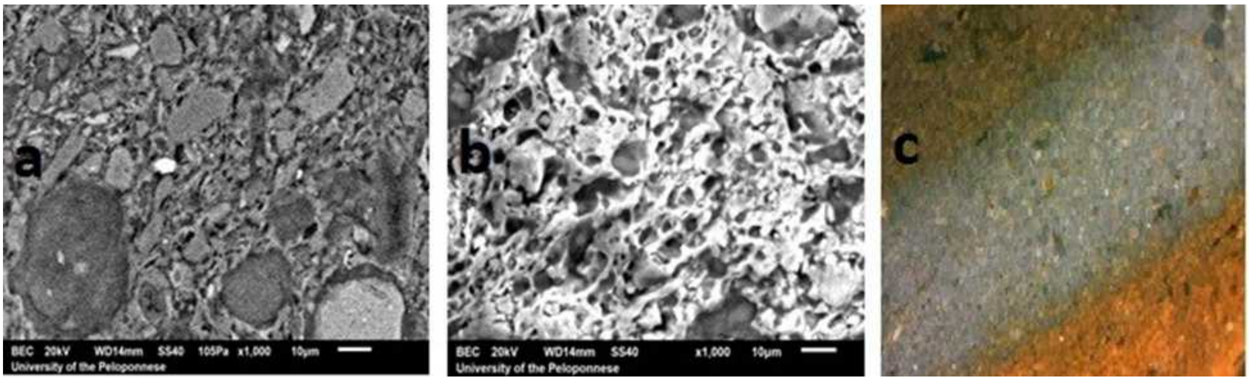


Figure 6. Representative images of a fired microstructure in: (a) Backscattered electron image of polished surface with extensive vitrification, Tmax-900-950 °C (calcareous clay); (b) Backscattered electron image of polished surface with continuous vitrification and medium bloating pores, Tmax- 1100-1050 °C (c) LED image (magnification X50) of fracture surface of the three-coloured core of M13 sample.

core (black-blue-orange) (Figure 6c). The colour of the core possibly indicates a lack of firing control during the kiln operation.

Besides the calcium content, the shape of vessels, namely the close or open forms, also leaves a macroscopic fingerprint on the material. It was observed that open vessels had a sandwich core while close vessels a bicoloured core (Molera *et al.* 1998). From the above, it can be concluded that the firing temperature and not the iron content (FeO) is the basic parameter for the variations of colours in these pottery groups.

Slip

Out of the 26 archaeological samples, surface slip was only detected in 11 samples. Two slips have been chosen for further examination here: a) the black (Figure 7b), which is the most common slip on Greek fine wares throughout the 4th and in the 3rd centuries BC; and b) the brown-red in its different hues (Figure 7d) (Mirti 2000). Surface slips were examined both macroscopically and microscopically. It was observed that: a) the colour of the slip varies from black to reddish brown and light red based on Munsell Soil Colour Chart characterizations; b) the slip is dull and fugitive; c) in some cases the slip seems to be absorbed by the clay body; and d) the slip shows signs of corrosion in some spots (Figure 7b, d). Thus, the slip is characterized as low quality. The chemical examination with the use of SEM/EDS reveals some micro-morphological differentiations such as: a) a variety in slip thickness' and b) a diffusion of grains through its width (Figure 7a, c). Finally, no significant differences were observed chemically regarding the corroded spots.

The Na_2O+K_2O versus CaO+MgO biplot of the analyzed slips and the respective clay bodies is presented in Figure 8. For the slips, the Na_2O+K_2O content ranges from 3 wt% to 5 wt% and the CaO+MgO content from 2 wt% to 8 wt% (Table A-3). The clay body in comparison presents greater heterogeneity, as the CaO+MgO content ranges from 2 wt% to 13 wt% (Table A-3). Thus, we can assume that the potters used the same slip recipe for different clay bodies. In M1 sample a high content of MnO (7.01 wt%) was detected (Table A-3), which resulted in the red hue of the slip.

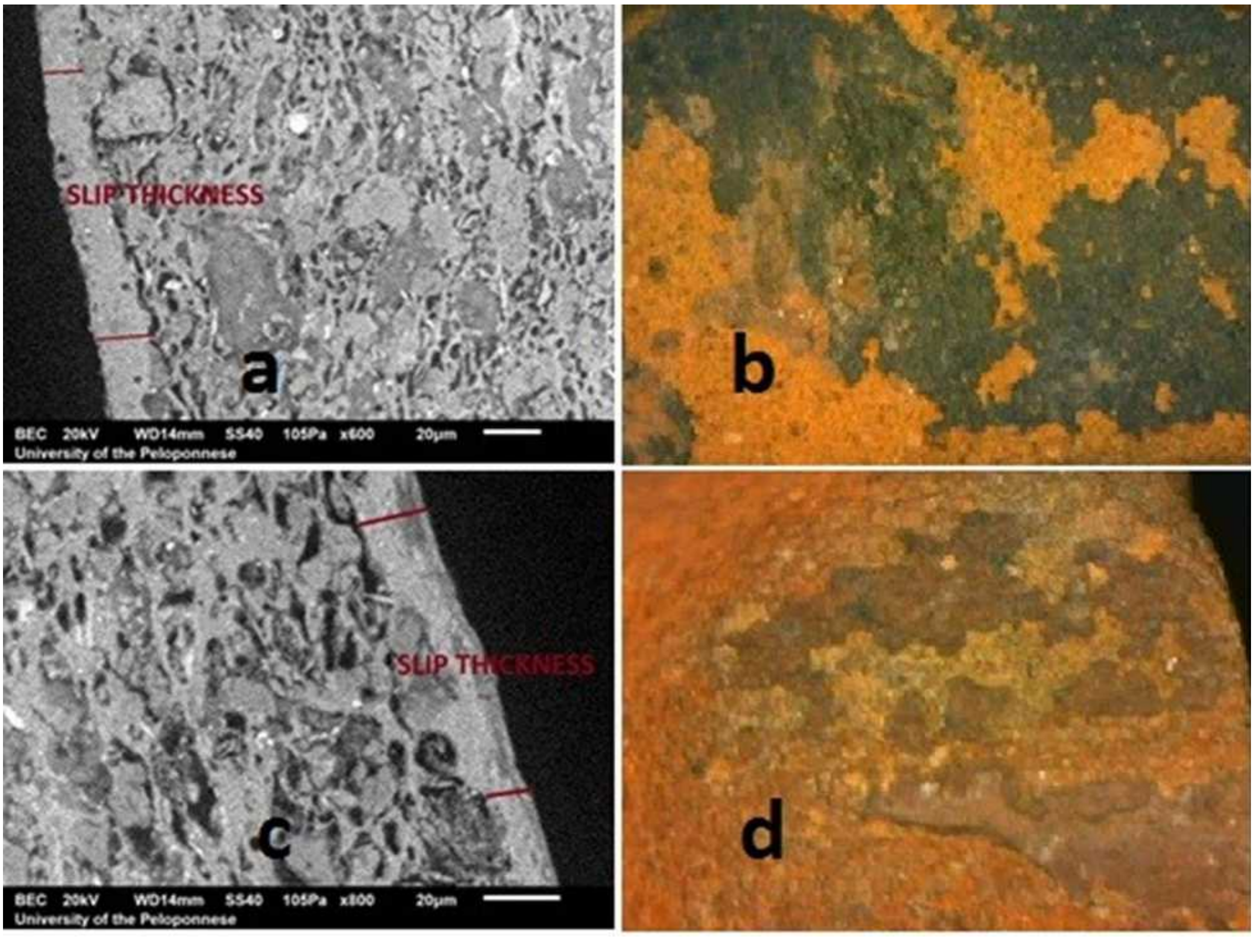


Figure 7. Slip and clay body of the same samples under the SEM/EDS (Backscattered electron images of polished surfaces) and LED microscope (magnification X50) (a, b) M6 sample (c, d) M15 sample

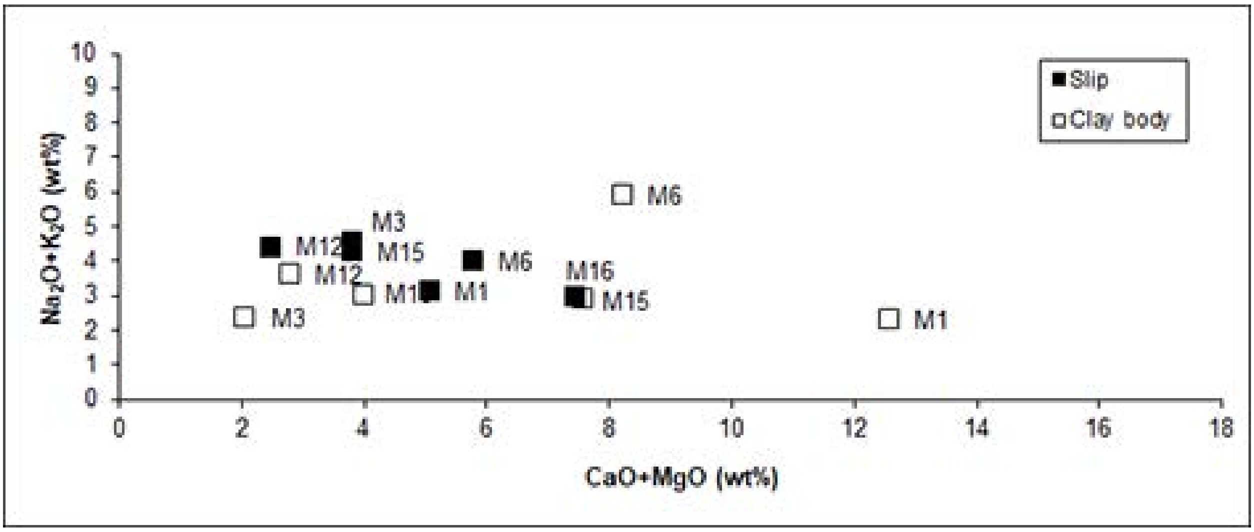


Figure 8. Na_2O+K_2O versus CaO+MgO ratio of the slips (black squares) and the related clay bodies (open squares)

Conclusions

The current macroscopic and microscopic examination along with the chemical analysis of the selected pottery groups from the Late Classical and Hellenistic assemblage of the south terrace of the Asclepieion complex in ancient Messene (Greece) constitutes the first step towards determining the character and provenance of the pottery from the site. The scientific study of the ceramic body in relation to the slip, the firing process, and provenance was performed through the combined use of analytical techniques (SEM/EDS, p-XRF). In addition, advanced statistical tools (PCA) were used in order to achieve a better overview of the chemical data from the SEM and p-XRF devices.

The examination of the visual traits (colour of clay fabric, colour of inclusions, frequency of inclusions, size and shape of inclusions, coarseness, porosity, etc.) indicates that there are 8 main fabrics (Fabric I, Fabric II, Fabric III, Fabric IV, Fabric V, Fabric VI, Fabric VII, Fabric VIII). The analysis revealed that the different colours observed macroscopically do not always correlate with a specific chemical composition. An exception is presented by samples M1, M17 from the Fabric I in which the high calcareous content, along with proper firing conditions, lead to whiter clay pastes. Also, samples M24 and M25 from Fabric VIII present both microscopical and chemical homogeneity as they belong to the same fabric and have low calcareous content.

For the identification of clay sources, both geological clay samples and relevant bibliographic data were used. Attica and Corinth were excluded as a provenance for the Messenian samples examined, while it was observed that the chemical composition Of the Messenian samples is comparable to that of S. Italian (Apulian) and Sicilian clays—a feature that is worth further exploration. Furthermore, the two geological samples collected from the neighbouring village of Valyra and their juxtaposition with the archaeological samples did not provide conclusive evidence in relation to the ancient clay sources that supplied Messenian potters with raw materials in the 4th and 3rd centuries BC. In order to draw safer conclusions, a more detailed geological research of Messenia needs to be done, and petrographic techniques need to be incorporated.

Regarding the technological traits of the assemblage, all examined slips were fugitive and easily absorbed by the clay body, suggesting a relatively poor quality. Additionally, a varied thickness of the slip and a significant diffusion of grains throughout its width were observed. In sample M1 the detected high levels of Mn imply the use of this element as a colourant.

Regarding the firing process, all the samples were fired with the known “iron reduction technique”, resulting from the mixing firing cycle (oxidation-reduction-oxidation), (Aloupi-Siotis 2020). The temperature ranged from 900 to 950 °C with the exception of the non-calcareous sample (M13) that seems to have been fired at a higher temperature close to 1050-1100 °C—and thus relatively bigger bloating pores make their appearance. In Ca-poor clay microstructures a deep textural re-arrangement appears only when the temperature reaches 1050 °C and the complete breakdown of the clay minerals occurs (Riccardi *et al.* 1999). Thus, the colour variation of fabrics correlated mainly with the firing temperature and not with the iron (FeO) content.

Overall, the detailed examination of various parameters like the visual traits, the chemical composition, and the technology production of the clay fabric samples presented here may contribute to a better understanding of the variety of Messenian pottery of the 4th and 3rd centuries BC.

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Table A-1. Chemical composition of the major elements (oxide form in wt%, normalized to 100%) as estimated by SEM/EDS (m: mean value; s: standard deviation; n.d: non detected)

	Major oxides (oxides wt%, normalized to 100%)										
Code	**Fabric**		**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**Fe_2O_3**
M1	Fabric I	m	0.90	3.20	17.27	49.89	2.20	1.79	15.58	0.93	8.24
		s	0.05	0.19	1.06	1.47	0.40	0.14	1.44	0.12	0.79
M2	Fabric IV	m	0.31	2.29	19.99	55.39	1.53	1.72	5.43	1.46	11.89
		s	0.17	0.05	0.18	0.88	0.43	0.05	0.93	0.25	1.60
M3	Fabric IV	m	0.39	1.32	23.42	61.83	0.40	1.66	1.39	0.80	8.80
		s	0.06	0.15	1.28	1.03	0.10	0.16	0.47	0.09	1.59
M4	Fabric IV	m	0.46	2.72	20.18	56.33	1.52	1.46	4.82	1.21	11.31
		s	0.29	0.63	0.86	2.89	0.36	0.31	1.71	0.21	1.71
M5	Fabric IV	m	0.93	4.29	18.51	53.81	0.90	2.80	6.74	0.88	11.70
		s	0.18	0.26	0.68	2.44	0.16	0.28	0.78	0.24	3.49
M6	Fabric IV	m	1.14	2.76	18.61	59.89	0.37	3.33	5.09	0.86	7.94
		s	0.03	0.15	0.39	0.69	0.20	0.23	0.48	0.18	0.27
M7	Fabric IV	m	0.50	2.73	19.68	50.58	2.78	2.23	8.85	1.14	11.50
		s	0.07	0.33	0.46	1.54	0.22	0.11	0.65	0.00	0.93
M8	Fabric IV	m	0.48	4.97	23.97	49.68	2.38	1.67	4.61	1.11	11.29
		s	0.22	0.44	0.54	0.53	0.12	0.12	0.35	0.16	0.53
M9	Fabric IV	m	0.53	2.42	16.39	54.23	1.79	1.74	12.98	1.13	8.80
		s	0.16	0.22	0.54	0.36	0.38	0.06	0.42	0.19	0.77
M10	Fabric IV	m	0.35	3.92	18.59	59.31	n.d.	2.84	5.53	1.04	8.41
		s	0.23	0.06	1.01	1.44	n.d.	0.32	0.57	0.22	0.13
M11	Fabric IV	m	0.50	2.44	19.18	57.46	1.31	1.84	5.58	1.15	10.55
		s	0.09	0.40	0.87	1.66	0.23	0.50	0.53	0.25	0.88
M12	Fabric IV	m	0.75	2.44	25.25	58.91	0.97	2.62	2.25	0.56	6.24
		s	0.18	0.26	0.78	1.00	0.05	0.20	0.17	0.20	0.25
M13	Fabric IV	m	0.85	2.63	22.67	58.26	0.74	2.83	1.78	1.04	9.20
		s	0.24	0.21	0.40	2.09	0.02	0.08	0.03	0.11	1.77
M14	Fabric IV	m	1.06	0.90	19.99	60.78	n.d.	1.68	5.88	0.84	8.88
		s	0.06	0.21	0.32	0.50	n.d.	0.17	0.85	0.06	0.38
M15	Fabric III	m	1.18	2.48	21.41	59.94	n.d.	2.88	5.97	0.77	5.37
		s	0.06	0.04	0.57	0.96	n.d.	0.15	0.56	0.33	0.31
M16	Fabric II	m	0.44	1.64	22.76	57.79	0.58	2.04	1.94	0.85	11.96
		s	0.38	0.56	2.32	6.85	0.33	0.94	1.69	0.09	3.60
M17	Fabric I	m	0.28	5.37	15.58	52.48	2.02	1.34	12.84	1.16	8.94
		s	0.07	0.62	1.11	2.78	1.26	0.13	0.72	0.12	0.53
M18	Fabric V	m	0.27	1.30	22.32	59.55	0.71	2.08	1.19	0.94	11.65
		s	0.20	0.08	1.20	1.14	0.49	0.06	0.14	0.14	2.16
M19	Fabric V	m	0.70	2.52	23.21	54.82	1.36	2.96	2.55	1.12	10.75
		s	0.30	0.31	1.98	3.36	0.78	0.24	0.50	0.36	2.01
M20	Fabric V	m	0.73	1.49	17.90	68.20	0.63	1.89	1.70	0.73	6.72
		s	0.08	0.04	1.44	2.58	0.32	0.11	0.31	0.13	0.66

	Major oxides (oxides wt%, normalized to 100%)										
Code	Fabric		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3
M21	Fabric VI	m	0.69	1.69	18.39	64.99	0.37	2.48	1.49	0.94	8.97
		s	0.36	0.22	1.49	3.47	0.03	0.38	0.22	0.26	1.14
M22	Fabric VI	m	0.51	3.30	25.06	50.00	2.25	2.30	6.04	1.09	9.45
		s	0.08	0.14	0.61	0.90	0.17	0.20	0.26	0.09	0.21
M23	Fabric VII	m	0.74	2.26	24.33	59.21	1.04	3.02	1.90	0.61	6.90
		s	0.03	0.22	0.71	0.26	0.16	0.41	0.48	0.01	0.54
M24	Fabric VIII	m	0.75	1.79	16.34	66.78	n.d.	2.91	3.58	0.72	7.13
		s	0.22	0.09	0.78	0.97	n.d.	0.10	0.28	0.08	0.53
M25	Fabric VIII	m	0.16	1.00	18.55	68.62	n.d.	1.53	0.84	1.01	8.29
		s	0.09	0.13	1.41	1.29	n.d.	0.30	0.06	0.14	2.59
M26	Fabric IV	m	0.47	3.74	19.53	50.09	0.69	3.21	11.57	1.02	9.67
		s	0.01	0.36	0.28	1.24	0.37	0.23	0.95	0.05	0.80
C1	Fabric IV	m	0.66	1.31	18.99	63.62	n.d.	2.47	0.68	0.56	11.69
		s	0.23	0.05	0.38	0.22	n.d.	0.20	0.19	0.25	0.40
C3	Fabric IV	m	0.95	1.51	15.33	56.33	n.d.	2.01	13.21	0.60	10.07
		s	0.28	0.07	0.69	1.62	n.d.	0.08	1.25	0.11	0.61
C4	Fabric IV	m	1.08	1.55	16.35	60.27	n.d.	2.14	8.33	0.72	9.58
		s	0.11	0.03	0.18	2.24	n.d.	0.10	2.80	0.18	0.64

Table A-2 Minor and trace elements concentration (in ppm) as estimated by p-XRF (m: mean value; s: standard deviation)

Code		Trace elements (ppm)																				
		P	S	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	Pb	Th	U
M1	m	5472	n.d.	9	106	406	19	135	72	74	22	43	233	32	147	7	9	3	23	54	20	6	nd
	s	463	n.d.	4	2	1	1	4	3	1	6	2	3	2	1	n.d.	2	n.d	2	93	2	1	nd
M2	m	3236	n.d.	58	155	316	25	153	91	82	7	49	105	31	176	8	11	2	14	268	13	6	nd
	s	1522	n.d.	20	11	11	1	3	9	8	1	2	6	1	8	1	3	1	4	465	1	1	nd
M3	m	2523	9	24	89	263	19	50	129	88	8	78	75	29	119	7	23	3	32	954	14	7	3
	s	1294	16	18	6	32	1	5	15	3	1	2	2	5	4	1	3	n.d	1	425	1	1	4
M4	m	5265	n.d.	30	76	485	21	105	119	109	16	52	127	31	120	7	17	3	24	539	17	6	1
	s	941	n.d.	8	3	117	1	14	12	2	3	3	2	2	5	1	4	n.d	1	933	1	1	2
M5	m	665	393	17	116	356	33	246	141	117	13	86	105	26	110	7	23	4	49	5277	16	8	nd
	s	141	76	17	10	18	10	41	5	3	1	16	17	1	8	2	6	n.d	6	9140	n.d	2	1
M6	m	1034	212	59	80	295	21	64	103	119	12	122	94	27	136	10	12	3	22	559	16	10	6
	s	58	46	6	8	5	2	5	2	6	1	8	8	2	7	1	7	n.d	7	660	1	1	1
M7	m	7469	n.d.	40	76	905	18	139	99	88	8	29	374	39	121	8	21	3	34	nd	14	5	nd
	s	1256	n.d.	9	14	82	1	5	8	8	2	2	85	2	7	1	1	1	5	nd	1	n.d	nd
M8	m	3319	n.d.	34	138	486	35	337	151	149	13	27	236	46	142	8	12	3	21	199	15	5	nd
	s	754	n.d.	25	11	29	2	8	7	4	1	6	70	2	4	1	6	n.d	5	345	1	n.d	nd
M9	m	4195	n.d.	6	133	394	20	170	94	65	7	29	172	38	132	7	18	3	29	85	14	5	nd
	s	725	n.d.	10	19	69	n.d.	5	4	9	1	3	8	1	11	1	2	n.d	2	147	1	n.d	nd
M10	m	1133	251	91	114	217	17	26	33	89	5	89	192	27	246	10	4	2	8	21	13	9	2
	s	85	85	38	8	10	1	5	2	6	1	7	8	3	26	1	4	n.d	4	36	1	1	1

		Trace elements (ppm)																			
Code		P	S	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	Pb	Th	U
M11	m	5758	n.d.	21	141	431	24	175	75	94	9	50	94	37	162	8	17	3	19	n.d	15	6	nd
	s	1558	n.d.	2	10	46	1	7	6	3	n.d	1	1	3	1	n.d.	2	n.d	1	n.d	1	1	nd
M12	m	4557	n.d.	25	95	219	21	50	154	115	14	78	122	31	156	8	18	3	29	929	17	8	nd
	s	1875	n.d.	31	14	31	2	n.d.	17	2	1	5	24	1	16	1	13	1	16	69	n.d	1	nd
M13	m	1338	221	167	102	432	56	62	91	120	9	109	132	34	158	8	19	3	36	3396	14	9	nd
	s	205	35	13	9	25	48	19	21	22	1	11	14	3	28	2	12	1	12	5881	1	1	nd
M14	m	1578	98	2	98	240	25	159	137	105	13	52	158	31	146	7	13	3	29	189	16	6	1
	s	774	169	4	16	33	2	26	25	19	5	4	6	2	6	1	3	n.d	4	215	2	1	1
M15	m	465	476	20	74	200	20	42	110	105	8	119	267	27	148	10	14	3	29	374	13	10	3
	s	162	4	18	10	9	1	7	7	4	1	2	102	5	7	n.d.	3	n.d	3	126	n.d	n.d	3
M16	m	2100	n.d.	3	79	191	18	48	98	96	9	97	137	26	136	8	18	3	34	679	15	9	nd
	s	90	n.d.	5	6	7	2	5	8	9	1	6	13	2	10	1	8	1	9	612	1	1	nd
M17	m	7098	n.d.	nd	81	478	27	189	127	95	9	22	185	38	125	6	10	3	20	294	14	4	nd
	s	2932	n.d.	nd	15	139	2	20	23	7	1	3	20	3	12	1	4	n.d	9	510	1	1	nd
M18	m	447	695	132	151	240	25	69	73	48	6	53	52	29	174	7	16	3	17	66	15	7	nd
	s	25	76	24	5	9	1	1	4	3	1	3	3	1	5	1	1	n.d	7	83	1	1	nd
M19	m	1836	9	147	119	887	30	139	95	130	10	105	235	34	177	11	6	3	15	499	14	9	2
	s	282	16	37	22	272	2	97	25	2	1	11	153	2	20	n.d.	4	n.d	2	435	1	1	3
M20	m	1392	486	149	91	892	22	43	152	55	45	65	79	35	171	9	9	3	15	312	25	8	nd
	s	56	37	16	1	91	2	4	2	2	8	3	3	3	6	1	5	1	3	385	1	0	nd
M21	m	440	1125	14	111	195	19	65	94	69	6	79	94	30	200	9	14	3	17	96	12	7	1

Trace elements (ppm)																						
Code		**P**	**S**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Sn**	**Sb**	**Ba**	**Pb**	**Th**	**U**
	s	67	142	22	3	7	2	2	13	6	1	3	7	2	12	1	3	n.d.	4	166	1	1	1
M22	m	3575	n.d.	9	123	292	57	178	149	136	18	50	145	29	174	7	14	3	21	6158	17	7	nd
	s	390	n.d.	10	7	33	46	23	16	19	2	2	7	11	14	2	10	n.d	4	10546	2	1	nd
M23	m	2482	n.d.	51	102	169	30	40	55	87	6	113	142	26	146	10	9	2	25	1348	13	10	nd
	s	125	n.d.	5	2	5	19	4	20	15	1	4	6	2	19	2	6	1	12	2335	1	1	nd
M24	m	207	777	41	79	344	19	106	120	91	8	102	89	33	144	10	14	3	15	186	14	9	2
	s	47	100	11	10	24	1	2	3	9	1	8	3	4	10	1	1	n.d	2	323	n.d	n.d	4
M25	m	199	933	85	128	175	21	44	75	99	17	75	57	25	204	8	14	3	19	n.d	18	8	nd
	s	70	102	27	19	15	1	3	15	17	4	7	4	1	16	1	4	n.d	5	n.d	1	1	nd
M26	m	1629	14	73	114	315	31	207	136	136	12	112	287	23	102	10	13	3	21	48	15	10	7
	s	499	24	13	6	34	1	6	9	8	1	1	6	1	4	1	2	n.d	1	84	1	1	4
C1	m	nd	nd	nd	nd	nd	27	323	108	73	10	29	nd	23	nd	nd	66	6	116	2867	15	nd	nd
	s	nd	nd	nd	nd	nd	1	3	2	1	1	nd	d	nd	nd	nd	1	n.d	n.d	69	1	nd	nd
C2	m	n.d.	1055	5	113	408	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	s	n.d.	127	1	5	1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C3	m	nd	nd	nd	nd	nd	21	313	128	60	9	29	nd	24	nd	nd	66	6	117	2349	15	nd	nd
	s	nd	nd	nd	nd	nd	n.d.	2	1	1	n.d	1	nd	1	nd	nd	n.d.	n.d	n.d	199	nd	nd	nd
C4	m	nd	nd	nd	nd	nd	22	318	124	64	9	29	nd	24	nd	nd	67	6	118	2547	15	nd	nd
	s	nd	nd	nd	nd	nd	n.d.	1	1	2	n.d	n.d.	nd	nd	nd	nd	n.d.	n.d	n.d	182	nd	nd	nd

Table A-3. Chemical composition of the major elements (oxide form in wt%, normalized to 100%) as estimated by SEM/EDS for the slip (S1) and the respective clay body (S2) (m: mean value; s: standard deviation; n.d: non detected)

Sample		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	FeO	MnO_2
M1	S1	1.12	1.4	18.52	61.01	1.47	2.02	3.67	1.12	2.65	7.01
	S2	0.52	3.07	11.98	65.28	1.26	1.81	9.48	1.07		5.52
	m	0.8	2.2	15.3	63.1	1.4	1.9	6.6	1.1	2.7	6.3
	s	0.3	0.8	3.3	2.1	0.1	0.1	2.9	0.0	0.0	0.7
M3	S1	1.16	2.02	17.51	66.81	1.01	3.42	1.78	0.56	5.73	n.d
	S2	0.32	1.07	12.21	78.11	0.59	2.04	0.98	0.38	4.3	n.d
	m	0.74	1.545	14.86	72.46	0.8	2.73	1.38	0.47	5.015	0.74
	s	0.59	0.67	3.75	7.99	0.30	0.98	0.57	0.13	1.01	0.59
M6	S1	0.66	1.59	22.72	56.21	2	3.36	4.17	0.85	8.44	n.d
	S2	1.36	1.82	16.37	62.55	1.52	4.55	6.39	0.57	4.87	n.d
	m	1.01	1.71	19.55	59.38	1.76	3.96	5.28	0.71	6.66	1.01
	s	0.49	0.16	4.49	4.48	0.34	0.84	1.57	0.20	2.52	0.49
M12	S1	0.85	1.59	19.58	60.59	0.97	3.57	0.89	0.75	11.21	n.d
	S2	0.47	1.8	17.77	66.82	0.74	3.15	0.99	1.53	6.73	n.d
	m	0.66	1.695	18.675	63.705	0.855	3.36	0.94	1.14	8.97	0.66
	s	0.27	0.15	1.28	4.41	0.16	0.30	0.07	0.55	3.17	0.27
M15	S1	1.19	1.53	22.72	56.72	0.44	3.1	2.28	0.67	11.35	n.d
	S2	0.56	2.12	15.56	65.36	0.84	2.35	5.45	0.7	7.05	n.d
	m	0.9	1.8	19.1	61.0	0.6	2.7	3.9	0.7	9.2	0.9
	s	0.4	0.4	5.1	6.1	0.3	0.5	2.2	0.0	3.0	0.4
M16	S1	0.8	2.36	23.62	58.29	0.46	2.16	5.07	0.67	6.57	n.d
	S2	0.33	2.34	21.37	63.32	0.98	2.68	1.63	0.8	6.56	n.d
	m	0.565	2.35	22.495	60.805	0.72	2.42	3.35	0.735	6.565	0.565
	s	0.33	0.01	1.59	3.56	0.37	0.37	2.43	0.09	0.01	0.33

From the Mycenaeans to the Romans: Reflecting on Early Glass Technology in Greece

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Abstract: The aim of this paper is to consolidate aspects of our understanding of how glass was produced, traded, and used from the Late Bronze Age through the Roman times in Greece. It is meant to concisely present the existing knowledge with respect to glass, critically assess the advancements in the field, and offer a springboard for further developing the theoretical framework gradually developed based on the existing data.

KEYWORDS: GLASS, MYCENAEAN GLASS, ARCHAIC GLASS, CLASSICAL ERA GLASS, HELLENISTIC GLASS, ROMAN GLASS, GLASS TECHNOLOGY, GLASS PROVENANCE, AEGEAN

Mycenaean Glass

It is reasonably certain, from an archaeological standpoint, that the expertise in glassmaking migrated to the Aegean region from Mesopotamia and Egypt, leveraging an existing technological foundation. The vitreous finds of the early Mycenaean period (1680-1425/1390 BC) are considered to be imported from the flourishing industries of Egypt and Mesopotamia, while finds from the Grave Circles in Mycenae are considered to be of Minoan origin. It is only by the end of the LBII onwards that we can talk with relative certainty about domestic glass processing, as the volume, variety, and standardization of finds lead to advocating with safety the existence of local glass workshops. Therefore, the study of Mycenaean glass could be organized based on two chronological axes: A first phase in the LBI and LBII period (1680-1425/1390 BC), and a second phase in LBAIIIA and IIIB (1425/1390-1190/1180 BC) (after Shelmerdine 2008).

The Mycenaean glass industry is clearly distinct when set against parallel glass centers in the Mediterranean and the Near East due to its almost exclusive dedication to glass jewelry adornments at the expense of larger-sized objects, such as vessels. The glass assemblages of this era comprise artifacts of mainly dark blue, light blue or turquoise colour, with very little white glass, while in Mesopotamia and Egypt other colours, apart from light blue, such as black, red, amethyst, yellow, white etc. are common. This has been seen as an index of glassworking, rather than glassmaking activity (Nightingale 2000, 2008; Panagiotaki *et al.* 2005) since there has been no concrete evidence — primarily associated to the absence of industrial remains in the archaeological record to date — to suggest the opposite. Therefore, the most plausible scenario based on the literature and existing data is that glass in the form of ingots — originating from an Eastern glass producing centre — was remelted and shaped into the desired artifact, an assumption reinforced by the discovery of such ingots in the Ulu Burun shipwreck (Pulak 1998, 2001, 2008; Brill 1999; Jackson and Nicholson 2010).

Motifs replicate or — to say the least — are inspired by characteristic themes of Minoan and Mycenaean art typically depicted on pottery, frescoes, and other materials. Glass was integrated into Mycenaean art and — instead of being developed to a certain degree autonomously based on its own special working features — it was manufactured with techniques first developed for metal. Thus, decorative elements adopted for metalwork, such as thickened, ribbed borders and granulation became characteristic of glass beads as well (Nightingale 2008; Kaparou 2017). Glass beads present a great deal of realism, although the decorative themes selected for jewelry exhibit a certain degree of conservatism (Nightingale 2000). It is characteristic that — for almost two consecutive centuries — there seems to be no development that somehow reflects the chronological evolution despite the variety and volume of the finds. As Higgins points out (1980: pp. 72-73), the only evolution is the increasing production of glass jewelry, the reduction of purely gold-made jewelry and its replacement with gold-plated jewels, which could reflect some kind of economic setback.

The Late Bronze Age glass artifacts were manufactured primarily on the basis of specific technological choices made by the glassmakers based on a tradition that was shaped and maintained for centuries in the various glass production centers of the era (Kaparou 2017).

From a practical point of view, producing and — in the case of the Mycenaeans most probably — working glass would have been feasible. There were already established ceramic workshops with high-temperature furnaces that could be used, at least at the onset of the new technology, before custom furnaces might be constructed. It would probably also have been attractive for the ancient craftsmen to work on such impressive materials, so similar to materials that were established as being of particular value, such as lapis lazuli, but also so easily accessible and "cheap" in economic terms, since the supply of raw materials did not differ much from the corresponding production of pottery. Even when glass production remains at the level of glassworking, a well-established trade network would secure the provision of raw glass rather easily as proven by the widespread occurrence and the simultaneous appearance on such early horizons in the Mycenaean reign in the absence of glassmaking evidence (Kaparou and Oikonomou 2022).

Thus, the typical glass of this period belongs to the type of Soda-Lime-Silica glass with high magnesia levels *c*.3-7 wt. %. In the literature this glass type is referred to as SLS-HMG glass (Soda-Lime-Silica, High Magnesia) and appears to be the predominant type used in Mesopotamia, SW Iran, Anatolia, Central Asia, Egypt and, of course, the Mycenaean world from around 1500 up until roughly 800 BC (Sayre and Smith 1961; Sayre 1964, 1965). This type of glass would have been manufactured using powdered quartz and the alkali source would have been ashes of halophytic plants (Henderson 2013). The close similarities in the deviation values of many non-coloring oxides in Egyptian, Mycenaean, and Mesopotamian glasses, noted by Sayre (1965), point towards conservatism in the evolution of technology over vast periods of time.

A lower magnesium content associated with the use of a different alkali source has been found in 14th-century BC glass from Tell Brak in Syria and Minoan Crete, and in glass artifacts from the 13th and 12th centuries BC from Pella, Jordan (Henderson 2000). These include less than *c*.1 wt. % magnesia, and the most likely explanation is that a rather pure mineral, i.e. natron, was used as an alkali source instead of plant ash. It seems, therefore, that at least two chemical types were used in the Late Bronze Age. This type has also been attested in Mycenaean assemblages (Polikreti *et al.* 2011; Zacharias *et al.* 2018; Kaparou *et al.* 2023), highlighting the possible early use of natron as an alkali source and moving its chronological exploitation a lot earlier (see below).

In Frattesina, Italy, a third chemical type of glass was identified for the first time with high potassium content levels of 6.5 to 14 wt. %, and a low magnesia content, at *c*.0.4-1 wt. %. In contrast, soda is low and amounts to about 6.5 wt.%. In any case, the total alkali content ranges from 14 to 16 wt. %. This type (LMHK/ Low Magnesia, High Potassium) entails glasses of a mixed type alkali source that have been found in various parts of Italy, and even in the largest quantities to date, in Western Ireland and Switzerland, as well as in Pylos (Polikreti *et al.* 2011), the North Aegean (Thassos), and Elateia of Fokida (Nikita and Henderson 2006). Up until now, workshop debris associated with glass finds of this type have not been identified, nor is the exact alkali source justified by the mixed type of alkali.

The Mycenaean predilection towards predominantly plant-based glasses, along with the more frequent occurrence of cobalt blue glasses in the archaeological record, have been seen as characteristic of Mycenaean glass production. As established by Sayre and Smith (1974), who used Neutron Activation Analysis (NAA) to analyze the cobalt colorant found in both Egyptian and Mycenaean glasses, it was accompanied by elevated levels of aluminum, zinc, nickel, and manganese. This has been seen, for instance, also in assemblages studied by the authors in the area of Peloponnese, namely Voudeni, Palaia Epidavros, Mycenae, Pylos etc. (Kaparou 2017; Zacharias *et al.* 2018). Exactly this pattern of cobalt and elevated trace elements was traced to an alum ore in the Kharga Oasis of the Egyptian Western desert (Kaczmarczyk 1986; Shortland *et al.* 2006) and matches analyses of cobalt-colored glass produced at Amarna. Along with the ingots from the Uluburun shipwreck, this restricted data has been used as a possible scenario for an Egyptian origin of Mycenaean cobalt blue glasses (Walton *et al.* 2009; Polikreti *et al.* 2011; Smirniou and Rehren 2012, 2013; Zacharias *et al.* 2018). In Ramesside, Egypt, a newly discovered source of the cobalt-blue colorant (Type R), which clearly differs from the traditional cobalt blue colorant derived from Zn-rich cobaltiferous alum from Dakhla Oasis, was used in blue glass and faience in the Memphite region. This new cobalt source is also different from that used after the Late Period in Egypt, as it can be clearly seen by the investigation of the accessory to cobalt trace elements and their variation in time (Abe *et al.* 2012). This evidence can serve as a springboard for further study of the Mycenaean cobalt blue glasses, offering insights and a better understanding of complex socio-economic issues.

Studies on trace elements have the capacity of assigning a possible provenance of glasses and this has been seen to vary from either Egypt or Mesopotamia. Shortland *et al.* (2007) analysed 54 LBA glass fragments (24 Mesopotamian and 30 Egyptian) with LA-ICP-MS and found that Mesopotamia is characterised by low values of Ti (<300 ppm) and Zr (<20 ppm), this being higher for Egyptian glasses. This find has been used in Mycenaean glass studies and has led to attributing glass artifacts to the Egyptian glass industry (Polikreti *et al.* 2011, Kaparou 2017; Zacharias *et al.* 2018; Kaparou *et al.* 2023).

This evidence of foreign-made raw glass transported into the Mycenaean world and fashioned into objects is of high scholarly interest, since it shows that the Mycenaean states relied, at least in part, on imported raw glass in the absence of industrial debris to suggest — at least currently speaking — a native industry. It is also noteworthy that no Egyptian glass has been found in Mesopotamia, nor have any Mesopotamian glasses been found in Egypt, whereas both seem to have supplied the Mycenaean world with raw glass.

When the Mycenaean palaces fell at the end of LHIIIB (around 1190/1180 BC), in the last phase of the Late Bronze Age (LHIIIC- 1190/1180–1065/1060 BC), the complex and sophisticated Mycenaean level of culture reverted to a much simpler one, accompanied by the disintegration of palatial society, economy, and of most palatial industries. While pottery and metalwork survived, the previously thriving common use of glass beads (alongside with faience ones) seems to have been gradually set aside. There is evidence that the number of beads used in Post-palatial times decreased before they disappeared to a great extent. In the Post-palatial period, the number of beads in tombs or even fragments of beads (already broken in antiquity) could likely be interpreted as tokens of an association to the glorious palatial Mycenaean past (Nightingale 2008).

First Millennium BC glass

In the course of the 1st millennium the overall situation starts to change significantly regarding glass production. The decline in every artistic expression after the collapse of Mycenaean centers is also evident in the Aegean and in the Greek mainland. During the beginning of the Early Iron Age, however, there is a significant rise in the numbers of glass objects retrieved from archaeological contexts. In particular, from the late 10th c. BC onwards various, mainly colourless glass beads are found in many places in Greece, such as in Aitolia, in the sacred deposits of Kameiros and Ialysos in Rhodes island, in Knossos and in Thera, while there are only few examples on mainland Greece (e.g. Orthias sanctuary in Sparta and Vitsa settlement in Zagori region, NW Greece). Most likely these objects were imported from Assyria or/and Mesopotamia from Greek and Phoenician traders following the trade routes of the Syropalestinian coast, the Dodecanese, Crete, the Aegean Sea and eventually mainland Greece (Triantafyllidis 2000- references therein).

Following the Early Iron Age, especially during the middle 7th c. BC there is a noticeable increase in the quantity of glass objects and especially glass vessels that are reported in the archaeological record. During this period, the introduction of core formed vessels, the so-called "Mediterranean bottles", occurs with the revival of the technique which first appeared possibly in Mesopotamia/Egypt during the LBA. These bottles constitute the largest numbers of glass vessels that circulated in the Mediterranean area and were manufactured in three successive industries between the mid-6th c. BC and the beginning of the 1st c. AD. They seem to share a common function and technology: as votive offerings in sanctuaries and perfume containers (Cosyns and Nys 2010). Moreover, most of their forms resemble the shapes of Greek ceramic and metalware (Grose 1999) of the Archaic, Classical, and Hellenistic periods — oenochoe, aryballos, amphoriskos, and alabastron just to name few of the forms. Various scholars believe that the earliest of these vessels were produced in Rhodes (Harden 1981; McClellan 1984; Grose 1989).

In addition, it is widely believed that from the late 5th c. BC onwards the colourless or/and transparent slightly coloured glass start to be manufactured or at least distributed in the Greek region parallel to the core-formed vessels (Weinberg 1992; Stern 1999). What is more, during this period, the so- called 'Pheidias workshop' in Olympia was in operation and it seems that glassworking activities took place rather regularly. In particular, vast numbers of decorative glass inlays of various shapes have been found along with their individual molds. These glass pieces most probably were used for the decoration of the throne and the attire the famous gold-ivory statue of Zeus or/and the tunic (chiton) of the statue of Nike (Stern-Nolte 1994). Moreover, a number of transparent/colourless glass vessels dating to the 4th c. BC and early 3rd are present in Greece and more specifically in Rhodes, Aitolia, and Macedonia and can be connected to the Achaemenid glass industry from Anatolia (Triantafyllidis 2000).

Glass production was taking place at a relatively small scale and the luxurious products were intended for people of higher status and this seems to be the reason why glass of this period is of exceptional quality and variety. Following the Hellenistic period, there is a growth in artistic production and technological advances, leading to an abundance of glass artefacts retrieved.

Regarding the glassmaking and glassworking activities in Greece during the 1st millennium BC., the archaeological evidence is very scarce and limited only to few examples especially during the end of the millennium. The assumption that a glassworking facility was in operation in Rhodes during the 7th c. BC is due to the excavation of more than 6000 transparent, almost colourless glass beads suggesting the existence of a secondary workshop (Triantafyllidis 2006). This is probably contemporary with the famous east-Hellenic faience workshop of Rhodes. Glassmaking activity in the 6th to 4th c. BC is relatively spatially restricted to Macedonia and Rhodes and should be connected mostly to the production of the core-formed vessels with occasional monochrome cast bowls, beads, head pendants, gems, and gaming pieces. However, no solid evidence, such as glassworking debris, raw materials or furnace constructions has been found so far. The most robust evidence for glassworking and glassmaking activities in Greece was found in Rhodes, where during a salvage excavation a deposit containing thousands of glassworking and glassmaking debris dating to the second quarter of the 2nd c. BC was retrieved (Rehren *et al.* 2005). Furthermore, for the late Hellenistic period two workshops have been located, one in Delos island, manufacturing glass tesserae and beads, and a second in Rhodes producing local skyphoi and phiale similar to the corresponding Syro-palestinian glass objects (Triantafyllidis 2006).

In glass technology of the 1st millennium BC we notice a major shift in the technological choices compared to the preceding Mycenaean glass industries. In particular, the plant alkali source was substituted by a mineral one, namely natron, and this change occurred *c.*800 BC. This shift for the Greek region most probably took place a bit later, around the end of the 7th c. BC, at least according to the current data. In addition, glass was made using as a basic raw ingredient, namely sand, rather than quartz pebble that were extensively used in the Mycenaean period. Most likely, during this period, glassmaking followed a centralized model which is evident in later periods (i.e. Roman period). According to this model, glass was fused in large quantities in dedicated glassmaking centers, which were located in favorable areas having access to the raw materials and the fuels needed to fuse the raw materials. After the production of the raw glass, it was then distributed in secondary glass workshops specializing in producing the final glass objects. Natron glass in this period dominated the Mediterranean area and subsequently the Aegean and Greek mainland for many centuries.

There are a lot of examples of different types of glass found in Greek contexts, such as beads, core formed vessels, open colourless vessels etc., all of which were made with natron (Oikonomou 2012; Oikonomou *et al.* 2012a; Oikonomou *et al.* 2012b; Triantafyllidis *et al.* 2012; Oikonomou *et al.* 2014; Blomme *et al.* 2016, 2017; Oikonomou 2018; Smirniou *et al.* 2018; Oikonomou 2019). There is no evidence of mixed alkali or plant ash glass during this period. The only exception so far attested is in Rhodes, where a significant number of glass beads and inlays were produced using plant ash as the main alkali. (Oikonomou and Triantafyllidis 2018).

In the later periods of the 1st Millennium BC, and more specifically during the middle and late Hellenistic, according to recent analytical data from Epirus, NW Greece we may assume that the primary glass was imported from major glassmaking sites in SE Mediterranean, such as Egypt and the Levantine coast, a tradition that continues in the Roman period (Oikonomou 2019; Oikonomou *et al.* 2020). However, there are indications of possible Italian origin of raw glass (or the finished object) for the core formed vessels of the particular period (Oikonomou 2018).

Overall, glass in 1st millennium BC was still considered as a luxury item as it used to be in the Mycenaean world due to its limited and laborious production. The types of glass used during this period include small bottles for perfumes and cosmetics, small dishes and bowls, jewelry pieces (mainly beads and pendants), and inlays used in architecture. Stylistically, the very strong colours (deep blue, green, and amber) and shapes follow the trends of each period (Archaic, Classical, Hellenistic). The techniques used for the manufacture of such objects are considered sophisticated, e.g. the mosaic technique, a rather complex technique, produced spectacular objects intended to highlight the status of the owners. Technologically it seems that 1st millennium glass set the foundations for the flourishing Roman glass production by experimenting and then adopting natron as a flux, and using sand instead of another silica source, such as quartz pebbles, as the main raw material. There is no evidence for primary production of glass in Greece (with the exception of Hellenistic Rhodes) and most of the glass was imported either as a raw material or as a finished object.

Roman glass

The ever desirable qualities of glass as material led to an increasing demand for vitreous artifacts just before the emergence of the Roman Empire. According to current archaeological evidence, the most important development in the history of glass, the discovery of the free blowing technique, occurred in the mid- 1st c. BC. More specifically, the earliest free blown perfume bottle was discovered in the cemetery of Engedi in Israel, which was abandoned in 40 BC (Harden 1969: 47). On a similar note, the earliest archaeological evidence that relates to the free blowing activity was uncovered in the Old City of Jerusalem in contexts that date between 37 and 4 BC (Israeli 2005). After a short period of experimentation, glass production underwent a massive expansion in the course of the first century AD. It supplied not only tableware for households of different social status across the Empire, but also furnished major public buildings with many tones of glass for windows and mosaics (MacMahon and Price 2005).

Nevertheless, the excavation of domestic contexts often yields a small quantity of glass. In rare cases, single vessels or entire groups have survived intact or almost intact, such as in sealed graves, in houses with short-lived occupation followed by collapse, or in buildings ruined by invasion or fire, where debris buries and, thus, protects use-deposits over time. Moreover, glass is often poorly preserved not only because it is fragile and suffers severe weathering, but also because, like metal, it was recycled. Glass vessels were easily broken during use, and then, according to literary evidence, disused vessels or sherds were often collected for melting and shaping a new (Stern 2012). In addition, the excavation of workshops and shipwrecks containing cullet, as well as the scientific analysis of samples, has demonstrated that both the long-distance trade in glass waste and the local production of vessels from recycled glass were features of a vital business in the Roman world (Silvestri *et al.* 2008; Freestone 2015; Schibille *et al.* 2017). Admittedly, the recognition of the extent of recycling in the composition of glass is still unclear and requires substantial work before this characteristic Roman aspect can be further understood (Rehren and Freestone 2015). Having said that, it is important to note that elevated concentrations of certain elements (normally Co, Zn, Sn, Cu and Pb) have been interpreted as indicators of glass recycling (Jackson 1997; Smirniou and Rehren 2013; Freestone 2015; Rehren and Brüggler 2015; Rehren and Brüggler 2020).

This problem is part of the overall issue of the in depth understanding of the Roman glass production process which involved more than one stage as well as more than one manufacturing center. Although glass working took place in virtually every area of the Roman world, the evidence for glass production is generally rather difficult to identify and interpret. There is a marked contrast between the wide range of vessels and objects that are constantly being discovered and "the ephemeral and episodic nature of the evidence for the production processes by which they are formed" (Price 2002, 81).

The study of the origin and the organization of Roman glass production goes beyond our current enquiry. Pliny's *Naturalis Historia* (77AD) strengthens much of our current understanding of Roman glassmaking materials including raw material sources, additives and the locations of production. Despite the ambiguities early texts may contain, the careful observation of archaeological evidence coupled with the findings of archaeometric investigations have resulted in the integrated interpretation of the most valuable literary source on ancient glass production in Antiquity (Freestone 2008). Pliny's writings point, indeed, to a rather complex multi-stage process which resulted in the production of lumps of fused material to be re-melted, color added and then reworked. In fact, strong scientific and archaeological evidence has proved that along the eastern Mediterranean coast raw glass was made by fusing Egyptian evaporitic soda (natron) and sand to produce large glass slabs in tank furnaces with capacities of 8-20 tones (Barfod 2020- references therein). These were broken up into blocks and were transported along with glass vessels and cullet to secondary glass workshops across the Empire for remelting and shaping into objects for use. Testimony to the movement of base-glass over large distances around the Mediterranean is evident from shipwreck cargoes (Siu *et al.* 2017- references therein) as well as from evidence linked to the final stage in the organization of production, the secondary object-forming furnaces which are also increasingly well documented (Papageorgiou 2014: 42-44 with references therein). This division of production in primary glassmaking and secondary glassworking continued until at least the ninth century AD.

Roman glass had a soda-lime-silicate basic composition and contained very little potash and magnesia (less than 1%). The mineral natron, the major soda source for glass, is chemically consistent, and this results in an overall homogeneous glass. On the other hand, the sand used may provide useful information of its origin as it introduces its geochemical signature into the glass batch. What is more, the study of its trace elements can be related to accessory minerals present in the sand such as feldspar, pyroxene, amphibole, zircon, monazite and more (Shortland *et al.* 2007). The major, trace and isotopic analyses of Roman and Byzantine glasses have already discerned at least six compositional groups (Shortland and Rehren 2020). More specifically, by looking into differences in the alumina, lime, and iron oxide contents, a number of natron-type glasses have been recognized that dominate the archaeological record in the Mediterranean and Northern Europe for most of the first millennium AD. These are thought to have been produced either on the Levantine coast (Levantine I: 6th to 7th c. AD and Levantine II: 7th to 8th c. AD), some Roman groups) or in Egypt (Egypt I and II: 8th-9th c. AD), high iron, manganese and titanium glass (HIMT: mid-4th to 7th c. AD) (Schibille *et al.* 2017- references therein). For the latter, it has been recently proposed that it was deliberately tinted yellow-greenish to allow it to be recognized and differentiated from the green-blue glass of the Levant, with which it competed in the marketplace but that had less favorable melting and working properties (Freestone 2018 *et al.* 185). These main glass groups are further divided into sub-groups based on their minor and trace element signatures.

Research has placed particular emphasis on the analysis of glass objects that date to the late Roman or early Byzantine periods most probably because the archaeological evidence that suggests a trade in raw glass ingots broken from larger slabs and their associated large tank furnaces date after the 6th c. AD (see for example relevant recorded evidence in sites in Israel in Gorin-Rosen 2000). In fact, recent glass overviews that explore the issue of the organization of glass making do not refer to the Roman period before the 6th c. AD (Rehren and Freestone 2015). As a result, there is a noteworthy gap concerning the organization of glass production during the early and middle Roman periods, despite the fact that the trade of raw glass around the Mediterranean is recounted in the *Periplus Maris Erythraei* (late 1st c. AD: Casson 1989: 127). Not to mention, archaeological evidence has not only confirmed the validity of the text, but it has also pushed the date of this practice backwards to the early 1st c AD (Jackson and Foster 2015, references therein). Nevertheless, Roman large glass factories similar to those that have been uncovered in Israel have not been published yet, which means that the primary production sites of Roman and HIMT glasses are still unknown (Nenna 2014). For the time being, isotopic data demonstrate that most Roman green-blue glass of the 1st to the 4th c. AD originate on the Levantine coast and that HIMT was produced in northern Egypt (Schibille *et al.* 2017- where references therein).

Further compositional distinction of Roman glasses is usually based on the chemical elements contained in the base-glass of the colored or the colorless samples. This is especially the case with the glassware of the 1st c. AD, when the production of highly colored objects was widespread. The marked differences in composition cannot be simply explained by the addition of minerals used to produce the different hues. In fact, the translucent emerald green and the opaque glasses of the period were made with the use of considerable amount of plant ash unlike the other colored or colorless natron glasses of the period in question and later. This compositional homogeneity within this group of glasses has led scholars to assume the existence of specialized production centers that would have produced each color or a group of colors. This hypothesis is reinforced by the discovery of brightly colored blue 1st c. AD raw glass (Jackson and Foster 2015). Current research attempts to identify the link between color and vessel form, while it does not exclude the possibility that there were workshops specializing in the production of specific vessel forms for which emerald green was selected. Probably, these workshops would have had easier access to a supply of the conspicuously colored emerald green glass (Cottam and Jackson 2018).

On another note, it has been found that high quality sand, low in iron, phosphorus and titanium, was used to produce the colorless artifacts of the 2nd and the 3rd c. AD. The presence of antimony and/or manganese at levels is also indicative of the deliberate addition as decolorizers. Noteworthy is the most recent investigation regarding the provenance of the antimony (Sb) decolorized Roman glass. The investigation of hafnium isotopes confirmed that the source for this highly desirable colorless glass, listed as "Alexandrian" in the Price Edict of Diocletian (301 AD), was indeed of Egyptian origin (Barfod *et al.* 2020). In contrast, their naturally colored pale blue, green or blue green counterparts were made with a carelessly selected sand rich in impurities (Jackson and Foster 2015).

The analytical investigations that have been put forward, regarding glass objects found in Greece are limited in number and, in fact, do not necessarily account for the Roman period. During the last decade an attempt has been made to cover part of the existing gap in research. The chemical analyses of glass objects, predominantly vessel glass, from Patras, Messene, Corinth, and Demetrias that chronologically range from the 1st. c. AD to the 6th c. AD has demonstrated that the glass compositions were overall in accordance with the typical Roman recipes and production processes (Papageorgiou 2014; Möncke *et al.* 2014; Papageorgiou and Zacharias 2012; Papageorgiou *et al.* 2012). It is understood that glass working activity in the aforementioned sites surrounded local secondary glass workshops that imported raw glass from the large glass making centers of the Eastern Mediterranean. Some isolated examples, whose composition does not match any published international reference glass group, are considered evidence of recycling. Strict control over the production process of the more special artefacts was also identified. In addition, it was possible to distinguish chemically the imported from the locally-produced objects.

Finally, the most recent work on Roman glass from the region of Greece was published in 2017 and concerns Roman and Late antique glass from Northern Greece (Silvestri *et al.* 2017). The use of oxygen and chemical isotopic compositions suggests that while the majority of the samples display a composition similar to the typical Roman glass imported from the Levantine coast, a minor assemblage may have been produced locally, in Thessaloniki.

Conclusions

It should be understood that glass is an important part of the archaeological assemblage as its study has the potential to not only yield valuable information regarding technological ability and transfer, but also to map out exchange networks, especially if the sites where the glass was made can be identified and characterized (Shortland and Rehren 2020). Furthermore, despite the difficulties in retrieving glass from the archaeological record, its discovery may yield complementary evidence concerning several aspects of everyday life. Hence, an increasing amount of work has been devoted to the study of glass, especially over the last twenty years.

Early glass technology in Greece has received some attention by Greek scholars particularly in the last decade. Most research has focused on specific sites and there has not been any collective work on ancient glass technology in Greece. In light of this evidence, there is great potential to proceed in systematic analysis of more glass collections in order to incorporate early glass technology in Greece into the already established system of production and exchange of glass in the Old World.

More specifically, the Mycenaean Aegean can be shown to have been a largely separate glass province on its own right, despite the absence of workshop debris that could pinpoint towards primary production. Glass beads, along with faience, unequivocally formed an integral part of Mycenaean culture. The data presented here concisely are part of a large research program that has managed to identify different traditions within close geographical areas and specific technological choices. Examples such as Palaia Epidavros, Argolid, and Voudeni, Patras, but also areas presented in the literature, boast localization of production following their own trends in fashioning and manufacturing glass artifacts. Following the traditional recipes of the LBA (with some interesting deviations that do not lie within the scope of this contribution), they followed the beaten track in the Mycenaean World with respect to the motifs chosen, but also produced their own unique artifacts (Kaparou 2017).

In addition, during the 1st Millennium BC it seems that there was a considerable amount of glass imported from major glassmaking centers, possibly located in the Levant and in Egypt. Therefore, we can at least currently accept the absence of any primary glassmaking industry in Greece with the only exception of Rhodes in Hellenistic period. Regarding technology, there is a profound change with the introduction of natron as a basic raw material which is evident throughout the Mediterranean. The production is not only limited in pendants and bottles, but also extended to other luxurious objects, such as bowls, dishes, eye beads etc. The analytical data obtained by various groups indicate that in most occasions there was continuity in the selection of raw materials through the different periods (Archaic, Classical and Hellenistic), showing that Greek sites had common suppliers, either of raw materials or of finished objects. However, small differences in specific compounds found in these assemblages indicate different glassmaking traditions and also the versatility of glass compositions.

Regarding Roman glass, the large amount of isolated case studies from the Roman world has already given way to the emergence of larger pictures, such as the understanding of the organization of production and the long-distance movement of glass. The case studies from Greece may be incorporated into that reference network contributing to a better understanding of local social and economic contexts. However, despite the widely admitted importance of glass, even as individual material, the plethora of findings from Greece has never been studied systematically. This systematic study should closely integrate the analytical results into meaningful archaeological and anthropological backgrounds. First of all, a full publication of typologies and chronological frameworks could establish a stronger connection between certain choices and the wider social contexts. Secondly, since Roman glass was characterized by chemical homogeneity, the detection of the workshops' characteristic style may illuminate us regarding the organization of production; from massive raw material production establishments to prestigious workshops that traded branded items, to small local workshops that recycled or worked on various glass objects depending on the resources available and the local needs. Finally, the social role of glass makers and/or workers as well as of the glass merchants is another interesting topic of research. So far, it has been poorly investigated, but should be considered as an integral part of the production and distribution of this major commodity in Roman times.

It is clear though that aspects of our understanding remain blurred in the absence of more scientific data, the combination of multiple analytical techniques, and the interpretation of the finds in a combined archaeological and archaeometric framework. Further research based on the integration of the latter will contribute to the study of social structures, socioeconomic aspects, technology, trade, cultural, and economic interconnections.

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A Detailed Study of a Sediment Contained in a Mycenaean Cooking Pot from Salamis, Greece by a Combination of Analytical Techniques (XRD, XRF, Raman and SEM/EDS)

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Abstract: During the excavations of the University of Ioannina at the Late Mycenaean building complex in Pyrgiakoni, in close proximity to the Mycenaean acropolis of Kanakia, on the southwest coast of Salamis, a quantity of Aeginetan cooking vessels, among other finds, was revealed. The vessels were used to prepare food as part of ritual gatherings which were taking place at the adjacent tumulus/cenotaph. These vessels include a three-legged cooking pot, located in a storage area of the building, which contained a sediment of bright red color inside. It should be noted that the specific color of the sediment has not been detected in any other area of the acropolis at Kanakia or in the building complex at Pyrgiakoni and therefore we can reasonably assume that this sediment is directly related to the contents of the cooking pot.

The primary aim of this study is to fully characterize the sediment using a set of complimentary analytical techniques to understand its use. Employing X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Raman Spectroscopy, the investigation yielded insightful results. XRD analysis identified calcite as the main mineralogical phase, corroborated by elemental XRF analysis revealing a high calcium content and Raman spectroscopy displaying calcite peaks at 282, 713, and 1086 cm^{-1}. Small amounts of hematite, likely contributing to the red color, were also detected. Raman spectroscopy further identified a red ochre pigment primarily composed of anhydrous iron oxides. SEM analysis on a pot wall fragment revealed an increased iron content on the inner surface, likely associated with the red ochre. Lastly, the ceramic body of the pot exhibited heightened vitrification and low porosity, suggesting firing at relatively high temperatures.

Based on these findings, it is plausible that the three-legged cooking pot was employed in the process of preparing red ochre by heating yellow ochre, a hydrated iron oxide mineral. The potential use of this vessel for transporting the red pigment should not be excluded. Notably, the large hypostyle hall in the Pyrgiakoni complex, spanning 60 m^2, featured remnants of white plaster coating on the floor. In the absence of frescoes, it is highly likely that the red ochre was used for decorating the floor and/or the rectangular hearth at the room's center.

KEYWORDS: RED OCHRE, MYCENAEAN POTTERY, SALAMIS, XRF, XRD, SEM, RAMAN

Introduction

The systematic excavations and other research work of the University of Ioannina in Salamis since the early 1990's under the direction of Prof. Yannos G. Lolos have brought to light a significant number of monuments, which highlight the crucial diachronic role of the island in the Saronic Gulf (Figure 1, left). Since 2000, the excavations in the wider area of Kanakia, on the southwestern coast of the island, have been revealing the Mycenaean administrative centre of the island, consisting of a hierarchically organized double acropolis, with a lower town; its associated cemetery, in its immediate vicinity known today as Pyrgiakoni, contains clusters of chambers tombs and cist graves (still unexcavated) and a cult area (Figure 1, right). Having a long habitation history, from the Late/Final Neolithic period onward, the acropolis had its last architectural phase in the LH III A2/III B1 period and was abandoned, in an organized exodus, at the very beginning of LH III C early.

The Mycenaean cult area at Pyrgiakoni comprises 3 elements: a tumulus, a low platform and a communal building (Figure 2, left). The tumulus, of roughly ellipsoid shape (20 x 25 m), incorporating a natural rock outcrop, has a height of more than 2 m, and is marked by a peribolos wall, with a diameter of ca. 45 m in a N.-S. axis. After the removal of the soil that had been piled on the top, two empty pits carved in the rock were revealed, associated with a simple rectangular limestone stele, which was found fallen on the east side of the tumulus. A few meters to the west, a low platform of roughly circular shape (diam. 6 m), constructed with cobble/gravel, was uncovered. On its surface was found a small quantity of sherds, including fragments of

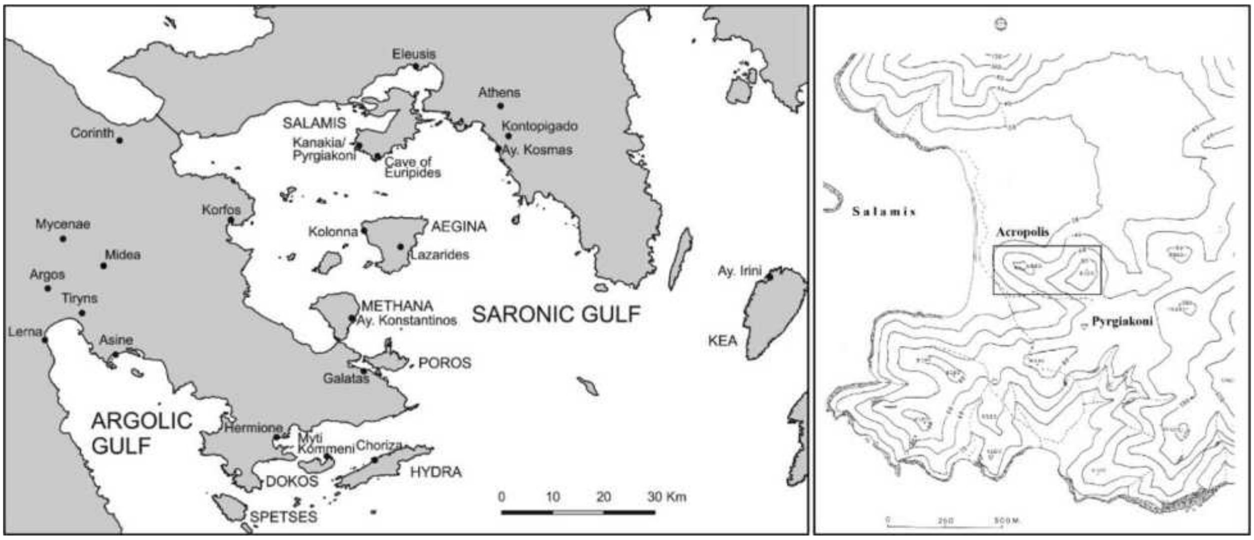


Figure 1. Map of the Saronic and Argolic Gulfs, with main Mycenaean sites (left). Salamis, Kanakia; map of the area of the Mycenaean acropolis and Pyrgiakoni (right).

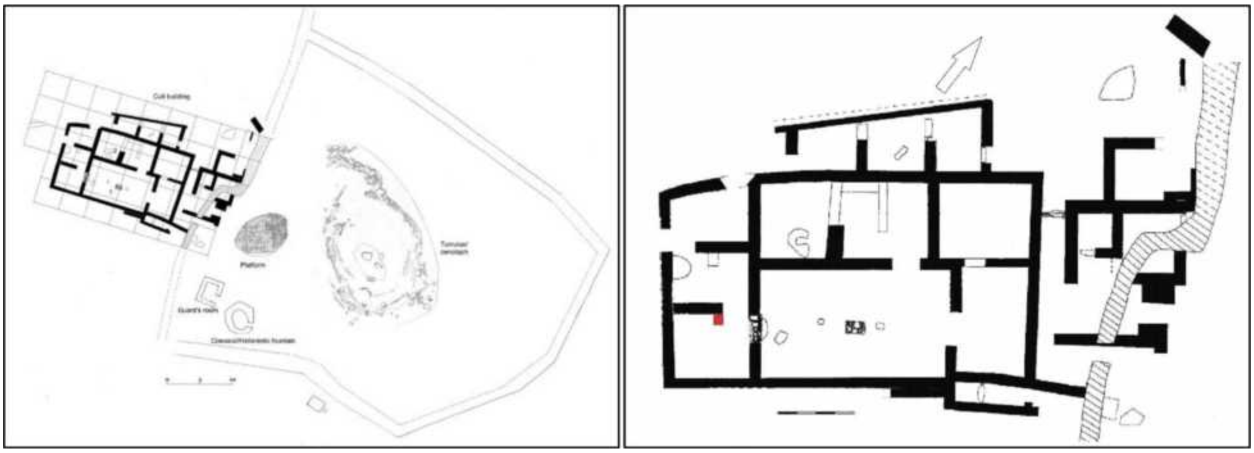


Figure 2. Salamis, Pyrgiakoni; plan of the Mycenaean cult area (left) and plan of the Cult Building (right). The find spot of the tripod cooking pot is marked in red (right).

kylikes, deep bowls and cooking pots of LH III B-III C early date, as well as two fragments of clay figurines and a small number of animal bones. Further to the west, on the same E.-W. axis and in relation to the tumulus, a well-built monumental structure has been excavated (Figure 2, right). Following the fate of the acropolis, the large cult building at Pyrgiakoni was also abandoned at the beginning of the LH III C early period (Lolos and Marabea 2017; Marabea 2019).

The focal point of the building is undoubtedly the large, megaron-type, hall, measuring 9.70-9.95 x 5.70-5.80 m, with a wide entrance on the west side. On the evidence provided by two stone bases for wooden columns in its long axis, the hall was pillared; it was also furnished with a rectangular hearth between them. Other rooms, of auxiliary and storage usage, flank the hall on the east, north and west side. The communication between the hall and the area of the tumulus to the east was accomplished by a long zigzag processional route on the north side, through successive doors, from the northwest to the east part of the building, and from there to the area of the low platform and the tumulus.

The combination of all evidence suggests that at the end of the 13th century B.C. the elite of the acropolis organized a formal cult at Pyrgiakoni, i.e. in the area until that time reserved exclusively for burial. It was obviously a hero cult, judging from the cenotaph at the top of the tumulus, most probably for a member of the highest status, who was not buried at home. This cult included gatherings in the megaron-type hall and the

Figure 3. Salamis, Pyrgiakoni, Cult Building. Aeginetan cooking pots in a storeroom (left), west of the large pillared hall. The analysed pot is the first from the right. The content of the analysed cooking pot (right).

related consumption of food and drink before or after the performance of symbolic acts in the area of the platform and the tumulus-cenotaph.

Among the pots retrieved in a storeroom on the west side of the hall was a number of Aeginetan cooking pots (Figure 3, left). One of the pots, of the carinated tripod type (Marabea 2019, 459, 465, Fig. 14: 27), which was resting on the floor, was full with a red substance (Figure 3, right). We should note that the specific sediment has not as yet been encountered either on the acropolis or at Pyrgiakoni, as part of the stratigraphy of these sites and, in all probability, we can safely surmise that the red substance is directly related to the content of the tripod pot. Within this framework, a series of analyses aimed at characterizing and identifying the content of the pot, in an effort to interpret its existence within the archaeological framework outlined above.

Materials and methods

In this study two different samples, the sediment sample and the ceramic sample, were examined with an array of analytical techniques. In particular, various subsamples from the red sediment were collected and prepared for XRF, XRD and Raman analysis. A small piece of the sediment was ground to a fine powder in an agate mortar. Part of it was pressed in a 12 mm diameter pellet by mixing 300 mg of sample powder with cellulose at a ratio of 10 wt. %, suitable for XRF analysis, and the rest was used for both XRD and Raman spectroscopy analysis. Furthermore, for SEM/EDS analysis, a small fragment of the tripod cooking pot was embedded in a resin block along with the red sediment which was firstly consolidated with Paraloid B72. The resin block was ground using silicon carbide papers of various grits (800, 1200, 2500, 4000) and was further polished with 3 μm diamond paste.

The XRD pattern of the red sediment was obtained using a D8 Advance Bruker diffractometer operating with CuKa (λ=1.5406 Å) radiation and a secondary beam graphite monochromator. Powder samples, obtained as described above, were scanned over an angular 2θ range from 2° to 60° in steps of 0.02° (2θ) at a rate of 2 s per step. To identify the mineralogical phases present in the samples, the PDF-4 database of the International Centre for Diffraction Data (ICDD) was used.

The major, minor and trace elements composition of the red sediment was determined through a home-built EDXRF spectroscopy facility (Papachristodoulou *et al.* 2006). X-rays emitted from annular radioisotopic ^{109}Cd and ^{241}Am sources were used to excite the characteristic X-rays of potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), zinc (Zn), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb), lead (Pb), barium (Ba), lanthanum (La), cerium (Ce) and neodymium (Nd). The WinQxas software package (IAEA, International Atomic Energy Agency, Vienna, Austria) was used for spectral analysis and elemental compositions were assessed with reference to the SOIL-7 certified material provided by the International Atomic Energy Agency (IAEA) and the JLs-1 "limestone" certified material provided by the Geological Survey of Japan (GSJ).

In addition, Raman spectroscopy was employed to further characterize the sediment. An InVia Reflex Renishaw photometer was used, equipped with a metallurgical microscope in which the x5 magnification lens was used. The samples were excited with the 785 nm laser line (488.0, 514.5 and 632.8 nm lines were tested, but the luminescence signal from the sample was stronger than the Raman spectrum with these lines) – in some cases the sample was irradiated with the laser light before collecting the spectrum in order

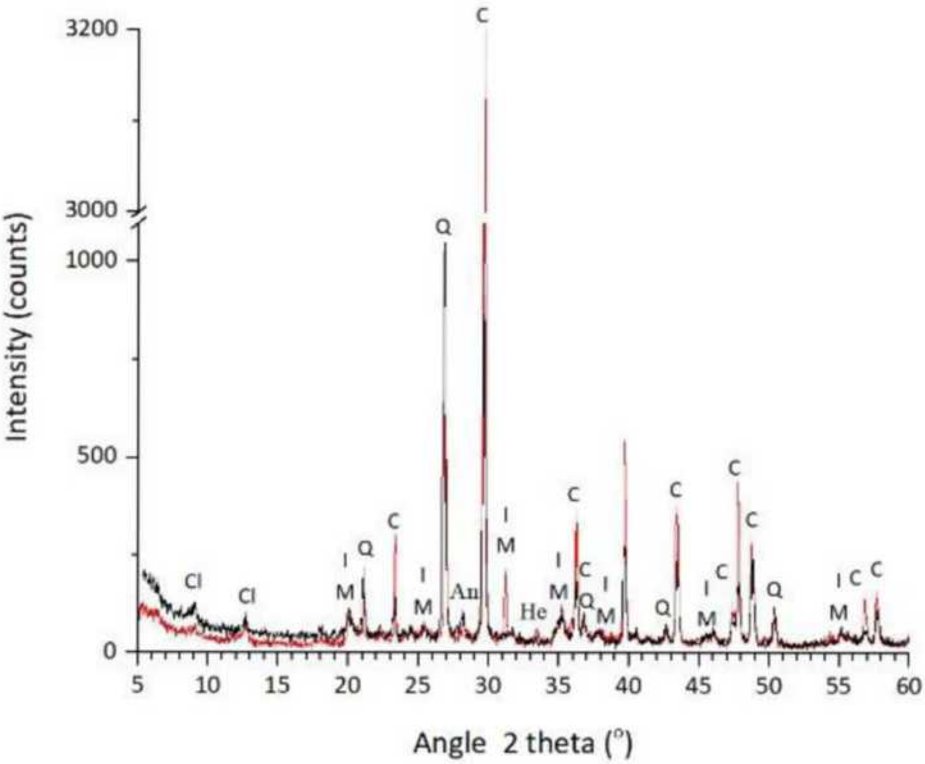


Figure 4. The XRD patterns of the red sediment (R.S.) (red line) and the surrounding sediment (S.S.) (black line). The basic crystal phases detected are: Q: quartz, C: calcite, M: muscovite, I: illite, An: anorthite, Cl: clinochlore, He: hematite

to reduce the luminescence effect (bleaching). The photometer resolution was set at ~ 1 cm^{-1}.

Finally, the sediment and the ceramic body of the pot were further investigated with a Zeiss/Evo 15 electron microscope (SEM) coupled with the Ultim Max EDS Detector (Oxford Instrument), having a 65 SDD detector. The operation voltage was set at 20kV, with a beam current at 1nA and a working distance of 8.5 mm.

Results and discussion

The mineralogical phases of the red sediment (R.S.) sample were identified with the XRD analysis. For comparison another sample of modern surrounding sediment (S.S.) was also analysed under the same conditions. According to the respective XRD patterns shown in Figure 4, the main mineralogical phase detected is calcite ($CaCO_3$) which is also in accordance with the XRF elemental data that showed a high calcium content in both the R.S. and S.S. samples (Table 1).

Apart from calcite, quartz, being extremely prevalent in soil samples, was also detected by XRD analysis. Furthermore, a few more mineralogical phases were identified, such as clinochlore (a magnesium rich chlorite), illite, muscovite (also known as common mica or potash mica) and anorthite ($CaAl_2Si_2O_8$), which are very common aluminosilicate phases in soil samples. Finally, the red colour of the R.S. sample might be attributed to the presence of hematite (Fe_2O_3). The hematite peak is slightly more intense in the XRD pattern of the R.S. compared to the S.S. sample, although the Fe_2O_3 content identified by XRF analysis is in both cases similar if we take into consideration the analytical errors e.g. in R.S. Fe_2O_3: 3.4±0.6 wt. % and in S.S. Fe_2O_3: 4.0±0.6 wt. %. In addition to the XRD and XRF analysis, Raman spectroscopy was applied on both samples. As expected, the strong calcite peaks were easily identified at 155, 282, 713 and 1086 cm^{-1} (two cation-anion relative translational T(Ca, CO_3) modes plus the internal ν_4 and ν_1 Raman active modes of the CO_3^{2-} anion respectively) (Figure 5). Moreover, the peaks at 220, 286, 402, 491 and 601 cm^{-1} can be attributed to hematite. Hematite can be found in red ochre pigments which consist mainly of anhydrous iron oxides and can be therefore categorized among the "iron oxide pigments" (Helwig 2007). The use of red ochre is attested in various contexts and dates back to more than three hundred thousand years ago, as there is archaeological evidence from Terra Amata, near Nice, France, suggesting that red ochre specimens were collected and transported (Schmandt-Besserat 1980).

Table 1. The composition of the two sediment samples, determined by XRF analysis (values are reported in wt. % and ppm).

	"Red sediment"	"Surrounding sediment"
K_2O (%)	2.0±0.4	1.6±0.4
CaO (%)	29±6	29±6
TiO_2 (%)	0.2±0.2	1.5±1.3
Fe_2O_3 (%)	3.4±06	4.0±0.6
Rb (ppm)	52±5	43±5
Sr (ppm)	145±8	214±10
Zr (ppm)	99±6	142±8
Nb (ppm)	6±1	9±1
Ba (ppm)	176±20	407±30
La (ppm)	24±3	40±3
Ce (ppm)	56±3	68±3
Nd (ppm)	24±2	35±2

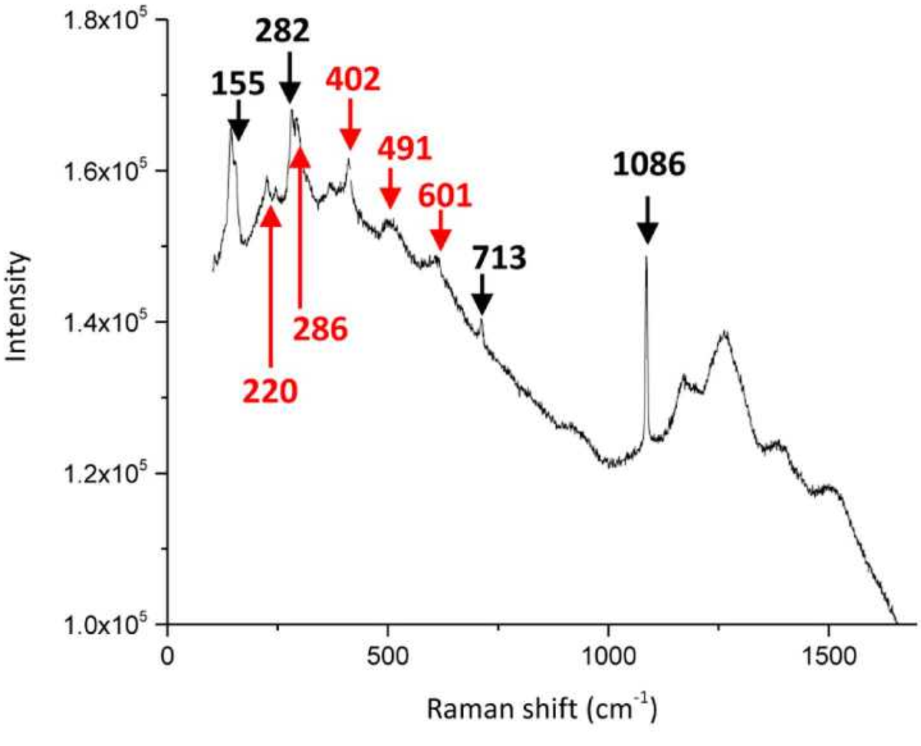
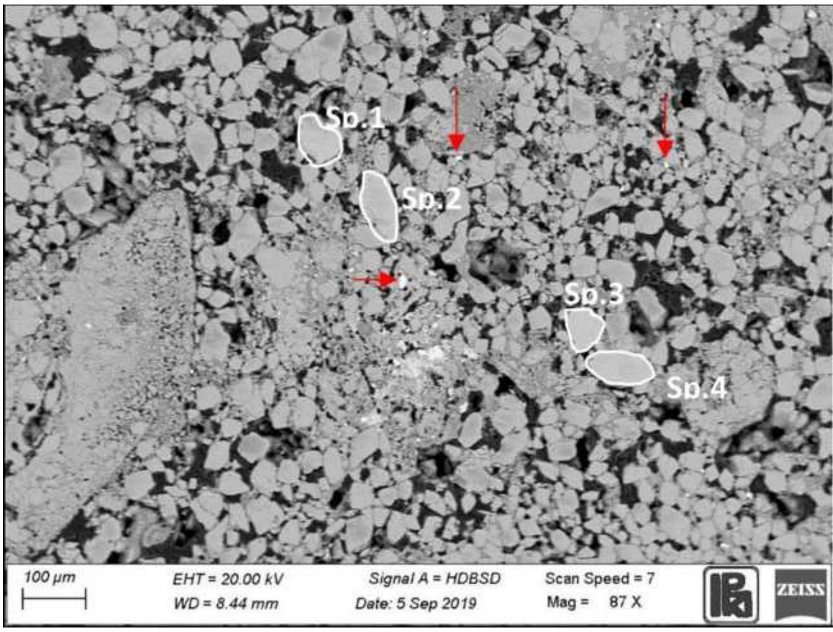


Figure 5. Raman spectrum of the red sediment (R.S.) taken with the 785 nm laser line. The characteristic peaks of calcite are indicated with the black colour and the peaks of hematite with the red colour.



Oxide (wt.%)	Sp. 1	Sp. 2	Sp. 3	Sp. 4
Al_2O_3	n.d.	n.d.	0.5	0.6
SiO_2	n.d.	n.d.	0.4	0.7
CaO	100	100	98.0	97.7
FeO	n.d.	n.d.	1.1	1.0

Figure 6. Backscatter electron image of the R.S. sample. There are calcite particles, some of them indicated with the white outline and smaller iron particles, some of them indicated with red arrows. The analysis of the corresponding areas is shown in the table. *n.d.: not detected.*

During the Palaeolithic period they were used extensively for both ritual and artistic purposes (Stringer and Andrews 2012). They were commonly used as pigments for rock painting but also for wall paintings and plasters. Apart from occurring in a natural deposit, red ochre can also be produced from the extensive heating of yellow earth, another common clay earth pigment dominated by iron oxide-hydroxide (goethite); during this procedure the excess of water which exists in the yellow earth evaporates leaving behind the anhydrous oxides and in particular hematite producing in such way the red ochre. This procedure has been noticed in the Assyrian cuneiform tablets indicating that the technique was already known in Mesopotamia (Thomson 1936). It has also been suggested that, even though this procedure might have been known in Egypt, there might have been no need for its practise because of the rich Egyptian red iron oxide deposits (Colinart *et al.* 1996; Lucas and Harris 1962).

The red sediment was further investigated by SEM analysis. The images (Figure 6) show that there is abundance of many calcite and iron oxide particles as it is indicated. In addition, it is worth noting that there are areas showing an intermediate binder, which contains a material with increased values of Al_2O_3, SiO_2, TiO_2 and FeO, as it is shown in Figure 7. This can be a result of the preparation procedure of a pigment e.g. red ochre (excess heating) or an intermediate medium additive used to keep the soil particles together.

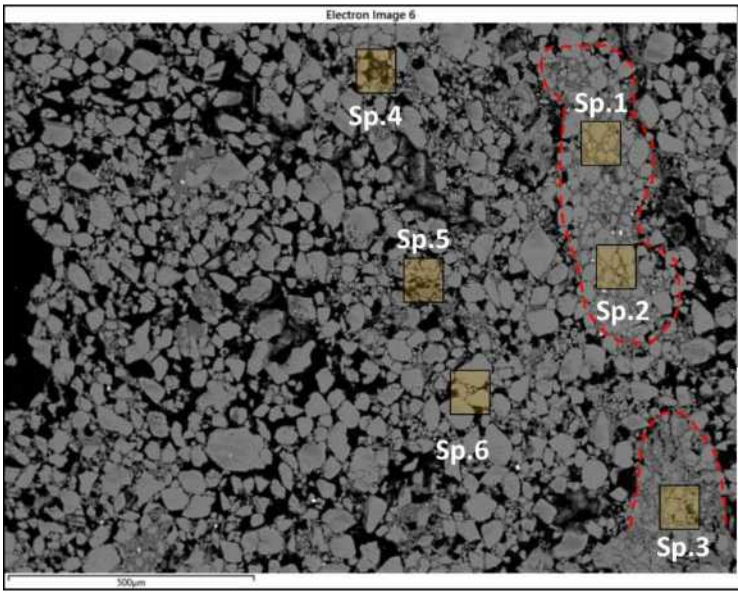
Following the analysis of the red sediment, a fragment of the tripod cooking pot with remnants of the red sediment attached to it was embedded in a resin block and was further examined in cross section with the Scanning Electron Microscope. According to the analysis the red sediment is attached to the fragment and its thickness varied between 20 and 25 µm (Figure 8). In addition, it has slightly higher amounts of iron oxide, most likely due to the existence of hematite.

Interestingly there is also an area between the red ochre and the ceramic body (indicated with the red dashed line Figure 8, Sp.3-4) having high amounts of lime concentration (over 75% wt.).

The main body of the tripod cooking pot shows a typical ceramic composition (Figure 8, Sp.5-6). Also, non-plastic inclusions of various sizes and shapes (Figure 9) are found, which are typical in the ceramic material (fabric) of the vessels. These inclusions are mainly quartz (SiO_2) and aluminosilicate particles. In addition, looking in more detail to the structure of the ceramic we notice areas showing signs of intense vitrification (Figure 10). This can be associated with the exposure of the pot at high temperatures during the manufacturing process.

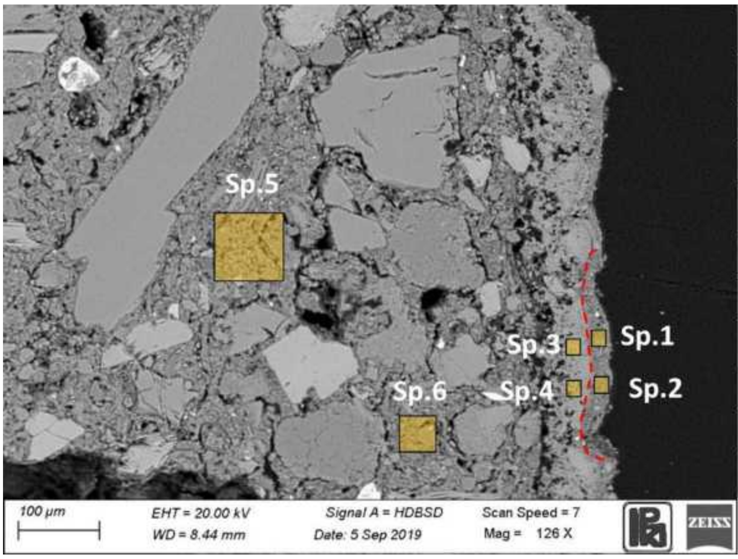
Conclusions

The red sediment, as it was shown from the analysis, contains hematite which is the main component of red ochre pigments. The tripod cooking pot was fired at high temperatures as many areas in the ceramic body showed extensive vitrification. Possibly the tripod cooking pot was used as a red ochre preparation vessel.



Oxide (wt.%)	Sp. 1	Sp. 2	Sp. 3	Sp. 4	Sp.5	Sp.6
MgO	1.2	1.3	1.2	1.0	1.2	0.9
Al_2O_3	14.8	13.8	13.5	7.8	9.8	5.9
SiO_2	21.3	19.5	23.1	11.1	14.4	7.8
K_2O	1.1	1.0	1.2	0.6	0.6	0.4
CaO	55.7	58.1	53.2	76.4	70.5	82.8
TiO_2	0.6	1.0	0.9	n.d.	n.d.	n.d.
FeO	5.3	5.4	6.7	2.7	3.2	1.9

Figure 7. A backscattered electron image of the interparticle area of the R.S. sample acquired by the AZTEC software of the EDS. The analysis of the areas indicated on the image is shown in the adjacent table. *n.d.: not detected.*



Oxide (wt.%)	Sp. 1	Sp. 2	Sp. 3	Sp. 4	Sp.5	Sp.6
Na_2O	0.4	0.2	n.d.	n.d.	1.4	1.9
MgO	2.4	2.2	2.3	2.3	2.5	1.2
Al_2O_3	17.5	21.5	5.3	7.5	18.2	20.0
SiO_2	51.2	51.4	7.7	10.9	63.9	63.1
P_2O_5	0.9	0.4	n.d.	n.d.	n.d.	n.d.
Cl	0.3	0.3	n.d.	n.d.	n.d.	n.d.
K_2O	3.5	2.7	0.4	0.5	1.8	2.0
CaO	15.9	15.0	82.8	77.0	4.4	4.1
TiO_2	0.7	0.6	n.d.	n.d.	1.2	0.9
FeO	7.3	5.6	1.3	1.7	6.3	6.5

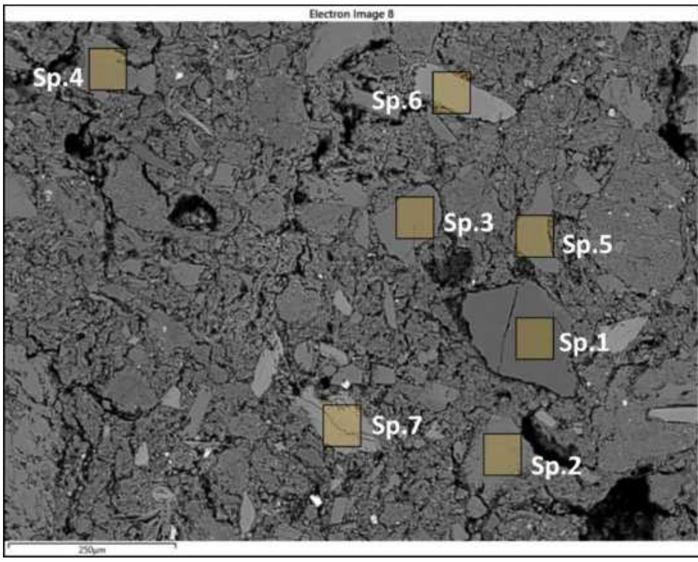
Figure 8. Backscattered electron image of the ceramic body of the cooking pot in cross section. The red line indicates the attached red sediment in the inner surface of the cooking pot. The analysis of the corresponding areas is shown in the table. *n.d.: not detected.*

When yellow ochre is subjected to high temperatures, water vaporizes from the hydrated iron oxides which are converted into hematite. In addition, its use as a container to transport the red sediment/pigment in the area of the building complex at Pyrgiakoni should not be excluded. In either case, the use of a tripod cooking pot for the preparation and/or transportation of red ochre or at least a red pigment having hematite, i.e. in a non-cooking context, is still rare in the Middle-Late Bronze Age of the Aegean, since only a few comparable cases have so far been reported (Koh *et al.* 2016; Veropoulidou *et al.* 2008).

The floor of the large pillared hall (with an area of 60 m^2) of the complex in Pyrgiakoni had remnants of white plaster and due to the lack of indications for frescoes, it is highly likely that this red pigment was used to decorate the floor and/or the rectangular hearth in the center of the hall.

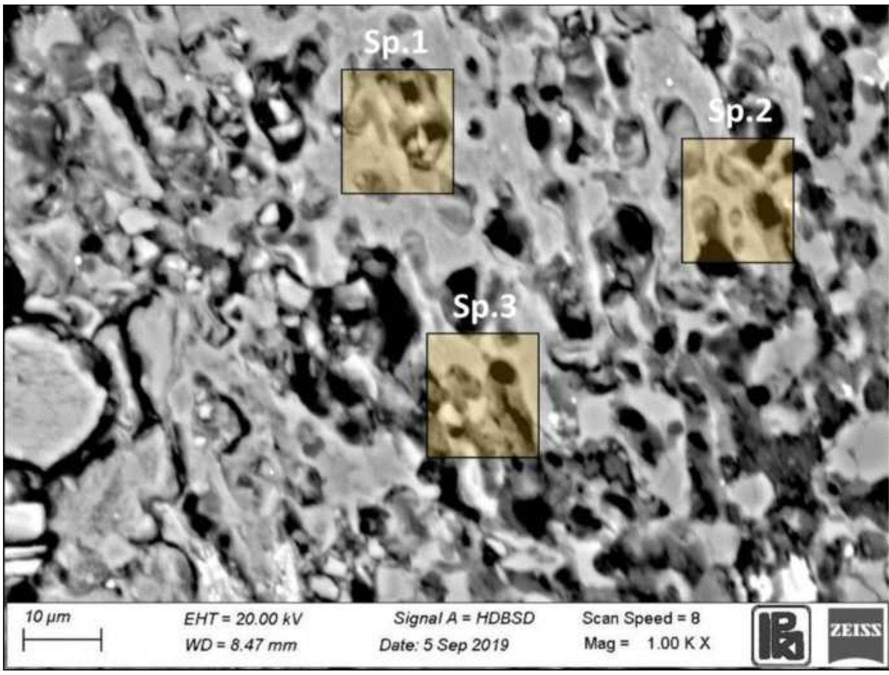
Acknowledgements

We are grateful to Prof. Yannos G. Lolos for his permission to work on the material and his constant support.



Oxide (wt.%)	Sp. 1	Sp. 2	Sp. 3	Sp. 4	Sp.5	Sp.6	Sp.7
Na_2O	n.d.	3.6	5.4	5.5	5.2	1.9	1.1
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	15.3	13.4
Al_2O_3	n.d.	30.9	28.2	28.0	28.7	13.3	9.6
SiO_2	99.7	51.3	55.7	56.0	55.0	43.7	47.2
K_2O	n.d.	n.d.	0.2	0.3	0.2	0.8	0.6
CaO	n.d.	13.8	10.2	10.0	10.6	12.2	11.6
TiO_2	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	1.1
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
FeO	0.3	0.5	0.3	0.4	0.3	11.1	14.7

Figure 9. Typical image of the ceramic fabric of the cooking pot acquired by the AZTEC software of the EDS. The analysis of the non-plastic inclusions is shown in the table. *n.d.: not detected.*



Oxide (wt.%)	Sp. 1	Sp. 2	Sp. 3
Na_2O	1.9	2.2	2.0
MgO	0.3	0.5	0.8
Al_2O_3	19.9	16.8	19.5
SiO_2	70.1	71.1	66.9
Cl	0.4	0.3	0.2
K_2O	2.0	3.4	2.6
CaO	2.3	2.1	2.8
TiO_2	0.5	0.5	0.6
FeO	2.8	3.2	4.6

Figure 10. In various points of the ceramic body of the cooking pot highly vitrified areas were noticed. The analysis of the corresponding feature is shown in the table. *n.d.: not detected.*

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Δυνατότητες και περιορισμοί στη διερεύνηση της τεχνολογίας και των υλικών κατασκευής λάκας αντικειμένου από την Κινέζικη συλλογή του Μουσείου Μπενάκη

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Abstract: This paper presents the research that was undertaken on an 18th century Chinese porcelain vase from the Chinese collection of the Benaki Museum. The object was coated with dark brown *urushi lacquerware* following the *raden* technique with inlayed mother of pearl and the *hyomon* technique with metal foil decoration forming a lakeside landscape with islands, a pavilion, a boat, bamboo groves, and figures of men. Originating from Jingdezhen, Jiangxi province of China, and dating from the Qing dynasty, this artifact was donated by G. Eumorfopoulos to the Museum.

Prior to conservation work was the investigation of artefact's technology and the composition of the coating on lacquer surface which was identified as a previous restoration material. It needs to be pointed out that Asian lacquer technology is an unknown and rare topic for the Greek Culture. The research methodology was based on analyzing samples from the artifact in comparison with reference samples of authentic urushi resins based on protocols of Asian Lacquer decorative techniques. The main questions of this research were related to the chemical composition and behavior of the materials: hydrophobic preparation, glossy lacquer stratigraphy and unknown restoration material. By characterizing the technological elements and the restoration materials, a hypothesis was expressed on the object's provenance, regarding that, if it was for local use or was exportable object, and whether the previous intervention was based on a western or an eastern approach of conservation.

Destructive and non-destructive techniques were employed for the examination and analysis of artifact's technology and materials. Examination of the lacquered surface by an infrared camera, with InGaAs sensor and detection range reaching up to 1100 nm, recorded traces of the lacquer attributed to the polishing method. Besides, examination under ultraviolet light detected the later restoration coating on the object's surface lacquer.

The examination of cross sections through polarized UV-Vis microscopy and SEM-EDS revealed the stratigraphy of the decorative layers. A hydrophobic foundation layer was primarily applied directly on the white porcelain. On top of that, two black lacquer layers, according to the *kiurushi* technique, having different grain sizes were detected containing the elements Fe, Si, and Al. Above the black lacquer layers, a transparent lacquer layer was applied with mother of pearl inlay decoration according to the *raden* technique and an inlay with metal foil (of Sn, and Pb alloys, as analyzed by SEM-EDS) following the *hyomon* technique was recorded through X-ray radiography. Besides protecting the decoration elements, the final clear lacquer layer that was detected also enhanced the lacquer's optical saturation effect and the deep black gloss of the decoration.

ATR-FTIR analysis was carried out on a detached sample of lacquer decoration from the vase, showing the characteristic spectrum of Asian lacquer which, was confirmed by comparison with spectra recorded from authentic reference samples made according to various standard lacquer techniques. Furthermore, significant amounts of organic salt (possibly, acetate) and calcium carbonate were detected in the foundation layers; the binding material was also found to be Asian lacquer.

This paper, taking into consideration the origin and the historic background of the Asian vase, demonstrates a relatively unknown topic for Greek researchers: the decorating techniques of the lacquered Asian artifacts. Furthermore, it presents a methodology involving analytical techniques used by the research team to identify the technology and deterioration of the object, in order to proceed with its conservation. Finally, this research points out the importance of investigating the technology and the materials of the artifact in the wider context of a multi-disciplinary approach which helps to better understand the origin and preservation condition of the object.

KEYWORDS: URUSHI LACQUERWARE, RADEN HYMON, NO DESTRUCTIVE TECHNIQUES, POLARIZE MICROSCOPY, SEM-EDS, ATR-FTIR.

Περίληψη: Η συντήρηση του κεραμικού αγγείου με διακόσμηση ασιατικής λάκας ΓΕ 2897 της Κινέζικης συλλογής του Μουσείου Μπενάκη επέβαλε τη μελέτη της τεχνολογίας κατασκευής και των υλικών διακόσμησης του αγγείου καθώς και τη διερεύνηση των μεταγενέστερων υλικών αποκατάστασης του. Τα δεδομένα αυτά ήταν απαραίτητα ώστε να κατανοηθεί η τεχνολογία κατασκευής του αντικειμένου, να συσχετιστούν τα υλικά που έφερε και τελικά να καταγραφούν οι μηχανισμοί αλλοίωσης και απολέπισης της διακοσμημένης επιφάνειας. Στο παρόν άρθρο παρουσιάζονται οι δυνατότητες και οι περιορισμοί που

Εικόνα 1 Όψη του αντικείμενου #ΓΕ 2897# της Κινέζικης συλλογής του Μουσείου Μπενάκη, φωτογραφία στο ορατό φάσμα.

αντιμετωπίστηκαν κατά τη διάρκεια της έρευνας (εικ. 1).

Η τεχνολογία του αγγείου είναι εξαιρετικά σπάνια για τον Ευρωπαϊκό και ακόμα ειδικότερα, για τον Ελληνικό πολιτισμό. Πρόκειται για αγγείο λευκής πορσελάνης με λευκή εφυάλωση και υπερκείμενη διακόσμηση μαύρης λάκας *urushi lacquerware* με ένθεση μάργαρου[1]/ σεντεφιού τεχνική που χαρακτηρίζεται με τον όρο *raden* και ένθεση μεταλλικών φύλλων, τεχνική που χαρακτηρίζεται με τον όρο *hyomon (Heckmann 2002)*. Για τη μελέτη της διακόσμησης από λάκα ακολουθήθηκε μεθοδολογία που στηρίχτηκε σε δείγματα από κλασσικά ανατολικά πρωτόκολλα αναφοράς κατασκευής τεχνικών λάκας, σε συνδυασμό με την ανάλυση των υλικών του αντικειμένου και τη σύγκριση τους με πρότυπα δείγματα αναφοράς.

Για την ταυτοποίηση των υλικών χρησιμοποιήθηκε συνδυασμός καταστρεπτικών και μη καταστρεπτικών τεχνικών. Με την κάμερα υπερύθρου, με αισθητήρα InGaAs και ευαισθησία που φτάνει τα 1100 nm διαπιστώθηκαν ίχνη της μεθόδου στίλβωσης της λάκας και με παρατήρηση σε υπεριώδη ακτινοβολία κατέστη δυνατή η καταγραφή παλαιότερων επεμβάσεων όπως η μεταγενέστερη ρητίνη στην επιφάνεια του αγγείου.

Η μελέτη μικροτομών στο πολωτικό μικροσκόπιο (ορατό – UV) και στο ηλεκτρονικό μικροσκόπιο σάρωσης SEM με στοιχειακή μικροανάλυση EDS ανέδειξε την στρωματογραφία της διακοσμητικής επιφάνειας. Στην επιφάνεια της πορσελάνης έχει αρχικά εφαρμοστεί στρώμα άκαμπτης και υδρόφοβης προετοιμασίας. Πάνω σε αυτήν την προετοιμασία, παρατηρήθηκαν τρία στρώματα όπου αποδίδουν το σώμα της μαύρης λάκας και διαφοροποιούνται λόγω της διαφορετικής τους κοκκομετρίας με παρουσία των στοιχείων Fe, Si, Al. Στο δεύτερο στρώμα μαύρης λάκας ήταν ένθετα τα διακοσμητικά στοιχεία όπως σεντέφι και μεταλλικά ελάσματα (από κράμα Sn, Pb), διακοσμητικά στοιχεία που αποτυπώθηκαν και με τη μέθοδο ακτινογράφησης. Η τελευταία επίστρωση λάκας, πλαισιώνει τα ένθετα προσοχή στο κόμμα! τα και ενισχύοντας την λάμψη τους μετά την στίλβωση τους κατά το τελευταίο στάδιο της κατασκευής.

Η ανάλυση με φασματοσκοπία υπερύθρου με μετασχηματισμό Fourier (μέθοδος ενισχυμένης ολικής ανάκλασης, ATR-FTIR) εκτελέστηκε σε αποκολλημένο δείγμα της λάκας, κατόπιν σύγκρισης με σύγχρονα δείγματα αναφοράς, έδειξε το αναμενόμενο προφίλ κορυφών της ασιατικής λάκας στην εξωτερική πλευρά του δείγματος. Επί πλέον, στο εσωτερικό λευκό στρώμα προετοιμασίας ανιχνεύθηκε μεγάλη ποσότητα οργανικού άλατος, ανθρακικό ασβέστιο, καθώς και συνδετικό υλικό που αντιστοιχεί σε ρητίνη *urushi.*

Το άρθρο αυτό στοχεύει στην τεχνολογική μελέτη της κατασκευής αντικειμένου με κινεζική λάκα της συλλογής του Μουσείου Μπενάκη, την ταυτοποίηση των υλικών κατασκευής του και με απώτερο σκοπό την αξιοποίηση των αποτελεσμάτων για τη συντήρηση του. Η διαθέσιμη μεθοδολογία αναλυτικών τεχνικών που εφαρμόστηκε παρουσίασε περιορισμούς ως προς την ανίχνευση όλων των στοιχείων της λάκας, παρόλα αυτά κατέστη δυνατός ο εντοπισμός της ασιατικής τεχνικής που σχετίζεται με τη ταυτότητα των υλικών και της τεχνολογίας κατασκευής.

Εισαγωγή

Το αντικείμενο με αριθμό ΓΕ 2897 είναι αγγείο της Κινέζικης συλλογής του Μουσείου Μπενάκη και αποτελεί ένα σπάνιο δείγμα κεραμικού με διακόσμηση τεχνικής με λάκα στην επιφάνεια του. Εξαιρετικά

[1] Το μάργαρο σχηματίζεται σταδιακά στο εσωτερικό του κελύφους ορισμένων οστράκων, είναι γνωστό και με τον όρο σεντέφι (*mother of pearl*). Ως μάργαρο αναφέρεται και η ουσία από την οποία δημιουργείται το μαργαριτάρι.

σπάνιο χαρακτηρίζεται το γεγονός ότι η διακόσμηση λάκας τοποθετήθηκε εξαρχής στο αγγείο και όχι μεταγενέστερα, όπως συνηθιζόταν, ώς τεχνική αποκατάστασης θραύσεων ή και κατασκευαστικών αστοχιών. Ένα ακόμη παρόμοιο αντικείμενο με αυτό του Μουσείου Μπενάκη ανήκει στη συλλογή του Royal Ontario Museum και στη σχετική δημοσίευση τονίζεται η σπανιότητα της διακοσμητικής τεχνικής με λάκα σε άθικτα κεραμικά αγγεία (Webb 2000, 22).

Το κινέζικο αντικείμενο της συλλογής ανήκει στην ευρύτερη κατηγορία αντικειμένων ασιατικής λάκας *urushi laquerware*. Τα αντικείμενα αυτά έχουν αρχαία καταγωγή και αποτελούν χαρακτηριστικά τεχνουργήματα των ασιατικών χωρών με κύριους εκπροσώπους την Ιαπωνία, την Κίνα και την Κορέα (Kopplin 2010). Αντικείμενα ασιατικής λάκας κατασκευάζονταν κυρίως από ξύλο και δευτερεύοντος από μπαμπού, μέταλλο, δέρμα, ταρταρούγα και σπάνια από κεραμικά και πορσελάνη (Webb 2000). Οι επιφάνειες των υλικών αυτών επικαλύπτονταν με πολλά στρώματα λάκας και στις περισσότερες περιπτώσεις είχαν ενσωματωμένες περίτεχνες διακοσμήσεις (Heckmann 2002). Χαρακτηριστικά δείγματα της τέχνης αυτής αποτελούν σκεύη, αντικείμενα καθημερινής χρήσης, εσωτερικά ναών, πανοπλίες. Ο κύριος ρόλος των αντικειμένων λάκας ήταν αισθητικός και ταυτόχρονα λειτουργικός και τελετουργικός, ενώ κατά την ασιατικό πολιτισμό αποτελούν φορέα της αισθητικής, της ιστορίας και της μεταφυσικής του παρελθόντος (Kitamura 1998). Το ίδιο το υλικό *urushi* ήδη από την αρχαιότητα είχε αναχθεί σε πολιτισμικό σύμβολο των χωρών αυτών και αντανακλούσε υλικά και άυλα στοιχεία κουλτούρας και επιρροών (Σαμπατάκος 2013).

Για την κατασκευή και διακόσμηση των αντικειμένων αυτών έχουν καθιερωθεί τεχνικές με αυστηρά τεχνικά πρωτόκολλα και υλικά κατασκευής, εκπληκτική σχολαστικότητα και τεχνικές απαιτήσεις που παρήγαγαν εντυπωσιακά έργα. Το κύριο συνδετικό μέσο για την κατασκευή της λάκας είναι η ρητίνη *urushi* και προέρχεται από τη χυμό του δέντρου *rhus verniciflluka (Webb 2000)*. Για τη συλλογή και επεξεργασία αυτής από το χυμό του δέντρου, υπάρχουν αυστηρές τεχνικές που ακολουθούνται και δίνουν *urushi* με διαφορετικές ιδιότητες διαφάνειας, χρωματισμού, στιλπνότητας, κολλητικών ιδιοτήτων και αντοχής (Kopplin 2010; Σαμπατάκος 2013). Η συγκεκριμένη ρητίνη είναι ένα φυσικό πολυμερές, υπό μορφή γαλακτώματος λαδιού-σε-νερό με κύριο συστατικό την *urushiol*, η οποία είναι μια πολυφαινόλη που με την παρουσία ένζυμων και σε συνθήκες υψηλής υγρασίας υφίσταται πολυμερισμό σχηματίζοντας δεσμούς διασταύρωσης (Du 1985). Το *urushi* είναι ένα θερμοσκληραινόμενο πολυμερές καθώς μετά τον πλήρη πολυμερισμό σχηματίζεται ως προϊόν αδιάλυτο σε όλους τους γνωστούς διαλύτες και το οποίο παρουσιάζει εξαιρετική χημική και μηχανική σταθερότητα (McSharry *et al.* 2007; Jaeschke 1994; Σαμπατάκος 2013).

Το *urushi* στην υγρή του μορφή είναι χημικά ενεργό και μπορεί να μεταβάλλει το χρώμα των περισσότερων φυσικών χρωστικών που αναμιγνύονται με αυτό, με αποτέλεσμα η παλέτα χρωμάτων λάκας να είναι περιορισμένη. Ο μαύρος χρωματισμός της ρητίνης τύπου *roiro urushi* επιτυγχάνονταν με χημική μεταβολή του *urushi* με προσθήκη υδροξειδίων του σιδήρου ή οξικού σιδήρου καθώς και με την προσθήκη ξυδιού από ρύζι (Barchalia 1988). Μαύρο *urushi* επίσης παρασκευαζόταν αναμιγνύοντάς το με τη χρωστική «μαύρο του άνθρακα» (carbonblack). Για τη δημιουργία κόκκινου *urushi*, τύπου *shu-urush* χρησιμοποιούνταν κιννάβαρι (θειούχος υδράργυρος), ή πιο σπάνια, αιματίτης (οξείδιο του σιδήρου) (Kitamura 1988; Webb 2000). Στο εύρος των υλικών που εφαρμόζονταν για τις τεχνικές διακόσμησης που χρησιμοποιούσαν συχνά οι καλλιτέχνες ήταν σκόνες και φύλλα από μέταλλα όπως χρυσό, ασήμι, κασσίτερος, μάργαρο, ελεφαντόδοντο, δέρματα, διαφόρων σχημάτων και διαστάσεων (Σαμπατάκος 2013; Kitano 2009; Webb 2000).

Η βασική τεχνολογία κατασκευής, στηρίζεται στη διαστρωμάτωση της λάκας πάνω στον εκάστοτε φορέα και αποτελείται από τα στρώματα προετοιμασίας σαν βάση, στην συνέχεια από τα πολλαπλά στρώματα λάκας με ενδιάμεσες στιλβώσεις που διαδοχικά αποκτούν διαφάνεια και πάνω ή μέσα σε αυτά διακρίνονται τα είδη διακόσμησης και σύνθεσης (Σαμπατάκος 2013). Τα συνολικά στρώματα μπορούν να ξεπερνούν σε πολλές περιπτώσεις τα 100 και ανάλογου αριθμού είναι οι ιστορικές τεχνικές διακόσμησης που έχουν καταγραφεί σε αντικείμενα (Heckmann 2002; Kopplin 2010).

Εξαιρετικού ενδιαφέροντος αποτελεί το γεγονός ότι ήταν σύνηθες για τα αντικείμενα που προορίζονταν για εξαγωγή στη Δύση να απλουστεύονται οι τεχνικές κατασκευής τους και να νοθεύονται τα υλικά για οικονομία και συντόμευση του χρόνου παραγωγής και παράδοσης (Kitano 2009; Heckmann 2002). Ως εκ τούτου τα αντικείμενα που ήταν κατασκευασμένα για να εξαχθούν στη Δύση σε πολλές περιπτώσεις παρουσιάζουν αδυναμία συνοχής των υλικών τους και μειωμένη αντοχή (Lambooy 2005). Σαν παράδειγμα αναφέρεται ότι το κύριο συνδετικό υλικό στα στρώματα προετοιμασίας *kiurushi*[2] αντικαθίστατο, στα αντικείμενα προς εξαγωγή, από ζωικές κόλλες (Heginbotham *et al.* 2016). Οι διαφορές των έργων αυτών σε σύγκριση με τα αντίστοιχα που προορίζονταν για την εγχώρια αγορά είναι τόσο μεγάλες που ομαδοποιούνται σε ειδική κατηγορία με την ονομασία «εξαγώγιμη λάκα»

[2] *Kiurushi* ονομάζεται το *Urushi* που χρησιμοποιείται μετά την συγκομιδή του χωρίς να έχει προηγηθεί σε αυτό κάποιο είδος επεξεργασίας. Περιέχει μεγάλη ποσότητα σε νερό, στοιχείο που του προσδίδει ιδιαίτερες συγκολλητικές ιδιότητες. Χρησιμοποιείται στα στρώματα προετοιμασίας.

exported lacquer. Λόγω της ιδιαίτερης κατασκευής και παθολογίας τους η μεθοδολογία αποκατάστασης τους διαφοροποιείται από αυτή που ακολουθείται στα αντίστοιχα έργα της ασιατικής αγοράς (Van Bellegem *et al.* 2010; Schellmann 2008).

Η δεοντολογία και η πρακτική αποκατάστασης / συντήρησης αντικειμένων από λάκα αποτελεί ένα αρκετά σύνθετο πεδίο με σαφείς διαχωρισμούς μεταξύ «ανατολικής» και «δυτικής» σχολής συντήρησης. Οι δύο σχολές παρουσιάζουν διακριτές διαφορές ως προς την ηθική προσέγγιση της συντήρησης που σε πρακτικό επίπεδο διαφοροποιείται ανάμεσα στην πλήρη αποκατάσταση και στην σταθεροποίηση - συντήρηση των έργων (Rivers 2005). Τα αντικείμενα αυτά, λόγω της χρήσης τους, φέρουν εκτεταμένες φθορές, απώλειες υλικού και διακόσμησης που σε συνδυασμό με τον λειτουργικό σκοπό τους και την υψηλή αισθητική τους έχουν μεγαλύτερη ανάγκη για αποκατάσταση. Η «ανατολική» προσέγγιση χρησιμοποιεί τα ίδια υλικά και τεχνικές αποκατάστασης με τα αυθεντικά, αποσκοπώντας στην επαναφορά της αισθητικής ακεραιότητας και της αυθεντικότητας των έργων και των υλικών τους. Στόχος της «ανατολικής» προσέγγισης αποτελεί η μετάβαση του νοήματος και της αισθητικής λεπτότητας του έργου στις επόμενες γενεές (Nakajima 1985). Η «δυτική» προσέγγιση αποκατάστασης πραγματοποιείται με σύγχρονα υλικά που είναι τελείως διαφορετικά σε χημική σύσταση από τα αυθεντικά, με στόχο την σταθεροποίηση της φθοράς και των απωλειών καθώς και την διακριτικότητα της επέμβασης (Rivers 2005; Miklin-Kniefcz 1999). Το εξαιρετικά περίπλοκο αυτό ζήτημα αντιμετωπίζεται ακροθιγώς στο παρόν άρθρο με σκοπό να επισημανθεί το γεγονός ότι τα αντικείμενα ασιατικής λάκας στη Δύση είναι δυνατό να φέρουν ποικίλα υλικά και φιλοσοφίες αποκατάστασης, ως αποτέλεσμα της διαδρομής και της βιογραφίας του κάθε αντικειμένου (Kitamura 1988; Σαμπατάκος 2013).

Από τον 16ο -17οαιώνα η αυξημένη ζήτηση ασιατικών αντικειμένων στο δυτικό κόσμο και η μειωμένη εξαγωγή τους από την Ασία δημιούργησαν την ανάγκη κατασκευής απομιμήσεων τους στην Δύση χρησιμοποιώντας ευρωπαϊκά υλικά, φυσικές ρητίνες και ξεραινόμενα έλαια. Τα αντικείμενα αυτά και η τεχνική απομίμησης της λάκας ονομάστηκαν ευρωπαϊκές λάκες ή *Japanning (Ballardie 1994)*. Οι τεχνικές αυτές κατέκτησαν αυτόνομη παρουσία στην κατασκευή διακοσμημένων τεχνουργημάτων και εξελίχθηκαν ως αυτόνομα έργα στους αιώνες που ακολούθησαν (McSharry *et al.* 2007). Στον τομέα της ταυτοποίησης, μελέτης και συντήρησης των αντικειμένων λάκας σε ορισμένες περιπτώσεις καθίσταται δύσκολο να διαφοροποιηθούν οι παραπάνω ευρωπαϊκές τεχνικές από τις ασιατικές. Για ορισμένα αντικείμενα δεν είναι δυνατό μακροσκοπικά, εικονογραφικά, ή μέσω των χαρακτηριστικών τους να καθοριστεί με βεβαιότητα αν αυτά κατασκευάστηκαν με ασιατικά ή ευρωπαϊκά υλικά και τεχνικές. Γίνεται λοιπόν αντιληπτό ότι ανάλογα κρίσιμα ερωτήματα καθορίζουν την ταυτότητα καθώς και την προσέγγιση συντήρησης του κάθε αντικειμένου (Webb 2000; Lambooy 2005).

Το πιο πάνω θεωρητικό πλαίσιο καθιστούσε σαφές την ανάγκη απάντησης ενός συνόλου ερωτημάτων πριν την διαμόρφωση της πρότασης για την συντήρηση του κινέζικου αγγείου του Μουσείου Μπενάκη. Παράλληλα, ήταν ξεκάθαρο ότι νέα δεδομένα σχετικά με την ταυτότητα των υλικών, την τεχνολογία κατασκευής και τις παλαιότερες επεμβάσεις θα εμπλούτιζαν τα ζητήματα προέλευσης και ιστορίας του αντικειμένου.

Σε διερευνητικό επίπεδο, ένα κύριο ζήτημα αφορούσε το ερώτημα εάν το αντικείμενο του μουσείου Μπενάκη ήταν έργο ασιατικής ή ευρωπαϊκής τεχνοτροπίας λάκας. Αν δηλαδή, τα κύρια υλικά κατασκευής περιείχαν ρητίνη *urushi* ή άλλες φυσικές ρητίνες. Στην περίπτωση που επρόκειτο για έργο ασιατικής λάκας κρίσιμο ήταν να εκτιμηθεί αν το αντικείμενο προορίζονταν για την ασιατική ή την ευρωπαϊκή αγορά. Ως εκ τούτου διατυπωθήκαν έμμεσα ερωτήματα σχετικά με την σύσταση υλικών και την ποιότητα κατασκευής της λάκας, τα μέσα στίλβωσης και διαστρωμάτωσης της (την σύσταση του προστύμματος συγκόλλησης του μάργαρου και των μεταλλικών φύλλων). Παράλληλα, καθοριστικής σημασίας ήταν να εντοπιστεί η σύσταση του επικαλυπτικού υλικού που εμφανώς αποτελούσε μεταγενέστερη επέμβαση, πιθανώς κατά τη διάρκεια προηγούμενης φάσης συντήρησης του αντικειμένου.

Μεθοδολογία

Το αντικείμενο της Κινέζικης συλλογής του Μουσείου Μπενάκη είναι διαστάσεων 35,5 εκ.(ύψος) με διάμετρο στομίου 7 εκ., μέγιστο άνοιγμα στο κέντρο 22 εκ. και διάμετρο βάσης 10 εκ. (εικ. 1). Πρόκειται για αγγείο με λευκή εφυάλωση και επικάλυψη μαύρης - σκούρας καστανής λάκας με ένθετη διακόσμηση, εγχάρακτα κομμάτια μάργαρου, τεχνική *raden* και μεταλλικών φύλλων, τεχνική *hyomon* που σχηματίζουν τοπίο με λίμνη, νησιά, περίπτερο, βάρκα, μπαμπού και μορφές ανδρών (εικ. 2). Το αντικείμενο προέρχεται από την Κίνα, επαρχία Jiangxi, από την πόλη Jingdezhen. Ανήκει στην Δυναστεία Qing όπου χρονολογείται στο 18ο αι. μ.Χ. και είναι δωρεά του Γεωργίου Ευμορφόπουλου (Ashton 1939).

Για τη μελέτη και τεκμηρίωση του αντικειμένου εφαρμόστηκαν καταστρεπτικές και μη καταστρεπτικές τεχνικές, η επιλογή των οποίων καθορίστηκε κυρίως από τη διαθεσιμότητα του εξοπλισμού στα συνεργαζόμενα ιδρύματα. Η φωτογραφική τεκμηρίωση[3]

[3] Η φωτογραφική τεκμηρίωση, η εξέταση του αντικειμένου στο

Εικόνα 2 Λεπτομέρεια από τη διακόσμηση του αντικείμενο #ΓΕ 2897#, φωτογραφία στο ορατό φάσμα.

πραγματοποιήθηκε με ψηφιακή κάμερα Nikon D3000 στο ορατό και υπεριώδες φάσμα και για τη διέγερση της επιφάνειας χρησιμοποιήθηκαν λαμπτήρες τεχνητού φωτισμού Philips Argaphoto – BM. Για την εξέταση και φωτογράφιση στην υπέρυθρη περιοχή (900-1100nm) χρησιμοποιήθηκε κάμερα υπερύθρου, με αισθητήρα InGaAs. Η εξέταση του φθορισμού στην ορατή περιοχή (420-700 mm) έγινε με διέγερση υπεριώδους ακτινοβολίας χρησιμοποιώντας φωτιστικές πηγές Black-Ray B100 nm. Για την ακτινογράφηση[4] του αντικειμένου χρησιμοποιήθηκε συσκευή digital radiography της General Electric (με συνθήκες 25V-6 mAs). Η επιφάνεια του αντικείμενου εξετάστηκε στο οπτικό στερεομικροσκόπιο Olympus SZ40 με φωτιστικές πηγές οπτικών ινών τύπου Olympus KL1500 σε X10 μεγέθυνση. Δύο αποκολλημένα τμήματα της διακόσμηση από το χείλος του αγγείου και από τη βάση του εξετάστηκαν με μικροσκοπικές μεθόδους. Αρχικά έγινε παρατήρηση και εξέταση της δομής των δειγμάτων στο πολωτικό μικροσκόπιο Olympus Provis AX70, με σύστημα ανακλώμενου φωτός (ορατού και υπεριώδους). Οι τομές μετά από την παρατήρησή τους στο πολωτικό μικροσκόπιο μελετήθηκαν και στο ηλεκτρονικό μικροσκόπιο σάρωσης SEM[5] (FEI Quanta Inspect), energy dispersive X-ray spectrometer (EDS) και στο ηλεκτρονικό μικροσκόπιο σάρωσης SEM[6](JEOLJSM-6510LV Quanta Inspect), energy dispersive X-ray spectrometer (EDS). Συγκριτικό πλεονέκτημα του SEM αποτελεί η μεγάλη δυνατότητα ανάλυσης, καθώς η στοιχειακή ανάλυση γίνεται σε επιλεγμένες περιοχές (Lambooy 2005; Kenjo 1985).

Η μοριακή ανάλυση της ασιατικής λάκας αποτελεί μια σημαντική πρόκληση, καθώς, όπως έχει ήδη αναφερθεί κατά τη διαδικασία πολυμερισμού, στο *urushi* σχηματίζεται ένα εξαιρετικά πυκνό σύστημα ενδομοριακών δεσμών διασταύρωσης (crosslinks) που καθιστούν τη ρητίνη αδιάλυτη σε οργανικούς διαλύτες, με εξαιρετική χημική και μηχανική σταθερότητα (Du 1985; McSharry *et al.* 2007. Η ιδιότητα αυτή της λάκας αποτελεί αφενός σημαντικό πλεονέκτημα σταθερότητας του υλικού, αφετέρου, καθιστά εξαιρετικά δύσκολη τη χημική ανάλυση της με συμβατικές μεθόδους και απαιτείται περεταίρω διαλυτοποίηση και χημική επεξεργασία του υλικού. Στην περίπτωσή μας, εφαρμόστηκε η υπέρυθρη φασματοσκοπία με μετασχηματισμό Fourier[7]με την τεχνική ενισχυμένης ολικής ανάκλασης (FTIR-ATR).

Αποτελέσματα

Τα Κινέζικο αγγείο του μουσείου Μπενάκη αποτελείται από στρώματα λάκας σε λευκή εφυάλωση. Η μαύρη

ορατό, υπέρυθρο και υπεριώδες φάσμα καθώς και εξέταση των δειγμάτων στο οπτικό στερεομικροσκόπιο και στο πολωτικό μικροσκόπιο, εκτελέστηκαν στα εργαστήρια συντήρησης του Μουσείου Μπενάκη.

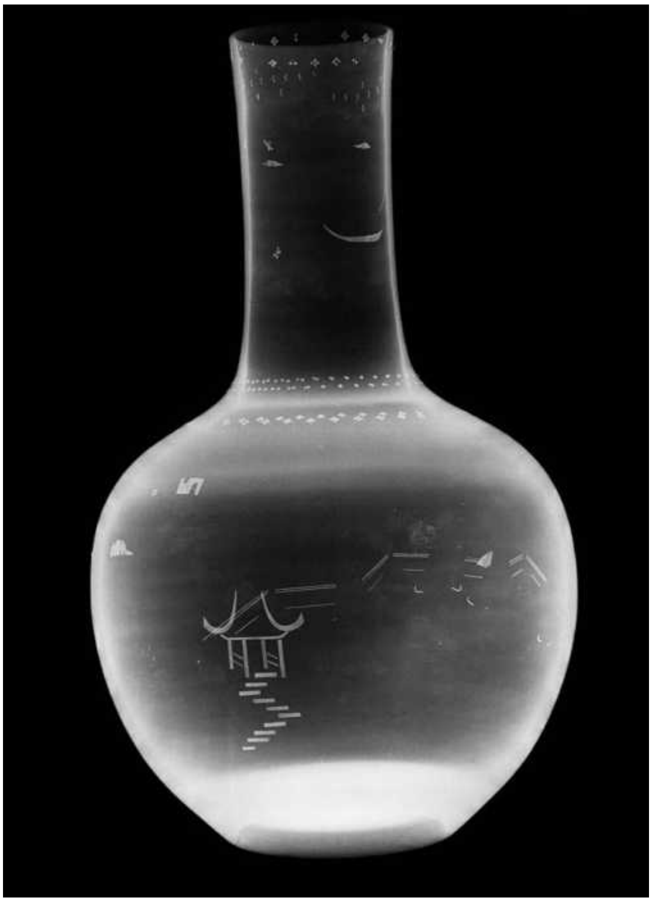
[4] Η ακτινογράφηση του αντικειμένου εκτελέστηκε στο διαγνωστικό κέντρο Ακτινοδιάγνωση.

[5] Η ηλεκτρονική μικροσκοπία εκτελέστηκε στις εγκαταστάσεις του ΕΚΕΦΕ «Δημόκριτος».

[6] Η ηλεκτρονική μικροσκοπία εκτελέστηκε στις εγκαταστάσεις του Πανεπιστημίου Δυτικής Αττικής.

[7] Η μέθοδος υπέρυθρης φασματοσκοπίας με μετασχηματισμό Fourier εκτελέστηκε στις εγκαταστάσεις του Πανεπιστημίου Δυτικής Αττικής.

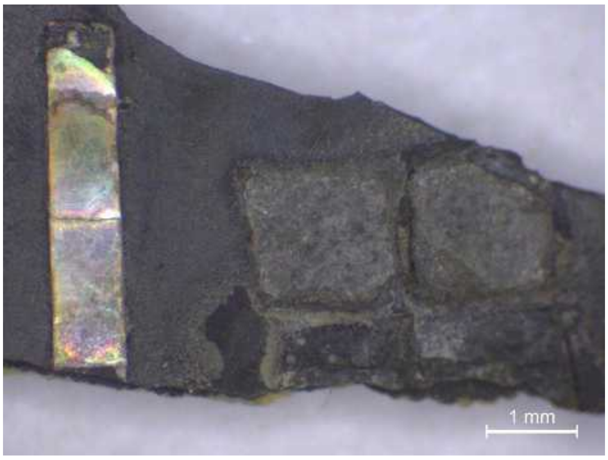
Εικόνα 3α Όψη του αντικείμενου #ΓΕ 2897# της Κινέζικης συλλογής του Μουσείου Μπενάκη, φωτογραφία στο ορατό φάσμα.



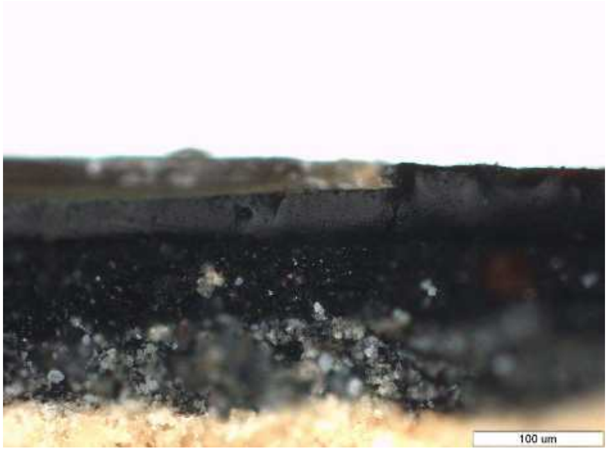
Εικόνα 3β Αποτύπωση των μεταλλικών διακοσμητικών με τη μέθοδο ακτινογράφησης.

λάκα φέρει ενσωματωμένη διακόσμηση από λεπτά φύλλα μάργαρου με την τεχνική *raden* και μεταλλικά φύλλα με την τεχνική *hyomon* (Webb 2000; Nakasato 1985). Η χρήση των δύο διαφορετικών διακοσμητικών υλικών στη σύνθεση των παραστάσεων δεν είναι άμεσα διακριτή, τα μεταλλικά τμήματα εντάσσονται αρμονικά στη διακοσμητική σύνθεση και παρουσιάζουν μικρό μέγεθος από 2 εκ το μεγαλύτερο έως 1,5 χιλ το μικρότερο. Πλήρης αποτύπωση των μεταλλικών διακοσμητικών έγινε κατά την ακτινογράφηση του αγγείου όπου και καταγράφονται οι θέσεις των μεταλλικών φύλλων (εικ. 3α, 3β) (Milam *et al.* 1985).

Τα ένθετα διακοσμητικά στοιχεία έχουν ενταχτεί στη διαστρωμάτωση, με τη διαδικασία εφαρμογής πολλαπλών επιστρώσεων λάκας πάνω στην επιφάνεια του αγγείου ακολουθώντας τα πρότυπα των τεχνικών raden και hyomon. Τα λεπτά φύλλα μάργαρου και τα μεταλλικά φύλλα πάχους 20 μm είχαν τοποθετηθεί πάνω στη επιφάνεια της μαύρης χρωματισμένης λάκας πριν αυτή στεγνώσει και κατόπιν επικαλύφθηκαν με πολλαπλές στρώσεις διάφανης λάκας με σκοπό να εγκιβωτιστούν μέσα στο στρώμα αυτό (εικ. 4).



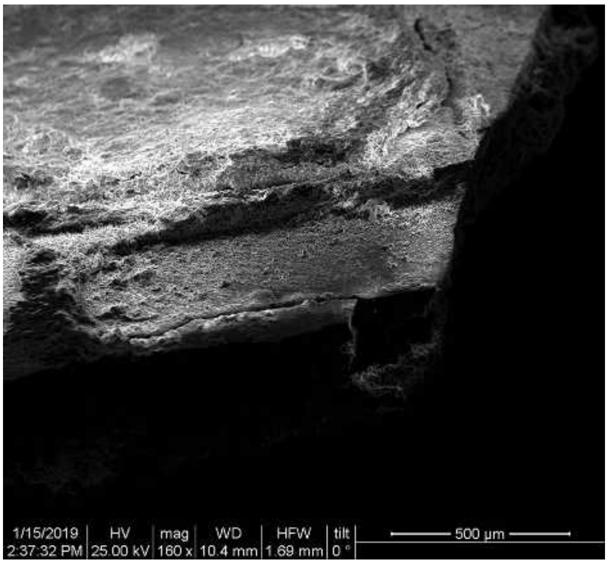
Εικόνα 4 Δείγμα διακόσμησης, εξέταση στο μικροσκόπιο. Διακρίνονται τα διακοσμητικά φύλλα από μέταλλο και μάργαρο που είχαν τοποθετηθεί πάνω στη επιφάνεια της μαύρης χρωματισμένης λάκας. Η επιφάνεια του δείγματος καλύπτεται από μεταγενέστερη ρητίνη συντήρησης που παρουσιάζει ρωγμάτωση, συρρίκνωση και χρωματική μεταβολή.

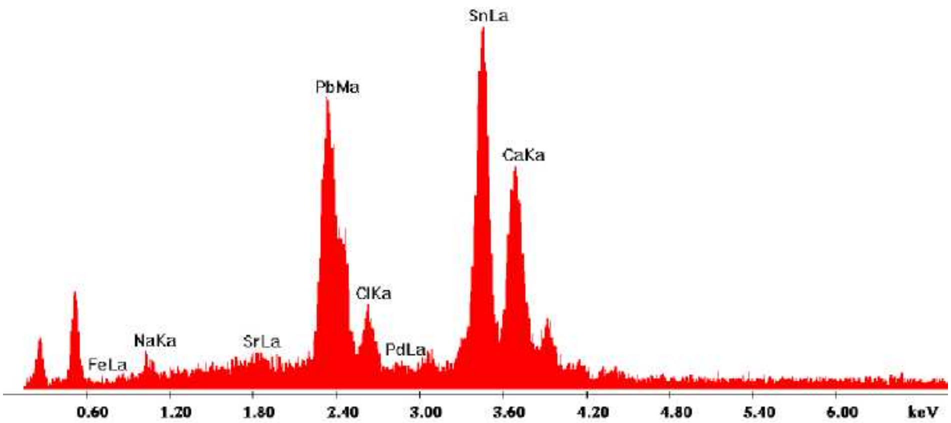


Εικόνα 5 Εγκάρσια τομή του δείγματος της διακόσμησης στο πολωτικό μικροσκόπιο, διακρίνεται ότι τα διακοσμητικά φύλλα είναι εγκιβωτισμένα στο στρώμα λάκας.

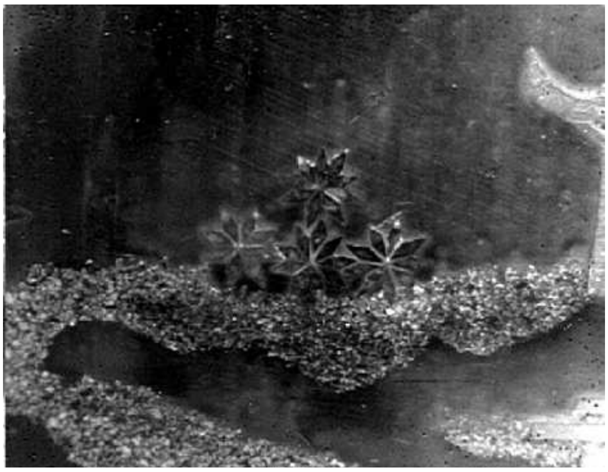
Η διαστρωμάτωση αυτή είναι εμφανής στο δείγμα που προήλθε από το στόμιο του αγγείου το οποίο έφερε διακόσμηση από μάργαρο και μέταλλο. Η τομή του δείγματος εξετάστηκε στο πολωτικό μικροσκόπιο με ανακλώμενο φωτισμό (ορατό και υπεριώδες) και ήταν διακριτά τέσσερα βασικά στρώματα στη τεχνολογία κατασκευής της διακοσμητικής επιφάνειας της λάκας (εικ. 5).

Κατά την εξέταση του δείγματος στο ηλεκτρονικό μικροσκόπιο σάρωσης SEM και με την εφαρμογή της στοιχειακής ανάλυσης EDS διαπιστώθηκε ότι το μεταλλικό φύλλο είναι κράμα μολύβδου - κασσίτερου και επιβεβαιώνεται βιβλιογραφικά η χρήση του στα αντικείμενα ασιατικής λάκας λόγω της σταθερότητας που παρουσιάζει στη διάβρωση (εικ. 6α, 6β) (Van Bellegemetal 2010).

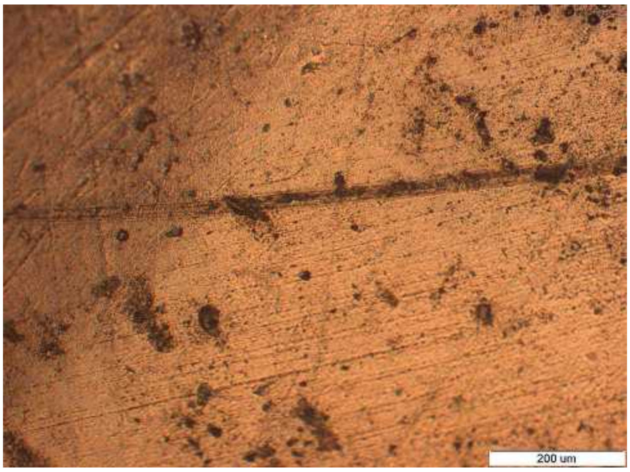




Εικόνες 6α, 6β Εξέταση του δείγματος διακόσμησης στο SEM (6α). Διάγραμμα στοιχειακής ανάλυσης EDS του μετάλλου, ανιχνεύτηκαν στοιχεία Pb, Sn (6β).



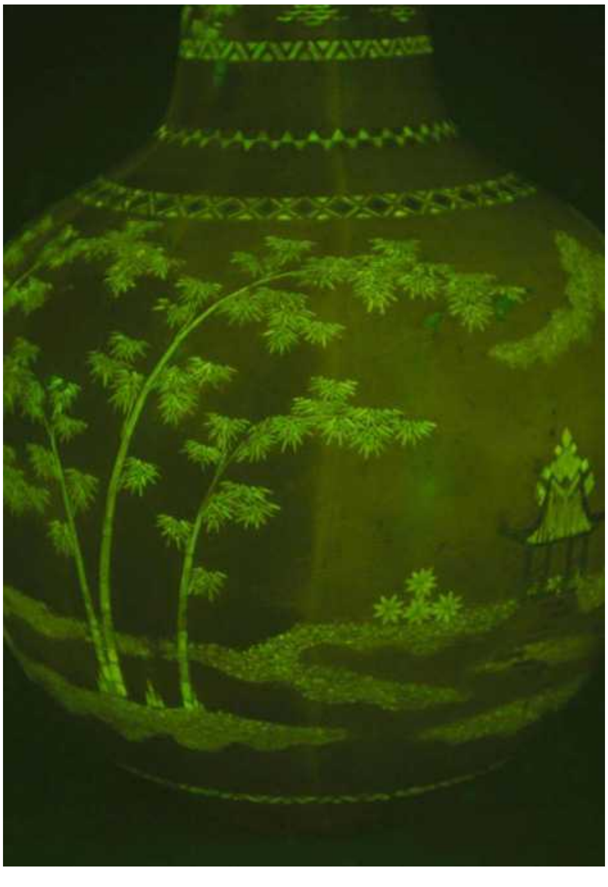
Εικόνα 7α Φωτογραφία στο υπέρυθρο φάσμα με την κάμερα υπερύθρου ως 1100 nm, διαπιστώθηκαν ίχνη από τη μέθοδο στίλβωσης της λάκας.



Εικόνα 7β Χαράξεις στίλβωσης σε δείγματα της επιφάνειας της λάκας στο πολωτικό μικροσκόπιο.

Με την εξέταση του αντικειμένου στο υπέρυθρο φάσμα με την κάμερα υπερύθρου που φτάνει τα 1100 nm, διαπιστώθηκαν ίχνη από τη μέθοδο στίλβωσης της λάκας. Αντίστοιχα χαράξεις στίλβωσης παρατηρήθηκαν και στα δείγματα από την επιφάνειας της λάκας τα οποία εξετάστηκαν στο πολωτικό μικροσκόπιο (εικ. 7α, 7β). Η στίλβωση της λάκας γινόταν με μέθοδο επαναλαμβανόμενης λείανσης της επιφάνειας με ψήγματα κάρβουνου ή/και σκόνης οστράκων (Webb 2000; Miklin-Kniefacz 1999).

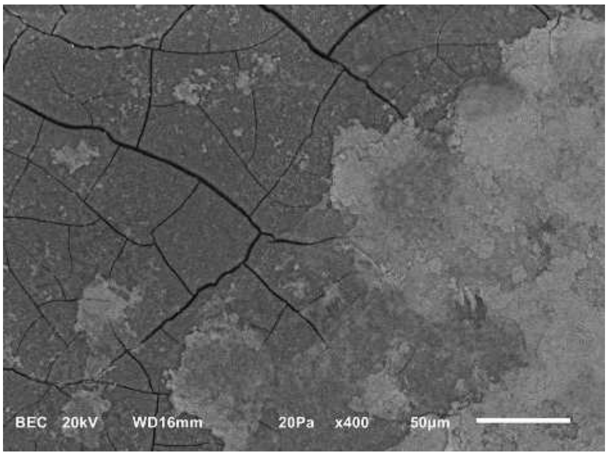
Το αντικείμενο διατηρούσε στην επιφάνεια του λεπτό στρώμα ρητίνης γεγονός που προβλημάτισε ως προς την προέλευση της, καθότι ρητίνες παρατηρούνται σε αντικείμενα ευρωπαϊκής καταγωγής με τεχνική απομίμησης της λάκας όπου ονομάζονται ευρωπαϊκές λάκες ή Japanning (Webb 2000; Lambooy 2005; Ballardie 1994). Η ρητίνη που διατηρούσε το αντικείμενο ήταν διαλυτή στο νερό, παρουσίαζε έντονη φωτοξείδωση και χρωματική αλλοίωση και εμφάνιζε διακριτό φθορισμό στο υπεριώδες φάσμα. Με βάση τα παραπάνω στοιχεία η ρητίνη μπορεί να χαρακτηριστεί ως υλικό μεταγενέστερης επέμβασης «ρητίνη συντήρησης» και αξιολογώντας την διαλυτότητα της στο νερό, θα μπορούσε να προσδιοριστεί ως φυτικής ή ζωικής προέλευσης όπως είναι το αραβικό κόμμι ή κουνελόκολλα (εικ. 8) (Mills *et al.* 1987). Διαπιστώθηκε επίσης απώλεια της στιλπνότητας και βάθος των χρωμάτων, γεγονός που οφείλεται στην οξείδωση της μεταγενέστερης «ρητίνης συντήρησης». Η τοπική χρωματική μεταβολή της μαύρης λάκας σε καφέ χρώμα, αξιολογήθηκε ότι οφείλεται σε φαινόμενο φωτοξείδωσης ως αποτέλεσμα της διαδικασίας φυσικής γήρανσης της λάκας (εικ. 9α, 9β) (Han *et al.* 2018; McSharry *et al.* 2007; Coueignoux *et al.* 2015; Jaeschke 1994).



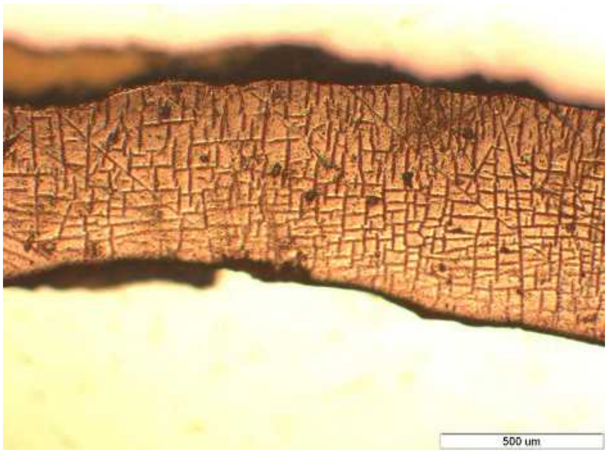
Εικόνα 8 Φωτογραφία στο υπεριώδες φάσμα, περιοχή με ρητίνη μεταγενέστερης επέμβασης παρουσιάζει διακριτό φθορισμό.

Το αντικείμενο παρουσίαζε αποκολλήσεις και τοπικές απώλειες της λάκας κυρίως στο στόμιο και στη βάση και εκτιμήθηκε ότι οφείλονται στη κακή συνοχή -προσρόφηση του στρώματος προετοιμασίας με την

Εικόνες 9α, 9β Το αντικείμενο παρουσίαζε αποκολλήσεις και τοπικές απώλειες της λάκας κυρίως στο στόμιο και στη βάση καθώς και κατά περιοχές χρωματική μεταβολή της μαύρης λάκας σε καφέ χρώμα.



Εικόνα 10 Φωτογραφία SEM καθώς διαπιστώθηκε ότι η επιφάνεια της λάκας έφερε μικρορωγματώσεις.

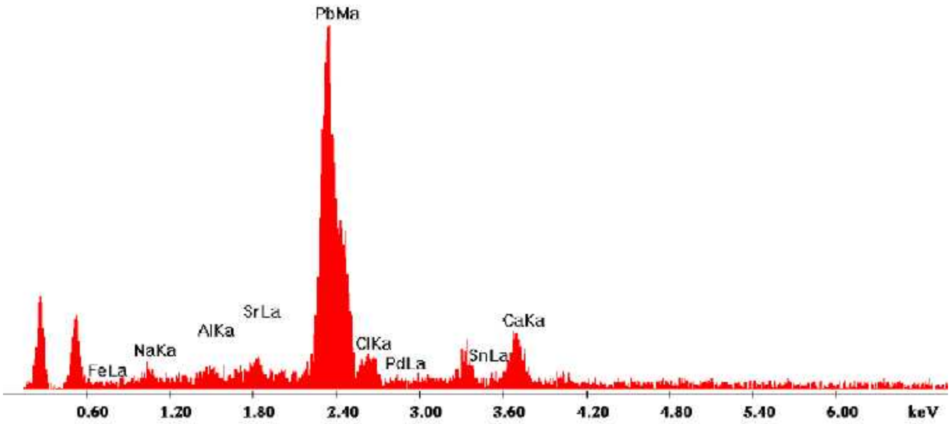


Εικόνα 11 Συρρίκνωση και ρωγμάτωση της ρητίνης, φωτογραφία στο πολωτικό μικροσκόπιο.

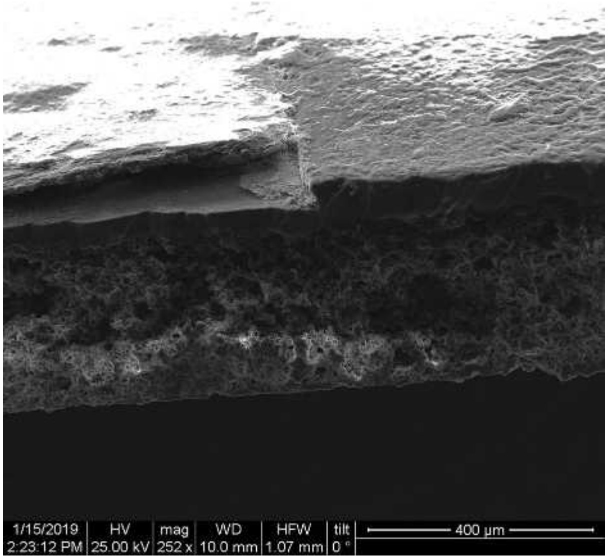
επιφάνεια της λευκής εμφιάλωσης του αγγείου (Lambooy 2005; Webb 2000; Shellman 2008). Τα ένθετα διακοσμητικά στοιχεία από μάργαρο και μέταλλο παρουσίαζαν ιδιαίτερη σταθερότητα και αυτό οφείλεται στην καλή συνοχή που έχουν μέσα στο στρώμα της διάφανης λάκας.

Κατά την οπτική παρατήρηση του αντικειμένου διαπιστώθηκαν ρωγμές που οφείλονται σε μηχανικές καταπονήσεις που προκλήθηκαν κατά τη διαδικασία αποκόλλησης του διακοσμητικού στρώματος. Το κόμμα να γίνει τελεία! Εκτός αυτού, κατά τη εξέταση των δειγμάτων λάκας στο ηλεκτρονικό μικροσκόπιο σάρωσης έγινε διακριτό επιφανειακό δίκτυο μικρορωγματώσεων της λάκας (εικ. 10). Η επιφάνεια της λάκας έφερε μεταγενέστερη ρητίνη, η οποία παρουσίαζε φαινόμενο συρρίκνωσης και ρωγμάτωσης όπως είναι διακριτό στις φωτογραφίες από το οπτικό και πολωτικό μικροσκόπιο (εικ. 4, 11).

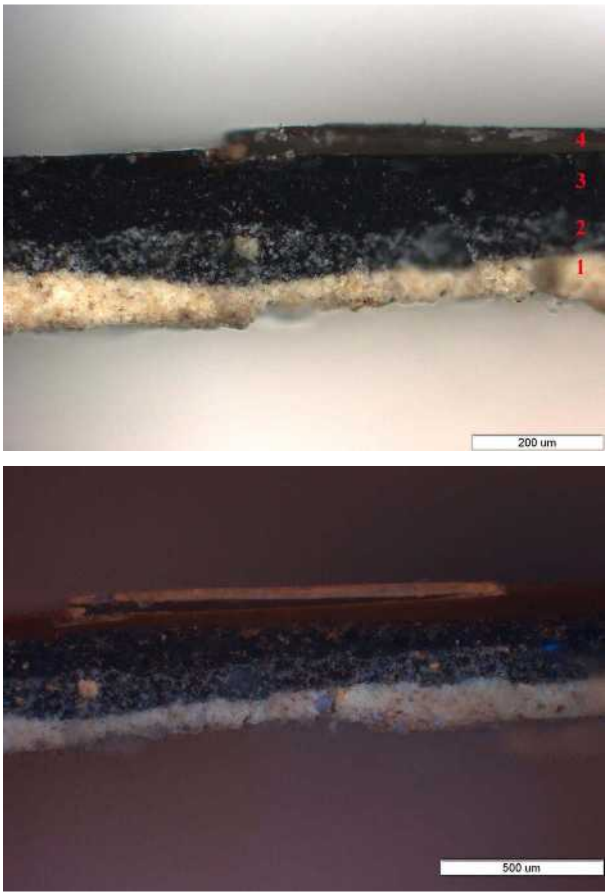
Τα μεταλλικά φύλλα παρουσίαζαν διάβρωση, εντονότερη καταγράφεται στα μεταλλικά στοιχεία της διακόσμησης στο στόμιο του αγγείου, η οποία προκλήθηκε πιθανότατα λόγω χρήσης του αγγείου. Μετά από εφαρμογή στοιχειακής ανάλυσης EDS στην επιφάνεια του μεταλλικού φύλλου ανιχνεύτηκαν κυρίως



Εικόνα 12 Διάγραμμα στοιχειακής ανάλυσης EDS από την επιφάνεια του μεταλλικού φύλλου, ανιχνεύτηκαν κυρίως στοιχεία του μόλυβδου.



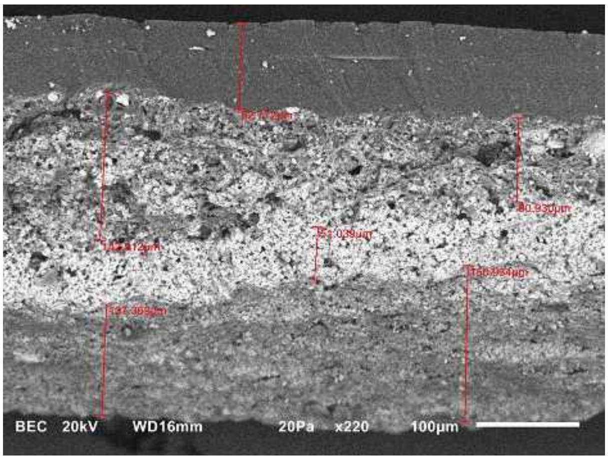
Εικόνα 13 Φωτογραφία στο SEM, στρωματογραφία εγκάρσιας τομής του δείγματος.



Εικόνες 14α, 14β Φωτογραφίες εγκάρσιας τομής του δείγματος της διακόσμησης στο πολωτικό μικροσκόπιο. Με διερχόμενο φωτισμό (14α), με υπεριώδη φωτισμό (14β).

στοιχεία του μόλυβδου, γεγονός που δικαιολογείται από τη διαδικασία διάβρωσης του κράματος κατά την οποία γίνεται μεταφορά και συσσώρευση οξειδίων του μολύβδου στην επιφάνεια του μεταλλικού ελάσματος (εικ. 12). Παρόμοια διάβρωση έχει διαπιστωθεί σε ελάσματα κράματος μόλυβδου που κοσμούν επιφάνειες λάκας σε 60 αντικείμενα ασιατικής τέχνης της συλλογής του Victoria and Albert Museum (Wolbers *et al.* 2014).

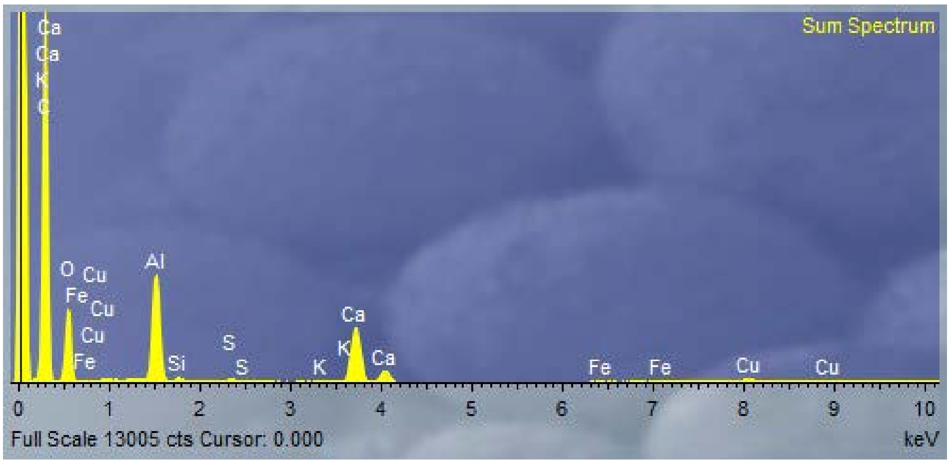
Με την εξέταση της εγκάρσιας τομής του δείγματος της διακόσμησης στο πολωτικό μικροσκόπιο και στο SEM κατέστη δυνατή η αποτύπωση της στρωματογραφίας του δείγματος. Το συνολικό πάχος της τομής είναι 247 μm και η δομείται από 4 βασικά στρώματα. Το πρώτο



Εικόνα 15 Φωτογραφία της εγκάρσιας τομής του δείγματος στο SEM.

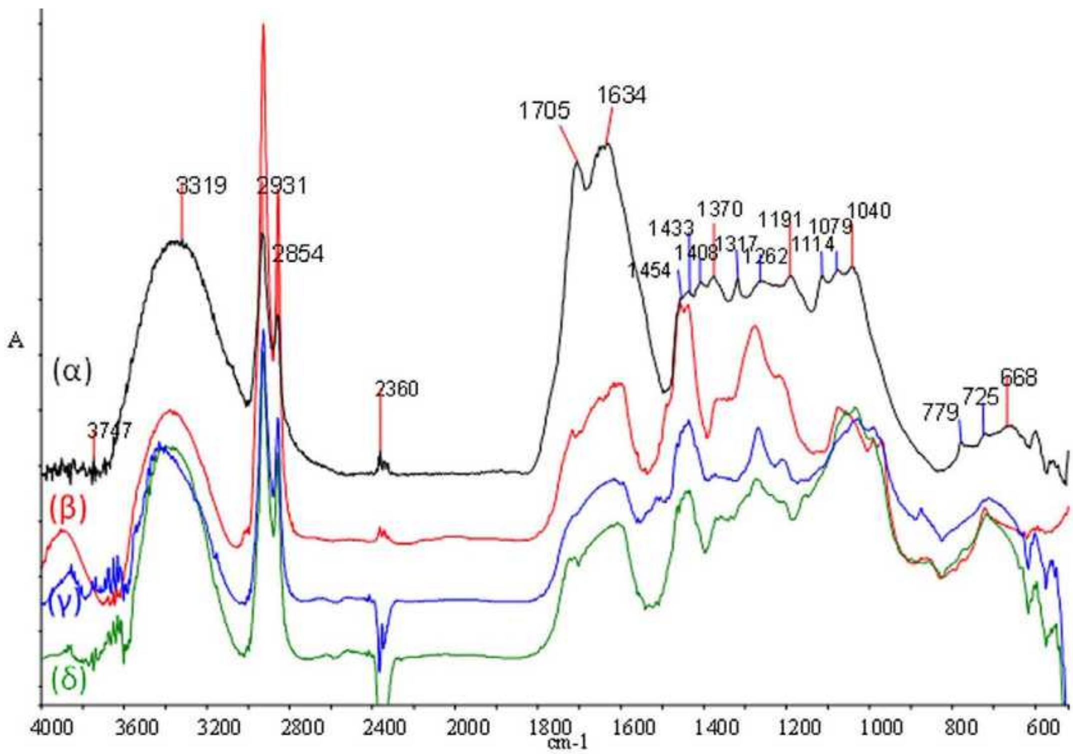
στρώμα είναι η προετοιμασία που βρίσκεται σε άμεση επαφή με την εφυαλωμένη επιφάνεια του αγγείου. Το δεύτερο και το τρίτο στρώμα αποτελούνται από μαύρη λάκα τα οποία διαφοροποιούνται μεταξύ τους ως προς το ποσοστό οργανικής ύλης που περιέχουν. Το τέταρτο και τελευταίο στρώμα αποτελείται από διάφανη λάκα και στο στρώμα αυτό εμπεριέχονται τα διακοσμητικά στοιχεία από μάργαρο και μέταλλο (εικ. 13, 14α, 14β).

Το πρώτο στρώμα πάχους 72 µm, αφορά την προετοιμασία η οποία παρουσιάζει πολύ λεπτή κοκομετρία και άριστη συνοχή με το επόμενα στρώματα της λάκας. Κατά τη στοιχειακή ανάλυση EDS που πραγματοποιήθηκε στο στρώμα αυτό ανιχνεύτηκε παρουσία αργιλίου (Al), ασβεστίου (Ca) και μικρή ποσότητα πυριτίου (Si). Συνεπώς, η προετοιμασία προσδιορίζεται ως πηλός αργιλικής σύστασης με προσμίξεις ασβεστίου και η



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	59.91	1.1024	65.25	0.31	74.13
O K	8.47	0.3864	26.31	0.30	22.44
Al K	2.75	0.8797	3.76	0.04	1.90
Si K	0.08	0.8942	0.11	0.01	0.05
S K	0.09	0.9508	0.11	0.01	0.05
K K	0.06	1.0561	0.07	0.01	0.02
Ca K	3.00	0.9777	3.68	0.05	1.25
Fe K	0.08	0.7839	0.12	0.03	0.03
Cu K	0.37	0.7434	0.59	0.08	0.13
Totals			**100.00**		

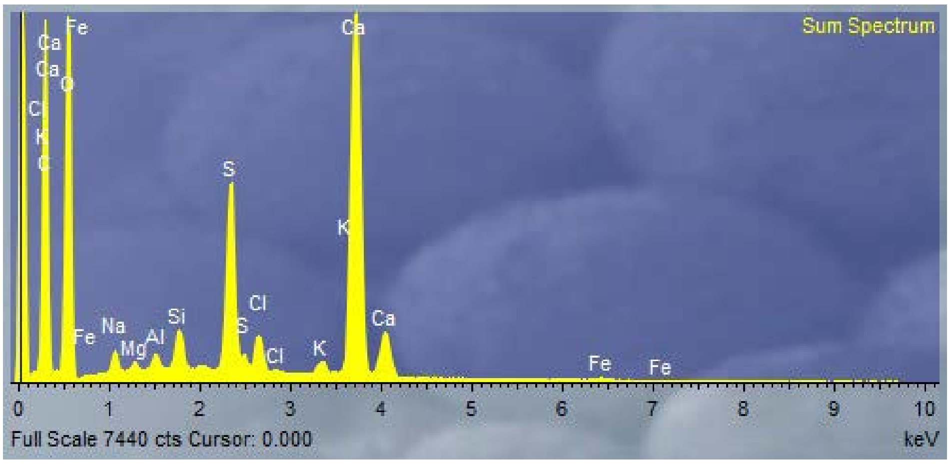
Εικόνες 16α, 16β Διάγραμμα και πίνακας κατανομής στοιχείων από τη στοιχειακή ανάλυση EDS στο πρώτο στρώμα της προετοιμασίας, ανιχνεύτηκε παρουσία Al, Ca, Si.



Εικόνα 17α Φάσματα ATR-FTIR: (α) μαύρη λάκα (Μουσείο Μπενάκη), (β) πρότυπη μαύρη ιαπωνική λάκα, (γ) πρότυπη ιαπωνική λάκα Bengara (δ) πρότυπη ιαπωνική λάκα DRM.

Κορυφή στο FTIR	Ερμηνεία
3400	νO-H
2925, 2855	νCH_2
1705	acidic component
1635	δC–O-H, phenolics
1452, 1433	δCH_2
1409	δC–O-H, acids
1374	δCH_3
1318	δ_{oop}C-OH
1262	νC–OH phenolics
1189	νC-O-C phenol ether
1078	quartz peak
778	quartz peak
598	$\delta(=CH_2)$
547	$\delta(=CH_2)$

Εικόνα 17β Πίνακας με την ερμηνεία των κορυφών του φάσματος ATR-FTIR του δείγματος ασιατικής λάκας στην εικ. 17α.



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	146.08	0.8951	31.98	0.36	44.09
O K	92.41	0.4104	44.12	0.33	45.67
Na K	0.59	0.7136	0.16	0.03	0.12
Mg K	0.76	0.6874	0.22	0.02	0.15
Al K	1.39	0.7992	0.34	0.02	0.21
Si K	2.53	0.8877	0.56	0.02	0.33
S K	4.71	0.9694	0.95	0.03	0.49
Cl K	1.28	0.8457	0.30	0.02	0.14
K K	1.31	1.1301	0.23	0.02	0.10
Ca K	106.97	1.0028	20.90	0.15	8.64
Fe K	1.03	0.7912	0.25	0.04	0.08
Totals			**100.00**		

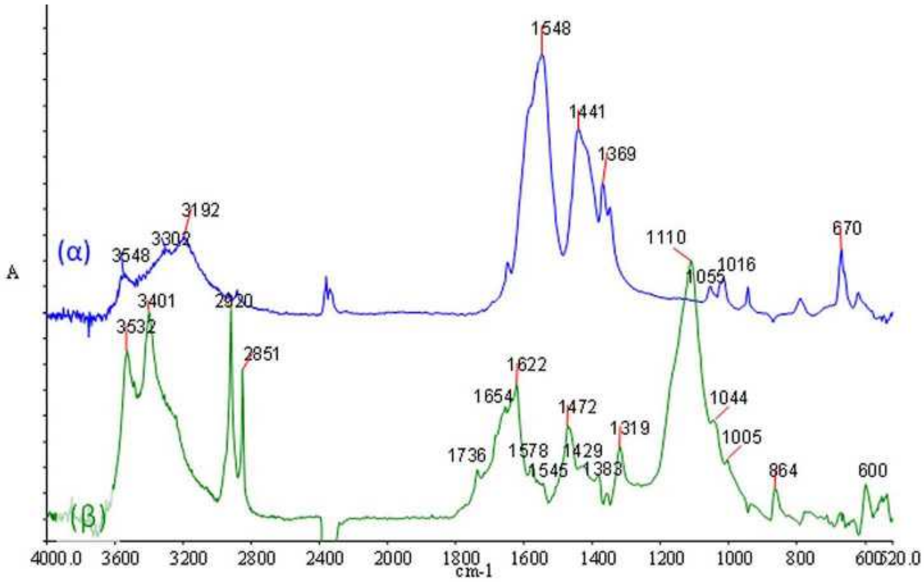
Εικόνες 18α, 18β Διάγραμμα και πίνακας κατανομής στοιχείων από τη στοιχειακή ανάλυση EDS στο 2^{o} και 3^{o} στρώμα της λάκας, ανιχνεύτηκε παρουσία Ca, S, Fe, Si , Mg, Al.

τεχνολογία αυτή συναντάται σε αντικείμενα ασιατικής τέχνης (εικ. 15, 16α, 16β) (Körber *et al.* 2016; Webb 2000; Lambooy 2005; Burmester 1985).

Η προετοιμασία δεν ήταν απορροφητική αλλά αντιθέτως παρουσίαζε σημαντική υδροφοβίωση. Με τη μέθοδο της υπέρυθρης φασματοσκοπίας (FTIR) αποτυπώθηκαν οι κύριες κορυφές του φάσματος που αντιστοιχούν σε ποσότητες *urushi (McSharry et al. 2007)*. Αποτυπώθηκαν επίσης οι χαρακτηριστικές κορυφές οργανικού άλατος που πιθανότατα αντιστοιχούν στο οξικό άλας του σιδήρου (εικ. 17α, 17β). Δεν ανιχνεύτηκαν στοιχεία πρωτεΐνης ή άλλης οργανικής ουσίας. Επομένως, διατυπώνεται το συμπέρασμα ότι το συνδετικό υλικό της προετοιμασίας είναι πιθανώς *kiurushi (Van Bellegem et al. 2010)*.

Το δεύτερο και τρίτο στρώμα συνολικού πάχους 122 μm, αποτελείται από μαύρη λάκα, η οποία στο ηλεκτρονικό μικροσκόπιο SEM εμφανίζεται ως λεπτόκοκκη, με άριστη συνοχή των στρωμάτων μεταξύ τους. Η στοιχειακή ανάλυση EDS των στρωμάτων κατέγραψε παρουσία ασβεστίου (Ca), θείου (S), σιδήρου (Fe) και μικρή ποσότητα πυριτίου (Si), μαγνησίου (Mg) και αργιλίου (Al).

Τέλος, πραγματοποιήθηκε μοριακή ανάλυση, και συγκεκριμένα, λήφθηκαν φάσματα ATR-FTIR από την



Εικόνα 19 Φάσματα ATR-FTIR από (α) τη λευκή προετοιμασία και (β) τη μεταγενέστερη ρητίνη συντήρησης.

επιφάνεια της λάκας (εικ. 17α, φάσμα α), την επιφάνεια της λευκής προετοιμασίας (εικ. 19, φάσμα α) και το στρώμα μεταγενέστερου επικαλυπτικού («ρητίνης συντήρησης», εικ. 19, φάσμα β). Για την ταύτιση του υλικού της μαύρης λάκας το φάσμα που λήφθηκε συγκρίθηκε με φάσματα από δείγματα αναφοράς διαφορετικών ειδών πρότυπης ασιατικής λάκας που παρασκευάστηκαν στο Μουσείο Ασιατικής τέχνης της Κολωνίας. Η ανάλυση της επιφάνειας της λάκας με την τεχνική αυτή, έδειξε την παρουσία ρητίνης *urushi,* παρουσιάζοντας χαρακτηριστικό φάσμα με πλήθος κορυφών που οφείλονται στη μεγάλη πυκνότητα δεσμών που σχηματίζονται κατά τον πολυμερισμό της ασιατικής λάκας (εικ. 17α) (Derrick *et al.* 1985; Derrick *et al.* 1999; Tamburini *et al.* 2016). Στον Πίνακα (εικ. 17β) φαίνονται οι ερμηνείες των κορυφών του φάσματος.

Το φάσμα ATR-FTIR που λήφθηκε από τη λευκή προετοιμασία (εικ. 19, φάσμα α) έδειξε ως κύριο συστατικό, άλας οξικού σιδήρου (βάσει των κορυφών στα 1548, 1441, 1055, 1016 και 670 cm^{-1}). Από το αποτέλεσμα αυτό μπορεί να στηριχθεί η υπόθεση ότι η λάκα είναι *Roiro-urushi*, για την οποία ο χρωματισμός πραγματοποιήθηκε με οξείδια του σιδήρου κατόπιν επίδρασης ξιδιού, πιθανώς από ρύζι (εικ. 18α, 18β) (McSharry *et al.* 2007). Το συστατικό αυτό πιθανότατα μαρτυρεί μια από τυπικές διαδικασίες μαύρου χρωματισμού της λάκας μέσω της χρήσης του συγκεκριμένου άλατος που οδηγεί στη δημιουργία μελανής σύμπλοκης ένωσης μεταξύ του σίδηρου και των πολυφαινολικών συστατικών της λάκας (McSharry *et al.* 2007).

Το φάσμα της μεταγενέστερης «ρητίνης συντήρησης» (εικ. 19, φάσμα β) έδειξε παρουσία γύψου (1622, 1111, 600 cm^{-1}), αραγονίτη (1472, 864 cm^{-1}), καθώς και παρουσία αμιδικού παραγώγου πολυσακχαριτικού υλικού (1654, 1578, 1383, 1319, 1044, 1005 cm^{-1}), που πιθανώς υποδηλώνει παρουσία χιτίνης, το κύριο οργανικό συστατικό του μάργαρου (Boyatzis 2022; Balmain *et al.* 1999; Olson *et al.* 2012). Στο ίδιο δείγμα, πρόσθετες κορυφές (2920, 2851, 1734, 1472, 1383 cm^{-1}) μαρτυρούν την παρουσία υπολειμμάτων ασιατικής λάκας ή/και άλλου εστερικού υλικού, πιθανώς κάποιας φυσικής ρητίνης ή ελαιώδους υλικού, τα οποία χρήζουν περεταίρω ανάλυσης.

Το τέταρτο επιφανειακό στρώμα λάκας παρουσιάζει διαφάνεια, δεν περιέχει πρόσμικτα και το στρώμα αυτό είχε άριστη συνοχή με το υποκείμενο στρώμα της μαύρης λάκας. Η εφαρμογή στοιχειακής ανάλυσης EDS στη επιφάνεια του στρώματος αυτού κατέγραψε πλήρη απουσία ανόργανων στοιχείων.

Συμπεράσματα

Η παρούσα έρευνα επιβεβαιώνει το γεγονός ότι η διεπιστημονική συνεργασία σε θέματα αρχαιομετρίας είναι ιδιαίτερα σημαντική για την κατανόηση, την μελέτη και την συντήρηση των έργων πολιτιστικής κληρονομιάς. Επιβεβαιώθηκε επίσης, σε όλη την διάρκεια της μελέτης, ότι σημαντική παράμετρος αποτελεί η γνώση της τεχνολογίας κατασκευής των αντικειμένων καθώς και του ιστορικού πλαισίου της δημιουργίας και χρήσης τους.

Κατά την έρευνα διαπιστώθηκε ότι τα έργα ασιατικής τέχνης με διακόσμηση λάκας απαιτούν εξειδικευμένη μεθοδολογία ανάλυσης των υλικών τους. Το ιδιαίτερα σταθερό πλέγμα δεσμών που παρουσιάζει η χημική σύσταση της ασιατικής λάκας καθιστά αδύνατη την ανίχνευση των μεμονωμένων στοιχείων της χωρίς να έχει προηγηθεί πυρόλυση του δείγματος.

Παρά τους περιορισμούς που υπήρξαν, στην χρήση των αναλυτικών διατάξεων, η παρούσα μελέτη κατέληξε σε σημαντικά συμπεράσματα ως προς την τεχνολογία κατασκευής και αποκατάστασης του αντικειμένου του Μουσείου Μπενάκη. Το αγγείο με λευκή εφυάλωση και υπερκείμενη διακόσμηση μαύρης λάκας *urushi lacquerware* δημιουργήθηκε με χρωματισμό κατόπιν κατεργασίας με FeO και ξύδι και αποδίδεται ως *Roiro-urushi*. Με τη μέθοδο της υπέρυθρης φασματοσκοπίας (FTIR) ανιχνεύτηκαν οι χαρακτηριστικές κορυφές οργανικού άλατος που πιθανότατα αντιστοιχούν στο οξικό άλας του σιδήρου, το εύρημα αυτό δείχνει μια πιθανή μέθοδο μαύρου χρωματισμού του στρώματος της λάκας, με σχηματισμό μαύρου συμπλόκου σιδήρου με τα πολυφαινολικά συστατικά χρησιμοποιώντας ως πρώτη ύλη το διαλυτό οξικό άλας σιδήρου. Διαπιστώθηκε ότι το κύριο συνδετικό υλικό στο στρώματα προετοιμασίας ήταν *kiurushi,* ακολουθώντας τα αυστηρά πρότυπα και υπάρχουν ενδείξεις ότι το αντικείμενο ήταν κατασκευασμένο για εσωτερική χρήση και όχι για εξαγωγή του στην Ευρώπη. Η ενσωματωμένη διακόσμηση του αντικειμένου ήταν από λεπτά φύλλα μάργαρου με την τεχνική *raden* και μεταλλικά φύλα κράματος μολύβδου - κασσίτερου ακολουθώντας πρότυπα της τεχνικής *hyomon*. Τέλος η ρητίνη που κάλυπτε την επιφάνεια της λάκας παρουσίαζε χαρακτηριστικά μεταγενέστερης δυτικού τύπου ρητίνης. Σε μελλοντική συνέχεια της έρευνας αυτής μπορεί να εφαρμοστεί σημειακή ανάλυση στη ρητίνη με μέθοδο micro-FTIR με στόχο την ταυτοποίηση της.

Η μελέτη του συγκεκριμένου αντικειμένου της Κινέζικης συλλογής του Μουσείου Μπενάκη και οι πληροφορίες που αποκαλύφθηκαν κατά τη τεχνολογική του μελέτη, επιβεβαιώνουν την ανάγκη της εποχής μας για την κατανόηση της τεχνολογίας έργων με πολυπολιτισμική και ανοικτή προσέγγιση, αναγνωρίζοντας τις ιδιαίτερες αξίες και τα χαρακτηριστικά των αντικειμένων, ενσωματώνοντας τα αποτελέσματα στον τρόπο προσέγγισης και διαχείρισης των έργων.

Ευχαριστίες

Θα θέλαμε να ευχαριστήσουμε για την υποστήριξή του στην έρευνα αυτή τον Επιστημονικό Διευθυντή του Μουσείου Μπενάκη Δρ. Γιώργη Μαγγίνη, καθώς και τον κ. Καραμπότσο, ΠΑΔΑ και τη Δρ. Αμέντα, ΕΚΕΦΕ «Δημόκριτος» για την πολύτιμη βοήθεια τους στην ηλεκτρονική μικροσκοπία σάρωσης. Το Tokyo National Research Institute of Cultural Properties και το Μουσείο Ασιατικής Τέχνης Κολωνίας για τη δυνατότητα κατασκευής των δοκιμίων αναφοράς Ιαπωνικής λάκας.

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The Marbles of the Quarries Ab-u Hayat and Ahmet Beyli in the Area of Ephesos

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Abstract: This paper presents the results of the investigations carried out at the marble quarries Ab-u Hayat and Ahmet Beyli in the area of Ephesos. An extensive investigation on the marble quarries in the area of Ephesos has been held the last years. Ahmet Beyli quarry is located *c.*20 km north of the ancient city of Ephesos. Ancient traces of tool marks as well as unfinished objects can be observed at the area of the quarry. It seems that this quarry was mainly used for the ancient city of Notion and the sanctuary of Klaros but no scientific data on the marbles has so far been available. The Ab-u Hayat quarry is about 4 km east of the ancient city of Ephesos. The recent investigation of the quarry showed indications that it was mainly used as a small sarcophagus production centre. Throughout the quarry there are many tool marks on the solid rock and abandoned marble objects. The methods applied in our research were petrographic investigations, chemical and isotopic analysis, and extractable salts (crush-leach analyses). The analysis of the new quarries contributes to the identification of archaeological artefacts coming from the ancient city of Ephesos and its surrounding areas.

KEYWORDS: WHITE MARBLE, PROVENANCE ANALYSIS, EPHESOS QUARRIES, EPHESIAN ARTEFACTS.

Introduction

The aim of this paper is to present the investigation carried out in two quarries in the area of Ephesos. In recent years, research (Yavuz 2011, Prochaska and Grillo 2012) has been undertaken on the Ephesian quarries and the marbles of Ephesian architecture. The different types of marbles mined in the area of Ephesos were not only important for the city itself, but also for the whole province of Asia with its many cities, such as, for instance, Pergamon (Pochaska and Grillo 2012). There are at least 40 locations-ancient quarries widely scattered in the region (Figure 1).

The different types of Ephesian marble are distinguished in two main groups, Ephesos I and Ephesos II. The marbles are grouped according to the similarities of their isotopic and chemical composition. The Ephesos I combines the locations of Ahmetli Koyu, Kentli Çiftliği, Urfalidaği-Tepesi Gölluce, Urfalidaği-Tepesi and some quarries of the area of Hasançavuşlar. The Ephesos II group includes the Belevi quarry, the Kuşini underground mine, and the small quarry near Sağlık (Pochaska and Grillo 2012).

Additionally, two smaller groups also belong to the marbles of Ephesos: the Aya Klirkiri and the Ab-u Hayat (former names: Tavşantepe or Farm, Yavuz *et al.* 2011). These two locations do not fit within the compositions of the two established main groups. A third location can be added to this list: the Ahmet Beyli quarry located 20 km north the ancient city of Ephesos (Pochaska and Grillo 2012).

A special and significant type of Ephesian marble occurs approximately 10km NE of the Belevi quarry near the village Hasançavuşlar. Located there are a series of quarries with white marble possessing typical black specks. This is the so-called Greco Scritto and it is well known in Roman architecture (Attanasio *et al.* 2009). This type of marble of Ephesian origin has been found not only at the region of Ephesos, but also in regions and cities such as Xanten, Germany and Sirmium (today's Belgrade) in Serbia (Pochaska and Grillo 2012).[1]

The geology of the area

The marble deposits in the region of Ephesos occur in different tectono-stratigraphic horizons. As a result, groups of marbles can be found which differ petrographically and chemically. According to the general view (e.g. Okay 2001; Güngör and Erdoğan 2002), the region around Selçuk/Ephesos belongs to the Cyclades complex in geological terms. This unit, characterized by an Eocene high-pressure/high-temperature metamorphosis, also includes parts of the Cycladic islands with their famous marble deposits (e.g. Paros, Naxos, and Samos). The occurrence of corundum

[1] For the analytical database of the Ephesian quarries, see: Prochaska *et al.* 2024

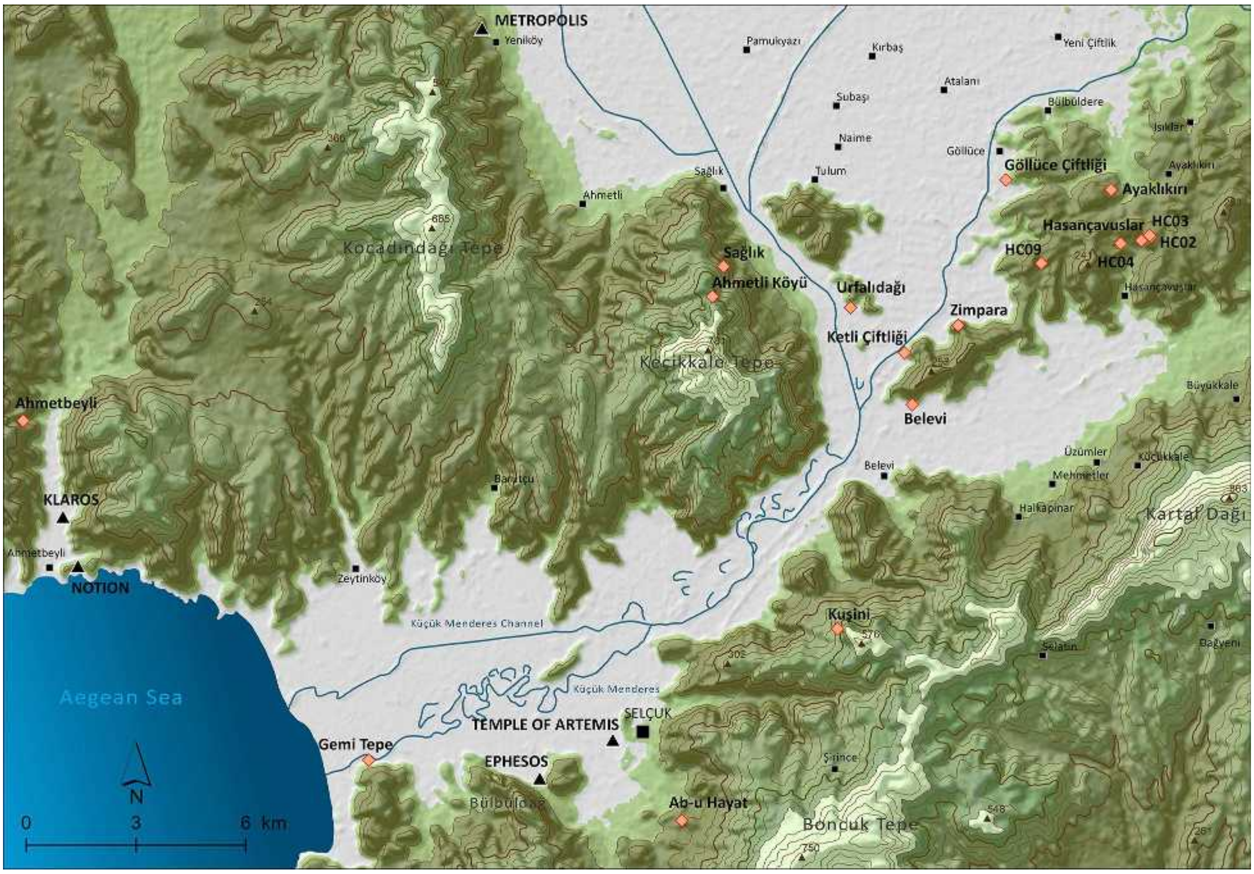

Figure 1. The quarries of the area of Ephesos (editor: Ch. Kurze, ÖAI-ÖAW).

in these series is characteristic—corundum lentils, for example, can be found in some meter long lenses in the ancient Belevi quarry. The Cyclades complex lies on the Menderes complex bordering to the east and is overlaid by the Vardar-Izmir-Ankara zone in the north.

The marbles of Ab-u Hayat quarry form a small lens. According to the geological map, the host rocks are Cretaceous metamelanges. No marble is noted on the geological map at the location of the quarry, but the lens may be too small and cannot be shown on this scale. This affiliation is supported by the fact that the composition of Ab-u Hayat marbles is clearly different from other Ephesian marbles. Another possibility is that these marbles belong to the Mesozoic to Cretaceous marble series that occur in the footwall of these meta-melange units and also include marbles from the Belevi or Sağlık quarry (Ephesos II marbles). However, as mentioned above, Ab-u Hayat marbles differ significantly in their chemical and petrographic parameters from Ephesos II marbles.

Experimental methods and marble database:

The samples were obtained in the form of a small chip taken from a suitable place of an already existing old or new break so that there was no loss of any archaeological/art historical information or aesthetic value.

The geological samples were characterized by petrographic, isotopic, chemical analyses traces element and trace elements analyses. More specifically:

- Stable Isotope Analysis, (13C /12C and 18O/16O)
- Petrographic analysis
- Trace element analysis
- Analysis of the fluid inclusions

For the statistical treatment, a large database of the most important quarries of the antiquity was used in combination with the extensive collection and analysis of the new quarries of the area of the Eastern Rhodopes. The programme packages STATISTICA and SPSS were used. The results provide additional data and complete the databases on marble provenance analysis. The collected samples were analysed at the Department of Geosciences and Geophysics at the University of Leoben Austria.

The Ab-u Hayat Quarry

The marble quarry with the modern name Ab-u Hayat is the closest mining site for white marble to the ancient

Figure 2. Aerial photo of the Ab-u Hayat Quarry (Ph. by Cr. Kurtze, ÖAI-ÖAW).

city of Ephesos. It is a quarry used in ancient times, primarily for sarcophagi, but also for agricultural equipment such as olive presses (Figure 2). The quarry is now privately owned and was excavated decades ago by the owner with the approval of the Antiquities Directorate in Ankara and under the supervision of the Museum in Ephesus. The exposed area measures 55 x 30 m and is processed to a maximum depth of 8 m below the original surface.

The quarry is currently perfectly cleaned to the bottom and the signs of mining from the last phase have been excellently preserved. The marbles of this quarry were first investigated by Yavuz *et al.* (2010) who also published some analytical data (EPR data and isotope analyzes).

In the course of our project, an archaeological documentation of the quarry was carried out, which resulted in a division into three different mining levels. It can be assumed that the ancient entrance was in the northwest, which is the lowest level today. This is characterized by large dumps of marble debris, negative impressions of blocks and traces of pick iron, and wedges with which the material was mined. The signs of degradation on the second, middle level can be seen particularly clearly. Drilled holes, chipping and wedge marks in parallel lines may be considered safe indicators for the removal of rectangular blocks. This is also evidenced by a pile of broken marble blocks in the south of the area. The walls on which the quarry work can be seen through numerous traces are particularly revealing. Quarry activity continued at the third, highest level. In particular, several olive presses or their impressions should be mentioned here. With a diameter of 1.3-1.7 m, they reach a considerable size and were certainly used in agricultural operations. On the edge of the quarry, near the assumed entrance, there are still unfinished rectangular marble blocks, a round marble part, a sarcophagus, and a lid.[2]

The Ahmet Beyli quarry

The marble quarry with the name Ahmet Beyli is only 4 km east of the archaeological site of Klaros. This was an

[2] For the analytical study of the Ab-u Hayat quarry, see: Anevlavi *et al.* 2021

Figure 3. The wall with the tool marks at Ahmet Beyli quarry, (Ph. by W. Prochaska, ÖAI-ÖAW).

ancient Greek sanctuary on the coast of Ionia. No later than the 3rd century BC, construction of the Temple of Apollo began. The Temple of Apollo, measuring 26 meters by 46 meters, was built in Doric style. The temple in the peripteros plan (6 by 11 meter columns) rises on a fifth crepis (Calrson and Aylward 2010). In 2005, research was conducted at the Kızılburun shipwreck on the Aegean coast of Turkey. The vessel transported eight column drums and an unfinished Doric capital intended for the Apollo temple at Klaros. Isotopic analysis of the stones from the shipwreck showed a possible provenance from Prokonnesos. However, isotopic investigations of architectural parts from the temple of Apollo showed more than one source of marble (Aylwand *et al.* 2012). At this point, it has to be mentioned that the local quarries in the area of Klaros-Ahmet Beyli have not been investigated before.

Since the Ahmet Beyli quarry was used in ancient times it was perhaps the main source of marble for the sanctuary. The current site of the quarry is abandoned. The small size of the quarry indicates only local use of the production. Different types of tool marks can be observed in the area of the quarry. Marks such as drill holes, chipping and wedge marks in parallel may be considered as signs of the removal of blocks (Figure 3). Debris can be found in different spots of the quarry and in various sizes. Walls of approximately 5 meters high combine all the tool marks on multiple levels. Abandoned objects, more specifically rectangular blocks with parallel pick marks, can be found.

Case studies

Two case studies are presented in this paper. The first is focused on the sarcophagus of the Octagon in Ephesos, and the second on the so-called Tavşantepe lion.

The so-called Octagon, an octagonal shaped mausoleum in the city of Ephesos, is located next to the Library of Celsus (Thuswaldner *et al.* 2009). It has been dated on stylistic grounds to between the mid-1st cent BC and the 2nd half of 1st cent AD, with most estimates ranging between 50 and 20 BC (Thür 1990). Recent investigations showed that the Octagon is dated to the Augustean Age (Waldner 2009). It is assumed that the mausoleum and the sarcophagus belong to Arsinoe IV (sister of Cleopatra VII), who was killed in Ephesos in 41 BC (Figure 4) (Thür 1990). The marbles of the rising architecture were analysed and appeared to be from the Ephesos I group (Prochaska and Grillo 2012).

The so-called Tavşantepe lion, made from white marble, is a sculpture depicting a lion ready to attack

Table 1. The analytical data of the quarries of Ab-u Hayat, Ephesos I, Ephesos II and Ahmet Beyli (Editor: V. Anevlavi, ÖAI-ÖAW).

	$MgCO_3$	Fe	Mn	Sr	Li/Na	Cl/Na	K/Na	Br/Na	I/Na	SO_4/Na	DS	∂[18]O	∂[13]C
Ab-u Hayat ø	1,55	109	69	218	1,8	1499	229	8,7	5,8	204,3	3722	-5,72	2,37
σ	1,13	67	58	44	0,9	117	72	6,5	1,4	107,7	2010	1,43	0,32
Ephesos I ø	3,85	207	23	125	1,4	2101	248	8,0	6,5	280,6	7173	-4,15	3,89
σ	4,85	104	14	35	1,5	305	205	4,6	5,8	523,0	5648	1,29	0,41
Ephesos II ø	1,20	128	20	73	1,2	1795	522	9,6	22,0	636	2252	-3,18	0,14
σ	1,50	69	8	18	1,2	972	313	11,7	14,2	1068	1997	0,39	0,57
Ahmet Beyli ø	1,19	78	10	185	1,2	1433	308	5,3	22,0	594,1	2906	-6,05	2,24
σ	0,19	31	7	24	0,4	247	128	1,6	13,5	366,3	1597	2,56	0,66

Figure 4. The sarcophagus of the Octagon, (Ph. by N. Gail, ÖAI-ÖAW).

its prey—a Hellenistic Age composition (Figure 5). It is 97 cm in length, 22 cm in width, and 10 cm in thickness (Erdemgil and Evren 1992). The sculpture was found isolated in the area of Tavşantepe buried close to the surface (Erdemgil and Evren 1992). Its base and general structure indicate that the statue was originally not located *in situ*, but was most likely placed in front of an important building (Erdemgil and Evren 1992). A first assumption about the provenance of the marble was based on the spot of discovery, meaning that it could possibly be connected with the quarry of the area: Ab-u Hayat.

Analyses and results

Ab-u Hayat: the coarse-grained marble has no schistosity and no directional structure can be found in the microscopic image. Likewise, silicate admixtures

Figure 5. The Tavşantepe lion (Ph. by W. Prochaska, ÖAI-ÖAW).

are not visible to the naked eye. The marble is white to light grey, slight bluish in colour, and the white varieties are very rare. Noticeable in the quarry site are large areas (up to one meter) of very coarse-grained recrystallizates, where the calcite crystals can reach a size of a few centimetres.

The examined marbles are coarse-grained to very coarse-grained metacarbonates with calcite crystals, which can reach a size of 6 mm. The most common grain size is approx. 4 mm. This coarse grain distinguishes the Ab-u Hayat marbles from other Ephesian white marbles. The microscopic structure is heteroblastic. Very typical of these marbles is a poikilitic texture with large calcite blasts growing around small calcite crystals. The grain boundaries are closely interlocked (Figure 6).

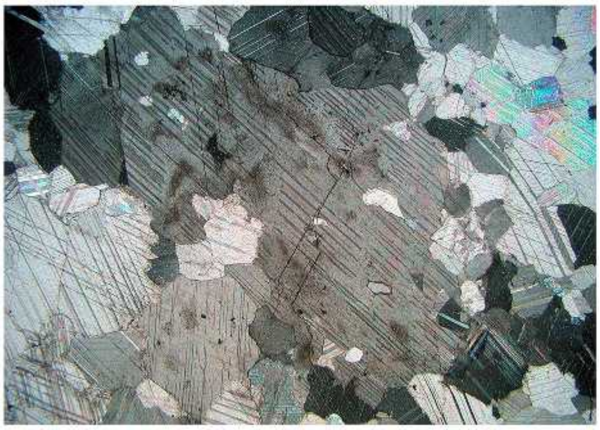

Figure 6. Heteroblastic, intergrowth structure, very large grain sizes (image length is 6mm), (Ph. by W. Prochaska, ÖAI-ÖAW).

What is striking about the marbles from Ab-u Hayat is the compactness and toughness of the rock. The reason for these special physical properties and resistance is probably due to the heteroblastic structure and the intensive interlocking of the individual grains. This probably explains the preferred use of these marbles for the production of sarcophagi and articles for daily use which required good wear resistance, e.g. in oil presses.

Ahmet Beyli: Petrographically, the Ahmet Beyli samples exhibit all features of strongly tectonized marbles. Due to this tectonic overprint, the calcite grains disintegrate on the grain boundaries to a groundmass of small, newly crystallized calcite crystals (Figure 7). According to this overprint the rock exhibits a slight schistosity. The maximum grain-size is between 1mm in the strongly deformed samples and 2,5mm in the less tectonized marbles. No considerable accessory minerals can be observed. Very small inclusions of organic matter (graphite) in the calcite crystals cause the slightly greyish tint of the marbles.

In Table 1, the data from four groups of marbles(?) are presented (average and standard deviation). The total

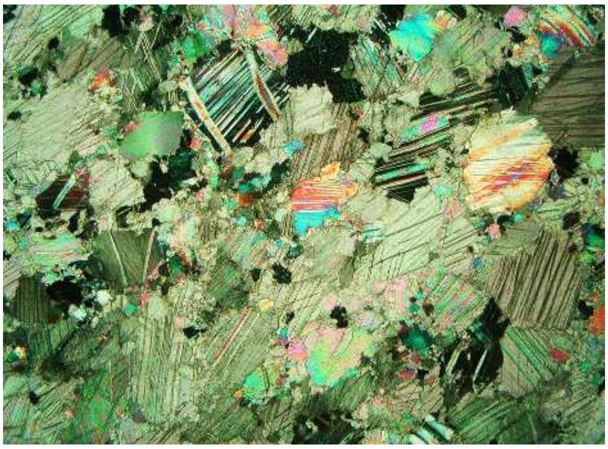

Figure 7. Strongly tectonized marble with relics of bigger grains decaying into a groundmass of small calcite grains, medium/small grain sizes (image length is 6 mm), (Ph. by W. Prochaska, ÖAI-ÖAW).

amount of the samples from these quarries-locations are approximately 350. As can be seen in Table 1 there are some significant differences among these four main groups in the region of Ephesos. The Ab-u Hayat average data show -5.72 ∂^{18}O and 2.37 ∂^{13}C while the Ahmet Beyli has -6,05 ∂^{18}O and 2,24 ∂^{13}C. The main difference between? the main Ephesos I and Ephesos II groups is that the C – isotope appeared with higher values compared to Ephesos I while ∂13C of Ephesos II is significantly lower. Elements such as Mg and Fe assist in identifying the differentiation among? the quarry groups. For example, Ephesos I has high values of Mg 3.85% on average. Ahmet Beyli has substantial lower Fe than the other groups (78ppm). Finally, Ab-u Hayat has higher average values of Mn (69ppm) and Sr (218ppm) than the three compared groups.

Case studies: The petrographic investigation of the sarcophagus showed that the marble is calcitic, very pure, with a low content of silicate minerals that is typical for Ephesos I marble (Prochaska and Grillo 2012). The colour of the marble is light grey. The marble of the lion has a white colour and is of a medium grained size.

The isotope analysis of the sarcophagus appears in the centre of the Ab-u Hayat ellipse. While the lion is at the centre of Ephesos I, ellipse show -4,27 ∂^{18}O and 3,69 ∂^{13}C. The data of the Ahmet Beyli quarry scatter and cover a large field in the diagram (Figure 8). However, as shown above, the macroscopical characteristics of the marble from the artefacts are very different from Ahmet Beyli's marble features.

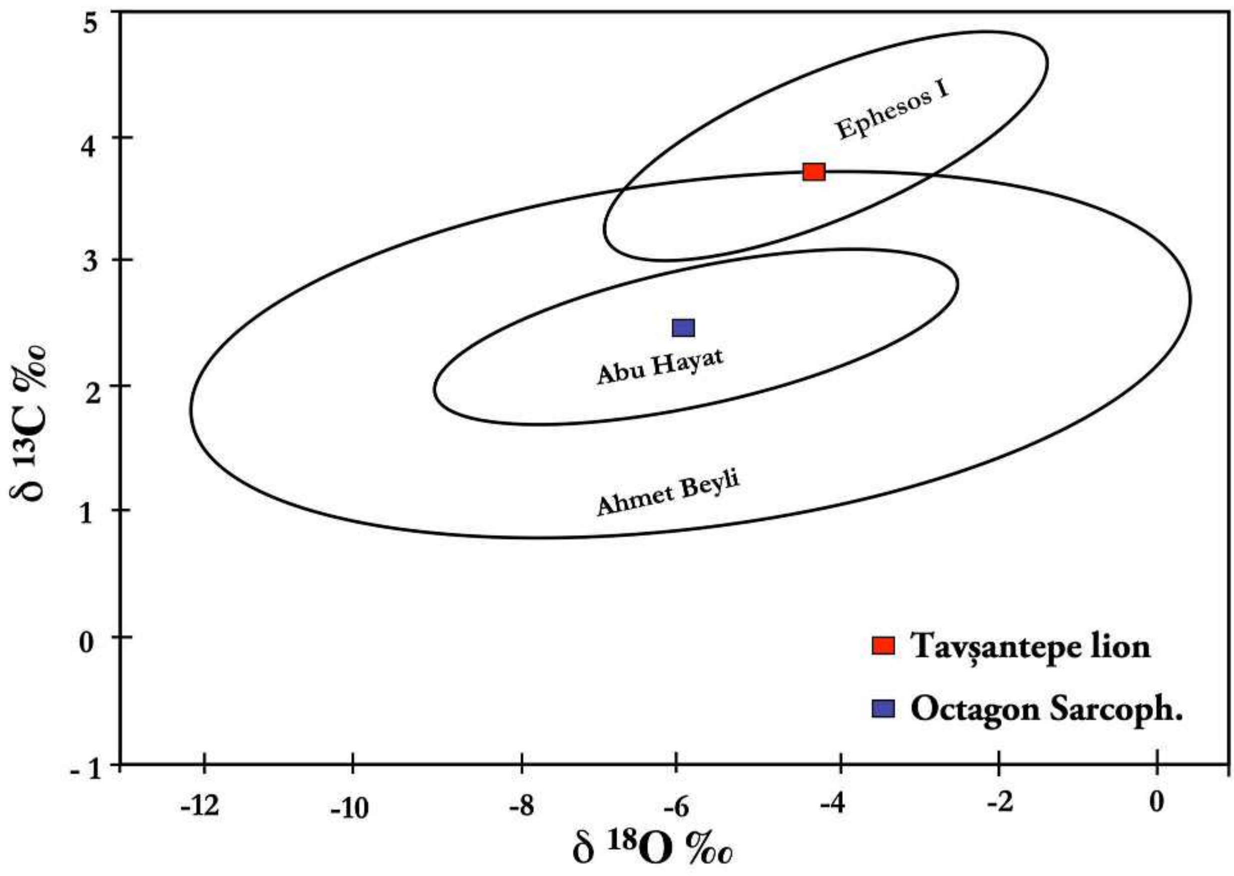

Figure 8. The isotope diagram of the lion sculpture and the Octagon sarcophagus (Editor: V. Anevlavi, ÖAI-ÖAW).

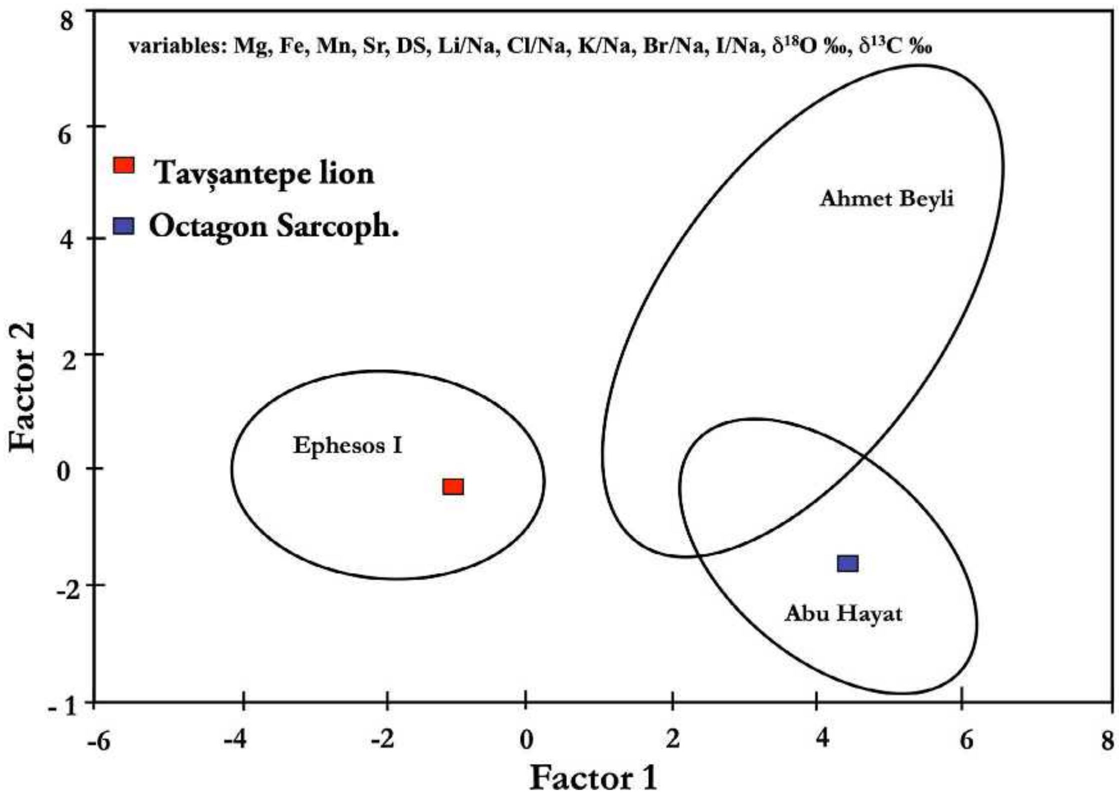

Figure 9. The multivariate diagram of the lion sculpture and the Octagon sarcophagus (Editor: V. Anevlavi, ÖAI-ÖAW).

A number of different, characteristic variables were considered for the discrimination analysis. These variables are: Mg, Fe, Mn, Sr, DS, Li/Na, Br/Na, Cl/Na, K/Na, I/Na, ∂^{18}O and ∂^{13}C. The multivariate diagram confirms the first diagram, and the provenance of these two artefacts is Ab-u Hayat and Ephesos I (Figure 9).

Conclusion

There are 40 locations around the region of Ephesos where white marble of appreciable quality was being mined and exported mainly during the Roman period. The last year's quarries and outcrops have been found and investigated from the spectra of archaeology and archaeometry.

The two new locations which were investigated and presented in this paper are the Ab-u Hayat and Ahmet Beyli quarries. Both of these quarries are small in size. Ancient tool marks can be observed in their entire areas in addition to unfinished objects scattered among the debris. A total of 60 samples from these two places were analysed with various techniques such as isotopes, chemical, and fluid analysis, as well as petrography. The results showed that there are various elements different from the two main groups Ephesos I and Ephesos II, for example, the Mg or Fe.

In the case of Ab-u Hayat, extensive exports of products are not to be expected due to the limited size of the quarry. The artefacts produced—as it turned out mainly sarcophagi—from this marble can only be found regionally. Two case studies of Ephesian artefacts are presented, a sculpture of a lion and the Octagon sarcophagus. Both of these originated from Ephesian marble sources. The sarcophagus was made of marble from the Ab-u Hayat quarry presented above. The sculpture of the "grave lion of Tavșantepe" was made of Ephesian white marble belonging to the group Ephesos I.

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Study of the Inlay Decoration of the Marble “Kosmites” of the Katholikon of the Daphni Monastery

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Abstract: The *Katholikon* of the Dafni Monastery, dating from the 11th century, is considered one of the most important monuments of the Middle Byzantine period, and is included in the list of monuments of the UNESCO World Heritage List. On the interior walls of the church are found horizontal marble cornices, “Kosmites”, decorated with an inlaid technique. The aim of the research is to determine the composition of the filling material, inlay, and to assess its condition. Optical examination showed variations in the shades of the inlay between the different decoration tiers of the church. Microscopic examination revealed a waxy texture and the presence of pigment, along with, evidence of decay. Selected samples from different areas were analysed by Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Scanning Electronic Microscopy in combination with X-Ray Spectroscopy (SEM-EDS). Analyses confirmed that the material is based on wax, and revealed information about the pigments and its alteration.

KEYWORDS: BYZANTINE LOW RELIEF DECORATION, INLAY, COLOURED WAX, SEM/EDS, FTIR

Introduction

The *Katholikon* (main church) of the Daphni Monastery in Attica, Greece, dedicated to the Assumption of Virgin Mary, is dated to the 11th century. It is considered one of the most important monuments of the Middle Byzantine period, due to its architecture and exceptional wall mosaic decoration, and is included in the UNESCO World Heritage List. The interior walls of the church are additionally decorated with horizontal marble cornices known as “Kosmites” in the relevant bibliography. These marble elements have an engraved decoration inlaid with a coloured material. The use of an inlay material on the marble architectural elements of the Byzantine period is mentioned in the literature, but to this date limited studies of related monuments or architectural members have been carried out.

The Daphni Monastery was built in an area with strong earthquake activity and has regularly suffered from intense earthquakes. In 1999 a strong earthquake in the area of Attica, caused extensive damage to the building and the wall mosaics of the church. Major projects aimed at the restoration-stabilization of the building and the conservation of its mosaics were carried out by the Hellenic Ministry of Culture (Miltiadou – Fezans 2008). The projects were co-funded by the European Union and completed in 2015.

The current research was initiated in the context of the conservation works carried out on the monument of the mosaics and other decoration elements carried out by the Directorate of Conservation of Ancient and Modern Monuments of the Hellenic Ministry of Culture. The marble cornices separate the mosaic decoration on the higher levels of the walls of the monument and access to them was facilitated by an extensive network of scaffolding erected for the conservation project. The aim of the research was to investigate the composition of the inlay in order to understand better this type of marble decoration and to assess its present condition.

Description (of kosmites) and historic background

“*Kosmites*” are defined as “architectural parts aiming to separate organically the areas of the interior walls of the church” (Bouras and Boura 2002). The name *kosmitis/es* refers to something that embellishes and derives from the phrase “*kosmitikai tainiai*” meaning (in Greek) decorative bands (Labakis 1889). *Kosmites* are elongated marble elements, cornices, usually with engraved decoration.

In relevant bibliography of Byzantine architecture and art, a flat relief decoration is generally mentioned for architectural elements and sculptures. In addition, an inlaid technique is described, where carving of the marble using low relief, was followed with an inlay. In general, the inlay material is referred to as *kiromastixi* [κηρομαστίχη] (Byzantine and Christian Museum Collections; Church of Porta Panagia at Pyli, Hellenic Ministry of Culture), literally meaning a mixture of wax and mastic resin. However, in his emblematic work *L’ Art Byzantin* (1983), Charles Delvoye describes a marble icon and mentions the possible use of inlay made of a coloured mixture of wax and marble dust on some areas of the relief, which are missing in the present day. Also, the mixture of wax, marble dust, and pigments was reported as a technique widespread in the eastern Mediterranean since the 2nd and 3rd centuries AD (Papadopoulou 2008). This inlaid decoration on marble elements is often described using the French term "*champlevé*". According to Charalampos Bouras "the flat reliefs should not be confused with the carvings known with the french term "champlevé. These are sculptures that were filled with some coloured material, wax, and were used mainly in the 11th, but also later in the 13th-14th century" (Bouras and Boura 2002). According to the same authors, the champlevé carvings are distinguished from the flat reliefs, since they have deeper lines while the walls surface remained rough in order to facilitate the attachment of the coloured filling. They also commented that there are no studies of the inlay composition and technique.

Specifically, for the *Katholikon* of the Daphni Monastery, the written sources mention the use of a dark black inlay at the engraved grooves of the marble (Labakis 1889). Moreover, the decoration of the *kosmites* at Daphni is characterized as a typical example of the *champlevé* technique (Bouras and Boura 2002).

The marble cornices, "*kosmites*", of the *Katholikon* of the Daphni Monastery are located at the interior walls of the monument, at the fifth and sixth level of the decoration zone, in a height of approximately 7.5m and 10.5m from the floor, respectively. We shall term them as the first and second *kosmitis.* The second and higher *kosmitis* is located under the base of the cupola. Both are made of whitish marble, with a height *c.*0.2 m and a length that varies from approximately 0.90 m to 1.3 m.

Material

Initial examination of the decoration was carried out prior to the conservation of the marble elements. In general, the inlay showed a waxy texture. Macroscopic and microscopic examination showed a variation in appearance of the material among the different locations of the church and in particular between the first and second *kosmitis*.

Although today the overall appearance of the inlay has a dark brown-black hue, examination at the base of the cupola revealed that the material in that area to have a reddish hue. The reddish hue of the material was not readily evident, as in most areas the external surface exhibited a greyish discolouration. Furthermore, at other areas, a material with a different (brownish) hue and method of application was noticed. This exhibited a rougher external surface, sometimes with apparent strokes, which in turn demonstrated a faster and perhaps unskilful application method. The appearance of the material possibly indicates a re-positioning of detached material of the decoration or a later addition.

The inlay material on the marble *kosmites* was classified into three types according to its colouring and condition: reddish with greyish external surface, homogeneous dark brown to black, and brownish with uneven surface.

Experimental

Prior to sampling, macroscopic and microscopic documentation of the marble elements and the inlay was carried out with an Olympus digital camera and a portable microscope –camera: Dino-Lite, AM211, Adjustable focus and Magnification ×10 ~ ×200.

Samples were then taken from the above-mentioned three types of material as they were distinguished in appearance and recorded during optical examination *in situ*: sample A, reddish, sample B, brown-black, and sample C, brownish. The samples were examined and documented under magnification without sample preparation, using stereomicroscopes in different lab facilities and the portable microscope-camera, Dino-Lite, AM211.

Analysis of the samples was carried out with Fourier Transformed Infrared Spectrometry (FTIR) of Attenuated Total Reflection (ATR) and Reflection-Absorption Spectra mode using a Perkin Elmer Spectrum GX FT-IR System, which was supplemented with Scanning Electron Microscopy, coupled with Energy Dispersive X-ray Spectrometry (SEM/EDS) with a JEOL JSM-6510 Oxford X-act Energy Dispersive X-ray Spectrometer, with INCA energy software. All analyses were carried out at the Department of Conservation of Antiquities and Works of Art of the University of West Attica.

Preliminary Results

Microscopic examination

The examination of the samples provided information about the nature, colouring, and presence or not of inclusions or pigment grains in the material.

Sample A: the sample was removed from the base of the cupola in small pieces due to the fragmentary nature of the material. It has a greyish external surface and an internal reddish hue. The external greyish surface was relatively flat with a variation of hue from light to dark grey. The strong difference in colour between the external and internal surface—grey and red respectively—is attributed to the decay of the material. The thickness of the external alteration zone, as

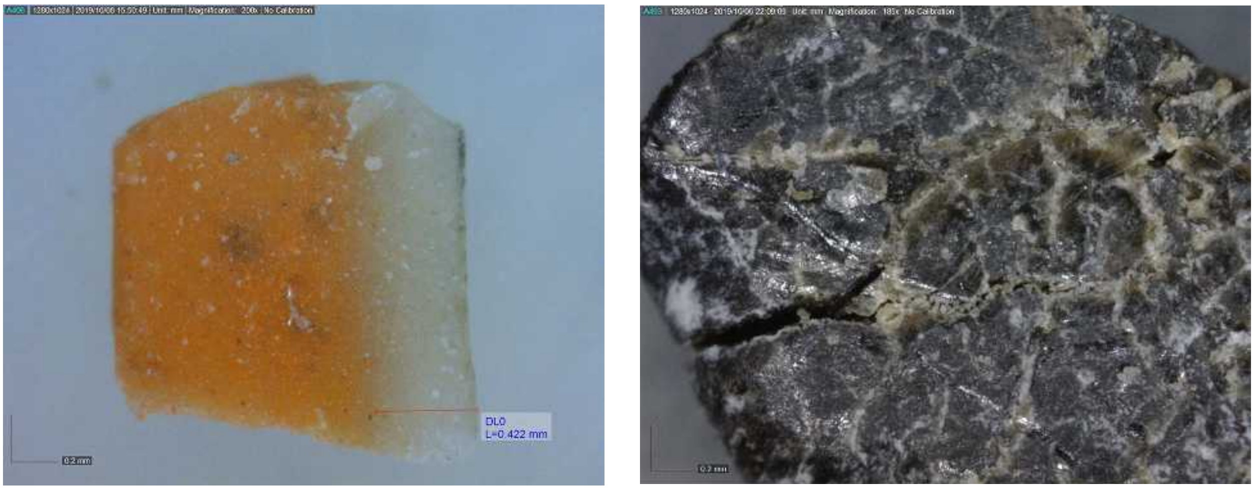

Figure 1. (a) Side view and measurement of the alteration zone on sample A small fragment and (b) Detail of the micro-cracking on the external surface of sample B.

measured on a freshly broken edge, was approximately 0.45 mm (Figure 1a). On the red areas, the presence of red grains was observed along with smaller black spots located at the more exposed sides, while in the grey areas no obvious grains were noticed.

Sample B: the sample had a dark brown-black hue and a more homogeneous nature. It was removed as a whole piece. The external surface is relatively flat and there is no obvious differentiation in colour between the external and internal surface. Microscopically the external surface exhibited micro-cracking and a more whitish colour. On fracture edges, areas of a yellowish, light brown hue were noticed of a texture that strongly resembled a waxy material. No grains were observed.

Sample C: the sample, a larger piece with a browner hue, was found detached and collected during conservation works. The external surface was rougher and the interior more uneven as compared to the other samples. This was due to the existence of cavities and apparent inclusions, mainly in the form of red and black elongated features and grains.

In general, all the fragments exhibited a duller hue on the external surface as compared to the freshly fractured surfaces. Occasionally, white deposits of mortar were observed on the external surface and in contact with the marble element. On the inner side the presence of detached marble grains was revealed. The detachment of grains indicates a strong bond with the marble and its deterioration.

SEM/EDS Analysis

Following optical examination under magnification, selected small fragments of the three samples were analysed with SEM/ EDS analysis.

SEM analysis of the red part of sample A showed an abundance of grains distributed in the matrix. In BSE images they appear very bright, thus indicating the presence of an element or elements with high atomic weight. The grains varied in shape, from small isolated ones distributed in the matrix, to larger ones that had the shape of a conglomerate.

Elemental analysis revealed that the grains were rich in lead, indicating the use of a red lead pigment for the red hue. Furthermore, calcium (Ca) was detected. The analysis of the greyish-whitish area of the same sample revealed the presence of similar grains, but in this case elemental mapping detected the presence of lead combined with sulphur (Figure 2).

In sample B, the micro-morphology of the material indicated a completely organic nature with no apparent grains. Elemental analysis detected calcium (Ca) only in areas where the presence of marble crystals was evident.

In sample C, in accordance to optical examination, a variety of inclusions, different in size and shape, were noticed in the matrix. At the same time, elemental analysis revealed a larger range of elements in low concentrations: Fe, S, Ba, Ca, Si, Al, Zn etc. Furthermore, the presence of specific crystals rich in barium (Ba) and sulphur (S) were detected (barite was identified through FTIR, spectrum not shown), as well as formations rich in iron (Fe) and grains with the combined presence of Si and Al (Figure 3).

FTIR analysis

The FTIR spectra of samples A and B showed absorbance bands that were attributed to wax (probably beeswax), while for sample C the presence of wax was less

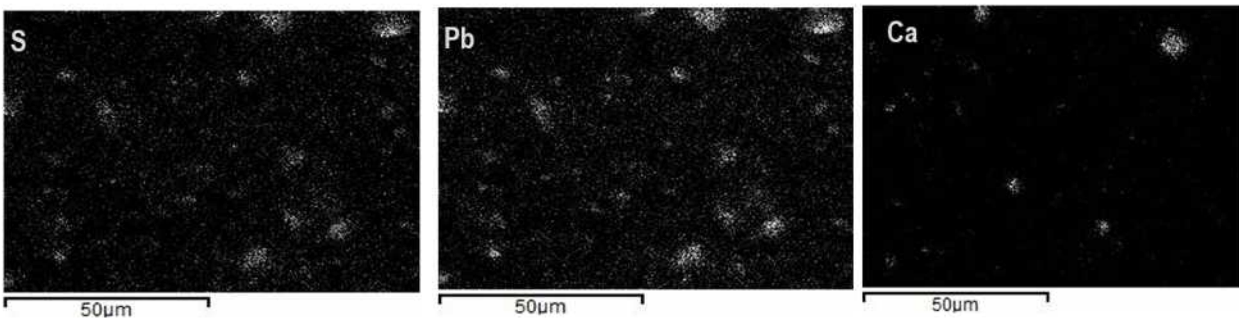

Figure 2. Sample A grey area- Elemental mapping for lead, sulphur and calcium, respectively.

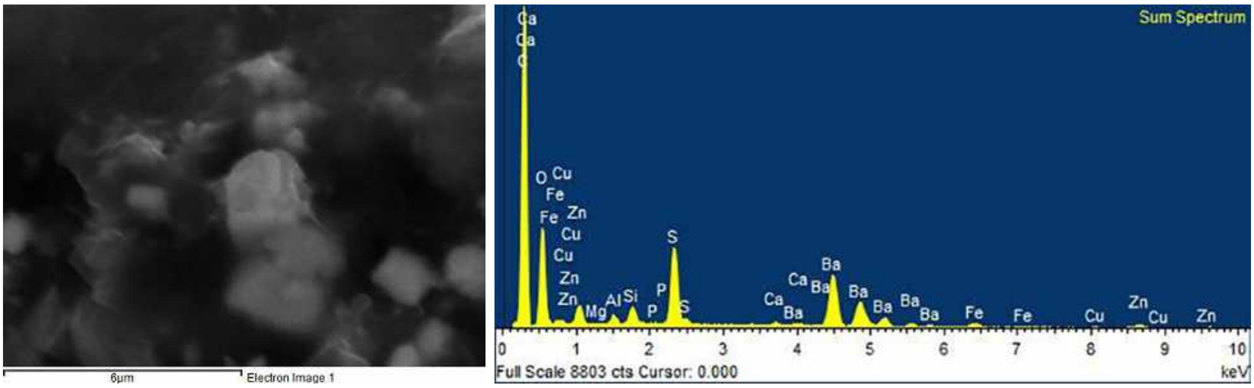

Figure 3. a, b Sample C., (a) SEM image of grains where barium and sulphur has been detected and (b) EDS spectrum

apparent, and a resin or a mixture of resins was more profound (Figure 4) (Table 1). The resulting spectra of sample C was compared to a modern mixture of the wax and resins (rosin and mastic) used in conservation-restoration.

The colour of sample B, where no obvious grains were detected, could be attributed to a carbon-based black pigment. This was investigated through FTIR of a xylene-extracted sample, where a strong sharp peak at 1585 cm^{-1} was evident (due to aromatic ring in carbon black graphite, spectrum not shown) (Rositani *et al.* 1987). It was not, however, possible to determine precisely the type of carbon pigment, i.e. flame carbon, char, or coke (Tomasini *et.al.* 2015).

In all the samples, the most common compound detected was calcium carbonate attributed to the marble grains. The presence of oxalates was also revealed on most spectra, along with bands of organic salts that indicate the degradation of ester or acidic organics, presumably the corresponding fraction of beeswax (Table 1).

Furthermore, the investigation focused on the difference in appearance optically recorded in sample A. This was considered as a strong indication of decay. ATR-FTIR analysis was carried out on both areas of sample A, the red and the greyish. The reduction of the spectra revealed the presence of oxalates (possibly, calcium), organic salts (possibly soap), and bands attributed to mixed sulphate phases including calcium (anhydrite) and lead (anglesite) (Figure 5).

The characteristic absorption bands of beeswax and the other main constituents are presented in Table 1 (Birshtein and Tul'chinskii 1977; Cuni, *et. al.* 2012; Font *et. al.* 2007; Galatis *et. al.* 2012; Mayo *et al.* 2004; Nevin *et al.* 2009; Theodorakopoulos *et. al.* 2007).

Discussion

The main component of the material of samples A and B is wax, and most probably beeswax. Bands attributed to the degradation of wax were also detected. The presence of soaps is not considered to be evidence of wax treatment (i.e. punic wax)—a common debate in analyzing painting with wax—since it does not appear to have been a necessary procedure in this type of decoration. On the contrary, the main component of sample C was resin, and most probably a mixture of resins, rosin, and mastic or dammar.

Elemental analysis detected lead as the main component of the grains in sample A. This indicates the use of red

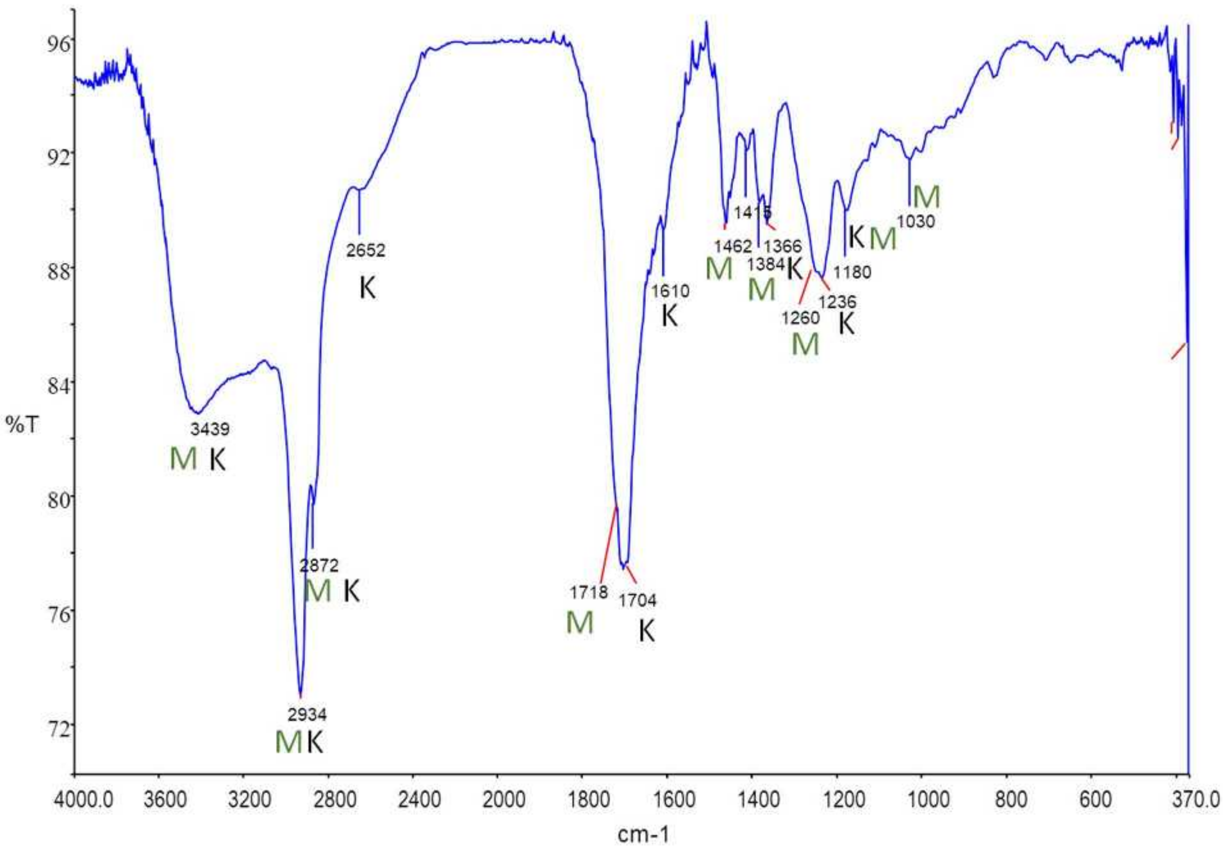

Figure 4. the FTIR spectra indicating a diterpenic resin (presumably, rosin/colophony), possibly mixed with mastic. Absorption bands attributed to: Rosin (K): 2934, 2872, 2652, 1704, 1610, 1366, 1236, 1180 cm^{-1} and Mastic (M): 1718 (shoulder), 1366, 1260, 1030 cm^{-1}

lead pigment similar to wall paintings. For the dark-brown, sample B, the absence of an inorganic element indicative of a pigment, in combination with the bands on FTIR spectra, suggests the use of a carbon- based black colorant. For sample C, various types of inclusions were detected with SEM/EDS analysis, such iron-rich grains. These demonstrate the use of a different red pigment from sample A and the possible presence of barium sulphate.

The different composition of sample C as detected with FTIR analysis, in combination with its macroscopic features and the results of elemental analysis with EDS, supports the initial hypothesis that this sample dates from a later intervention.

Calcium (Ca) was detected in all the samples with elemental analysis and as calcium carbonate bands in FTIR spectra. However, as the samples were analysed as received, the calcium carbonate could either have derived from the external environment, marble and/ or lime mortar, and/ or it could be an initial component of the mixture.

The presence of oxalates is not an unusual feature, as in recent years they have been recognised as common deterioration products on monuments made of various materials and were also detected on the external surface of a tessera deriving from the wall mosaics of the same monument (Loukopoulou 2019).

Coloured wax was used from antiquity for the decoration of marble sculptures, while the most widespread use of wax is in painting, like in encaustic technique. Furthermore, wax was employed in wall paintings from Roman period, and a recent study verified its use also in the wall painting of a Byzantine church in Egypt (Gehad 2015).

Although in the relevant bibliography the inlay for the Byzantine champlevé sculptures is commonly described as a mixture of wax and resin, the present research revealed the use of only wax for the two samples considered to be original material. To the authors' knowledge, the only study of similar material derives from the sculpture decoration at the altar piece of a church dated to the Byzantine period, though this

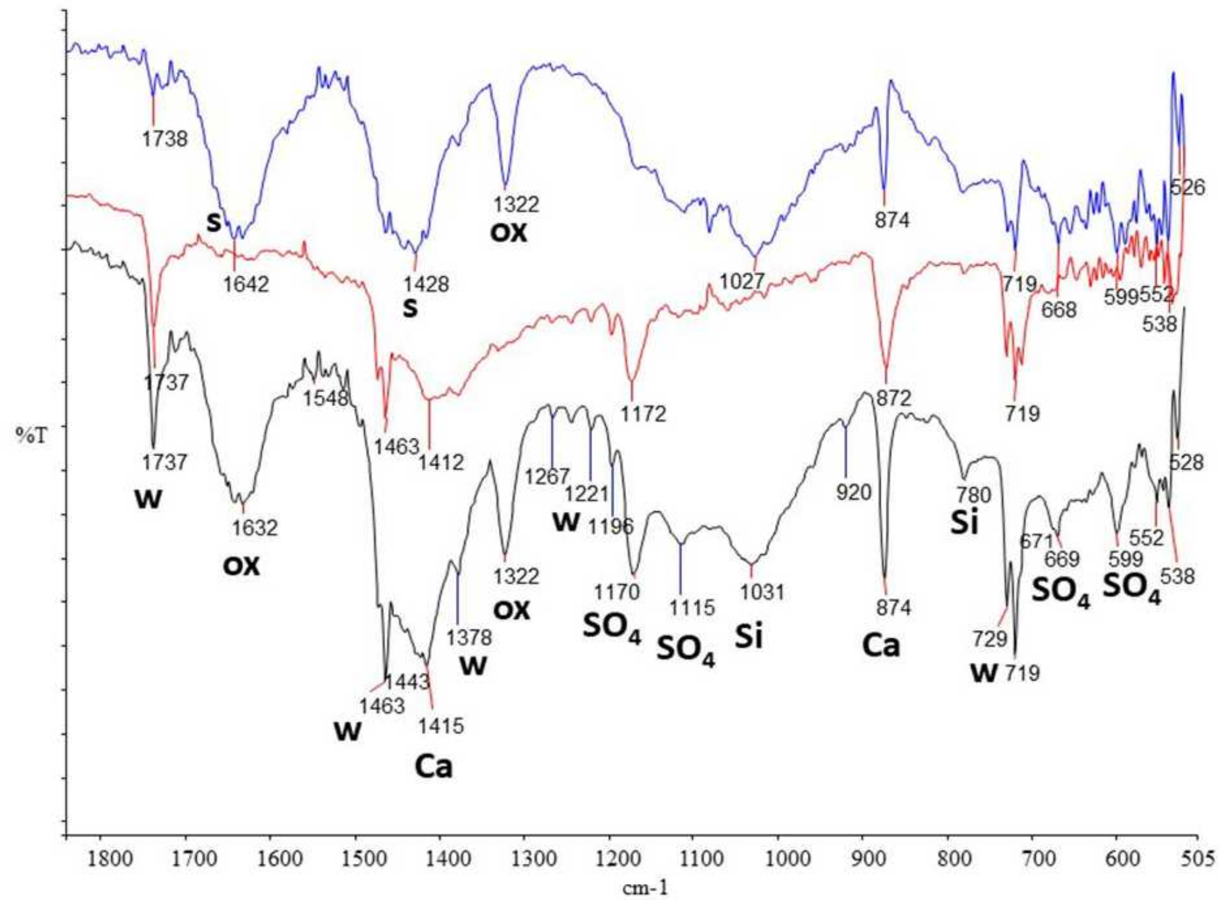

Figure 5. Sample A, FTIR spectra from grey area (bottom), the red area (middle) and after reduction (top) indicated the presence of beeswax peaks (W), Calcium Carbonate (Ca), mixed sulphate phases, Oxalate (calcium) (OX) and organic salt, possibly soap (S).

Table 1. Infrared peaks and assignments (ATR spectrum)

Beeswax related		**Other**	
2919, 2851(s)	νC-H in long alkyl chains of hydrocarbons, fatty acids and esters (wax components)	3412	νOH in water
1738	νC=O in esters (wax components)	1643, 1633(br)	δOH in water (silicates), $\nu_{as}COO^-$ in oxalate salts
1712	νC=O in fatty acids (wax components)	1585	Aromatic ring vibration in carbon black
1464	δCH_2, $\delta_{as}CH_3$ of long alkyl chains of hydrocarbons, fatty acids and esters (wax components)	1423	$\nu_{as}CO_3$ in calcite
1380	$\delta_s CH_3$ of long alkyl chains of hydrocarbons, fatty acids and esters (wax components)	874, 712 (overlapped)	δCO_3 in calcite
1171	νC-O in esters (wax components)	1032	νSi-O in silicates
729, 720	ρCH2 (doubly split, due to crystallized hydrocarbon content)	552, 538	δSO_4 in silicates
		783	δCOO^- in oxalate salts
		1323	$\nu_s COO^-$ in oxalate salts
		1177, 1115, 1080	$\nu_{as}SO_4$ in barite
		635, 609	δSO_4 in sulphate salt (barite)

remains an unpublished work that was carried out in the framework of a Conservation Project (Galanou A. and Dogani G., 2008 personal communication). The analysis of the material in question was carried out using Gas Chromatography - Mass Spectrometry, and again only the presence of beeswax was detected.

At the same time, the use of wax as a medium in painting has been studying extensively, along with published data for wax alteration and the analysis of objects made of wax. The use of coloured wax and the wax-based painting technique in antiquity is well documented, particular for the encaustic technique. A recent experimental study of ancient encaustic technique provided data on the changes of wax samples (prepared as films) after artificial ageing. These changes were constituted of colour alteration towards a whitish hue for most, and a white powdery texture or the development of cracks (Stacey *et al.* 2018). These results are in accordance with the observed morphology of the external surface of the waxy inlay material from the Daphni Monastery.

The alteration of lead-based pigments and in particular of the red lead that leads either to the darkening or the lightening-whitening of the paint layer, was also documented. The usual degradation products reported are: anglesite PbSO4, cerussite PbCO3, hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$, black lead dioxide (β-PbO_2), and lead sulphide PbS (Aze 2006, Aze 2008). The fading of the external surface of the red paint layers in wall paintings was attributed to the transformation of red lead to anglesite $PbSO_4$ and cerussite $PbCO_3$ because of the chemical reactions of carbonation and sulphation, respectively (Aze 2006). Furthermore, in the study of red lead (minium) alteration of outdoor wall paintings of a church dated from the 17th century, anglesite was detected (Sotiropoulou *et al.* 2008).

The colour change of sample A, as the difference observed between the external and internal surface, could be attributed to the decay of wax in combination with the alteration of the red pigment (lead tetroxide). In this case, the alteration of the red lead pigment tended possibly towards anglesite PbSO4 (greyish) as the presence of lead carbonate was not verified.

Conclusions

The chemical characterisation of the inlay material from the marble kosmites of the Daphni Monastery, through FTIR and SEM/EDS analysis, combined with morphological features, enabled us to reveal the nature of the material, the identification of pigments, and degradation phenomena.

The analysis verified the organic nature of the basic material of the inlay and showed that the two samples were composed of wax (beeswax) only, while the third one was composed of a mixture of wax and resins. Although in the literature a mixture of wax and resin is often reported, in our study this was detected only in the sample considered to be a later addition.

The study further demonstrated the use of the FTIR technique and SEM/EDS as an initial tool for the analysis of the inlay material. The alteration of the reddish inlay towards a grey hue was detected and attributed to the combined effect of the alteration of wax and the pigment's grains. In the future, further analysis could provide more data about the basic material of the samples and their alteration, along with the type of the carbon – based black pigment used in the black inlay.

Acknowledgements

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Materials and Techniques of Two Late 19th Century Greek Icons: An X-ray Techniques-Based Investigation

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Abstract: Two late 19th century Greek popular religious panel paintings ("icons") were subjected to analytical investigation through portable/handheld and micro X-ray fluorescence spectrometry, supplemented by X-ray radiography. A two-dimensional elemental distribution mapping technique that employs a conventional tabletop micro-XRF device equipped with an x-y stage and open-source analysis software is demonstrated. This approach led to a non-destructive characterization of the materials and techniques employed in the production of the two artifacts. Identified materials include a calcium sulfate compound that was used as priming/ground, and the pigments lead white, lead-chrome yellow, red iron ochre, minium, and carbon black. In addition, thin brass leaves and high-purity silver alloy decorative elements were used for the embellishment of halos and other pictorial elements. Even though both artifacts were painted by a single craftsman who used the same painting techniques, the analytical investigation revealed considerable differences with regards to the materials employed. This study is a first attempt to compensate for the notable literature gap in the analytical investigation of late post-Byzantine Greek icons.

KEYWORDS: IMAGING X-RAY FLUORESCENCE, X-RAY RADIOGRAPHY, PIGMENT, POST-BYZANTINE ICONS.

Introduction

Traditional post-Byzantine icon painting declined in Greece during 19th century, and was largely replaced by westernized and "academic" religious painting (Φριλίγγος 2002; Γραικός 2011). Nevertheless, several folk painters still adhered to the traditional Byzantine-style painting. The artefacts in this study are characterized by stylized representations and deliberate deviation from realism, two-dimensionality, enhanced linear pictorial elements (contours), and the rendering of dark and lighter hues by non-intermixed colour tones. Although artists of the latter type were not appreciated by their contemporaries, more recently folk painting has been viewed as an important, authentic expression of instinctive artistic creation. It is indicative that the works of specific folk artists, such as Theophilos Chatzimichail, for example, have gained great popularity and are very much admired by art historians (Τσαρούχης 1966; Χατζηγιαννάκη 2007).

In the context of a recent field research on Greek folk religious painting, two idiomorphic late 19th/early 20th century religious panel paintings ("icons") that depict St Fanourios were spotted (Figure 1). Their style of painting is very naive and characteristic, and they exhibit notable stylistic similarities that indicate that they were painted by a single craftsman. Indeed, one may note that in both icons St Fanourios is depicted in exactly the same posture, while the sketches follow the same characteristic and very much stylized outlines. In addition, the inscriptions lack accents and are written in the same handwriting, while both icons bear a particularly broad black border outline. Moreover, both icons were painted on wooden panels of practically identical dimensions and made of very similar softwoods (Figure 1).

The great similarity and simplicity of these paintings triggered analytical investigation. The primary aim of this study was the identification of the priming materials ("gesso"), pigments, metallic decorative elements, and the elucidation of the techniques by

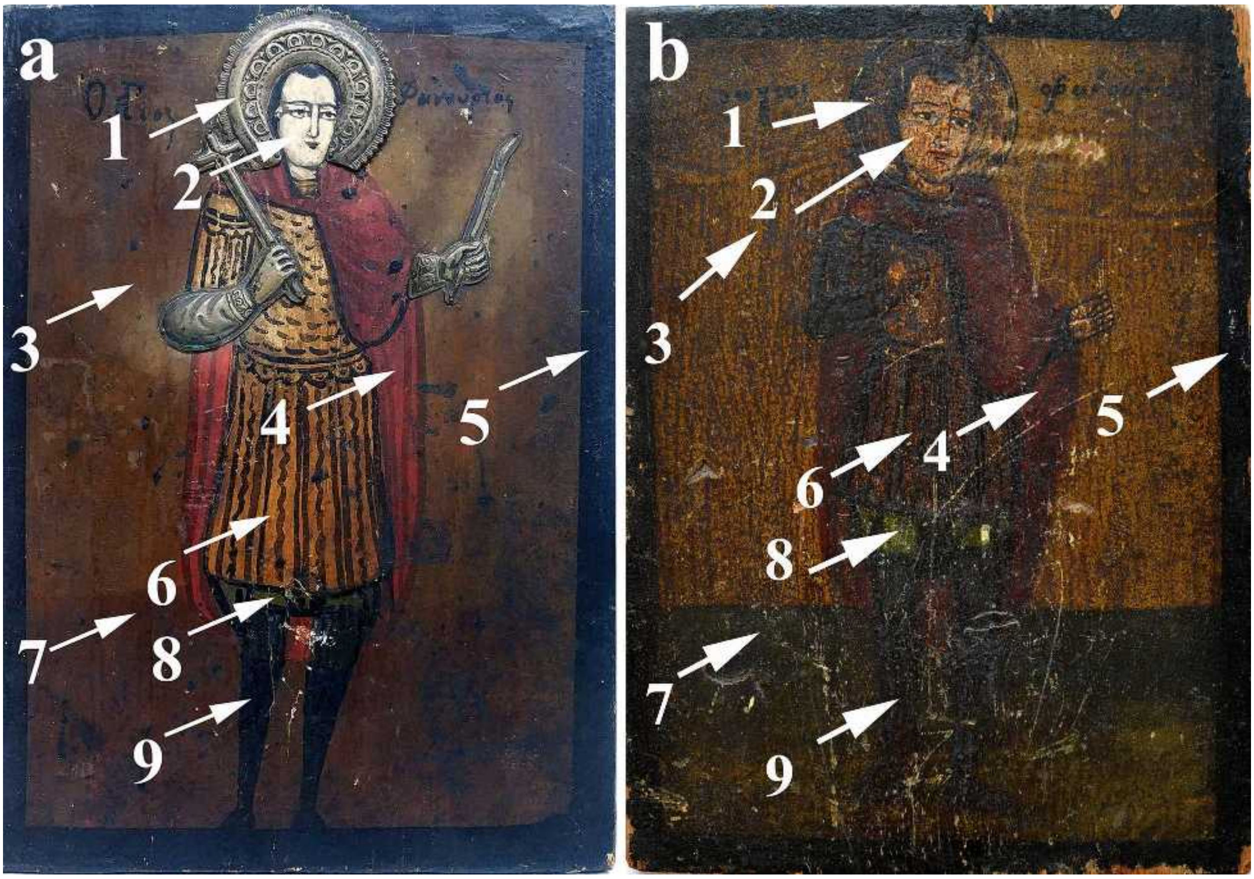

Figure 1. The two St Fanourios icons in consideration. Numbers and arrows indicate the points analyzed by p-XRF (Tracer 5i – Bruker).

which these materials were used by the artist. Such a study is interesting since despite the rather extended bibliography on older (pre-19th century) Greek post-Byzantine religious icons (Karapanagiotis, *et al.* 2013; Mastrotheodoros, *et al.* 2016; Sotiropoulou and Daniilia 2010), scholars have very rarely focused on later artifacts. Besides, to the authors' knowledge, this is the first work that focuses on the analysis of this type of late (circa 1900) Greek popular religious panel paintings.

The valuable character of cultural heritage assets requires, whenever possible, the application of non-destructive protocols for their investigation. When it comes to analyzing archaeological/cultural heritage items, X-ray fluorescence (XRF) techniques offer rapid and accurate elemental characterization in a practically non-invasive way (Mantler and Schreiner 2000).

In the case of the icons in consideration, the authors have implemented a non-destructive analytical protocol that exclusively employs X-ray based techniques. Specifically, two X-ray spectrometers, a handheld and a tabletop one, were employed in the current study. An important novelty of our study is the successful generation of sufficiently-detailed 2D elemental distribution mappings by employing a conventional tabletop spectrometer and adequate open-source software (see Methodology for details). It should be noted that elemental distribution mapping through complex scanning macro-XRF set ups, is currently regarded amongst the most promising tools in painting analysis (Romano, *et al.* 2017; Janssens, *et al.* 2016).

As a supplement to XRF techniques, digital X-ray radiography (DR) was employed. Hard X-rays penetrate throughout paint layers and wooden supports—their absorbance depending on the atomic number of the analyte constituents. Therefore, DR is routinely employed in the context of painting analysis for investigating manufacturing materials and techniques, and for assessing the preservation state of wooden panels and paint layers (investigation of wood defects, insert metallic elements, crevices/lacunae etc.) (Hassel 2005; Gavrilov, *et al.* 2014).

Methodology

A Philips Bucky diagnost (TH2/CS4) device equipped with an Agfa digital detector (DR 17e G) was employed for recording radiographs from the icons in consideration. Specific points on both artifacts were

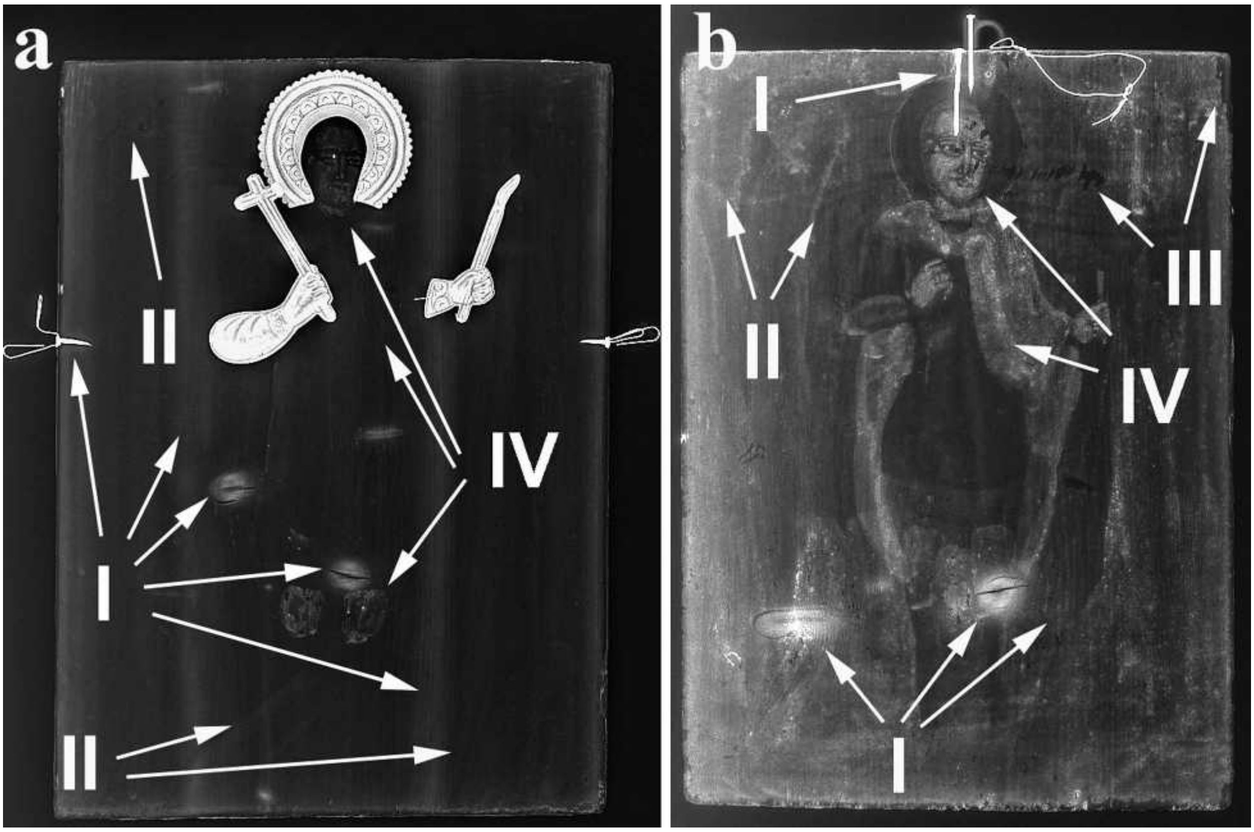

Figure 2. Digital radiographs. Arrows "I" point to wood characteristics/inserted elements; "II" show gesso application gestures; "III" paint losses; and "IV" characteristic paint layers.

analyzed with a handheld XRF spectrometer (Tracer 5i, Bruker) equipped with a Rh anode X-ray tube and a silicon drift detector (energy resolution: 145 eV @ Mn Kα-energy). The tube voltage was set to the maximum 50 kV, the current was fixed to 30 μA, and a set of filters (25 μm Cu/25 μmTi/300 μm Al) was used; every single point was measured for 5 s. The compact set-up geometry allows for the detection of elements as low as Na. In addition, the M1-Mistral tabletop spectrometer (Bruker) was used for the determination of the lateral distribution (map) of detectable elements. The device is equipped with a micro-focus X-ray tungsten tube and a high-resolution SSD detector. X-ray fluorescence mapping (XFM) acquisition is done by raster scanning the sample under the beam using the step-by-step mode. The beam spot is determined by a circular mask of 700 μm nominal diameter, and the lateral resolution of the system was about $0.8 \times 0.8 mm^2$ (Papagiannis 2020). The W X-ray tube operated at its maximum power of 50 kV high voltage and 800 μA current; a total number of more than 1,000 spectra were recorded in each case, and every point was measured for 5 s. Spectra were analyzed using the PyMca program (Solé, *et al.* 2007), which allows peak identification based on theoretical XRF emission lines. Atomic elements below potassium are undetectable due to the spectrometer's sensitivity.

Results and discussion

Digital X-ray radiography (DR)

For reasons of convenience from now on the two St Fanourios icons will be designated as "a" and "b" according to Figure 1. Note that the corresponding dimensions are $33.5 \times 24.5 \times 1.9\ cm^3$ ("a") and $34.0 \times 24.5 \times 1.6\ cm^3$ ("b").

The bulk metallic decorative elements that exist on icon "a" hindered the examination of the subject painting during DR investigation, and also acted as high-contrast areas, slightly obscuring the details of the painting. Nevertheless, the latter problem was largely surpassed through proper digital image processing of the radiograph (Figure 2a). The radiographs reveal the presence of metallic elements (nails) that were inserted into the wooden supports (probably for purposes of hanging), while the wood anatomic characteristics and defects (grain and knots) were also clearly recorded (Figure 2, arrows I). Note that the knots give off resin and also create tensions that may gradually lead to paint losses. For these reasons, they were ordinarily avoided or received special treatment prior to painting (Véliz 1998). Hence, it appears that the "anonymous" painter used rather improperly prepared wooden panels. It is also apparent that both panels correspond to radial wood cuts and were manufactured by using similar wood species (most probably evergreen coniferous trees as was indicated by macroscopic examination). In addition, DR revealed that in both icons the priming material (ground/"gesso") was freely applied on the panels through broad and rather quick brushstrokes (Figure 2, arrows II). Interestingly, the higher x-ray absorption of icon "b" ground implies the use of a different material than the one used in icon "a". Similarly, it is evident that the red cloak of St Fanourios was rendered by using different pigments in the two icons, while the flesh tones exhibit very similar X-ray absorbance (Figure 2, arrows IV). Minor paint losses are recorded only in the case of icon "b".

Point XRF analysis results

Several spots on the icons were analyzed through the handheld XRF device. The pertinent analytical results are summarized in Table 1 and discussed in detail below.

The halo of icon "a" is covered by a relief decorative metal sheet (oklad) manufactured by a silver-copper alloy (debased silver). In contrast, Cu and Zn are the major elements detected in the halo of icon "b", revealing the use of a brass foil gilding (Mastrotheodoros, *et al.* 2018). The detection of minor amounts of Ca, Sr, and S in the same spot is presumably related to the ground layer (calcium sulfate compound) that lies below the leaves (Mastrotheodoros, *et al.* 2016). On the other hand, the detected minor amount of Fe and traces of Pb relate to the glue/mordant used for applying the leaves on the ground. Similar results (i.e. detection of Cu, Zn and Ca as major elements) were obtained upon analyzing the armors in both icons and the greaves in icon "b" (spots No6 and 9, Table 1-Figure 1). The use of brass leaves in these cases was verified as well. Note that the technique of applying brass instead of gold leaves is often described as "false gilding" (Perez-Rodriguez, *et al.* 2018).

In both artifacts the flesh parts show enhanced Pb along with minor Fe, which imply rendering in a lead white plus iron-ochre pigments mixture (spots No2 in

Table 1 Point XRF analysis results. Major detected elements appear according to the magnitude of their fluorescence emission lines intensity. In parenthesis are shown the minor or trace elements. Question marks denote uncertainty on specific identifications.

Analyzed Spot	Detected elements (icon a/b)	Attribution
Halo (1)	a: Ag, Cu, As, Pb (Au, Zn, Fe)	Silver-copper sheet
	b: Cu, Ca, Zn, Sr, Fe, Pb (S)	Brass foil, Pb-Fe-containing mordant, Ca-S ground
Flesh (2)	a: Pb, Fe (Ca, Mn)	Pb-white, Fe-red
	b: Pb, Sr, Ba, Ca, Fe (Cu)	Pb-white, Fe-red, Ca-Sr (& Ba): ground (?)
Background (3)	a: Ca, Pb, Fe, Sr, Cr, Ba, Mn (Zn, Cu)	Pb/Cr-yellow, Fe/Mn-ochre
	b: Pb, Ca, Fe, Cr, Sr, Mn, Ba (Zn, Cu)	Pb/Cr-yellow, Fe/Mn-ochre
Red cloak (4)	a: Ca, Fe, Sr, Pb (Zn, Cu)	Fe-ochre
	b: Pb, Ba, Ca, Sr, Fe (Cu)	Pb-red
Black borderline (5)	a: Fe, Pb, Ca, Sr, Cr, Mn, Ba (Zn, Cu)	C-black (?)
	b: Pb, Fe, Ca, Cr, Sr, Mn, Ba (Cu, Zn)	C-black (?)
Armor (6)	a: Cu, Ca, Zn, Sr, Fe (Pb, S)	Brass foil
	b: Cu, Ca, Zn, Sr, Fe (Pb, S)	Brass foil
Ground (7)	a: Pb, Fe, Ca, Cr, Mn, Sr, Ba (Cu, Zn)	Pb-Cr yellow + red Fe-ochre
	b: Pb, Fe, Cr, Ca, Mn, Sr, Ba (Cu, Zn)	Pb-Cr yellow + organic blue (indigo?)
Green garment (8)	a: Ca, Pb, Fe, Sr, Ba, Cr, Mn (S, Cu, Zn)	Green earth + Pb-Cr yellow (?)
	b: Pb, Ca, Fe, Cr, Sr, Cu, Zn (Ba, S, Mn)	Pb-Cr yellow + organic (or Prussian) blue (?)
Greaves (9)	a: Fe, Ca, Pb, Cr, Mn, Ba (Zn, S, Cu)	C-black (?)
	b: Cu, Pb, Ca, Fe, Zn, Sr, Cr (Mn, Ba)	Brass foil

Figure 1 and Table 1). Besides, mixing a white pigment with a red one is the most common way of rendering flesh parts in Orthodox iconography (Διονύσιος 1997). Nevertheless, XRF revealed significant presence of Ba, Ca, and Sr in the case of the flesh of icon "b". The first element indicates the presence of barium sulfate, while calcium and strontium may also pertain to a calcium carbonate or sulfate compound. Both baryte and chalk (along with other white components) were often added as adulterants in lead white (Eastaugh, *et al.* 2008).

In case of the yellowish backgrounds (spots No3) in both icons, Pb and Cr are detected, suggesting the use of yellow lead chromate, a pigment widely used during late 19th century (Kühn and Curran 1986). Fe and Mn indicate the presence of an ochre-type component, while the elements Ca and Sr are probably related to the subject calcium sulfate ground layer (Mastrotheodoros, *et al.* 2016). However, the notable differentiations with regard to the elemental peak intensities in the corresponding spectra indicate the use of different pigment mixtures in the two icons (Figure 3a). Different pigments were also used for the rendering of the red cloaks (Figure 1): the p-XRF data indicates that a red iron ochre was used in icon "a" while the same pictorial element was rendered in a Pb-rich red pigment (probably minium) in icon "b" (spots No4, Table 1, Figure 3b). Due to the high X-ray absorbance of lead compounds, this differentiation is graphically depicted in the digital radiographs as well (Figure 2). On the other hand, the elements detected on the borderlines are the same as the ones detected on the yellowish backgrounds, indicating thus that the black lines were rendered in carbon black and applied directly onto the background (Table 1, spots 5).

The ground on which St Fanourios stands is rendered in a pale brown/orange hue in icon "a" and in green in icon "b" (Figure 1, spots 7). On the basis of the corresponding p-XRF spectra, it seems that the painter used a lead chromate yellow pigment mixed with an iron red ochre in case "a", while the green tone of ground "b" may have been achieved by mixing the same yellow pigment (Pb-Cr) with an organic blue one, presumably indigo. The latter is, in fact, one of the most widely-used blue pigments in Greek post-Byzantine painting (Mastrotheodoros, *et al.* 2020). The p-XRF spectra collected from the green garments (spots 8) show notable differentiations, indicating the use of different pigment mixtures in the two icons. In the case of icon "a" the somewhat enhanced (in comparison to icon "b") iron peak may pertain to the use of green earth or Prussian blue (Eastaugh, *et al.* 2008; Mastrotheodoros, *et al.* 2020). Finally, the greaves in icon "a" (spot 9) appear blackish, and, on the basis of the corresponding XRF spectrum, it is considered probable that they were rendered in carbon black that was applied directly on the pale brown background.

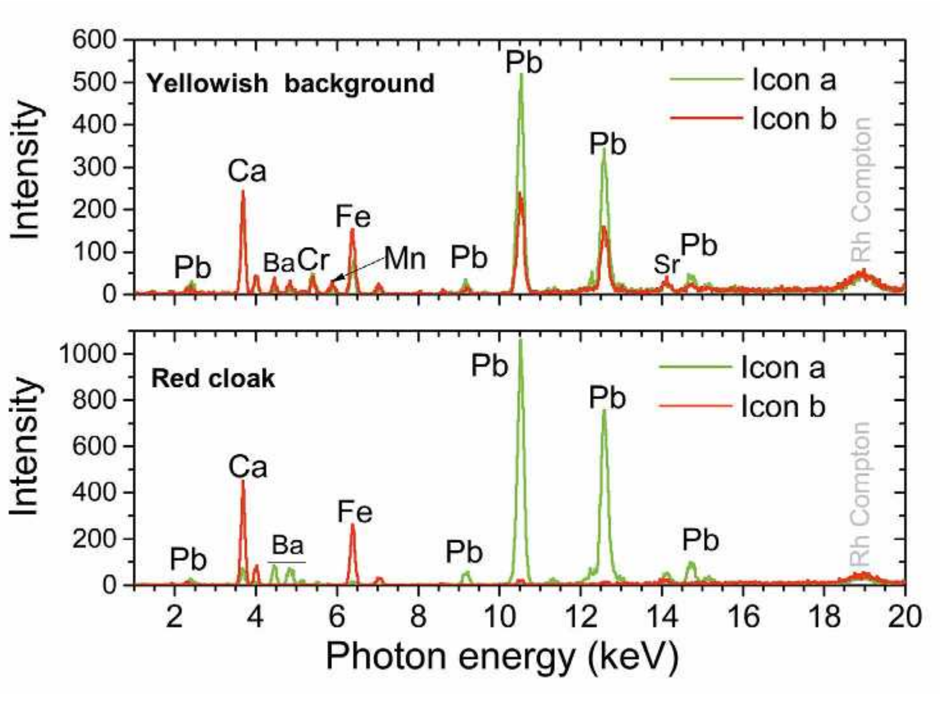

Figure 3. a: Overlapping of two XRF spectra collected from spots on the yellowish backgrounds of icons "a" and "b" (green and red lines respectively). b: XRF spectra from the red cloaks of icons "a" and "b" (green and red lines respectively).

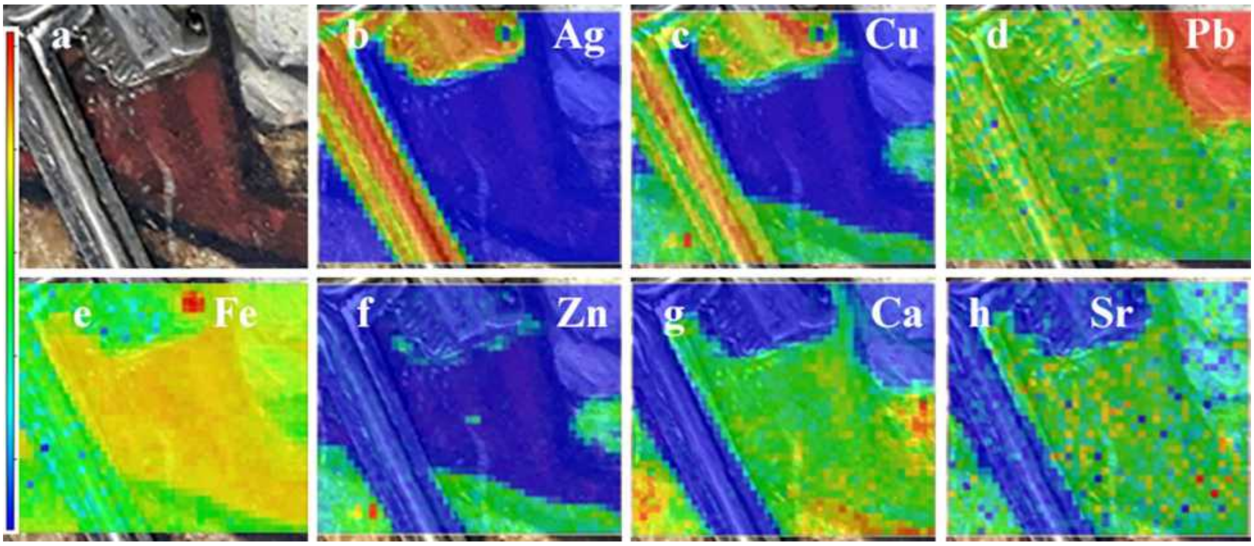

Figure 4. Various 2D elemental distribution maps, icon "a".

XRF two-dimensional elemental mapping

In the context of the current investigation the possibility of generating 2-D elemental distribution maps through the use of a conventional tabletop/bench top XRF spectrometer was explored [Papagiannis 2020]. In this framework, various areas on both icons were scanned and indicative mappings are presented and discussed below (Figure 4).

In case of icon "a" an area measuring 3.0×2.5 cm^2 that lays on the left part of St Fanourios' chest and includes both painted areas and metallic decorative elements was scanned (Figure 4a). In this case, the scanning step was 0.75 mm and a total of 1394 (41×34) points were measured (spectrum acquisition time: 5s). The elemental mapping analysis was performed with the PyMca program, using both the region of interest method (RoI) around characteristic element emission lines (typically a few tens of eV around the Kα or Lα fluorescence emission lines of the elements of interest) and the least square fitting method (Solé, *et al.* 2007).

The distribution maps of the elements Ag, Cu, Pb, Fe, Zn, Ca and Sr are shown in Figure 4. The scanned area consists of several well-defined areas. The cross is made of a silver-copper alloy, as is deduced from the Ag Kα and the Cu Kα intensity distributions (Figure 4b-c). Note that the sudden intensity drop observed in the upper-right part of the graph corresponds to the point where an iron nail has been placed to support the cross (see also the mapping of Fe-Figure 4e). The other intensity variations originate from height and surface orientation differentiations due to the sample's morphology, and do not pertain to composition variation. In order to determine quantitatively the weight concentration of the elements that compose the metallic decorative elements, a measurement was performed on a flat position on the cross. The analysis was performed by applying the PyMca code and lead to the following weight concentrations: 81% Ag, 17% Cu, 0.6% Fe, 0.8% As and 0.1% Au; also, elements Pb and Zn are detected at trace levels (<0.1 wt%).

On the other hand, the Pb Lα intensity distribution (in Figure 4d it is represented in logarithmic scale due to the high Pb-intensity) highlights the saint's flesh parts rendered in lead white. The very high intensity of Pb Lα peaks reveals the presence of a thick Pb layer, and this observation is consistent with the results obtained by X-ray radiography (Figure 2a). Similarly, the iron distribution in Figure 4e is shown in logarithmic scale as well due to the high intensity originating from the nail that holds the metallic cross in place. The intense iron distribution in the saint's red cloak reflects the use of red iron ochre (see also Table 1), while the intensity of iron drops drastically in the areas covered by the metallic cross.

On the other hand, the Zn Kα intensity distribution (Figure 4f) correlates well with that of Cu in the areas of armor, verifying the use of brass sheets in these particular pictorial elements. The Ca Kα intensity distribution (Figure 4g) outlines the areas covered by the metallic cross as Ca Kα photons cannot pass through the Ag-Cu metal sheet. What is more, no Ca Kα photons are detected in the flesh regions too; the rather thick Pb layer absorbs entirely the Ca Kα photons (energy of 3.7 keV), which originate from the ground/preparatory layer (probably a $CaSO_4$ compound). Interestingly, the Sr Kα distribution (Figure 4h) escorts the Ca distribution (Sr/Ca twins) probably because strontium sulfate is a common impurity of gypsum (Mastrotheodoros, *et al.* 2016). Nevertheless, one may note that there is a considerable Sr Kα photon distribution in flesh where no calcium was detected: Sr Kα photons are of significantly higher energy than Ca Kα ones (14.4 keV and 3.7 keV respectively). Therefore they manage to penetrate through the Pb layer.

Finally, we note the existence of three small regions that exhibit an enhanced Ca intensity without a 'corresponding' increase of Sr Kα intensity. The observed reduced Sr/Ca Kα intensity ratio in the latter areas indicates the presence of an additional calcium compound, which is not accompanied by the expected level of Sr. Strictly speaking, however, the Sr/Ca ratio depends both on the compound and its origin. Interestingly, the aforementioned Ca Kα enhancement appears in the areas where Cu and Zn are detected, hence it is assumed that the increase in calcium intensity is due to the use of a $CaCO_3$ compound in the brass foil gluing agent (mordant) (Antunes, *et al.* 2014).

Conclusions

Through the complementary use of various X-ray analytical techniques, the inorganic materials and the painting techniques employed in two late 19th century icons were identified. The two works depicting St Fanourios were made by the same folk painter who used typical—for the late 19th century—materials, such as bronze foils ("false gilding"), lead white, lead chromate yellow, Ba-containing pigments, etc. Interestingly, in some instances the painter used different pigments for the rendering of the same pictorial elements in the two icons, e.g. in the case of the St Fanourios' red cloak. The identification of the pigments and metallic elements was achieved through X-ray spectroscopy analysis, while X-ray radiography allowed for the observation of the anatomic characteristics of the wooden supports and revealed wood defects and inserted metallic elements. The authors explored the possibilities for creating 2-D elemental distribution maps by using a conventional tabletop XRF device and open source software. The latter approach allowed for the generation of relatively small (yet sufficiently detailed) maps in reasonable time spans, which revealed invisible (by both the naked eye and X-ray radiography) technical details. Moreover, elemental distribution mapping data revealed that the Sr/Ca ratio can be used for the detection of superposition of different calcium compounds.

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Χαρακτηρισμός των δομικών υλικών και εντοπισμός της φθοράς τους στους "Τάφους των Βασιλεών", Πάφος, Κύπρος

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Περίληψη: Η περιοχή έρευνας εντοπίζεται στον αρχαιολογικό χώρο της νεκρόπολης της Νέας Πάφου, η οποία βρίσκεται στο βόρειο και ανατολικό τμήμα της πόλης, ακριβώς έξω από τις οχυρώσεις. Το βόρειο τμήμα της νεκρόπολης είναι γνωστό με την ονομασία οι «Τάφοι των Βασιλέων» και καλύπτει μια έκταση περίπου 1,2 km^2. Οι «Τάφοι των Βασιλέων» είναι ταφικά μνημεία εξολοκλήρου λαξευμένα μέσα στον βράχο. Θεωρούνται ως ένα από τα σημαντικότερα αρχαία μνημεία που σώζονται, καθώς αποτελεί ένα από τα λίγα παραδείγματα ελληνιστικής αρχιτεκτονικής που μπορεί να συναντήσει κάποιος στην Πάφο. Αυτός είναι ο λόγος για τον οποίο περιλαμβάνονται στον κατάλογο της UNESCO για την παγκόσμια πολιτιστική κληρονομιά, και η διατήρησή τους θεωρείται κρίσιμη. Επιπλέον, είναι γνωστό πως από την Ελληνιστική ως την Ρωμαϊκή εποχή ο χώρος λειτούργησε ως λατομείο.

Οι «Τάφοι των Βασιλέων» αποτελούνται από 8 ταφικά μνημεία. Στην παρούσα εργασία μελετήθηκαν οι τάφοι 3 & 4. Οι στόχοι της εργασίας είναι δύο: πρώτον ο ιστολογικός και ορυκτολογικός χαρακτηρισμός του πετρώματος δόμησης, ώστε σε κάθε προσπάθεια συντήρησης ή αποκατάστασης να χρησιμοποιείται ο ίδιος ή παρόμοιων χαρακτηριστικών δομικός λίθος. Δεύτερον, διερευνώνται οι υφιστάμενες φθορές και η αναγνώριση των αστοχιών που σχετίζονται με την ποιότητα του πετρώματος. Για την επίτευξη των στόχων έγιναν μετρήσεις του προσανατολισμού των βασικών τεκτονικών ασυνεχειών - ρωγματώσεων του βράχου, λήφθηκαν δείγματα για την πετρολογική μελέτη, καθώς και φωτογραφικό υλικό από τις θέσεις φθοράς και αστοχιών του ευρύτερου χώρου. Επίσης, πραγματοποιήθηκε μικροσκοπική μελέτη των δομικών λίθων από την οποία προέκυψε ότι όλοι χαρακτηρίζονται ως βιογενείς ασβεστόλιθοι. Από την ορυκτολογική μελέτη προέκυψε ότι ο ασβεστίτης είναι το κυρίαρχο ορυκτό και τα αποτελέσματά της είναι σε πολύ καλή συμφωνία με την μικροσκοπική μελέτη.

Η λειτουργία του χώρου ως λατομείου είχε ως αποτέλεσμα την εκτεταμένη απόληψη δομικών λίθων για την οικοδόμηση της πόλης της Πάφου και της ευρύτερης περιοχής. Αυτή η διαδικασία είχε ως αποτέλεσμα την φθορά των δομικών λίθων του μνημείου σε βάθος, γεγονός που επηρέασε και επηρεάζει την ποιότητά του στον χρόνο. Εντοπίστηκαν τόσο στα επιφανειακά όσο και στα υπόγεια τμήματα του μνημείου υφιστάμενες αστοχίες. Εξαιτίας της αλλοίωσης που έχει υποστεί το μνημείο από τις ποικίλες χρήσεις καθίσταται πολύ δύσκολη η διάγνωση και η εύρεση της προέλευσης των αστοχιών. Παρόλα αυτά, με βάση τα στοιχεία που έχουν συγκεντρωθεί από βιβλιογραφικές αναφορές, καθώς και τις παρατηρήσεις στο πεδίο γίνεται προσπάθεια εύρεσης των αιτιών φθοράς του μνημείου. Από τη μελέτη προέκυψε ότι πιθανές αιτίες είναι η μικρή απόσταση από την παραθαλάσσια ζώνη της Πάφου, η αυξημένη υγρασία της περιοχής, καθώς και οι άνεμοι ο οποίοι μεταφέρουν σταγόνες θαλασσινού νερού εμπλουτισμένες με άλατα ακόμα και κόκκους άμμου που έχουν ως τελικό αποτέλεσμα την ανάπτυξη του φαινομένου της κυψέλωσης. Επίσης, μελετήθηκαν οι υπάρχουσες ρωγμές στο μνημείο οι οποίες πιστεύουμε ότι συνδέονται με ρήγμα το οποίο πιθανώς να βρίσκεται κάτω από το μνημείο σε διεύθυνση Βορρά – Νότου, όπως και οι ρωγμές. Συνεπώς, η μικρό-σεισμικότητα της περιοχής διαδραματίζει σημαντικό ρόλο στην φθορά του μνημείου.

ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ: ΤΑΦΟΙ ΤΩΝ ΒΑΣΙΛΕΩΝ, ΠΕΤΡΟΛΟΓΙΚΟΣ ΠΡΟΣΔΙΟΡΙΣΜΟΣ, ΦΘΟΡΑ ΥΛΙΚΩΝ

Abstract: The study area is located at the archaeological site of the necropolis of Paphos at the north-east side of the city, outside the fortification. The north side of this site is known as "Tombs of the Kings" and covers an area of about 1.2 sq. km. The Tombs of the Kings are rock-hewn burial monuments (entirely cut into the native rock) and are considered as one of the most important ancient surviving monuments, since it is one of the few examples of Hellenistic architecture that can be found in Paphos. This is why it is included in UNESCO's list of world cultural heritage and its preservation is considered critical. Furthermore, it is known that the archaeological site, from the Hellenistic to the Roman era, was used as a quarry.

The site of the "Tombs of the Kings" consists of 8 burial monuments. This paper examines tombs 3 and 4. The goals of the paper are two: first, to classify the rock mass from a histological and mineralogical perspective, so that the same or similar kind of building stones may be used in case of further maintenance or restoration of the monument; and second, to study the existing failures which are related to the quality of the rock. In order to achieve the aforementioned objectives, the orientation of the basic tectonic discontinuities – fracturing of the rock were measured, samples were taken for a petrological study, as well as photographic material from the sites of damage and failure in the wider area. Furthermore, a microscopic study of the building blocks was performed which revealed that all of them fall under the category of biogenic limestones. The mineralogical study showed that calcite is the dominant mineral and its results are similar to the microscopic study.

The use of the site as a quarry resulted in the extensive removal of stone blocks for the construction of the city of Paphos and the wider area. This process resulted in the deterioration of the depth of monument stone block, which affected and affects its quality over time. Existing deficiencies were also identified on both the surface and underground sections of the monument. Due to the deterioration that the monument has undergone as a result of the various ways in which it has been used, it is very difficult to determine and trace the origin of the failures. However, based on the data collected from bibliographical references as well as observations in the field an attempt has been made to identify the causes of the deterioration of the monument. The study has showed that the possible causes are the short distance from the coastal zone of Paphos, the increased humidity of the area, as well as the winds that carry drops of sea-water enriched with salts and even sand grains that eventually result in the development of the "honeycomb" phenomenon. Finally, existing cracks on the monument were studied, which we believe are related to a fault that may be located beneath the monument towards a north – south direction, where the cracks are also directed. Therefore, the micro-seismicity of the area plays an important role in the deterioration of the monument.

KEYWORDS: TOMBS OF THE KINGS, FAILURES, PETROLOGICAL PERSPECTIVE

Ιστορικά στοιχεία μνημείου

Η ευρύτερη περιοχή της πόλης της Πάφου η οποία περιλαμβάνει και τη νεκρόπολη, γνωστή ως «Τάφοι των Βασιλέων», κατοικήθηκε για πρώτη φορά κατά την εποχή του Χαλκού, όταν στα δυτικά παράλια της Κύπρου ανθούσε ο ομώνυμος πολιτισμός (Τμήμα Αρχαιοτήτων Κυπριακής Δημοκρατίας). Δεν έχουν εντοπιστεί στην ευρύτερη περιοχή της πόλης της Πάφου ίχνη της Πρώιμης, Μέσης και Ύστερης εποχής του Χαλκού. Ένα μόνο εκτενές νεκροταφείο στην τοποθεσία Ισκεντέρ που έχει χρονολογηθεί στη Γεωμετρική, Αρχαϊκή, Κλασσική και Ελληνιστική περίοδο φανερώνει την κατοίκηση αυτή την περίοδο (Θεοδούλου 2006).

Τόσο η ανάπτυξη της πόλης, όσο και η ανέγερση των οχυρώσεών της είχε ως αποτέλεσμα την μεταφορά των νεκροταφείων έξω από τα τείχη της πόλης. Οι Πτολεμαίοι έδωσαν ιδιαίτερη σημασία στην Πάφο, εξαιτίας της θέσης της, που βρισκόταν απέναντι από την Αλεξάνδρεια την πρωτεύουσα της Μεσογείου. Οι στενές σχέσεις ανάμεσα στην κυπριακή πρωτεύουσα και την Αλεξάνδρεια αντικατοπτριζόταν τόσο στην αρχιτεκτονική, όσο και στον τρόπο κατασκευής των ταφικών μνημείων των δυο πόλεων. Για να είναι δυνατή η ικανοποίηση των συνεχώς αυξανόμενων αναγκών του πληθυσμού σε χώρους ταφής, χρησιμοποιήθηκε ολόκληρη η περιοχή που περιβάλλει την αρχαία πόλη. Η περιοχή προσφέρεται για κατασκευή λαξευτών τάφων εντός του μεγάλου πάχους ασβεστολιθικού υποβάθρου που είναι κατάλληλο τόσο για λατόμευση και λάξευση, όσο και για την οικοδόμηση της πόλης.

Η μνημειακή όψη και μεγαλοπρέπεια των τάφων στα Παλαιόκαστρα ώθησε τους λόγιους της Πάφου κατά το δεύτερο τέταρτο του 20ου αιώνα να ονομάσουν την περιοχή «Τάφοι των Βασιλέων». Η μυθοπλασία γύρω από τα μεγαλόπρεπα υπόσκαφα που βρίσκονται στο βορειότερο μέρος της περιοχής Παλαιόκαστρα αποτελούσε πρόκληση για τους κυνηγούς των θησαυρών, αλλά και για διάφορους περιηγητές που άφησαν κληρονομιά αξιοπρόσεκτες περιγραφές.

Η χιλιετής λατόμευση έχει ως αποτέλεσμα την καταστροφή της αρχικής εικόνας του μνημείου. Μια θέση για την πραγματική εικόνα του νεκροταφείου μπορεί να προσδιοριστεί στο νοτιοανατολικό τμήμα στο οποίο η επέμβαση ήταν πιο περιορισμένη. Μια σειρά από τύμβους καλύπτει τα βραχώδη εξάρματα που εσωκλείουν μικρότερους θαλαμωτούς τάφους. Ο αρχαιολογικός χώρος καταλαμβάνει συνολική έκταση περίπου 200.000 τετραγωνικών μέτρων. Αποτελείται από οκτώ τύμβους, με μεγάλη ποικιλία αρχιτεκτονικών τύπων. Ωστόσο η μελέτη της παρούσας εργασίας εστιάζει στον Τάφο 3 και στον Τάφο 4.

Στοιχεία των τάφων

Τάφος 3

Αποτελείται από ένα μεγάλο αίθριο με περίστυλη αυλή. Είναι προσιτός μέσω καλυμμένου κλιμακοστασίου που αποτελείται από 12 σκαλοπάτια. Η κάθε πλευρά της στοάς του αίθριου υποβαστάζεται από τέσσερις κολόνες δωρικού ρυθμού που επιστεγάζονται με το ανάλογο θριγκό. Το επιστύλιο είναι απλό, ενώ ακολουθεί διάζωμα από τρίγλυφα και μετόπες. Κάτω από κάθε τρίγλυφο υπάρχει λαξευτός κανόνας και οι απαραίτητες σταγόνες.

Κάτω από την ανατολική στοά διατηρείται το μεγάλο θυρεό άνοιγμα που περιβάλλεται από λάξευμα σε σχήμα Π, προς απομίμηση των θυρωμάτων των λεγόμενων Μακεδονικων Τάφων. Το θύρωμα επικοινωνεί με μεγάλο καμαρο-σκέπαστο θάλαμο του οποίου το δάπεδο έχει αλλοιωθεί από τη λατόμευση. Πιθανό να διατηρούσε κλίνες για εναπόθεση νεκρών στην αρχική του χρήση. Απέναντι ακριβώς από το κεντρικό θάλαμο στο δυτικό τοίχωμα υπάρχει ο νεκρικός θάλαμος που διατηρεί αριθμό θηκών λαξευμένων στα πλευρά του. Ο θάλαμος

Εικόνα 1. Άποψη του Τάφου 3 λήψη από πάνω από την ανατολική προς την δυτική πλευρά

είναι καμαρο-σκέπαστος και διατηρεί σε μεγάλο βαθμό το κονίαμα που αρχικά κάλυπτε όλες τις επιφάνειες του τάφου. Στο βόρειο τοίχωμα κάτω από την στοά που καλύπτει και το λάκκο υπάρχει μικρή οστεοθήκη. Ένας αριθμός λακκοειδών τάφων βρισκόταν κάτω από την ανατολική και νότια στοά. Στη βορειοανατολική γωνιά του τάφου υπάρχει ένα άνοιγμα που οφείλεται σε τυμβωρύχους και οδηγεί στο θάλαμο άλλου ταφικού συγκροτήματος του οποίου η είσοδος βρίσκεται στα βορειανατολικά του κεντρικού τομέα.

Τάφος 4

Αποτελεί τον καλύτερα διατηρημένο τάφο με περιστύλιο αίθριο. Είναι προσιτός μέσω κλιμακωτού δρόμου με 13 σκαλοπάτια. Το κλιμακοστάσιο είναι αρχικά παράλληλο με τη δυτική στοά του αίθριου και στην συνέχεια, σχηματίζει γωνία και καταλήγει στο αίθριο. Μέρος του δρόμου ήταν αρχικά στεγασμένο με πλάκες, όπως υποδηλώνει η λαξευμένη υποδοχή στην επιφάνεια του βράχου.

Στα δεξιά της κατάληξης του δρόμου κάτω από τη νότια στοά βρίσκεται ο λάκκος. Ο νεκρικός θάλαμος βρίσκεται στο κέντρο της ανατολικής στοάς και είναι προσιτός μέσω θυραίου ανοίγματος και σκαλοπατιού λαξευμένου κάτω από την στοά. Ο θάλαμος είναι εφοδιασμένος με τουνελόσχημες θήκες για απλές ταφές. Τις στοές υποβαστούν ανά τέσσερις κολόνες δωρικού ρυθμού. Ο θρίγκος διατηρείται και στις τέσσερις πλευρές ενώ η επιφάνεια των στοών είναι λαξευμένη με τρόπο που υποδηλώνει την ύπαρξη κτιστών αρχιτεκτονικών μελών, πιθανότατα κάποιας σύμης για την συγκέντρωση των όμβριων υδάτων. Οι κολόνες της δυτικής στοάς είναι ασυμπλήρωτες και έχουν τη μορφή πεσσών. Στο δάπεδο κάτω από τη βόρεια και νότια στοά βρίσκονται λακκοειδείς τάφοι.

Γεωλογία της παράκτιας ζώνης της Πάφου

Οι γεωλογικοί σχηματισμοί που απαντώνται στην περιοχή της Πάφου χωρίζονται σε τρεις μεγάλες κατηγορίες: την αλλόχθονη σειρά που περιλαμβάνει όλα τα πετρώματα της σειράς του συμπλέγματος των Μαμωνιών, τα αυτόχθονα πυριγενή της οφιολιθικής σειράς του Τροόδους και την αυτόχθονη σειρά των ιζηματογενών πετρωμάτων του ανώτερου Μεσοζωϊκού έως τις πρόσφατες αποθέσεις (Κωνσταντίνου 2004, Ρήγας 2008). Η παράκτια πεδιάδα της Κύπρου εκτείνεται από τον ποταμό Χαποτάμι και φτάνει ως την περιοχή Πέγεια. Το μήκος που καταλαμβάνει είναι περίπου 35 km, ενώ το πλάτος της αγγίζει περίπου τα 6 km (Χατζηιορδάνη 2008, Πογιατζής 2011). Η πεδιάδα της Πάφου καλύπτεται από θαλάσσιες αναβαθμίδες η μελέτη των οποίων μπορεί να δώσει σημαντικά στοιχεία για την τεκτονική της περιοχής και τον ρυθμό ανόδου της παράκτιας ζώνης. Η παράκτια ζώνη της Πάφου θεωρείται μια από τις πιο ψηλές θαλάσσιες αναβαθμίδες της ΝΔ Κύπρου με ύψος 400 ως 410 m από την επιφάνεια της θάλασσας (Zomenia 2012, Harrison *et al.* 2013).

Εικόνα 2. Άποψη της ανατολικής πλευράς του Τάφου 4 λήψη από επάνω από την δυτική πλευρά

Από την περιοχή Κισσόνεργα προς το αεροδρόμιο της Πάφου η θαλάσσια αναβαθμίδα έχει πλάτος 3 km και σχετίζεται με την ανύψωση της παλαιο-ακτής κατά 50 με 55 m από την επιφάνεια της θάλασσας σύμφωνα με την ηλικία των κοραλλιών που βρέθηκαν σε ύψος 3 m περίπου από την θάλασσα και χρονολογούνται 130.000 χρόνων, περίπου. Επιπλέον, η αναβαθμίδα φαίνεται να ακολουθεί μια πιθανή θέση της επιφανειακής εμφάνισης ενός ρήγματος εφφίπευσης (Κκάλλας 2009).

Λιθολογικά οι αναβαθμίδες αποτελούνται από ασβεστιτικούς ψαμμίτες, άμμους, χαλίκια και ιλύες, δηλαδή υλικά των θαλάσσιων αναβαθμίδων . Επιπλέον, συναντώνται Ολοκαινικές αποθέσεις οι οποίες αποτελούνται από κολούβια, δηλαδή από ριπίδια. Οι αλλουβιακές αποθέσεις καλύπτουν τις πλημμυρικές και δελταϊκές περιοχές των χειμάρρων. Οι αλλουβιακές αποθέσεις αποτελούνται από κροκάλες, άμμο, ιλύ και άργιλο.

Κλιματολογικά στοιχεία Κύπρου

Το κλίμα της Κύπρου χαρακτηρίζεται ως Μεσογειακό. Η συνολική μέση βροχόπτωση στους μήνες Δεκέμβριος, Ιανουάριος και Φεβρουάριος αντιστοιχεί περίπου με το 60% της ετήσιας βροχόπτωσης. Τόσο το υψόμετρο, όσο και η απόσταση από την παραλία παίζουν καθοριστικό ρόλο στη διαμόρφωση των τιμών της σχετικής υγρασίας του αέρα. Στη διάρκεια της μέρας κατά το χειμώνα και σ' όλες τις νύχτες του χρόνου η σχετική υγρασία κυμαίνεται κυρίως μεταξύ 65 και 95 %.

Στην περιοχή της ανατολικής Μεσογείου οι γενικοί άνεμοι είναι ασθενείς ως μέτριοι δυτικοί ή νοτιοδυτικοί το χειμώνα και βόρειοι - βορειοδυτικοί το καλοκαίρι. Οι πολύ ισχυροί άνεμοι θεωρούνται σπάνιοι. Οι τοπικοί άνεμοι είναι οι θαλάσσιες και απόγειες αύρες στις παράλιες περιοχές και οι αναβατικοί και καταβατικοί άνεμοι στις ορεινές περιοχές. Οι θαλάσσιες και απόγειες αύρες παρατηρούνται σε παράλιες περιοχές και μπορούν να γίνουν αισθητές σε απόσταση ως 35 Km από την παραλία. Οι θαλάσσιες αύρες στις παράλιες περιοχές και οι αναβατικοί άνεμοι στις ορεινές περιοχές έχουν τη μεγαλύτερή τους ένταση κατά τους καλοκαιρινούς μήνες. Όσον αφορά την ταχύτητα οι άνεμοι στην περιοχή της Κύπρου είναι κυρίως ασθενείς ως μέτριοι. Σύμφωνα με το Τμήμα Μετεωρολογίας της Κυπριακής Δημοκρατίας οι πολύ ισχυροί άνεμοι (ταχύτητα ανέμου 34 κόμβοι και πάνω) είναι σπάνιοι, ενώ πνέουν κυρίως στις προσήνεμες περιοχές όταν επηρεάζουν την Κύπρο συστήματα με πολύ χαμηλές πιέσεις. Σημειώνονται χαρακτηριστικές αλλαγές στην κατεύθυνση του αέρα κατά την διάρκεια της ημέρας στην περιοχή της Πάφου, που είναι τυπικές των Μεσογειακών παραλίων. Ο επικρατών άνεμος κατά την διάρκεια της ημέρας είναι Δυτικός, ενώ αλλάζει σε Βορειανατολικό κατά την διάρκεια της νύχτας.

Εικόνα 3. Περιοχή με έντονα τα σημάδια της χιλιετούς Λατόμευσης στην Βορειοδυτική πλευρά Τάφου 4

Κατά τη διάρκεια των εργασιών στο μνημείο παρατηρήθηκε ότι στη Βόρεια πλευρά του Λατομείου 3 η κυψελοειδής φθορά του μνημείου ήταν πιο έντονη απ' ότι στο Λατομείο 4. Πιθανώς να σχετίζεται με την έκθεση του στις καιρικές συνθήκες και με την διεύθυνση που πνέουν οι άνεμοι στην περιοχή.

Παρουσίαση επιφανειών φθοράς και υφιστάμενων αστοχιών στο μνημείο

Όπως έχει ήδη αναφερθεί ο ευρύτερος αρχαιολογικός χώρος λειτούργησε από τα Ελληνιστικά έως τα Ρωμαϊκά χρόνια ως λατομική περιοχή (Εικόνα 3 & Εικόνα 4). Κατά τη διάρκεια αυτών των χρόνων έγινε εκτεταμένη απόληψη δομικών λίθων για την οικοδόμηση της πόλης της Πάφου και της ευρύτερης περιοχής. Αυτή η διαδικασία είχε ως αποτέλεσμα τη φθορά του σχηματισμού, δηλαδή του ασβεστιτικού ψαμμίτη σε βάθος, γεγονός που επηρεάζει την ποιότητα της βραχόμαζας στον χρόνο.

Εστιάζοντας στην περιοχή μελέτης η αναγνώριση και η εξέταση των υφιστάμενων αστοχιών που σχετίζονται με την ποιότητα των ασβεστολιθικών πετρωμάτων αποτελούν στόχο της παρούσας εργασίας. Αστοχίες εντοπίστηκαν τόσο στα επιφανειακά, όσο και υπόγεια τμήματα του μνημείου. Βέβαια, σύμφωνα και με τους Kyriakides *et al.* (2016) λόγω της αλλοίωσης που έχει υποστεί το μνημείο από τις ποικίλες χρήσεις καθιστά πολύ δύσκολή τη διάγνωση και την εύρεση της προέλευσης των αστοχιών. Παρόλα αυτά, με βάση τα στοιχεία που λήφθηκαν από τις παρατηρήσεις στο πεδίο γίνεται προσπάθεια εύρεσης των αιτιών φθοράς του μνημείου.

Κατά την πορεία της μελέτης τέθηκαν τα ερωτήματα σχετικά με τους λόγους της φθοράς του πετρώματος. Ως πιθανή αιτία θεωρήθηκε η μικρή απόσταση από την παραλία της Πάφου, εφόσον ο χώρος των Τάφων των Βασιλέων απέχει από την παραλιακή ζώνη της Πάφου περίπου 150 m. Συνεπώς, η αυξημένη υγρασία της περιοχής, καθώς και οι άνεμοι οι οποίοι μεταφέρουν σταγόνες του θαλασσινού νερού εμπλουτισμένοι με άλατα ακόμα και κόκκους άμμου έχουν ως αποτέλεσμα την ανάπτυξη του φαινομένου της κυψέλωσης.

Η κρυστάλλωση αλάτων αναφέρεται στη μηχανική φθορά των πορωδών λίθων και δομικών υλικών, μέσω της ανάπτυξης μηχανικών τάσεων στο εσωτερικό των υλικών (πόρους) από κρυστάλλους αλάτων και διάρρηξη της συνέχειας του υλικού όταν οι τάσεις ξεπεράσουν την αντοχή του. Οι κύριες πηγές αλάτων σε τοιχοποιίες είναι η τριχοειδής αναρρίχηση από το έδαφος, τα γειτονικά υλικά όπως το τσιμέντο, και συχνά το ίδιο το συνδετικό κονίαμα. Τα άλατα μεταφέρονται και μέσω σταγόνων νερού.

Εικόνα 4. Σημάδια έντονης Λατόμευσης στον ευρύτερο χώρο των Τάφων των Βασιλέων.

Πιο αναλυτικά με τον όρο Κυψέλωση ή Κυψελοειδής φθορά χαρακτηρίζεται η εμφάνιση μικρών οπών σποραδικά ή σε συστάδες και είναι αποτέλεσμα συνήθως βιολογικής δράσης που δεν είναι πλέον ενεργή. Επίσης, ως κυψέλωση ονομάζουμε την ιδιόμορφη διάβρωση που παρουσιάζει ο λίθος λόγω δυνατών ανέμων, αιωρούμενων σωματιδίων και αλάτων. Στην περίπτωση αυτή δημιουργούνται στην επιφάνεια του λίθου ασύμμετρες οπές και κοιλότητες που πολλές φορές οδηγούν σε σπηλαιώδεις καταστάσεις. Στη συνέχεια, παρατίθενται εικόνες από το μνημείο στις οποίες παρατηρείται το φαινόμενο η βιβλιογραφία πρέπει να μπει στο τέλος της προηγούμενης πρότασης (Εικόνα 5 & Εικόνα 6).

Επίσης, κατά τις ψυχρές εποχές το νερό που εισέρχεται στους πορώδεις σχηματισμούς με την πτώση της θερμοκρασίας παγώνει. Η αλλαγή στην κατάσταση του νερού συνοδεύεται από διαστολή και αύξηση του όγκου που έχει ως αποτέλεσμα την διάνοιξη κενών στο πέτρωμα. Όταν η θερμοκρασία αυξάνεται τότε το νερό εξατμίζεται και τα κενά διευρύνονται. Ο τύπος αυτός της φθοράς εμφανίζεται μακροσκοπικά με τη μορφή της κυψέλωσης, δηλαδή την αποκόλληση τμήματος του διερρηγμένου υλικού.

Επιπλέον, είναι γνωστό όπως έχει αναφερθεί και νωρίτερα, ότι η περιοχή της Πάφου έχει πληγεί κατά το παρελθόν από ισχυρούς σεισμούς (Βελδεμίρη 2006, Papadimitriou and Karakostas 2006). Τα συνήθη μεγέθη σεισμού στην περιοχή είναι συνήθως μεταξύ M= 5,5-6 χωρίς να αποκλείονται ισχυρότεροι σεισμοί (Wdowinski *et al.* 2006, Cagnan and Tanircan 2010). Η ύπαρξη ρωγμών σε κάποιες θέσεις στο μνημείο σύμφωνα με τους Kyriakides *et al.* (2016) θεωρείται ότι συνδέεται με ρήγμα το οποίο πιθανώς να βρίσκεται κάτω από το μνημείο σε διεύθυνση Βορρά – Νότου όπως και οι ρωγμές. Σύμφωνα με Πανταζοπούλου (2017), υπάρχει πιθανότητα εκδήλωσης αστοχιών στους υπό μελέτη τάφους σε προυπάρχουσες επιφάνειες τεκτονικών ασυνεχειών. (Εικόνα 7 & Εικόνα 8)

Χαρακτηρισμός δομικών υλικών

Η φθορά ενός υλικού εξαρτάται όχι μόνο από τα μηχανικά χαρακτηριστικά του λίθου αλλά και από την ορυκτολογική του σύσταση. Πολλές φορές η αλλοίωση των συστατικών ενός πετρώματος και ο τρόπος που εκδηλώνεται αυτή η αλλοίωση ελέγχουν και πιθανώς καθορίζουν την έκταση, αλλά και την ένταση της φθοράς ενός μνημείου και διαδραματίζουν σημαντικό ρόλο στον τρόπο συντήρησης ή και αποκατάστασης (Μοροπούλου 2007).

Διεθνώς αποδεκτό είναι ότι μια αποκατάσταση δεν πρέπει απλά να είναι αισθητικά επιτυχημένη, αλλά το νέο υλικό που θα τοποθετηθεί στο μνημείο να έχει παρόμοια ορυκτολογικά και φυσικομηχανικά χαρακτηριστικά. Έτσι, επιτυγχάνεται η ορθολογικότερη αποκατάσταση ενός μνημείου με τη λιγότερο δυνατή επέμβαση σε αυτό. Από τα παραπάνω γίνεται εύκολα αντιληπτό ότι εκτός των άλλων απαιτούνται και εξειδικευμένες ορυκτολογικές και πετρολογικές μελέτες των στοιχείων ενός μνημείου για να είναι επιτυχημένη η συντήρηση ή η αποκατάστασή του.

Μικροσκοπική μελέτη

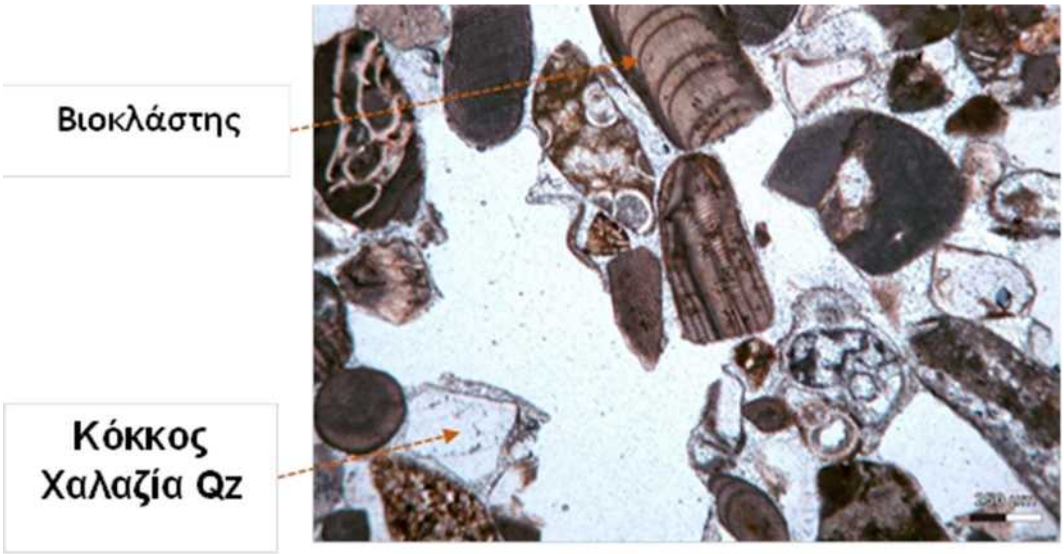
Από την εξεταζόμενη περιοχή και συγκεκριμένα από τους τάφους 3 και 4, αλλά και από τον υπόλοιπο αρχαιολογικό χώρο των Τάφων των Βασιλέων που λειτούργησε κατά τα ιστορικά χρόνια ως λατομείο, αξιολογήθηκαν μακροσκοπικά τα πετρώματα που εμφανίζονται και διαπιστώθηκε ότι όλα ανήκουν στο χαρακτηριστικό πορώδη ασβεστόλιθο της περιοχής της Πάφου. Έτσι, επιλέχθηκε αντιπροσωπευτικό δείγμα ασβεστόλιθου από το οποίο κατασκευάστηκε λεπτή τομή για μελέτη στο πολωτικό μικροσκόπιο.

Εικόνα 5. Κυψελοειδής φθορά λόγω ανέμων οι οποίοι μεταφέρουν σταγονίδια με υψηλή περιεκτικότητα σε άλατα Λατομείο 4

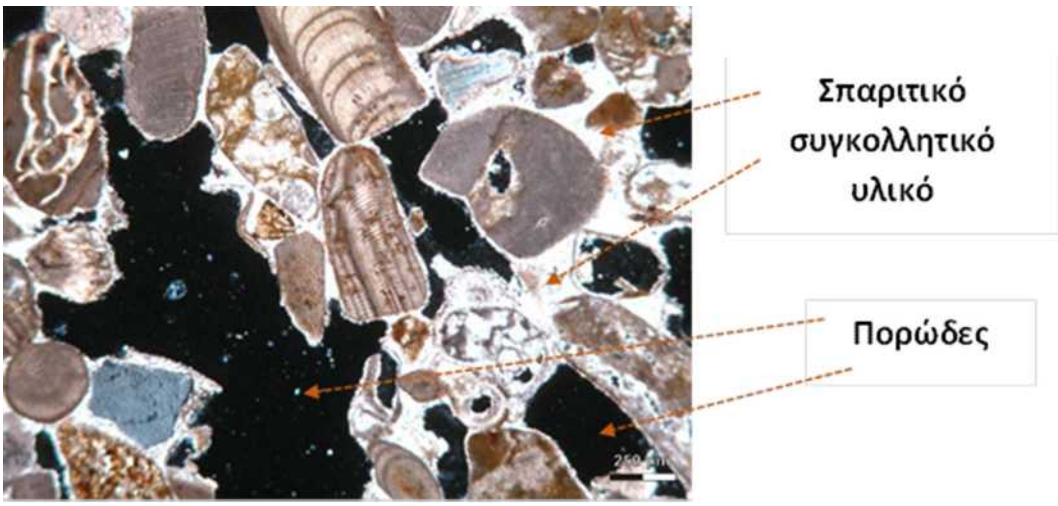
Εικόνα 6. Κυψελοειδής φθορά λόγω ανέμων οι οποίοι μεταφέρουν σταγονίδια με υψηλή περιεκτικότητα σε άλατα Λατομείο 3

Εικόνα 7. Αποκόλληση τεμάχους στην Βόρεια πλευρά του Τάφου 4 γεγονός που θα πρέπει να εξεταστεί και να ενισχυθεί η ευστάθεια του πρανούς γιατί βρίσκεται σε επαφή με το βόρειο πρανές του Τάφου 4

Εικόνα 8. Αποκόλληση τεμάχους στην Νότια πλευρά εξωτερικά Τάφου 3



Εικόνα 9. Μικροσκοπική παρατήρηση εξεταζόμενου δομικού λίθου, N//, μέγιστη διάσταση φωτογραφίας 0,25mm



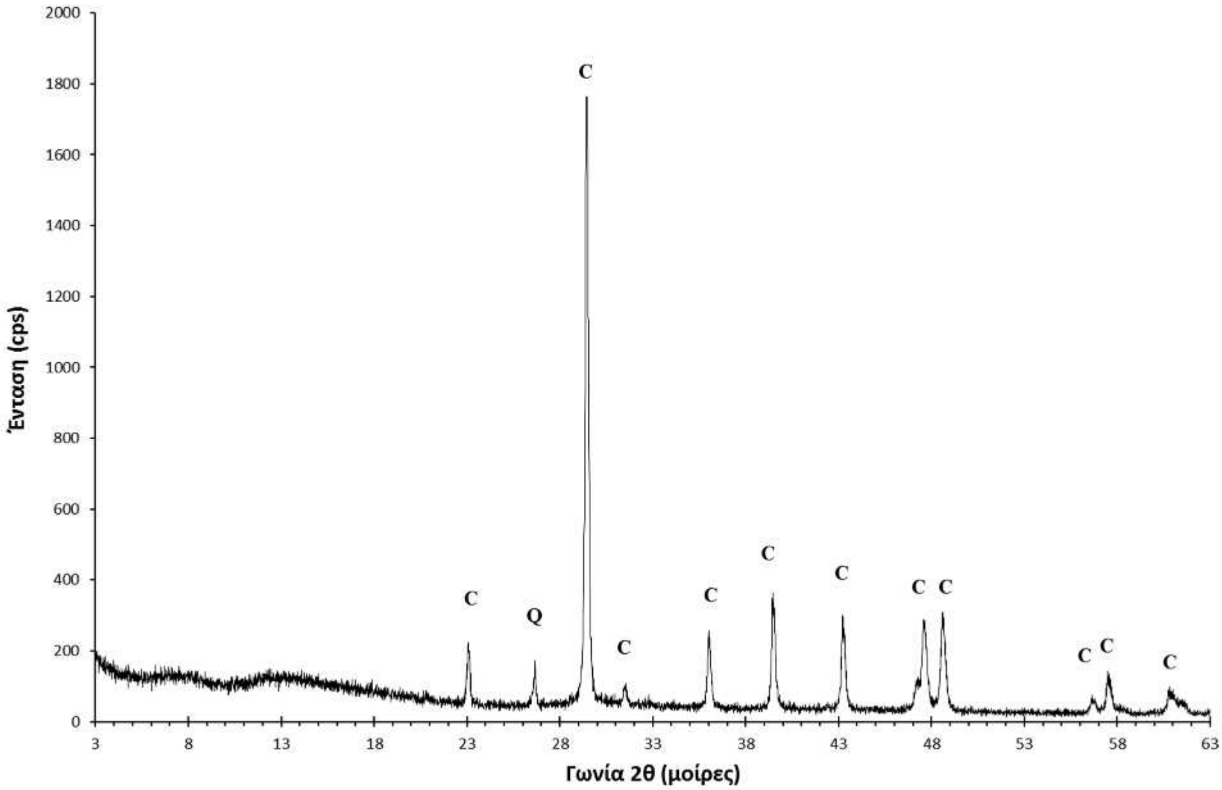
Εικόνα 10. Μικροσκοπική παρατήρηση εξεταζόμενου δομικού λίθου, N⊥, μέγιστη διάσταση φωτογραφίας 0,25mm

Από την εξέταση της λεπτής τομής διαπιστώθηκε ότι το υπό μελέτη δείγμα χαρακτηρίζεται μικροσκοπικά ως βιογενής ασβεστόλιθος. Το μέγεθος των κόκκων κυμαίνεται από 0,5 mm ως και 2 mm. Το κύριο του συστατικό είναι οι βιοκλάστες (απολιθώματα) σε ποσοστό που ξεπερνά το 50 % ενώ το συγκολλητικό υλικό είναι σπαριτικό (αδροκρυσταλλικός ασβεστίτης). Τα μη ασβεστιτικά συστατικά του πετρώματος είναι χαλαζίας και πλαγιόκλαστο. Από την παράθεση των παρακάτω εικόνων (Εικόνα 9 και 10) γίνονται αντιληπτά ο ιστός του πετρώματος, το πορώδες, η μεγάλη παρουσία βιοκλαστών, καθώς και η ύπαρξη του σπαριτικού συγκολητικού υλικού. Επίσης, διακρίνονται οι λιθοκλάστες (κόκκοι χαλαζία και πλαγιοκλάστου).

Το εξεταζόμενο δείγμα ταξινομήθηκε με βάση τα προαναφερθέντα συστατικά του κατά Folk (1959) και Dunham (1962). Αποτέλεσμα αυτής της ταξινόμησης είναι ο χαρακτηρισμός του ως Βιοσπαρίτης σύμφωνα με τον Folk (1959) και ως Κοκκόλιθος σύμφωνα με τον Dunham (1962).

Ορυκτολογική μελέτη

Η μέθοδος της περιθλασιμετρίας ακτίνων Χ (XRD) χρησιμοποιήθηκε με στόχο τον προσδιορισμό ποιοτικά και ημιποσοτικά της ορυκτολογικής σύστασης του εξεταζόμενου δείγματος. Για την εφαρμογή της μεθόδου πάρθηκε αντιπροσωπευτικό υλικό από το



Εικόνα 11. Περιθλασιόγραμμα του υπό μελέτη δείγματος

εξεταζόμενο δείγμα, το οποίο κονιοποιήθηκε με το χέρι σε αχάτινο γουδί, σε μέγεθος κόκκων <20 μm. Στη συνέχεια, το κονιοποιημένο δείγμα τοποθετήθηκε σε ειδικές αντικειμενοφόρες πλάκες και δημιουργήθηκε το παρασκεύασμα κόνεως, τυχαίου προσανατολισμού.

Για την ακτινογραφική εξέταση χρησιμοποιήθηκε ακτινοβολία χαλκού σε περιθλασίμετρο τύπου PHILIPS PW1710/00 και φίλτρο Ni για την παραγωγή μονοχρωματικής ακτινοβολίας $Cu_{K\alpha}$ σε συνθήκες λειτουργίας 35 kV και 25 mA, ταχύτητα γωνιομέτρου 1,2 °/min και περιοχή σάρωσης 3-63° 2θ. Το περιθλασιόμετρο ακτίνων-Χ βρίσκεται στον Τομέα Ορυκτολογίας-Πετρολογίας-Κοιτασματολογίας του Τμήματος Γεωλογίας του Αριστοτελείου Πανεπιστημίου Θεσσαλονίκης.

Ο ημιποσοτικός προσδιορισμός των ορυκτών πραγματοποιήθηκε με βάση τις απαριθμήσεις συγκεκριμένων ανακλάσεων, οι οποίες δεν επηρεάζονται από άλλη ανάκλαση, λαμβάνοντας υπόψη την πυκνότητα και τον συντελεστή απορρόφησης μάζας για ακτινοβολία $Cu_{K\alpha}$ των ορυκτών που προσδιορίστηκαν. Διόρθωση των αποτελεσμάτων έγινε με την αξιολόγηση πρότυπων μιγμάτων από τα ορυκτά που αναγνωρίστηκαν στο εξεταζόμενο δείγμα, μετά από σάρωση στις ίδιες συνθήκες (Καντηράνης κ.α. 2004).

Με βάση τα αποτελέσματα της περιθλασιμετρίας ακτίνων–Χ, το υπό εξέταση δείγμα αποτελείται από ασβεστίτη σε ποσοστό 96,2% κ.β. και χαλαζία 3,8% κ.β.

Μέτρα προστασίας

Όσον αφορά τις επιπτώσεις από την εμφάνιση της κυψελοειδούς φθοράς που σχετίζεται με την κρυστάλλωση των αλάτων θα πρέπει να μελετηθούν εκτενέστερα και να προταθούν συγκεκριμένες λύσεις. Μία πιθανή λύση θα μπορούσε να είναι η εφαρμογή ενός ακρυλικού πολυμερούς στα φυσικά πρανή των λατομείων, μέσω ψεκασμού υδάτινου αιωρήματος του ακρυλικού πολυμερούς το οποίο έχει την ιδιότητα να προκαλεί συσσωμάτωση των κόκκων αυξάνοντας την συνεκτικότητα αυτών με αποτέλεσμα τη δημιουργία ενός λεπτού και αδιαπέρατου στρώματος στην επιφάνεια του πρανούς που εφαρμόζεται (Bosco *et al.* 2013). Η εφαρμογή αυτή θα οδηγούσε στην αύξηση της αντοχής σε τριβή άρα και στην αντοχή σε υδατική και αιολική διάβρωση των λίθων χωρίς να αλλοιώνει τη φυσική όψη του πρανούς.

Όσον αφορά την παροχέτευση των όμβριων υδάτων από το αίθριο των τάφων προτείνεται η χρήση συστήματος καναλιών με σχάρες που θα οδηγούν εκτός του χώρου τα νερά. Οι σχάρες προτείνεται να καλυφθούν με χαλίκι που θα προέρχεται από την θραύση ίδιου ή παρόμοιου δομικού λίθου με στόχο να μην υποβαθμίζεται η εικόνα του μνημείου.

Για την επίτευξη της ευστάθειας του εξωτερικού πρανούς του Λατομείου 4, το οποίο βρίσκεται σε επαφή με το βόρειο πρανές του Τάφου 4, προτείνεται η τοποθέτηση ανοξείδωτων συρματοκιβωτίων. Τα συρματοκιβώτια είναι ορθού τετραγωνικού σχήματος κιβώτια-κλουβιά κατασκευασμένα από μεταλλικό, εξαγωνικής οπής πλέγμα το οποίο πληρώνεται με βραχώδη υλικά. Η διαδοχική καθ' ύψος και κατά πλάτος τοποθέτηση οδηγεί στη διαμόρφωση της κατασκευής αντιστήριξης. Μέσω αυτού του μέτρου επιτυγχάνεται ενίσχυση του πρανούς, ευκαμψία, διαπερατότητα. Είναι ένα μέτρο οικολογικής κατασκευής το οποίο μπορεί να αφομοιωθεί στο περιβάλλον.

Για την τοποθέτηση των συρματοκιβωτίων θα πρέπει να ακολουθηθεί η εξής διαδικασία. Αρχικά θα πρέπει να κατασκευαστεί μια στρώση έδρασης-στράγγισης στη βάση πριν την τοποθέτηση των συρματοκιβωτίων, η οποία βελτιώνει τη διαπερατότητα του εδάφους και προστατεύει από την τριχοειδή υγρασία και τα επιφανειακά νερά του υπεδάφους. Στη συνέχεια, θα τοποθετηθεί η πρώτη σειρά συρματοκιβωτίων με λίθους και κροκάλες από την περιοχή με στόχο την εναρμόνιση με το περιβάλλον. Θα πρέπει να τονιστεί ότι στόχος είναι να μην υποβαθμιστεί η εικόνα του μνημείου συνεπώς πριν την τοποθέτηση των συρματοκιβωτίων το πλέγμα θα πρέπει να βαφεί στο ίδιο χρώμα με το πέτρωμα, καθώς και τα πετρώματα που θα τοποθετηθούν να είναι τμήματα του περιβάλλοντος χώρου. Λόγω του μικρού όγκου των πιθανών ασταθών τεμαχών δεν απαιτούνται μεγάλης έκτασης επεμβάσεις με συρματοκιβώτια. Εναλλακτικά, αντί για συρματοκιβώτια, θα μπορούσε να γίνει στοχευμένη κατασκευή ξερολιθιών σε ύψος και πλάτος ικανό για την αντιμετώπιση των πιθανόν αστοχιών.

Προτείνεται να ελεγχθούν και να μελετηθούν οι ήδη ανοιχτές ασυνέχειες με στόχο να σφραγιστούν με κάποιο ειδικό υλικό-κονίαμα μέσω του οποίου θα αποτραπεί η περαιτέρω διάνοιξή τους και θα προληφθεί η αποκόλληση τεμάχους σε περίπτωση εκδήλωσης σεισμικής ενέργειας. Από αναλύσεις ευστάθειας που έχουν πραγματοποιηθεί στο μνημείο (Πανταζοπούλου 2017) η πιθανότητα εκδήλωσης αστοχιών είναι υπαρκτή, αλλά ο όγκος του υλικού που θα αστοχήσει είναι πολύ μικρός. Βέβαια σε έναν αρχαιολογικό χώρο που κινείται σημαντικός αριθμός επισκεπτών, ακόμα και η πιο μικρή πιθανότητα εκδήλωσης αστοχίας θα πρέπει να μηδενιστεί. Τέλος προτείνεται η μελέτη και η εφαρμογή ενός συστήματος γεωτεχνικής και δομητικής παρακολούθησης της φθοράς του μνημείου με το χρόνο. Στόχος αυτού του μέτρου είναι η πρόληψη και αποφυγή αποκολλήσεων ή/και καταπτώσεων τεμάχων του μνημείου.

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Ανθεμωτή ανάγλυφη επίστεψη από τον κυκλικό τάφο Δερβενίου Θεσσαλονίκης

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Περίληψη: Η ανθεμωτή ανάγλυφη επίστεψη του Δερβενίου, χρονολογείται στα τέλη του 4ου και στις αρχές του3ου αι. π.Χ. και σήμερα κοσμεί τον ειδικό χώρο της έκθεσης του Αρχαιολογικού Μουσείου Θεσσαλονίκης. Το σπουδαίο αρχιτεκτονικό στοιχείο αυτό ανακαλύφθηκε στον κυκλικό τάφο του αρχαίου νεκροταφείου του Δερβενίου Θεσσαλονίκης. Αναλύθηκαν τα στοιχεία της κατασκευής του ανθεμίου, η λίθινη βάση, η λευκή προετοιμασία και οι χρωστικές. Η πιο σημαντική πληροφορία για ορυκτολογική σύσταση των χρωστικών έχει ληφθεί κατά την εξέτασή τους στο πολωτικό μικροσκόπιο. Ο τελικός προσδιορισμός των συστατικών της ζωγραφικής διακόσμησης πραγματοποιήθηκε με τη βοήθεια των φυσικοχημικών αναλύσεων (XRF, SEM-EDX, FTIR και HPLC-PDA). Από τα αποτελέσματα της μελέτης των τεχνολογικών στοιχείων συμπεραίνεται η χρήση κυρίως ανόργανων χρωστικών (αιματίτης, κιννάβαρη, κιμωλία, άνθρακας, μαλαχίτης, αιγυπτιακό μπλε) και μίας οργανικής χρωστικής με πηγή προέλευσης το άγριο ριζάρι. Τα αποτελέσματα από τη μελέτη του ανθεμίου συγκρίθηκαν με τις τοιχογραφίες του κιβωτιόσχημου γυναικείου τάφου 1 του αρχαίου νεκροταφείου Δερβενίου της ίδιας χρονολογίας.

ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ: ΖΩΓΡΑΦΙΚΗ, ΧΡΩΣΤΙΚΕΣ, ΡΙΖΑΡΙ, PLM, M-XRF, SEM-EDS, FTIR, HPLC-DAD.

Εισαγωγή

Η ανθεμωτή ανάγλυφη επίστεψη του Δερβενίου, που χρονολογείται στα τέλη του 4ου και στις αρχές του3ου αι. π.Χ., σήμερα κοσμεί τον ιδικό χώρο της έκθεσης του Αρχαιολογικού μουσείου Θεσσαλονίκης. Το σπουδαίο αρχιτεκτονικό μνημείο αυτό (Τζαναβάρη 2002) ανακαλύφθηκε το 1998 σε έναν από τους τάφους γνωστού στους αρχαιολόγους μελετητές, νεκροταφείου του Δερβενίου. Ο αρχαιολογικός χώρος του αρχαίου νεκροταφείου απλώνεται στο ύψος 9-10ου χλμ. της εθνικής οδού Θεσσαλονίκης-Καβάλας. Στο σχήμα 1 παρουσιάζεται η ανθεμωτή ανάγλυφη επίστεψη του Δερβενίου.

Το ανθεμίου βρέθηκε στον κυκλικό τάφο του Δερβενίου. Πρόκειται για μία ταφική αρχιτεκτονική, η οποία είναι ασυνήθιστη στον ελλαδικό χώρο, με κυκλικό θάλαμο και πολύ μακρύ «νεκρικό» διάδρομο. Η ζωγραφική εντοίχια διακόσμηση και τα έγχρωμα επιχρίσματα φαίνεται πως αρχικά κάλυπταν τα τοιχώματα του τάφου, αλλά καταστράφηκαν και κατά την ανασκαφή αποκαλύφθηκαν στην επίχωση του τάφου. Η περίφημη ανθεμωτή επίστεψη βρέθηκε στο δρόμο του κτιρίου και φαίνεται πιθανό ότι διακοσμούσε την πρόσοψη του τάφου, ίσως στη κορυφή του ανοίγματος της θύρας (Τζαναβάρη 2002).

Η διακόσμηση της πώρινης επίστεψης είναι πολυσύνθετη και αντανακλά το χαρακτηριστικό για τη «μακεδονική» τέχνη το στυλ του «εκλεκτικισμού» με στενή συνεργασία συχνά των «απροσδόκητων» στοιχείων και υλικών. Περιλαμβάνει δύο τύπους διακόσμησης: ανάγλυφη και ζωγραφική. Το ανάγλυφο τμήμα της σύνθεσης αποτελεί το ανθέμιο τοποθετημένο κεντρικά, τα ζωγραφικά φυτικά θέματα αναπτύσσονται περιμετρικά του ανθεμίου. Μία πλούσια χρωματική παλέτα χρησιμοποιούνταν άφθονα σε όλα τα στοιχεία διακόσμησης, ζωγραφικά και ανάγλυφα, καλύπτοντας όλη την επιφάνεια του ανθεμίου. Η μεγάλη ποσότητα της ύλης που αποτελούσε έγχρωμα στοιχεία της

Σχήμα 1. Ανθεμωτή ανάγλυφη επίστεψη του Δερβενίου κοσμεί τον ειδικό χώρο της έκθεσης του Αρχαιολογικού Μουσείου Θεσσαλονίκης.

διακόσμησης έχει χαθεί, σε πολλά σημεία διατηρούνται μόνο ελάχιστα ίχνη των αρχικών χρωμάτων, όπως π.χ. συμβαίνει με το μαύρο χρώμα, τα υπολείμματα του οποίου βοηθάνε στην αναπαράσταση του φυτικού μοτίβου που περιέκλειε το ανθέμιο.

Το ανθέμιο ήρθε στο φως ολόκληρα σκεπασμένο με χώματα, τα οποία ήταν γερά προσκολλημένα και στην ζωγραφική επιφάνεια. Κατά τη διαδικασία της απομάκρυνσης των χωμάτινων επικαθίσεων από την επιφάνεια του ανθεμίου, παρατηρήθηκε πως κόκκοι χρωστικών σώζονταν πάνω στο χώμα. Στη μελέτη χρησιμοποιήθηκαν μόνο αυτοί μεμονωμένοι κόκκοι των χρωμάτων που συλλέχτηκαν κατά την διαδικασία συντήρησης προκειμένου να αποφευχθεί η δειγματοληψία από τα ελάχιστα σωζόμενα διακοσμητικά στοιχεία.

Πειραματικό μέρος

Επιλογή της μεθοδολογίας εξέτασης.

Η μελέτη της αρχαίας ζωγραφικής πάντα είναι μια δύσκολη και περίπλοκη υπόθεση. Οι δυσκολίες οφείλονται τόσο στην κατάσταση διατήρησης των συστατικών της ζωγραφικής, τα οποία συνήθως, λόγω της παραμονής σε διαβρωτικό περιβάλλον, παρουσιάζουν έντονη αλλοίωση μέχρι την πλήρη αποσύνθεσή τους, αλλά, κυρίως, λόγω της σύστασης και της φύσης των ίδιων των συστατικών της ζωγραφικής.

Πιο συγκεκριμένα στο θέμα της σύστασης θα πρέπει να αναφερθεί πως στην κατασκευή ενός ζωγραφικού στρώματος κατά κανόνα συμμετέχουν: α) υπόστρωμα-βάση, β) προετοιμασία γ) χρωστικές, ανόργανες ή/ και οργανικές, μεμονωμένες ή τα μίγματά τους (έχοντας υπόψη και τα επάλληλα στρώματα των χρωμάτων) και δ) συνδετικό μέσο. Έτσι η διερεύνηση της ζωγραφικής με τη χρήση των μη επεμβατικών τεχνικών (XRF, Raman) συνήθως δεν δίνει από μόνη της μια ολοκληρωμένη εικόνα για την ταυτοποίηση των ανόργανων στοιχείων του χρωματικού στρώματος.

Στις μελέτες μας, προκειμένου να εξαχθούν πιο ασφαλή αποτελέσματα δίνεται ιδιαίτερη προσοχή στην προκαταρκτική εξέταση των υλικών με τη χρήση οπτικών μέσων ανάλυσης, συγκεκριμένα, στην εξέταση των μικροσκοπικών κόκκων της ζωγραφικής στο πολωτικό μικροσκόπιο (Τζαναβάρη 2002, Τσιμπίδου-Αυλωνίτη 2012, Αχειλαρά κ.ά., 2012, Βιβντένκο 2015). Οι κόκκοι αυτοί συλλέγονται κατά την διαδικασία αρχικού καθαρισμού της ζωγραφικής από επιφανειακές εναποθέσεις χωμάτων, καθώς, λόγω της αποσύνθεσης του συνδετικού στα χρώματα, έχουν αποκτήσει ισχυρότερη πρόσφυση με το χώμα παρά με το ζωγραφικό στρώμα από το οποίο προήλθαν. Με τον τρόπο αυτό συλλέχθηκαν και στην παρούσα εργασία τα δείγματα των χρωμάτων από την ίδια τη συγγραφέα Σβετλάνα Βιβντένκο, η οποία έκανε σωστική και τελική συντήρηση του ανθεμίου και έπειτα η διερεύνηση των στοιχείων κατασκευής του.

Στη μεθοδολογία που εφαρμόστηκε κατά την αρχαιομετρική διερεύνηση της ανθεμωτής επίστεψης μετά από τις προκαταρκτικές οπτικές εξετάσεις πραγματοποιήθηκαν φυσικοχημικές αναλύσεις (XRF, SEM-EDX , FTIR και HPLC).

Εξέταση των λεπτών τομών στο πολωτικό μικροσκόπιο.

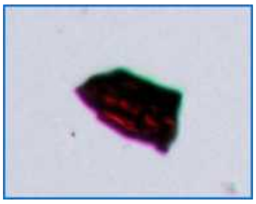
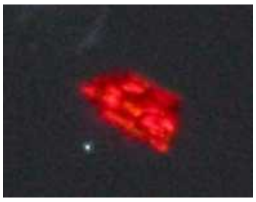
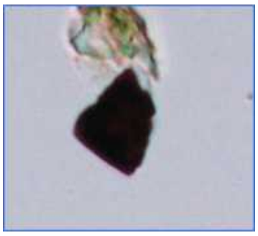
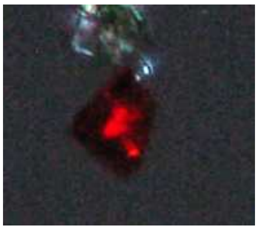
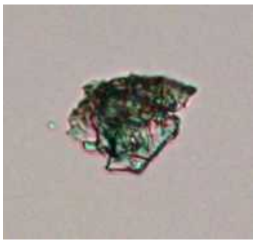
Οι λεπτές τομές από τους κόκκους χρωστικών και υποστρωμάτων εξετάστηκαν και φωτογραφήθηκαν στο πολωτικό μικροσκόπιο Zeiss με σκοπό να ληφθούν οι πρώτες πληροφορίες σχετικά με την ορυκτολογική σύσταση των δειγμάτων. Οι λεπτές τομές παρασκευάστηκαν με υγρό καταβύθισης, Βάλσαμο Καναδά, ενώ χρησιμοποιήθηκαν κόκκοι των δειγμάτων διαμέτρου της τάξης των 0,5-1,5 mm. Το γεγονός ότι η εξέταση στο πολωτικό μικροσκόπιο μπορεί να πραγματοποιηθεί και με πολύ μικρό μέγεθος κόκκων δείγματος οφείλεται στο χαρακτηριστικό των ορυκτών να διατηρήσουν τις οπτικές τους ιδιότητες και μετά τον τεμαχισμό τους.

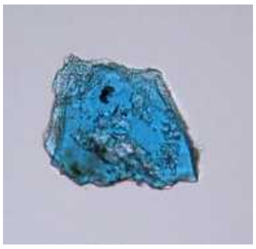
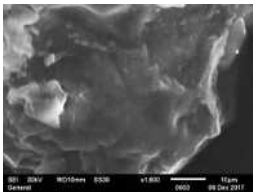
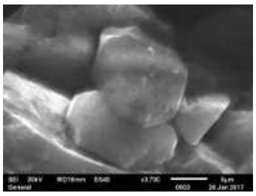
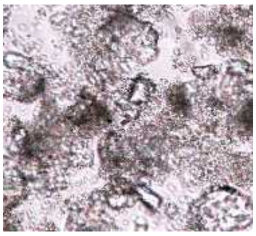
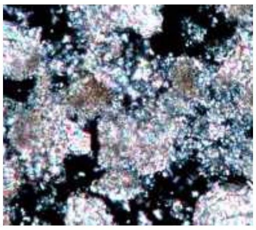
Προκειμένου να προσδιορισθούν τα ορυκτά συστατικά των χρωμάτων στη λεπτή τομή του δείγματος εξετάζονται οι οπτικές ιδιότητες των κόκκων του δείγματος: χρώμα, πλεοχροϊσμός, ανάγλυφο, δείκτης διάθλασης, διπλοθλαστικότητα, χρώματα πολώσεως, κατάσβεση, σχισμός, διδυμία κ.α. Για την κάθε τομή έχουν ληφθεί δυο αντιπροσωπευτικές φωτογραφίες, σε παράλληλα και σε διασταυρωμένα Nicols, έτσι ώστε να έχουμε μια ολοκληρωμένη άποψη της ορυκτολογικής μορφής του εξεταζόμενου δείγματος. Πρέπει να σημειωθεί, ότι η εξέταση μεμονωμένων κόκκων των χρωστικών αποκλείει τη βλαβερή επίδραση των άλλων συστατικών του εξεταζόμενου δείγματος και επιτρέπει την λήψη πιο αξιόπιστης πληροφορίας για ορυκτά συστατικά. Οι φωτογραφίες των ορυκτών, οι οποίες παρουσιάζονται στη μελέτη, πραγματοποιήθηκαν στο πολωτικό μικροσκόπιο Zeiss, με Nicols παράλληλα N II (το πεδίο είναι φωτισμένο) και Nicols διασταυρωμένα N× (το πεδίο είναι σκοτεινό) και μεγέθυνση × 120 και × 240 × 240, από τη χημικό Σβετλάνα Βιβντένκο. Οι κύριες οπτικές ιδιότητες των υπό εξέταση χρωστικών αναφέρονται στον πίνακα 1.

Μελέτη δειγμάτων με SEM

Πραγματοποιήθηκαν με τη χρήση ηλεκτρονικού μικροσκοπίου σάρωσης SEMJSM-6510 του Οίκου JEOL με Δευτερογενή ηλεκτρόνια (SE). Η πίεση εντός του θαλάμου είναι 10-270Pa.

Πίνακας 1:Κύριες οπτικές ιδιότητες των ορυκτών που εντοπίστηκαν στις υπό εξέταση χρωστικές

Ορυκτό	Μικροφωτογραφία. Πολωτικό μικροσκόπιοPLM (NII, N ×). Ηλεκτρονικό μικροσκόπιο SEM	Οπτικές ιδιότητες. Διαγνωστικά στοιχεία
Ορυκτό κινναβαρίτης, cinnabarite Θειούχος υδράργυρος με χημικό τύπο HgS. Η κοινή ονομασία της χρωστικής κιννάβαρη, ***vermilion.***	 	Μορφή : μακροσκοπικά οι κρύσταλλοι της κιννάβαρης είναι σκούρου κόκκινου ή γκρίζο-μαύρου χρώματος. Οι κρύσταλλοι είναι πινακοειδείς, πρισματικοί ή ρομβοεδρικοί. Το σύστημα κρυστάλλωσής:τριγωνικό. Μονάξονα θετικό. Σχισμός : τέλειος κατά {1010} Δείκτης διάθλασης n_{ω}= 2,81 , n_{ε} = 3,14. Διπλοθλαστικότητα είναι εξαιρετικά μεγάλη δ = 0,33. Διαγνωστικά στοιχεία : πολύ μεγάλη διπλοθλαστικότητα και τέλειος πρισματικός σχισμός.
Ορυκτό αιματίτης,***hematite.*** Τριοξείδιο του δισιδήρου (III) με χημικό τύπο Fe_2O_3. Αποτελεί το βασικό συστατικό της κόκκινης χρωστικής με κοινή ονομασίακόκκινη ώχρα.	 	Μορφή : μακροσκοπικά οι κρύσταλλοι του αιματίτη είναι γκρίζου-μαύρου χρώματος, σε γεώδη μορφή έχει κόκκινο χρώμα, συχνά εμφανίζεται σε κοκκώδη (γεώδη και φυλλώδη) συσσωματώματα. Οι κρύσταλλοι είναι πινακοειδείς, ινώδεις και πλακοειδείς. Το σύστημα κρυστάλλωσής: τριγωνικό. Μονάξονας αρνητικός. Σχισμός: απουσιάζει. Δείκτης διάθλασης n_{ω} = 2,78, n_{ε} =3,01. Διπλοθλαστικότητα είναι εξαιρετικά μεγάλη δ = 0,23. Διαγνωστικά στοιχεία: πολύ μεγάλη διπλοθλαστικότητα και απουσία σχισμού.
Ορυκτό **μαλαχίτης**, ***malachite.*** Διβασικός ανθρακικός χαλκός με χημικό τύπο $CuCO_3 \cdot Cu(OH)_2$	 	Μορφή: στη φύση σχεδόν πάντα βρίσκεται μαζί με τον κυπρίτη και τον αζουρίτη. Στα έργα ζωγραφικής, οξειδώνοντας εύκολα, μετατρέπεται σε κυπρίτη με αλλαγή του χρώματος έως το καστανέρυθρο. Το χρώμα των κρυστάλλων του φυσικού μαλαχίτη μεταβάλλεται από το έντονο πράσινο έως το σχεδόν λευκό. Οι κρύσταλλοι είναι πρισματικοί ή ινώδεις. Το σύστημα κρυστάλλωσής :μονοκλινές. Σχισμός: τέλειος κατά {201}. Δείκτης διάθλασης n_{α} = 1,66, n_{β} = 1,88, n_{γ} = 1,91. Εξαιρετικά μεγάλη διπλοθλαστικότητα δ = 0,25. Διαγνωστικά στοιχεία : πολύ μεγάλη διπλοθλαστικότητα και τέλειος σχισμός, ο οποίος εμφανίζεται κάτω από το μικροσκόπιο σε μορφή μικρών ρωγμών στην επιφάνεια των κρυστάλλων. Στο υδροχλωρικό οξύ διαλύεται με εκχύλιση του διοξειδίου του άνθρακα.

Αιγυπτιακό μπλε, **χαλκούχο γυαλί** (υαλώδης φάση της τεχνητής χρωστικής) με γενικό χημικό τύπο $CaO \cdot CuO \cdot 4SiO_2$ ($CaCuSi_4O_{10}$)	 	Μορφή : Οι κόκκοι έχουν χρώμα από το γαλάζιο μέχρι το μπλε. Το σύστημα κρυστάλλωσής : είναι άμορφο υλικό. Σχισμός : δεν υπάρχει. Δείκτης διάθλασης n = 1,61. Διπλοθλαστικότητα δ = 0,00. Είναι ισότροπο. Διαγνωστικά στοιχεία : Χρώμα των κόκκων, χαμηλός δείκτης διάθλασης και ισότροπα
Ορυκτό ***cuprorivaite*** (κρυσταλλική φάση στο **αιγυπτιακό μπλε**) με χημικό τύπο $CaCuSi_4O_{10}$	 	Μορφή : μακροσκοπικά οι κρύσταλλοι είναι ανοιχτού γαλάζιου χρώματος. Εμφανίζεται και σε κοκκώδη φυλλώδη συσσωματώματα. Οι κρύσταλλοι είναι πινακοειδείς. Το σύστημα κρυστάλλωσής: τετραγωνικό. Μονάξονας αρνητικός. Σχισμός: τέλειος {001} Δείκτης διάθλασης n_{ω} = 1,633 n_{ε} = 1,59. Διπλοθλαστικότητα είναι χαμηλή δ = 0,043. Διαγνωστικά στοιχεία: χρώμα, χαμηλή διπλοθλαστικότητα και τέλειος σχισμός.
Ορυκτό **ασβεστίτης *calcite*.** Ανθρακικό ασβέστιο με χημικό τύπο $CaCO_3$ Η αντίστοιχη λευκή χρωστικήονομάζεται **λευκό*meudon*.**	 	Μορφή: μακροσκοπικά ο ασβεστίτης είναι λευκός ή άχρωμος, συχνά εμφανίζεται σε κοκκώδη συσσωματώματα. Το σύστημα κρυστάλλωσής: τριγωνικό. Μονάξονας αρνητικός. Σχισμός: τέλειος ρομβοεδρικός {1011}. Δείκτης διάθλασης: n_{ω} = 1,658, n_{ε} = 1,486. Διπλοθλαστικότητα είναι εξαιρετικά μεγάλη δ = 0,172. Διαγνωστικά στοιχεία: πολύ μεγάλη διπλοθλαστικότητα, τέλειος ρομβοεδρικός σχισμός και ο αναβρασμός με αραιά οξέα.

Στοιχειακές χημικές αναλύσεις XRF.

Πραγματοποιήθηκαν με τη χρήση φορητής συσκευής φθορισμομετρίας ακτίνων Χ (portable X-Ray Fluoresence, Bruker, TracerIVμε ανιχνευτή Silicon Drift, SDD). Η τάση και το ρεύμα επιτάχυνσης ρυθμίστηκαν στα 40 kV και 0,1mA. Ο χρόνος απόκρισης ήταν 60 sec.

Χρωματογραφία HPLC.

Για την εξέταση της οργανικής ρόδινης χρωστικής χρησιμοποιήθηκε υγρή χρωματογραφία υψηλής πίεσης με ανιχνευτή παράτασης διόδων HPLC-DAD της εταιρείας DIONEX. Η διάταξη περιλαμβάνει αντλία βαθμωτής έκλουσης (Ultimate 3000 LPG) με ενσωματωμένο απαερωτή κενού, αυτόματο δειγματολήπτη, (Ultimate 3000 Autosampler, WPS-3000 SL), χρωματογραφική κλίνη (TCC-3000SD) σταθμισμένη στη θερμοκρασία των 35°C και ανιχνευτή παράταξης διόδων (UltimateDAD-3000). Για τις αναλύσεις χρησιμοποιήθηκε χρωματογραφική στήλη AlltimaHPC18 5μm, 250mmx 3.0mm, (AlltechAssociates, USA). Το πρόγραμμα βαθμωτής έκλουσης που χρησιμοποιήθηκε περιγράφεται στον πίνακα 2.

Πίνακας 2. Πρόγραμμα βαθμωτήςέκλουσης

Χρόνος (min)	Ροή (mL min^{-1})	H_2O + 0.1% TFA (%)	CH_3CN + 0.1 % TFA (%)
0.0	0,5	95	5
0.0	0,5	95	5
1.0	0,5	95	5
15.0	0,5	70	30
20.0	0,5	40	60
23.0	0,5	40	60
33.0	0,5	5	95
35.0	0,5	5	95
38.0	0,5	95	5

A: H2O + TFA 0.1% (v/v).
B: ACN + TFA 0.1% (v/v).

Για την εκχύλιση χρωστικής, το δείγμα προκατεργάστηκε σε θερμό (100oC) λουτρό με αναλογία μεθανόλη/νερό/υδροχλωρικό οξύ (1:1:2) για 10 min. Έπειτα, το υδροχλωρικό οξύ εξατμίστηκε με προσθήκη αζώτου σε θερμοκρασία 60°C και το ίζημα διαλυτοποιήθηκε σε 200μL διμεθυλοσουλφοξύδιο (DMSO). Στη συνέχεια το δείγμα φυγοκεντρήθηκε για 3 min στις 3000 στροφές και το υπερκείμενο υγρό, απαλλαγμένο πλέον από στερεά σωματίδια, αναλύθηκε με την προτεινόμενη μέθοδο υγρής χρωματογραφίας. Η επιλεγμένη μέθοδος εκχύλισης αποτελεί προϊόν εκτενών μελετών (Mantzouris *et al.* 2011, Βιβτένκο 2015)

Φασματοσκοπία FTIR.

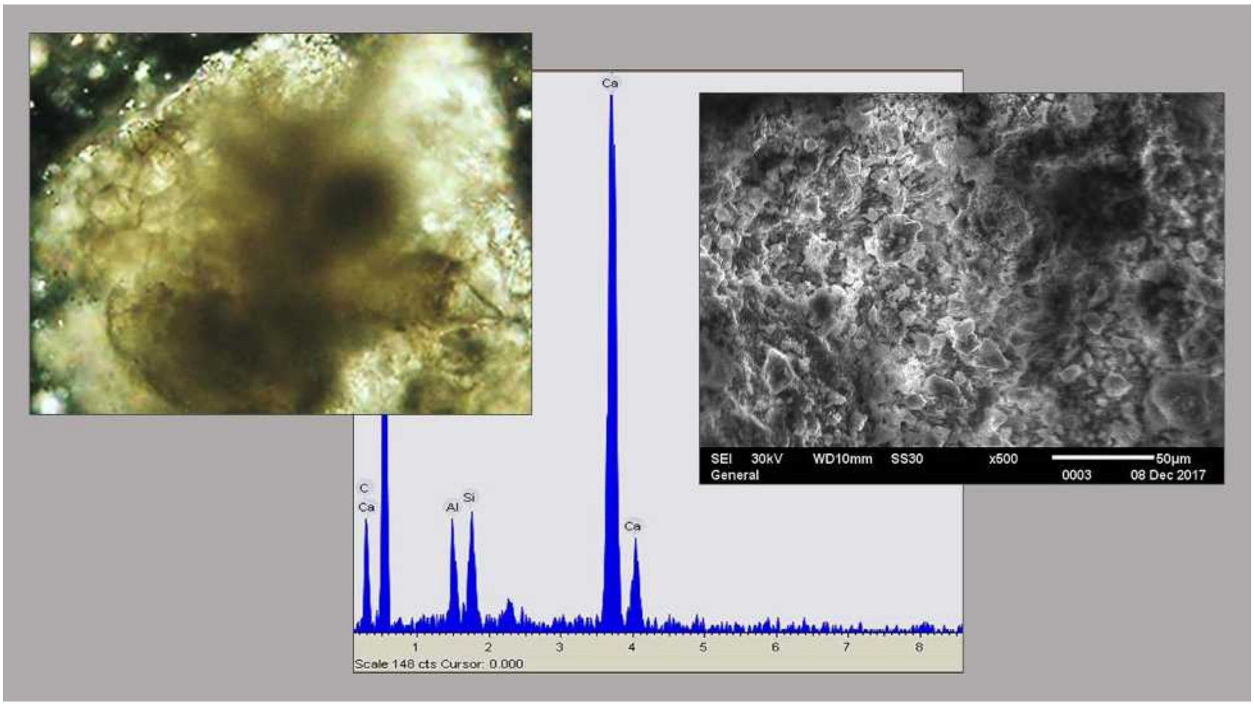
Η ανίχνευση των οργανικών συνδετικών μέσων πραγματοποιήθηκε με φασματοσκοπία FTIR. Χρησιμοποιήθηκε Φασματόμετρο Υπέρυθρου με μετασχηματισμό Fourier (FTIR) του οίκου Perkin-Elmer εξοπλισμένο με μικροσκόπιο εφοδιασμένο με πηγή λευκού φωτός (LED Illumination),υψηλής απόδοσης ανιχνευτή ψύξεως υγρού αζώτου, εξάρτημα μετρήσεων ανάκλασης διάχυσης (diffuse reflectance) και λειτουργικό λογισμικό SPECTRUM400. Τα φάσματα συλλέχθηκαν με φασματική διακριτική ικανότητα 4cm^{-1} στη φασματική περιοχή 4000-500cm^{-1} και 32 σαρώσεις.

Αποτελέσματα και συζήτηση

Στην εξέταση υποβλήθηκαν οι κόκκοι του υλικού από τη λίθινη βάση, την προετοιμασία και επτά δείγματα χρωμάτων. Παρακάτω παρουσιάζονται τα αποτελέσματα των εξετάσεων.

Λίθινη βάση ανθεμίου

Δείγμα προς εξέταση αποτέλεσαν οι μικροί κόκκοι του πωρόλιθου αποκολλημένοι από τη δομή κατά τη μεταφορά του ανθεμίου στο εργαστήρια συντήρησης.



Σχήμα 2. Ασβεστιτική σύσταση της λίθινης βάσης του ανθεμίου. Πολωτικό μικροσκόπιο, N×. *Ηλεκτρονικό μικροσκόπιο* SEM.

Στη σύσταση του δείγματος ανιχνεύονται κυρίως συσσωματώματα μικροκρυσταλλικού ασβεστίτη $CaCO_3$ με τα βασικά οπτικά χαρακτηριστικά του (Winchell and Winchell 1953; McCrone 1982), τα οποία είναι η πολύ μεγάλη διπλοθλαστικότητα και ο τέλειος ρομβοεδρικός σχισμός (πίνακας 1). Από τα αποτελ*έσματα της* XRF *και* EDS *ανάλυσης προκύπτει ότι* το κύριο χημικό στοιχείο που εντοπίστηκε στο δείγμα είναι το ασβέστιο Ca (σχήμα 2). Στις μικροφωτογραφίες του δείγματος της λίθινης βάσης στο πολωτικό και στο ηλεκτρονικό μικροσκόπιο σάρωσης διακρίνονται οι μικρόκοκκοι του ασβεστίτη. (σχήμα 2). Συμπεραίνεται ότι η λίθινη βάση κατασκευάστηκε από τον τραβερτίνη, ασβεστολιθικό ιζηματογενές πέτρωμα χημικής προέλευσης.

Προετοιμασία του ζωγραφικού στρώματος

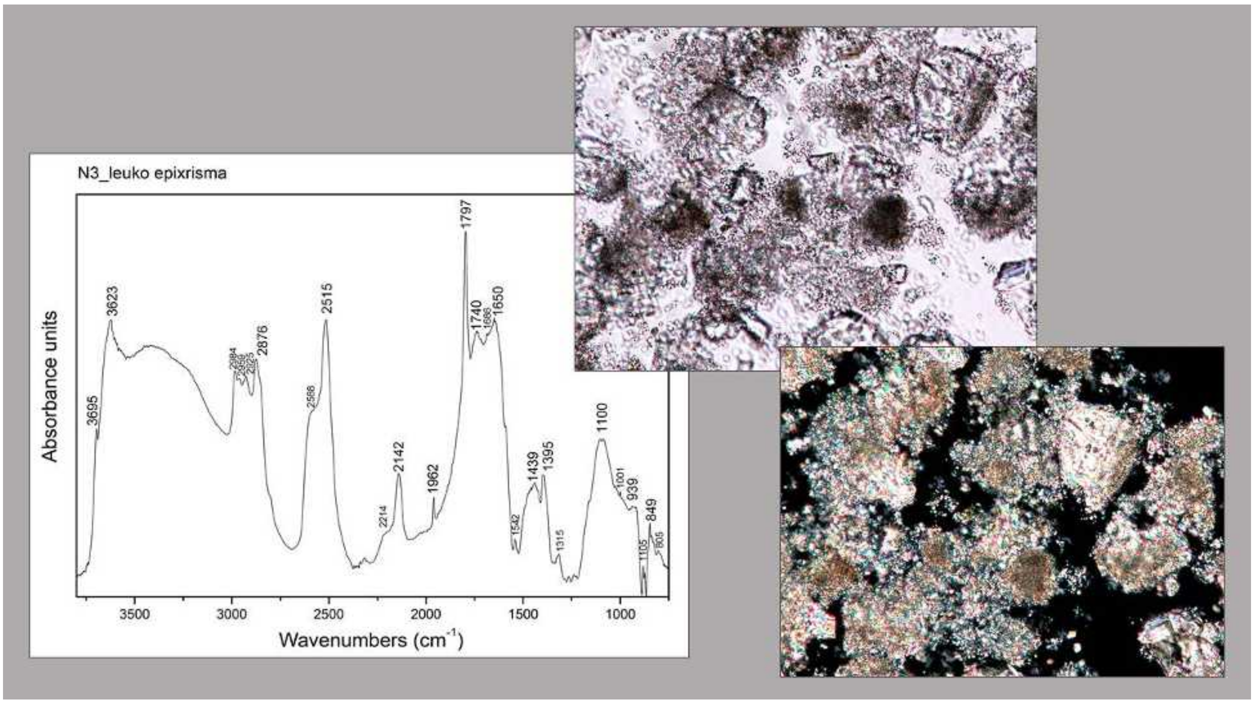
Στην επιφάνεια του πωρόλιθου σώζονται μόνο ίχνη προετοιμασίας υπόλευκου χρώματος, πάχους 0,2-1,5 mm. Στο σχήμα 3 απεικονίζονται τα αποτελέσματα της εξέτασης της προετοιμασίας. Στη σύσταση της προετοιμασίας ανιχνεύονται κυρίως συσσωματώματα κρυπτό και μικροκρυσταλλικού ασβεστίτη και με μέτρια συχνότητα αργιλικά ορυκτά. *Από τα αποτελέσματα* XRF *και* EDS *προκύπτει ότι* το κύριο χημικό στοιχείο του δείγματος είναι το ασβέστιο Ca και με χαμηλότερη συχνότητα πυρίτιο Si και αργίλιο Al. Και τα αποτελέσματα FTIR υποδεικνύουν ότι η προετοιμασία αποτελείται από ασβεστίτη με πρόσμιξη αργιλικού ορυκτού, καολινίτη και επίσης μικρή προσθήκη οργανικού υλικού, όπως είναι τα κόμμεα. Η απορρόφηση O-H εντοπίζεται στην περιοχή 3400-3650 cm^{-1}. Στα 2515 cm^{-1} και στα 1439 cm^{-1} εντοπίζεται απορρόφηση C-O του ασβεστίτη. Στα 2984 cm^{-1} 2876 cm^{-1} και 1797 cm^{-1} εντοπίζονται οι δονήσεις C=O από το ανθρακικό ιόν του ασβεστίτη (Galván-Ruiz *et al.* 2009, Gunasekaran *et al.* 2006). Οι απορροφήσεις στα 1650 cm^{-1}, στα 1395 cm^{-1} και στα 1100 cm^{-1} είναι χαρακτηριστικές των κόμμεων. Η απορρόφηση στα 1650 cm^{-1} αποδίδεται στη δόνηση τάσης των δεσμών C=O και C-N του πρωτοταγούς αμιδίου. Στα 1542 cm^{-1} εντοπίζεται η δόνηση κάμψης του δεσμού N-H και στα 1395 cm^{-1} εντοπίζεται ο δεσμός C-H του δευτεροταγούς αμιδίου. Στα 1100 cm^{-1} εντοπίζεται η δόνηση C-O-C στο δακτύλιο της γλυκοζαμίνης στα κόμεα (Ibekwe *et al.* 2017, Rajabi *et al.* 2019, Tahsiri *et al.* 2019).

Χρώματα από την έγχρωμη διακόσμηση του ανθεμίου

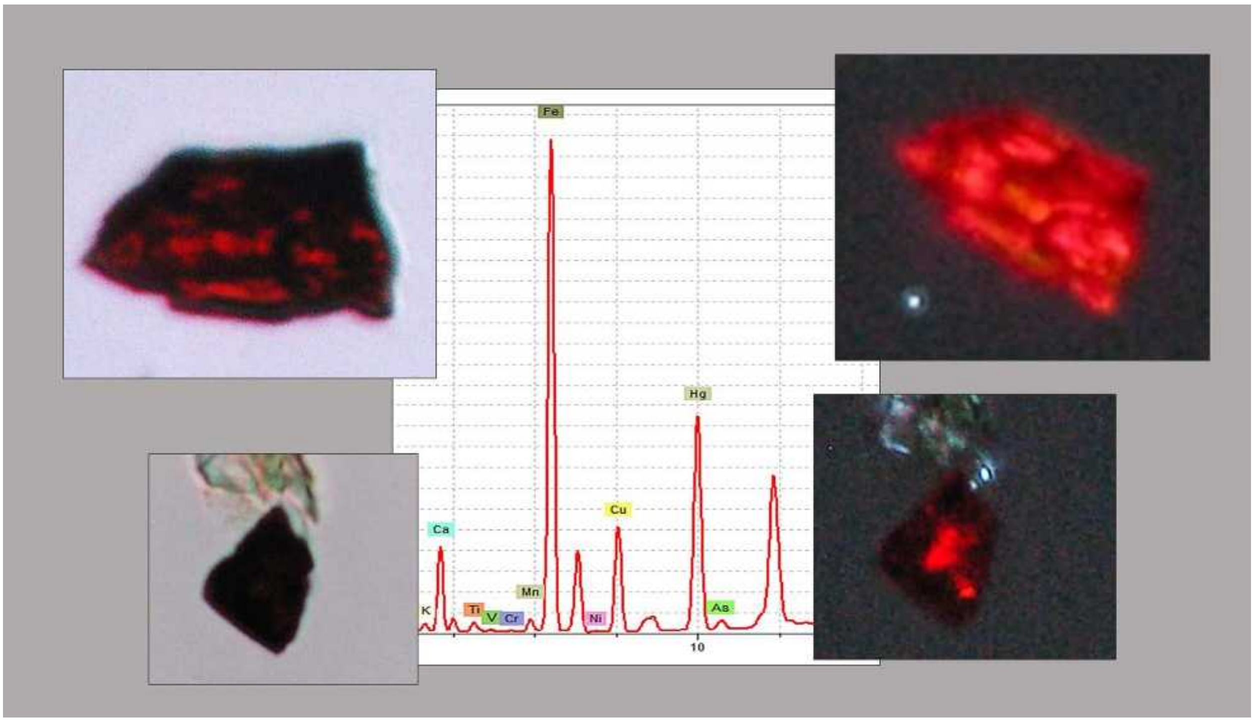
Βαθύ ερυθρό χρώμα.

Το χρώμα εντοπίστηκε στις κεντρικές ανάγλυφες ζώνες της διακόσμησης, δηλαδή στον τρίφυλλο πυρήνα άκανθας, στα φύλλα της άκανθας, στους κυρτούς οφθαλμούς των ελίκων, στο περίγραμμα του κάλυκα, στο κεντρικό ανάγλυφο λουλούδι ανάμεσα στους κεντρικούς βλαστούς και στην περιοχή με ζωγραφική διακόσμηση καθώς επίσης και στα δύο λουλούδια με οξυκόρυφα πέταλα στο πλαγινό πλαίσιο της σύνθεσης.

Στο σχήμα 4 παρατηρούνται τα αποτελέσματα εξετάσεων του ερυθρού χρώματος στο πολωτικό μικροσκόπιο και της XRF ανάλυσης. Στο δείγμα του



Σχήμα 3. Προετοιμασία. Φάσμα υπερύθρου και μικροφωτογραφίες στο πολωτικό μικροσκόπιο πάνω σε παράλληλα και κάτω, αντίστοιχα, σε διασταυρωμένα Nicols (πάνω NII, κάτω N×). Διακρίνονται συσσωματώματα άχρωμων κόκκων ασβεστίτη και νεφώδη συσσωματώματα γκρίζου χρώματος των αργιλικών υλικών.



Σχήμα 4. Φωτεινό ερυθρό. Στη σύστασή του εντοπίστηκαν κόκκοι δυο ορυκτών. Στο κέντρο απεικονίζεται το φάσμα *της μ*- XRF ανάλυσης. Αριστερά και δεξιά βρίσκονται μικροφωτογραφίες στο πολωτικό μικροσκόπιο του κόκκου κινναβάρεως (επάνω) και του κόκκου αιματίτη (κάτω) σε NII και N× αντίστοιχα.

ερυθρού εντοπίστηκε μίγμα των ορυκτών. Οι κόκκοι σκούρου κόκκινου χρώματος με χαρακτηριστικά διαγνωστικά στοιχεία του ορυκτού αιματίτη, όπως είναι πολύ μεγάλη διπλοθλαστικότητα και απουσία σχισμού (πίνακας 1). Μαζί με τα συσσωματώματα κόκκων γαιώδους αιματίτη παρατηρήθηκαν και οι μεμονωμένοι μεγάλοι κρύσταλλοι του αιματίτη (McCrone 1982) κόκκινου χρώματος με μεγάλη διπλοθλαστικότητα. Στους κρυστάλλους του δεύτερου είδους, φωτεινού κόκκινου χρώματος, παρατηρήθηκαν χαρακτηριστικά διαγνωστικά στοιχεία (Winchell and Winchell 1953, McCrone 1982) του ορυκτού κινναβαρίτη (πίνακας 1), δηλαδή πολύ υψηλός δείκτης διάθλασης, πολύ μεγάλη διπλοθλαστικότητα και τέλειος πρισματικός σχισμός. *Τα* κύρια στοιχεία που εντοπίστηκαν στο δείγμα ερυθρού χρώματος, με τη χρήση XRF *και* EDS (*σχήμα* 4) *είναι* ο σίδηρος (Fe) και ο υδράργυρος (Hg). Τα αποτελέσματα από τις φασματοσκοπικές τεχνικές συνηγορούν με αυτά της οπτικής μικροσκοπίας. Το βαθύ ερυθρό χρώμα οφείλεται στην παρουσία μίγματος των χρωμοφόρων ορυκτών αιματίτη και κινναβαρίτη.

Ρόδινο ανοιχτό χρώμα

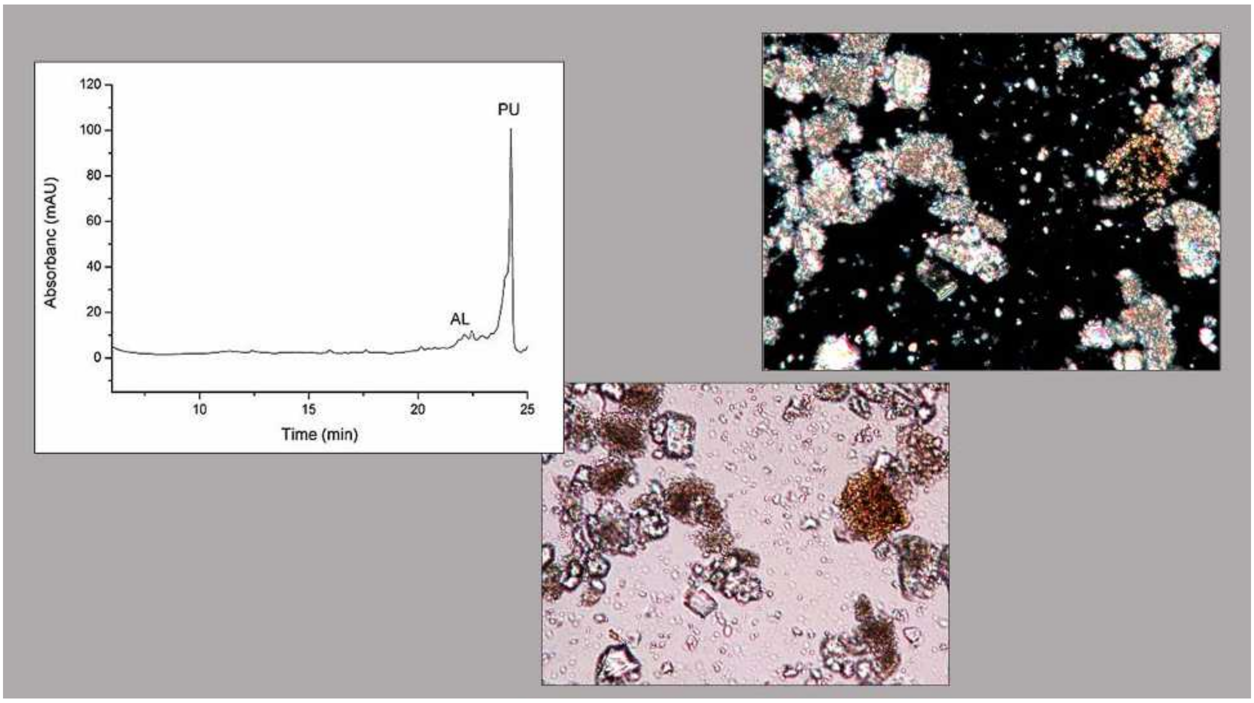
Το χρώμα αυτό ανιχνεύεται σημειακά στις αρχές και στις απολήξεις των φύλλων του ανθεμίου. Φαίνεται πως αρχικά κάλυψε μεγαλύτερο μέρος της επίπεδης επιφάνειας ανάγλυφων φύλλων του ενδεκάφυλλου ανθεμίου.

Στο δείγμα εντοπίστηκαν κόκκοι κόκκινης χρωστικής αρκετά μεγάλου μεγέθους έως 0,06-0,1 mm και πολυάριθμοι κόκκοι μικροκρυσταλλικού ασβεστίτη. Στους κόκκους κόκκινου χρώματος παρατηρήθηκαν χαρακτηριστικά διαγνωστικά στοιχεία του ορυκτού κινναβαρίτη, όπως είναι πολύ υψηλός δείκτης διάθλασης, πολύ μεγάλη διπλοθλαστικότητα και τέλειος πρισματικός σχισμός (πίνακας 1).Τα αποτελέσματα XRF και EDS δείχνουν την παρουσία του στοιχείου υδραργύρου που διαβεβαιώνει την υπόθεση ότι το βασικό ορυκτό ροζ χρώματος ήταν η κιννάβαρη. Ως αραιωτικό μέσο χρησιμοποιήθηκε ο μικροκρυσταλλικός ασβεστίτης σε μορφή κιμωλίας. Το ρόδινο χρώμα αποτελείται από μίγμα κινναβαρίτη με ασβεστίτη.

Ιώδες ανοιχτό χρώμα

Το ιώδες ανοιχτό χρώμα βρίσκεται στο εσωτερικό του κεντρικού άνθους και στα δύο συμμετρικά ημικύκλια σημεία (Τζαναβάρη 2002), τα οποία θεωρούνται τα ελάχιστα στοιχεία μίας φυτικής διακόσμησης η οποία αναπτυσσόταν από πλάγιες πλευρές και σε μεγάλο βαθμό έχει χαθεί.

Στο σχήμα 5 παρουσιάζονται τα αποτελέσματα εξετάσεων για το ανοιχτό μοβ χρώμα. Από τα αποτελέσματα XRF και EDS στο σύνολο των χημικών στοιχείων κυριαρχεί το ασβέστιο Ca.



Σχήμα 5. **Ανοιχτό μοβ χρώμα.** Αριστερά είναι χρωματογράφημα (400-500 nm) του δείγματος με κορυφές πουρπουρίνης (PU) και αλιζαρίνης (AL). Δεξιά είναι μικροφωτογραφίες στο πολωτικό μικροσκόπιο των κόκκων ασβεστίτη με οργανική χρωστική μοβ χρώματος σε NII και N× αντίστοιχα.

Στο πολωτικό μικροσκόπιο διακρίνονται τα συσσωματώματα των κόκκων του ασβεστίτη, στους οποίους ομοιόμορφα κατανέμεται μία ισότροπη ουσία με χρώμα, που σημειακά μεταβάλλεται από ανοιχτό μοβ προς ρόδινο και ανοιχτό πορτοκαλί. Οι οπτικές ιδιότητες και ο μεταβαλλόμενος σημειακά χρωματισμός υποστηρίζουν την υπόθεση για τη χρήση της χρωστικής οργανικής προέλευσης. Ως φορέας για οργανική χρωστική χρησιμοποιήθηκε μικροκρυσταλλικός ασβεστίτης (πίνακας 1).

Το δείγμα αναλύθηκε με υγρή χρωματογραφία υψηλής πίεσης (HPLC-PDA). Ταυτοποιήθηκε η ένωση της πουρπουρίνης και σε ίχνη ταυτοποιήθηκε η ένωση της αλιζαρίνης (σχήμα 5). Το αποτέλεσμα αυτό υποδηλώνει τη χρήση ριζαρίου ως χρωστική για τη διακόσμηση του ανθεμίου. Η μικρή ποσότητα αλιζαρίνης (σε σχέση με την πουρπουρίνη) που ανιχνεύθηκε αποτελεί ισχυρή ένδειξη ότι το ριζάρι που χρησιμοποιήθηκε προήλθε από το φυτό *Rubia peregrine* L. (άγριο ριζάρι).

Πράσινο φωτεινό χρώμα

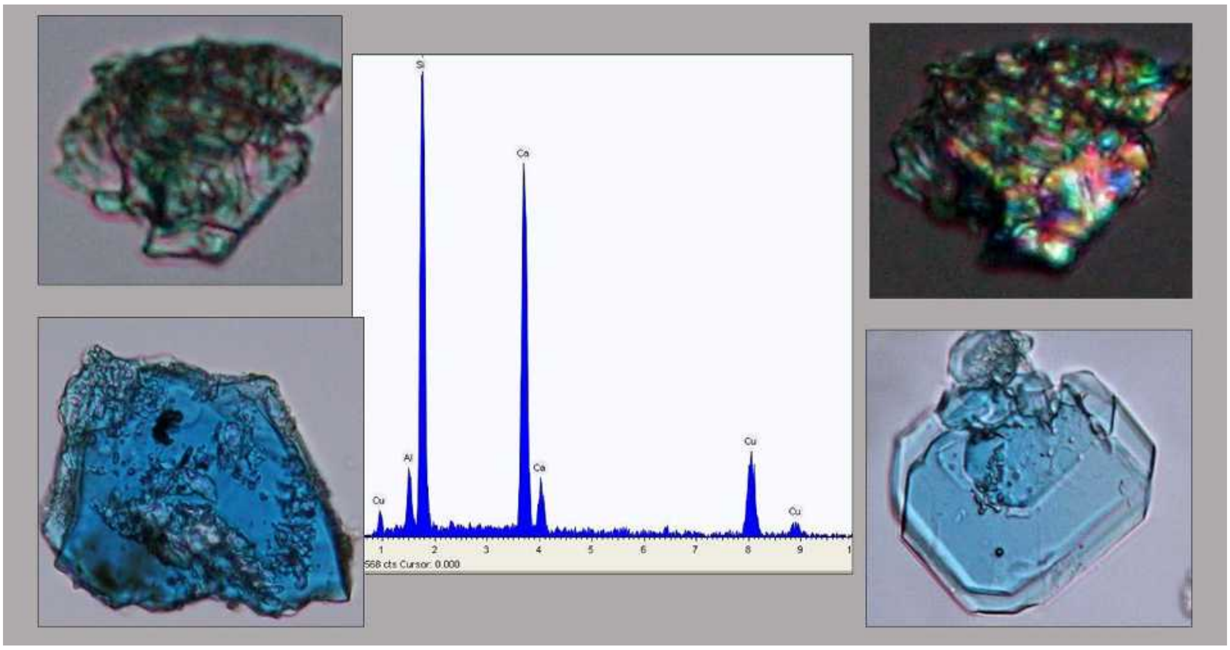
Ίχνη πράσινου χρώματος, εντοπίστηκαν μόνο σε δύο σημεία της διακοσμητικής σύνθεσης, δηλαδή στα σέπαλα του κάλυκα και στις νευρώσεις των πλαϊνών φύλλων του ακάνθου.

Με τη χρήση πολωτικού μικροσκοπίου στους κόκκους πράσινου χρώματος παρατηρούνται τα χαρακτηριστικά στοιχεία (Winchell and Winchell 1953, McCrone 1982) του ορυκτού μαλαχίτη, τα οποία είναι το χρώμα και η υφή της επιφάνειας των κρυστάλλων, ο μέτριος δείκτης διάθλασης, η εξαιρετικά υψηλή διπλοθλαστικότητα και ο τέλειος σχισμός (πίνακας 1). Στο δείγμα πράσινου χρώματος με βάση τα αποτελέσματα από XRF και EDS -αναλύσεις, κυριαρχούν το ασβέστιο (Ca) και ο χαλκός (Cu). Το πράσινο φωτεινό χρώμα οφείλεται στην παρουσία του ορυκτού μαλαχίτη.

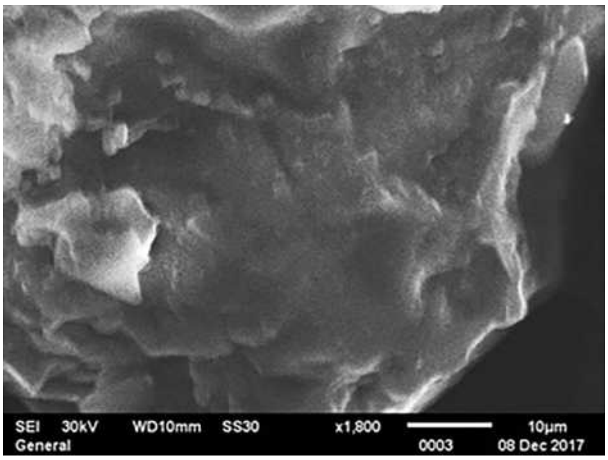
Κυανό χρώμα

Το χρώμα κάλυπτε μεγαλύτερο μέρος της επιφάνειας του ανθεμίου, δημιουργώντας ένα πλούσιο, έντονα χρωματισμένο βάθος, στο οποίο με επιτυχία προβάλλονται ανάγλυφα και έγχρωμα γραπτά στοιχεία διακόσμησης.

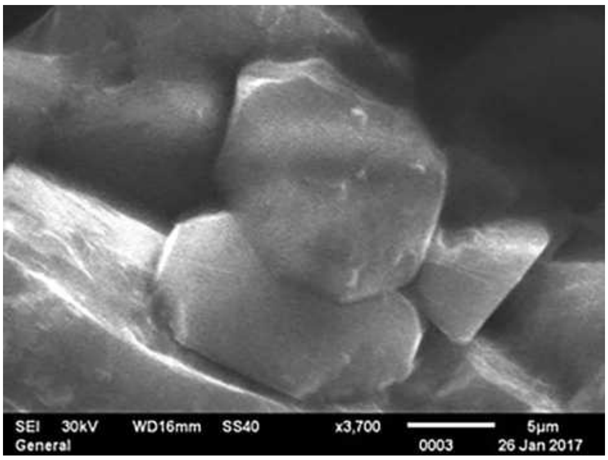
Στο δείγμα διακρίνονται ισότροποι κόκκοι γαλάζιου χρώματος (McCrone 1982) που αποτελούνται από υαλώδες υλικό (σχήμα 6). Μετά από την αξιολόγηση των αποτελεσμάτων των χημικών αναλύσεων με XRFκαι EDS (σχήμα 6), από τις οποίες προέκυψε χαλκός (Cu), ασβέστιο (Ca) και πυρίτιο (Si) συμπεραίνεται ότι πρόκειται για το χαλκούχο γυαλί. Εν τούτοις, στο δείγμα του κυανού χρώματος, μαζί με το χαλκούχο γυαλί, εντοπίστηκαν και μικροί κρύσταλλοι με οπτικές ιδιότητες του ορυκτού *cuprorivaite* [15], (πίνακας 1). Επίσης και στις εικόνες που έχουν ληφθεί από το SEM στο δείγμα του κυανού χρώματος παρατηρούνται



Σχήμα 6. Επάνω παρουσιάζονται μικροφωτογραφίες του κόκκου μαλαχίτη πράσινου χρώματος στο πολωτικό μικροσκόπιο, NII και N×. Κάτω αναφέρονται τα αποτελέσματα εξέτασης των κόκκων του αιγυπτιακού μπλε. Στο κέντρο απεικονίζεται το φάσμα της EDS ανάλυσης της χρωστικής, ενώ αριστερά και δεξιά βρίσκονται οι μικροφωτογραφίες των κόκκων του αιγυπτιακού μπλε στο πολωτικό μικροσκόπιο σε παράλληλα Nicols. Συγκεκριμένα, αριστερά είναι εικόνα του γαλάζιου κόκκου υαλώδους φάσης, ενώ αντίστοιχα δεξιά, του γαλάζιου κόκκου cuprorivaite κρυσταλλικής φάσης.



Σχήμα σ1 Αιγυπτιακού μπλε. Περιοχή με το χαλκούχο γυαλί. Ηλεκτρονικό μικροσκόπιο SEM.



Σχήμα σ2 Αιγυπτιακού μπλε. Κρύσταλλοι ορυκτού cuprorivaite. Ηλεκτρονικό μικροσκόπιο SEM.

περιοχές με υαλώδες υλικό και με κρυστάλλους *cuprorivaite* (σχήμα σ1 και σ2 συνοδευτικό υλικό).

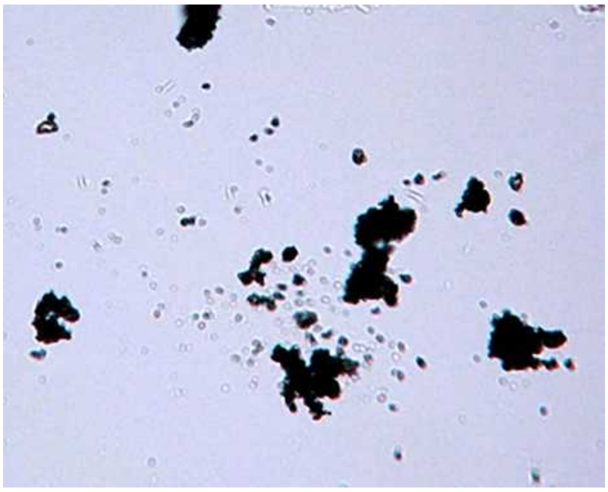
Συμπεραίνεται, ότι η χρωμοφόρα ουσία στο κυανό χρώμα του ανθεμίου ήταν η τεχνητή χρωστική, αιγυπτιακό μπλε, στο οποίο συνυπήρχαν δύο φάσεις, μία υαλώδης και μία κρυσταλλική, χαλκούχο γυαλί και μικροκρυσταλλικός cuprorivaite.

Παρόμοια σύσταση του αιγυπτιακού μπλε εντοπίστηκε κατά την εξέταση του κυανού χρώματος από την εντοίχια διακόσμηση του κιβωτιόσχημου γυναικείου τάφου 1 Δερβενίου, ο οποίος βρίσκεται στο ίδιο νεκροταφείο και χρονολογείται στις αρχές του 3 αιώνα π.Χ. Κατά την πετρογραφική ανάλυση των κόκκων αιγυπτιακού μπλε από το βάθος της παραπάνω τοιχογραφίας διαπιστώθηκε, ότι οι μερικοί κόκκοι ήταν ισόμορφοι, σχηματίζοντας υαλώδη φάση, ενώ σε άλλους διακρινόταν ζώνες κρυσταλλοποίησης με χαρακτηριστικές οπτικές ιδιότητες του ορυκτού cuprorivaite.

Ο συνδυασμός παρόμοιων φάσεων κρυσταλλικού και υαλώδους υλικού παρατηρήθηκε στα δείγματα του αιγυπτιακού μπλε που εξετάστηκαν και από άλλα έργα αρχαίας ζωγραφικής (Chakoumakos *et al.* 1993, Kakoulli 2009).

Μαύρο χρώμα

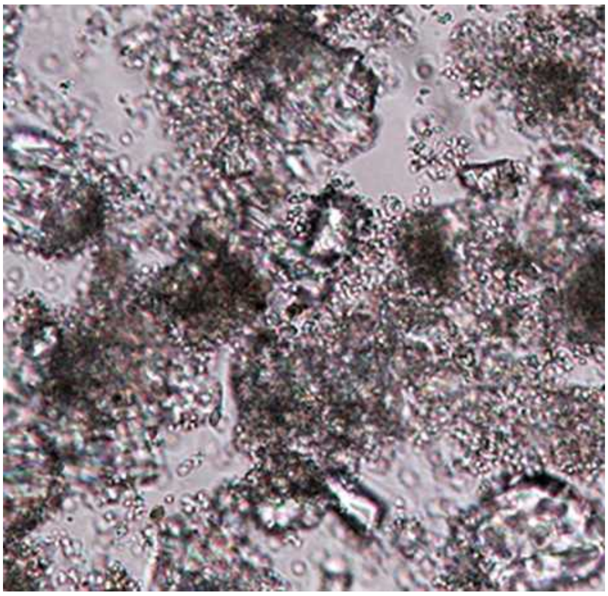
Μαύρο χρώμα έχει χρησιμοποιηθεί στα περιγράμματα των ζωγραφικών στοιχείων. Με το πολωτικό μικροσκόπιο όπως φαίνεται στο σχήμα σ3 στο συνοδευτικό υλικό, στο δείγμα ανιχνεύονται συσσωματώματα των ισότροπων κόκκων ανθρακοποιημένου οργανικού υλικού. Στα φάσματα XRF και EDS εντοπίστηκε ο άνθρακας που είναι το βασικό χρωμοφόρο στοιχείο του μαύρου των φυτών. Το σχήμα των κόκκων του άνθρακα και η χημική σύστασή του υποδηλώνουν τη χρήση της χρωστικής του μαύρου των φυτών (Βιβντένκο 2015).



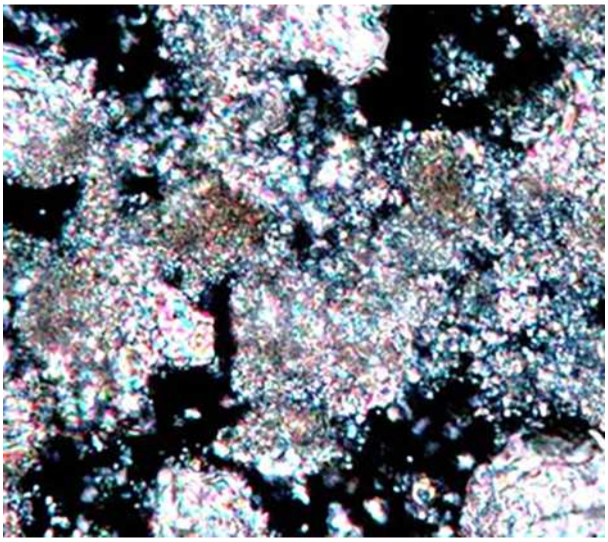
Σχήμα σ3 Κόκκοι μαύρου των φυτών. Πολωτικό μικροσκόπιο. Ν ΙΙ
Χρωστική: Μαύρο των φυτών, λαμβάνεται με το ψήσιμο των κληματόβεργων των πυρήνων ροδάκινου, των κελυφών αμυγδάλου και καρυδιών, του φύλλου και φλοιού των δέντρων κλπ. Έχει αυξημένη περιεκτικότητα σε C (95%), ενώ οι προσμίξεις των ανθρακικών ασβεστίου και καλίου αποτελούν μόνο 5% της συστάσεως.

Λευκό χρώμα

Λευκό χρώμα καλύπτει τους ανάγλυφους κρίνους. Στη σύσταση του λευκού χρώματος (σχήμα σ4 και σ5 συνοδευτικό υλικό) κυριαρχούν συσσωματώματα κρυπτό και μικροκρυσταλλικού ασβεστίτη (πίνακας 1). Από τα φάσματα XRF και EDS (σχήμα σ6 συνοδευτικό υλικό) το στοιχείο που κυριαρχεί στη σύσταση του δείγματος είναι το ασβέστιο Ca. Το λευκό χρώμα αποτελείται από ασβεστίτη που παρουσιάζεται σε μορφή κιμωλίας.



Σχήμα σ4. Κόκκοι ασβεστίτη στη σύσταση λευκού χρώματος. Πολωτικό μικροσκόπιο. ΝΙΙ.

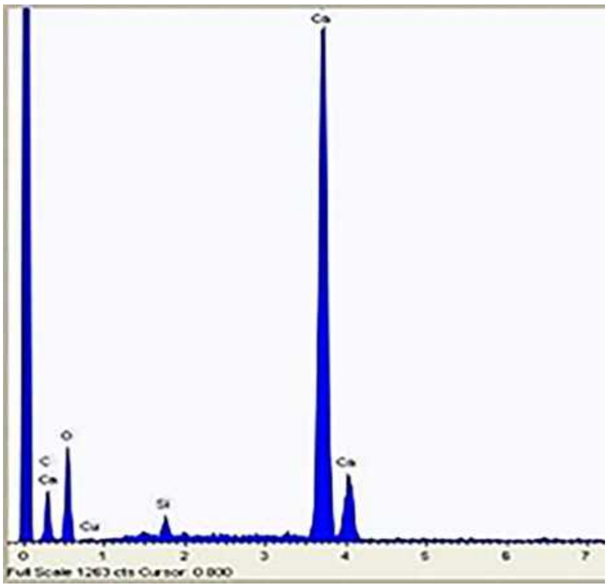


Σχήμα σ5. Κόκκοι ασβεστίτη στη σύσταση του λευκού χρώματος. Πολωτικό μικροσκόπιο. Ν×.

Τεχνική της ζωγραφικής

Κατά την αρχική προκαταρκτική εξέταση του ανθεμίου καταλήξαμε στο συμπέρασμα ότι στη διακόσμηση της επιφάνειας του ανθεμίου χρησιμοποιήθηκε τεχνική *tempera* [1]. Στα πρώτα αυτά συμπεράσματα συμβάλλανε οι παρακάτω παρατηρήσεις.

Στο ανθέμιο δεν υπήρχε υπόστρωμα με το απαραίτητο πάχος για την τεχνική *fresco*. Όταν εφαρμόζεται η τεχνική *fresco* το υπόστρωμα πρέπει να έχει αρκετά μεγάλο πάχος για να μην στεγνώνει γρήγορα. Το υπόλευκο επίχρισμα που εντοπίστηκε επάνω στην



Σχήμα σ6. Φάσμα της EDS ανάλυσης λευκού χρώματος.

πέτρινη βάση ανθεμίου έχει πάχος μόλις 0,2-1,5 mm. Ενδεικτικός για την τεχνική *tempera* είναι και ο τρόπος της χρήσης του αιγυπτιακό μπλε για δημιουργία του βάθους στα ανάγλυφα μέρη του ανθεμίου, όταν κάλυπτε μεγάλη ζωγραφική επιφάνεια. Η χρωστική απλώθηκε σε μορφή συσσωματωμάτων αρκετά μεγάλου μεγέθους που δύσκολα εφαρμόζονται σε μία κάθετη επιφάνεια ζωγραφικής. Ως κατά το ένα μέρος υαλώδες υλικό το αιγυπτιακό μπλε, από τη φύση του παρουσιάζει χαμηλή πρόσφυση στην επιφάνεια της προετοιμασίας και προκειμένου να σταθεροποιηθεί απαιτεί τη χρήση συνδετικού μέσου με καλές συγκολλητικές ιδιότητες.

Σύμφωνα με τα αποτελέσματα των τελευταίων αναλύσεων στη σύσταση της προετοιμασίας μαζί με τον ασβεστίτη και καολινίτη εντοπίστηκαν και ίχνη μίας οργανικής ουσίας με συγκολλητικές ιδιότητες (κόμμι). Η ζωγραφική τεχνική που χρησιμοποιήθηκε στο ανθέμιο ήταν η τεχνική *tempera.*

Συμπεράσματα

Από τα αποτελέσματα της αρχαιομετρικής μελέτης της ανθεμωτής πέτρινης επίστεψης συμπεραίνεται η χρήση κυρίως φυσικών ανόργανων χρωστικών με κύρια ορυκτά (αιματίτη, κινναβαρίτη, μαλαχίτη, ασβεστίτη σε μορφή κιμωλίας και άνθρακα) και μίας τεχνητής ανόργανής χρωστικής, του αιγυπτιακού μπλε. Την παλέτα πλουτίζει και μία οργανική χρωστική ανοιχτού μοβ χρώματος.

Το αιγυπτιακό μπλε, συμμετέχοντας στη δημιουργία του βάθους των ανάγλυφων στοιχείων του ανθεμίου, χρησιμοποιήθηκε στη διακόσμηση περισσότερα από τις άλλες χρωστικές. Στη χρωστική διαπιστώθηκε συνύπαρξη δυο φάσεων: κρυσταλλικής, του ορυκτού *cuprorivaite*, και υαλώδους, του χαλκούχου γυαλιού, το οποίο ήταν καθαρό, χωρίς προσμίξεις άλλων χημικών στοιχείων, όπως π.χ. μόλυβδος ή κασσίτερος.

Για λόγους σύγκρισης αναφέρουμε επίσης και την πληροφορία σχετικά με το αιγυπτιακό μπλε, που εντοπίσθηκε στις τοιχογραφίες του γυναικείου κιβωτιόσχημού τάφου 1 Δερβενίου. Η τεχνητή αυτή χρωστική, όπως και το κυανό στο ανθέμιο, χρησιμοποιήθηκε στην ταφική διακόσμηση συχνότερα από τις άλλες χρωστικές, συμμετέχοντας στη δημιουργία του γαλανού φόντου στην ανώτερη ζώνη διακόσμησης, της ορθομαρμάρωσης της κάτω περιοχής και των πολυάριθμων στοιχείων του πλοχμού.

Όπως και στο ανθέμιο, στο αιγυπτιακό μπλε των παραπάνω τοιχογραφιών εντοπίσθηκε cuprorivaite και χαλκούχο γυαλί, αλλά σε αντίθεση με το κυανό του ανθεμίου, το γυαλί εδώ περιείχε μεγάλη ποσότητα μολύβδου και μπορούμε να υποθέσουμε ότι κατά την κατασκευή της χρωστικής χρησιμοποιήθηκαν παλαιά χάλκινα αντικείμενα, τα οποία στο κράμα τους είχανε σημαντική πρόσμιξη μολύβδου.

Εντυπωσιακή είναι και η θέση της πολύτιμης χρωστικής κιννάβαρης, η οποία, παρά το μεγάλο κόστος της, φαίνεται να ήταν η δεύτερη στη συχνότητα χρήσης στη ζωγραφική του ανθεμίου, μετά το κυανό. Η κιννάβαρη εντοπίστηκε σε όλες τις χρωστικές ανθεμίου με κόκκινη απόχρωση: στο βαθύ ερυθρό ήταν αναμεμιγμένη με τον αιματίτη, ενώ στο ρόδινο, όπου έπαιζε τον ρόλο του βασικού χρωμοφόρου, αραιωνόταν με την κιμωλία. Παρόμοια ευρεία χρήση της κιννάβαρης παρατηρήθηκε και στο κιβωτιόσχημο τάφο 1 Δερβενίου. Η πολύτιμη χρωστική χρησιμοποιείται σε καθαρή μορφή στα στοιχεία του περιστεριού και περιμετρικά σε όλο τον τάφο στο φωτεινό κόκκινο του δωρικού κυματίου. Η κιννάβαρη εντοπίστηκε και στα σύνθετα χρώματα: στο ιώδες ανοιχτό σε ανάμιξη με το αιγυπτιακό μπλε, ενώ στο ρόδινο ήταν αναμεμιγμένη με κιμωλία, όπως και στο ανθέμιο.

Η ευρεία χρήση της πολύτιμης χρωστικής υποδεικνύει τη μεγάλη αξία των υπό εξέταση μνημείων του Δερβενίου.

Ίχνη μαλαχίτη εντοπίστηκαν μόνο σε δύο σημεία της διακοσμητικής σύνθεσης του ανθεμίου. Την ίδια περιορισμένη χρήση μαλαχίτη, μόνο στο στεφάνι, παρατηρούμε και στο προαναφερόμενο ταφικό μνημείο.

Από τις οργανικές χρωστικές διαπιστώθηκε η χρήση στο μοβ ανοιχτό χρώμα του ριζαρίου, το οποίο θεωρείται από τις αρχαιότερες και πιο διαδεδομένες στον ελλαδικό χώρο κόκκινες φυτικές βαφές. Στη χρωστική αυτή, η εξαιρετικά μικρή ποσότητα του ενός συστατικού του ριζαρίου, της αλιζαρίνης σε σχέση με το άλλο, την πουρπουρίνη, αποτελεί ισχυρή ένδειξη ότι το ριζάρι που χρησιμοποιήθηκε προήλθε από το φυτό RubiaperegrinaL (άγριο ριζάρι).

Τον ρόλο του φορέα της οργανικής χρωστικής έπαιξε η κιμωλία.

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ΤΙΤΛΟΙ ΠΙΝΑΚΩΝ

Πίνακας 1:**Κύριες οπτικές ιδιότητες των ορυκτών που εντοπίστηκαν στις υπό εξέταση χρωστικές.**

Πίνακας **2:**Πρόγραμμα βαθμωτής έκλουσης.

The Burial Monument of Amphipolis through the Absolute Dates of the Gradual Coverage of the Soil Layers and Stratigraphy of Kastas Hill

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Abstract: The aim of this survey (2013–2017) is to answer some of the questions that were created following the revelation of the burial monument of Amphipolis in Kastas hill in 2014, foremost the origin of the filling sediments of the interior and the creation of Kastas hill (artificial or natural). The methodology included field work, such as macroscopic observations, sample drillings, sediment sampling, and photographic documentation. Minerological analyses were carried out following the XRD method, sedimentary (granulometric analysis) and absolute radiocarbon dating (^{14}C) and bibliographic information.

The sum of the elements of our research shows that Kastas hill is natural and not a tomb, though the use of excavation machinery has caused temporal strong interventions. With the extensive removal and coverage of soil layers in the years 2014 and 2015 the environmental alteration of its natural structure continued. The only ancient deposits are located over the burial monument and are bounded by the slopes of the trench that was opened for its construction. This is the only part of the hill considered as a tomb.

The internal backfill of the monument was made with sediments supernated to the hill *c.*70 BC, after all the valuables and artifacts had been removed from its interior. The fragments of charcoal, along with sand that penetrated from the seismic opening of the western wall at the northwest end of the burial chamber, are older than the burial monument and were dated to the Archaic period, *c.*620 BC.

The dimensions of the trench that hosts the burial monument, as well as the position and dimensions of the box-shaped grave at the north and deepest end, leads to the conclusion that the box-shaped grave is later than the burial monument. The absolute dating of the combustion detected above the arch of the monument and under its clay overlap, gives us a terminus for the time of construction. It is more likely between the second and third quarter of the third century BC, that is, 271-231. Furthermore, during the correlation of the burial monument with the Macedonian tomb C of the third century BC—located on the southern outskirts of Kastas— important common elements were revealed.

KEYWORDS: KASTAS HILL STRATIGRAPHY, BURIAL MONUMENT EMBANKEMENT, DATING SEDIMENTS, LAZARIDIS EXCAVATION, PERISTERI EXCAVATION

Introduction

Kastas hill is located in East Macedonia in Greece, about 2 km northeast of Amphipolis, on the southern part of Strymon River and the south-west fringes of Mountain Pangeo (Figure 1).

The revelation of the burial monument on this hill in 2014 initiated a discussion within the archaeological community concerning a variety of issues, including the dating of its construction phases, the origin of the sediment repletion in its interior, and the creation of the Hill (natural or tomb).

The archaeological excavation on Kastas hill that had begun in 1964 by D. Lazaridis finished in 1982. In 1965 Lazaridis revealed the first 40.8 m of the supporting precinct and estimated its circumference at 487 m, considering it a large tomb. During the excavations he uncovered an extensive cemetery on the upper surface of the hill of about 80 burials, dating from the Iron Age, the Archaic until the Early Classical period. The uncovered graves were at a depth of 1.20 m, 3 m, 3.80 m and deeper from the surface of the hill, and were opened in the natural terrain (Kabouroglou *et al.* 2017; Lazaridis 1973). In 1982 Lazaridis excavated the north and west part of the hill, revealing terra rossas in horizontal layers alternating with sands. As a benchmark, he left four Witnesses of his excavations, appearing in his aerial photo of 1988 (D. Lazaridis archive) (Figure 2).

In 2010, C. Peristeri began excavations, initially around the centre of the hill, and in 2012 in its surrounding region at the base of the hill, which revealed part of

Figure 1. Geophysical map of Eastern Macedonia.

Figure 2. Aerial photography of Kastas hill with four Witnesses (1-4) (Lazaridis D. archive; 1988).

the supporting precinct.She argued that there is a Macedonian tomb that is chronologically placed to the last quarter of the fourth century BC, that is, the period after the death of Alexander the Great (Newspaper TODAY'S, of Serres, 09 October 2012). Thus, she pre-dated a still unknown burial monument of Kastas hill. The excavation continued in 2013, with the finding of the rest of the supporting precinct, and in 2014, with the finding of the important burial monument of Kastas hill.

This article presents the results of our research that began in 2013 during the revelation of the supporting precinct, and continued from 2014 —with E. M. Kabouroglou as a member of the excavation team of the burial monument— until 2017. The aim of this paper is to answer some of the questions that were raised during the revelation of the burial monument in 2014: the origin of the sediment repletion in the interior of burial monument of Kastas hill, the dating of its construction phases, and the creation of Kastas hill (natural or tomb).

Methodology

The methodology followed, included: field work, such as macroscopic observations along the excavations during the revelation of the precinct and the gradual interior coverage of the soil layer of the burial monument; sample drillings inside the burial chamber; sediment samplings; photographic documentation; and bibliographic information from all excavations from 1964 onwards. We searched for corresponding stratigraphical horizons with Kastas hill in the wider region and compared our own data with those of the excavations of D. Lazaridis, C. Peristeri, and the geological map of S. Xidas (IGME, 1978).

Minerological analyses were carried out using the XRD method and granulometric analysis, with the aim of defining the structure, character, and mineral identification of the specimens, as well as the interpretation of their storage conditions. The absolute radiocarbon dating (^{14}C) helped us to clarify the temporal deposition of sediments inside the burial monument and during its construction time.

During the excavations, the sediments of the upper stratigraphical horizon of terrestrial origin were removed in the upper part of the hill from the temporal removal of accumulated soil. The remaining sediments around its centre were covered to a large extent by the fillings realized in 2014 and 2015. Important help in solving this problem was offered by the published data of the excavation research of D. Lazaridis and his photographic archive. Also for the complete documentation of our views, we used the drawings of the excavation of 2010 by C. Peristeri located in the department of drawings of the Museum of Amphipolis in comparison with photographs from her excavation, which she had send to us online.

Stratigraphy of the hill

The wider geomorphological environment, in which the hill of Kastas is located, is hilly to semi-hilly. This is mainly due to the display of loose to semi-hard rocks, which originate from old (Neogenous) and newer sedimentary deposits of the basin of the Strymon River. These are mainly torrential, deltaic, lacustrine to brackish sediments with limited interference of sea deposits. (Syrides 2000; Xidas 1978)

Kastas is a hilly knob with a base at an altitude of 88 m and a present-day peak at 107.57 m, measured at the basement of the building around the centre of the hill. Its total thickness is 19.57 m. The shape of its base is circular for the most part with a diameter of about 160 m. Cyclicity has changed on its south-western part and the base has been magnified due to the rejection of sediments from past excavations in the upper part of the hill.

Today at the top of the site there are two residual structures with steep slopes. The southernmost of these structures was created by the removal of accumulated soil from the excavations of D. Lazaridis, as we were informed by the former chief guardian A. Kohliaridis. The northernmost is the remainder of witness 1 after the excavation of C. Peristeri in 2010. On the base of these structures, an extended, almost horizontal surface area of more than 10,000 m^2 has been created as a result of the intense sediment removal from past excavations. Here the geological background was displayed. The height of the vertical east slope of witness 1 from its base is about 6.5 m.

As has been shown, the hill consists of two different sedimentary sequences (Kabouroglou and Mitsis 2020; Kabouroglou *et al.* 2022). The upper sedimentary sequence consists of terrestrial sediments, mainly from horizontal layers of terra rossa, which alternate with sandy sediments—thicker in the east side of the hill—aged in the Pleiocene period (Xidas 1978) without fossils, and also from lower sedimentary sequence of lacustrine–brackish sediments with limited sea interference, aged in the Upper Miocene–Pleiocene period (Syrides *et al.* 2017; Xidas 1978) with fossils. These sediments occupy a wider area north and east of the hill of Kastas.

These two sedimentary sequences are separated by angular incompatibility found throughout the circumference of the hill (Kabouroglou *et al.* 2022; Kabouroglou and Kampouroglou, forthcoming) and bounded by the supporting precinct. On the northeast slopes of the hill, in the oldest formation, green-blue clays are involved, alternating with sandy layers, as in the other areas of the hill. The sandy sediments bear fossils such as Pecten regiensis, Ostrea s.p., etc.

The first to reveal these layers on the west side was D. Lazaridis (Lazaridis 1965), who mentioned the gradual coverage of hard soil layers of hypo green colour accumulated in turns with layers of fine sand. While he

Figure 3. Revealing the northeast end of the north wall of the building and the continuation of stratigraphy in north (Lazaridis D. archive; 1972).

described the sediments correctly, the interpretation he gave was incorrect. Lazaridis also revealed the edge of the north wall of the building around the centre of the hill (Lazaridis 1972a) (Figure 3), which he considered as its probable mark. He mentioned the presence of sandy terra rossa layers alternating with layers of pure sand and indicated that this wall was based on an undisturbed thin-sand layer (Lazaridis 1973).

In the excavation section the specific layers continue to the north without interruption. Corresponding layers appear on the northern slopes of the hill with a bent to the east and are about 75 m from its centre (Kabouroglou and Kampouroglou, forthcoming). Terra rossas also appear on the southwest area of the hill and in the extended moat addressed A–D north of the centre of the hill (Kabouroglou *et al.* 2022; Lazaridis 1973).

In 1982, D. Lazaridis left four Witnesses from his excavation sections on the upper part of the hill (Figure 2). The horizontal layers of terra rossas are distinguished. Then, in 2010 C. Peristeri excavated the upper part of the hill and a topographic plan of this section was made (Figure 4), (S. Goudas being the topographer and N. Medesidou the designer). In this project, the floor plan of the construction revealed by D. Lazaridis is displayed, among others, and the positions of four excavation sections–witnesses are noted. Also, 18 tombs are captured at different altitudes ranging from 96.15 m to 100.86 m. Of the 18 tombs and the 80 revealed by D. Lazaridis, today only 5 are preserved. We do not know whether the rest 93 were destroyed or recovered. Witness 1, 23.5 m long, includes the centre of the hill with the building that Lazaridis himself revealed. Witness 2, 31.5 m long is a continuation of witness 1 and is separated from it by a ditch. Before the opening of the ditch, there was a single stratigraphic horizon. Witness 3 is located south of 1 and was created by the removal of accumulated soil. Witness 4, 11 m long, is located south of Witness 2. This plan agrees with the aerial photo of 1988 where the four hilly knobs (Figure 2) and the horizontal stratigraphy are shown.

In the second drawing of 2010 (N. Medesidou being the designer) (Figure 5) the stratigraphy of the four witnesses from the excavation of the same year is presented. In the stratigraphic section of witnesses 1 and 2—whose total length was 55 m— and in the upper territorial horizon the underlying layers are red clay in horizontal layers, alternating with white-yellow sand along the length of 55 m.

C. Peristeri sent us photographs of the excavation, and asked us whether the sediments are natural or artificial. Our answer was that these are perfectly natural formations. In photo (Figure 6) Witnesses 2 and 4 are presented before they were destroyed. The arrows mark horizontal layers of terra rossas alternating with sandy layers as in the excavation section of D. Lazaridis in 1973. The underlying sediments belong to lacustrine–brackish deposits. The dividing surface known as angular discrepancy is inserted between them though not perfectly clear due to the coverage of the soil by the excavator. It is likely to be near the level created by the digging machine.

The excavation section of Witnesses 1 and 2 is compared to their physical appearance (Figure 7) at the time of their design. The terra rossa alternating with white-yellow sands in horizontal layers are distinguished throughout the length of 55 m. The designed section (N. Medesidou being the designer) fully agrees with its natural appearance. After the 2010 excavation, Witnesses 2 and 4 were destroyed.

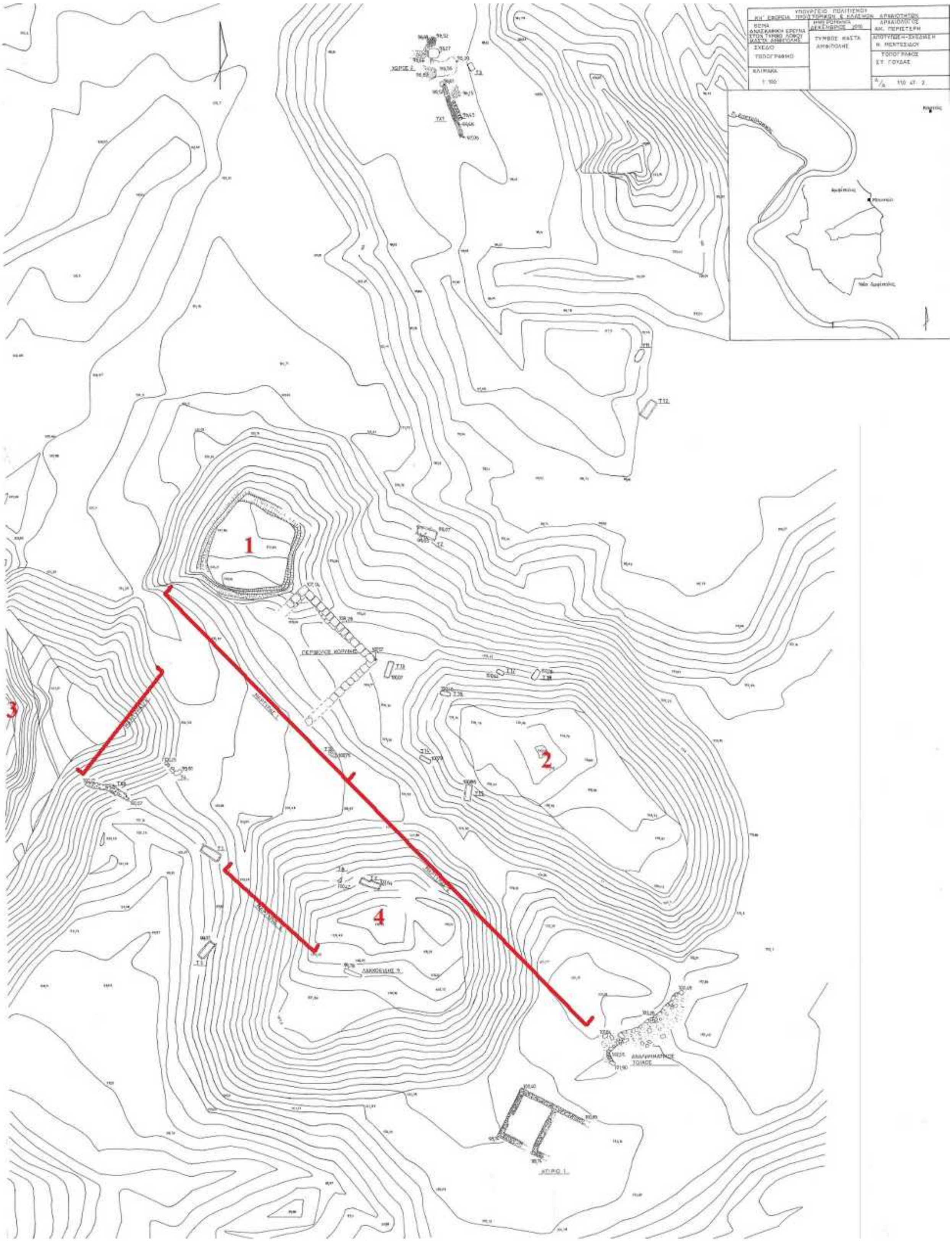

Figure 4. Topographical plan of KH EPCA (2010) around the centre of the hill after the excavation of C. Peristeri with four witnesses (department of drawings of the Amphipolis Museum).

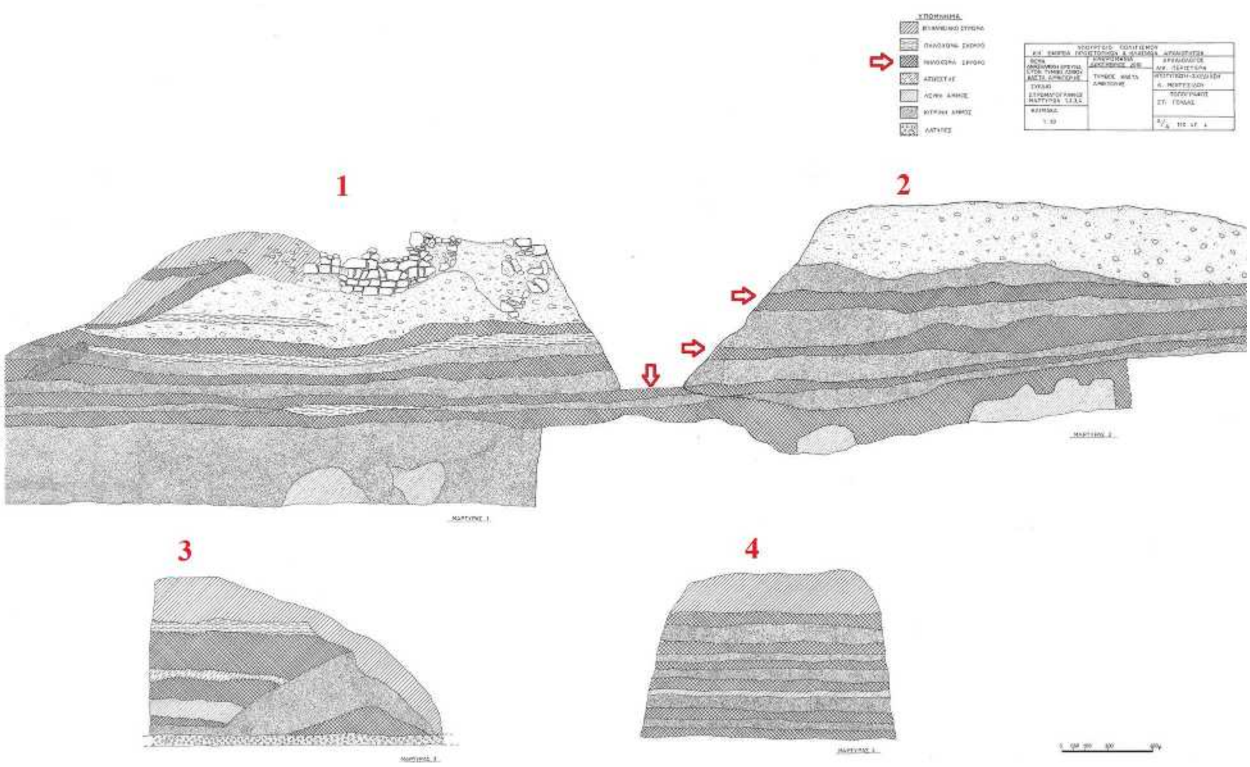

Figure 5. The four sections of witnesses after the excavation of C. Peristeri (KH EPCA 2010 - department of drawings of the Amphipolis Museum).

Figure 6. Excavation section of C. Peristeri in 2010 (Peristeri archive; 2010).

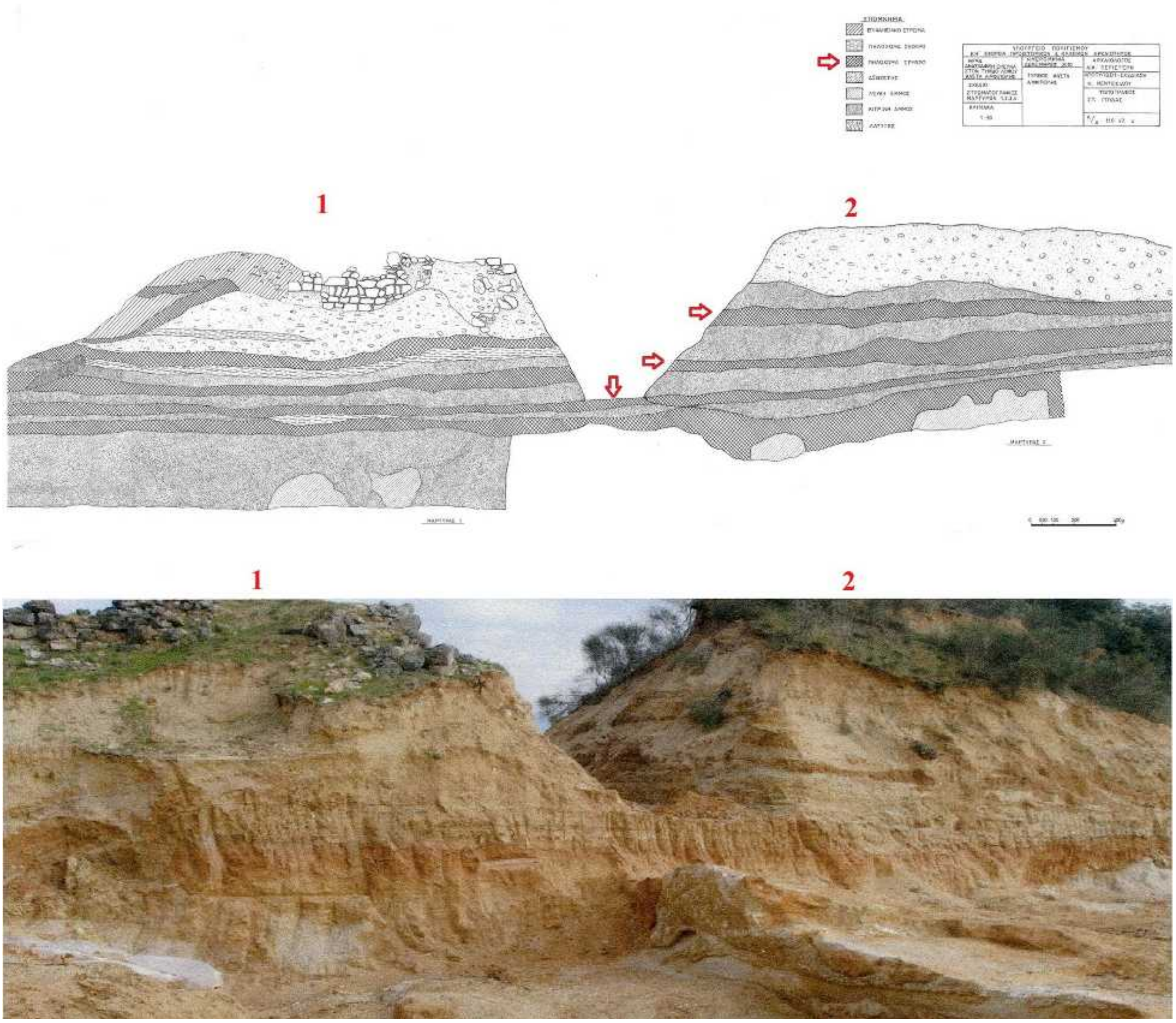

Figure 7. Cross section with W1-W2 witnesses (department of drawings of the Amphipolis Museum; photography C. Peristeri; 2010).

In 2013 when we started our own investigation there was only one section left from Witness 1. In 2014, Witness 1 (Figure 8) was covered in the north, and in 2015 it was covered in the south after the installation of geotextile. The continuous use of excavation machinery in the excavation of 2014 resulted in: i) the continuation of the deterioration of the morphology of the upper part of the hill; ii) the creation of conditions of instability on its slopes, on the supporting precinct, and on the burial monument; and iii) the destruction of many elements related to its structure (Kabouroglou and Mitsis 2020).

Due to the aforementioned conditions of instability, geostatic problems were created, resulting to a significant part of the supporting precinct (bigger than 100 m) being violently swallowed by the continuous landslides of the slopes. The continuation of the coverage of the soil layers by others north east, north and west of the centre of the hill, contributed to the further alteration of its morphology and the loss of many archaeological and stratigraphic elements (Figure 9a).

In a survey undertaken after the end of the excavation in 2014 (Syrides *et al.* 2017), the natural sediments of the hill were separated from the human material using a 3D digital model. Two types of filling material of the hill were observed: the ancient one linked to the construction of the burial monument, and the recent one from the excavations of D. Lazaridis. They are not mentioned in the fillings that took place in 2014 on the upper surface of the hill around its centre.

From the surface research we have seen the existence of terra rossa in the entire length of the western areas of Pageo (more than 18 km). These cover a significant

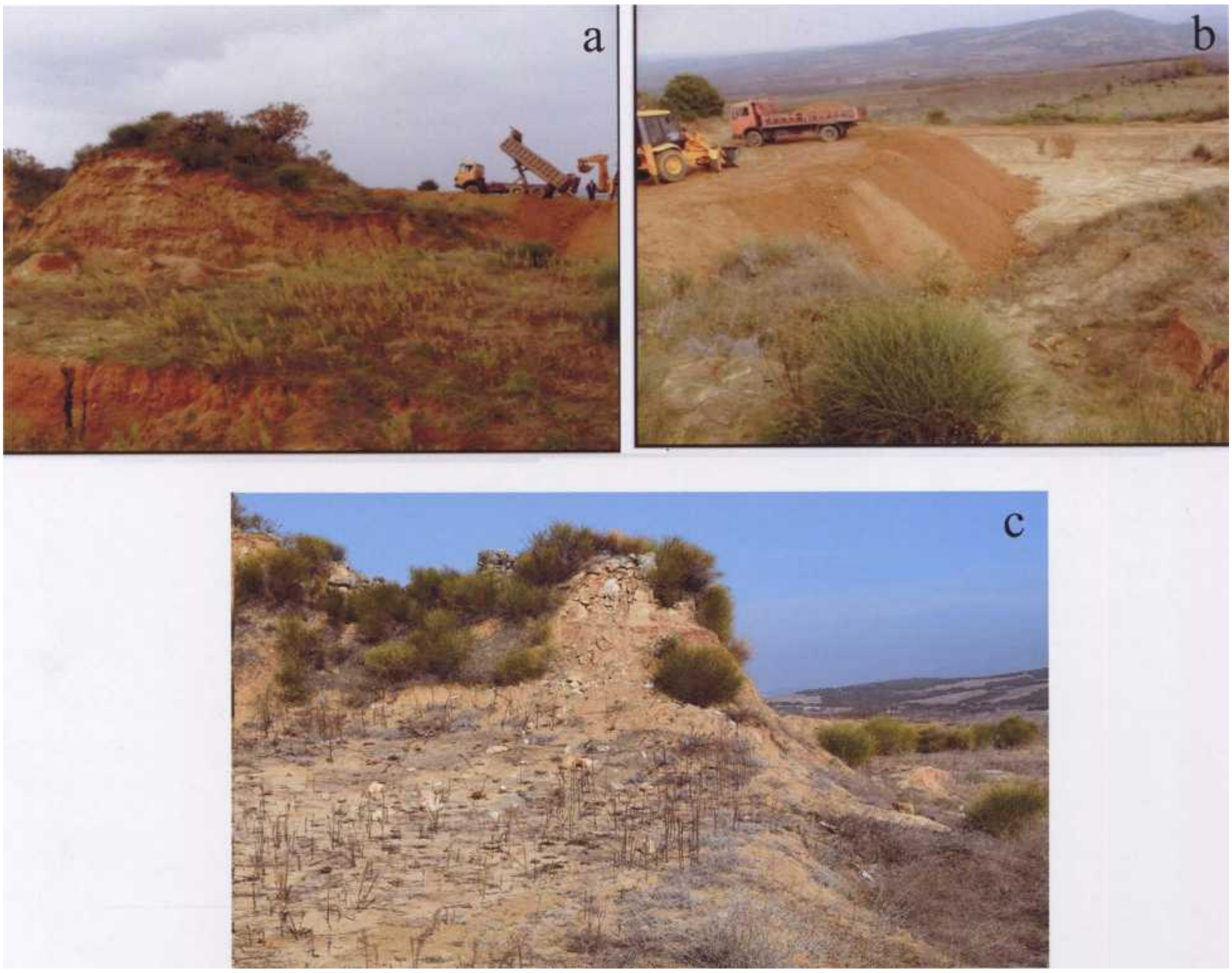

Figure 8. The embankment fill around the witness W1 in a) b) 2014 and c) 2015.

Figure 9a–b. a) Present view of the Kastas hill from aerial photography (Google 2019); b) revelation of burial monument entrance in 2014.

Figure 10a–b. a) Hill in north site of Kastas Hill (2016); b) a horizontal layer of terra rossa is displayed near the top of the hill (2016).

part of the lowland area. There are several hills with similar morphology and corresponding stratigraphy, such as the one pictured in Fig 10, located north of Kastas. In the natural section of this hill (of a length greater than 160 m), a horizontal layer of terra rossa is displayed near the top and presented in detail in Fig 10b. S. Xidas, in 1978, in the geological map of IGME, sheet Rodolivos, which Kastas belongs to, mentioned the existence of horizontal coats of red soil of terrestrial origin for the whole area west of Pageo. He placed this formation chronologically at the higher levels of the Neogene (Pleiocene). As for the formation of terra rossas, it is indicated that they were deposited with angular discord on the underlying formations of the Neogenic, just as on Kastas hill.

As for the morphology and shape of the hill we derive important information from the first topographical plan of the area (Figure 11) (Lazaridis 1971). This is the only plan that corresponds more fully to its shape since the extensive removal and accumulation of soil had not occurred. The contours were designed every 5 m in detailed outline, showing the almost circular base of the hill and its asymmetrical morphology in relation to the centre. The east slope is more inclined to the west due to the density of the contours. The 110 m contour delimits a plateau located higher and east of the centre of the hill. The 111 m contour was included in the detailed plan, which is surrounded by the 110 m contour. In topographical section A–B directed A–D passing through the centre of the hill, asymmetric morphology appears where the east slope is higher than the west. This asymmetric morphology does not accord with the existence of a tomb, the centre of which had to be higher than its sidewalls.

In the topographic plan of 2010 of the excavation of C. Peristeri, (Figure 4) four hilly knobs with the proportional contours are delimited around its centre. These knobs correspond to the Witnesses that D. Lazaridis had left from his excavation and appear in the aerial photograph of 1988 (Figure 2). Witnesses 2 and 4 located east and southeast of the centre have altitudes of 110.67 m and 110.57 m respectively, while Witness 1 (including the centre of the hill) has an altitude of 107.57 m. The centre is more than three meters lower. This elevation difference between the centre and the eastern area of the hill agrees with the topographic plan of D. Lazaridis of 1971. From the aforementioned comparative data we can conclude that the stratigraphic and topographic elements of the excavations of D. Lazaridis (1964 –1982) and C. Peristeri in 2010 fully agree and that they reveal horizontal layers of terra rossa which alternate with sandy sediments at a length of at least 55 m in the upper part of the hill. They also agree with our geological elements (2013 – 2017) and those of S. Xidas (1978).

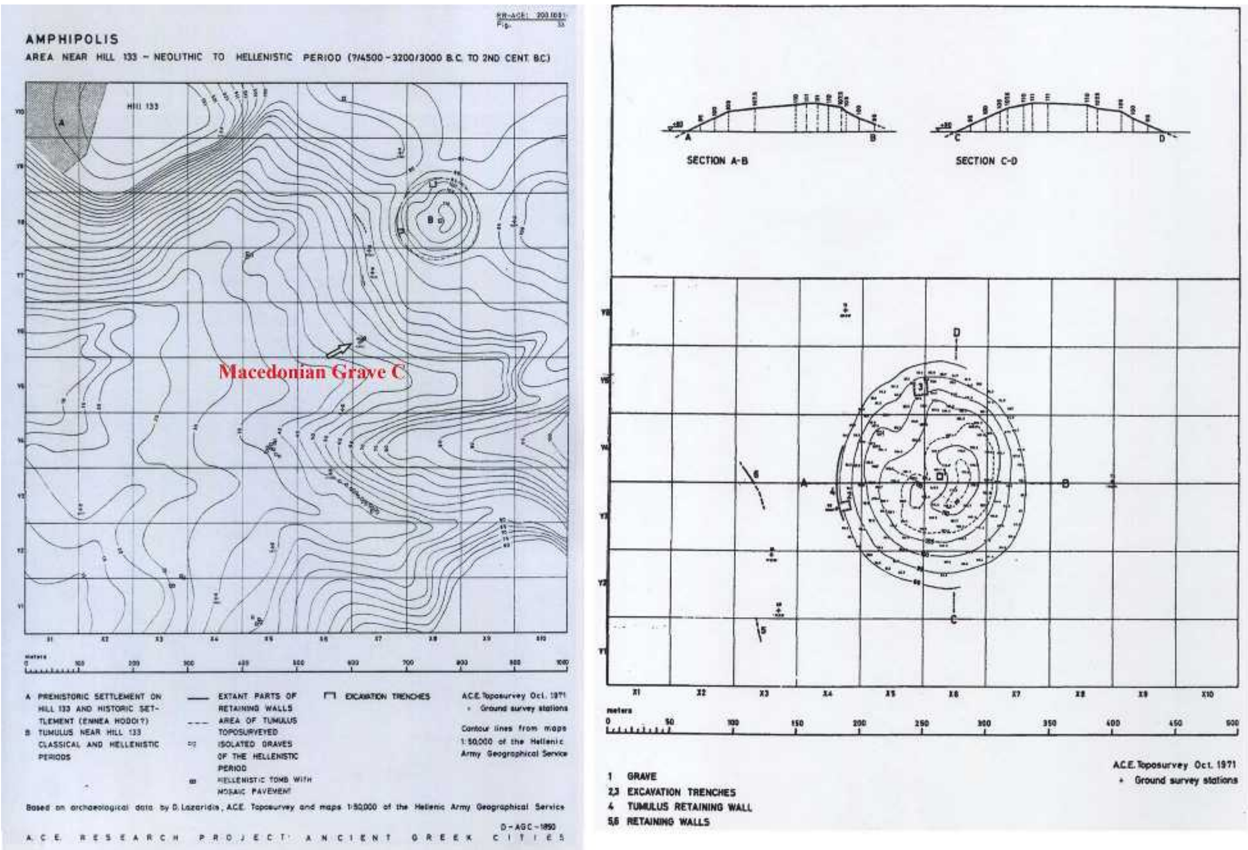

Figure 11. Topographic plan of Kastas Hill (Lazaridis D. archive, 1971).

The sediments and the gradual coverage of the soil around the tomb

The removal of accumulated soil that took place in 2015 around the burial monument for flood protection, the natural stratigraphy of the hill, west, north and east, was revealed above the burial chamber (Figure 12).

These are alternating quartz sands with clays in a layered arrangement and contain fossils mainly from Ostrea sp., Pecten etc. The same figure displays sand with fossils underlying on a horizontal layer of clay. These are lacustrine, mainly brackish deposits of Neogene. The same sediments were traced on the vertical sidewalls of the 3 m depth trench, which was opened on the floor of the burial chamber and hosts the box-shaped tomb. The stratigraphy continues in the trench, 2 m below the floor of the box-shaped grave with the same sediments that emerged from the elements of the drillings (Kabouroglou and Mitsis 2019).

From the elements of our research we designed the cross section along the main axis of the burial monument (Figure 13). On the north of the burial monument (left side of the cross section), the natural stratigraphy of the hill is displayed.

In 2014 the embankments at the northern end of the burial chamber reached a height of 1.65 m, while at the southern end of 3.15 m above the floor before it was unloaded. This was tilted to the north as in the section between the Sphinx and the Cariatides. In the embankments were found mixed: two broken marble door leaves as well as the bones of at least five human skeletons, the femoral bone of an equid (press release of the Ministry of Culture on 19/01/2015), in addition the head of one Sphinx, parts of the marble wings of the Sphinxes, part of the mosaic with Persephone, and fossils identical to those of the sediments of the hill. All the findings were outside the plundered box-shaped tomb at various heights and at least 1 m higher than it.

From the mineral diagnostic and sedimentary analysis it emerged that the deposits exhibit an identical structure with the supernated sediments of the hill (Kabouroglou and Mitsis 2020). Consequently, the monument was covered by the supernated sediments of the hill and not by flood deposits of the Strymon River. After all, the existence of the two sealing walls (in front of the Sphinxes and in front of the Cariatides), exclude the case of natural causes.

On the northwest end of the burial chamber there is a 70 x 68 cm recess that was partially filled by quartz

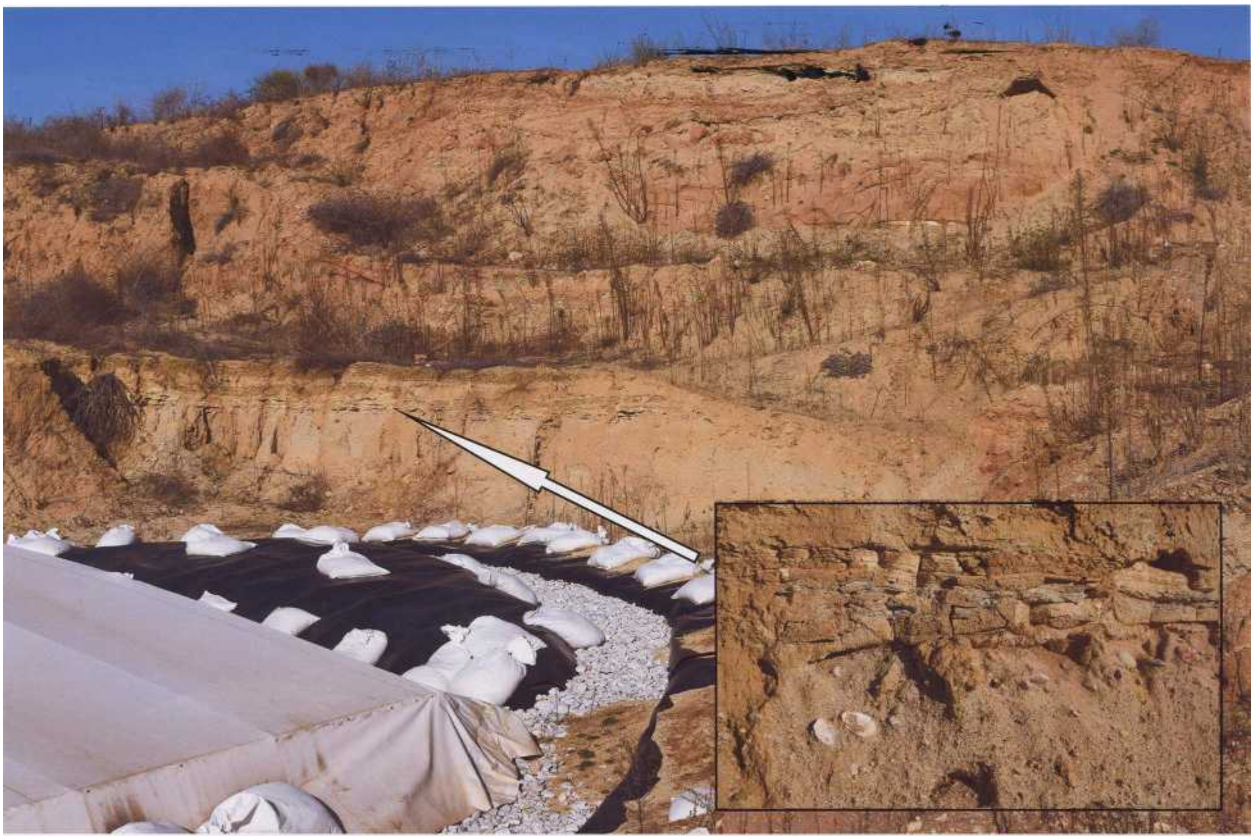

Figure 12. Physical stratigraphy N and NE of the burial monument (2016).

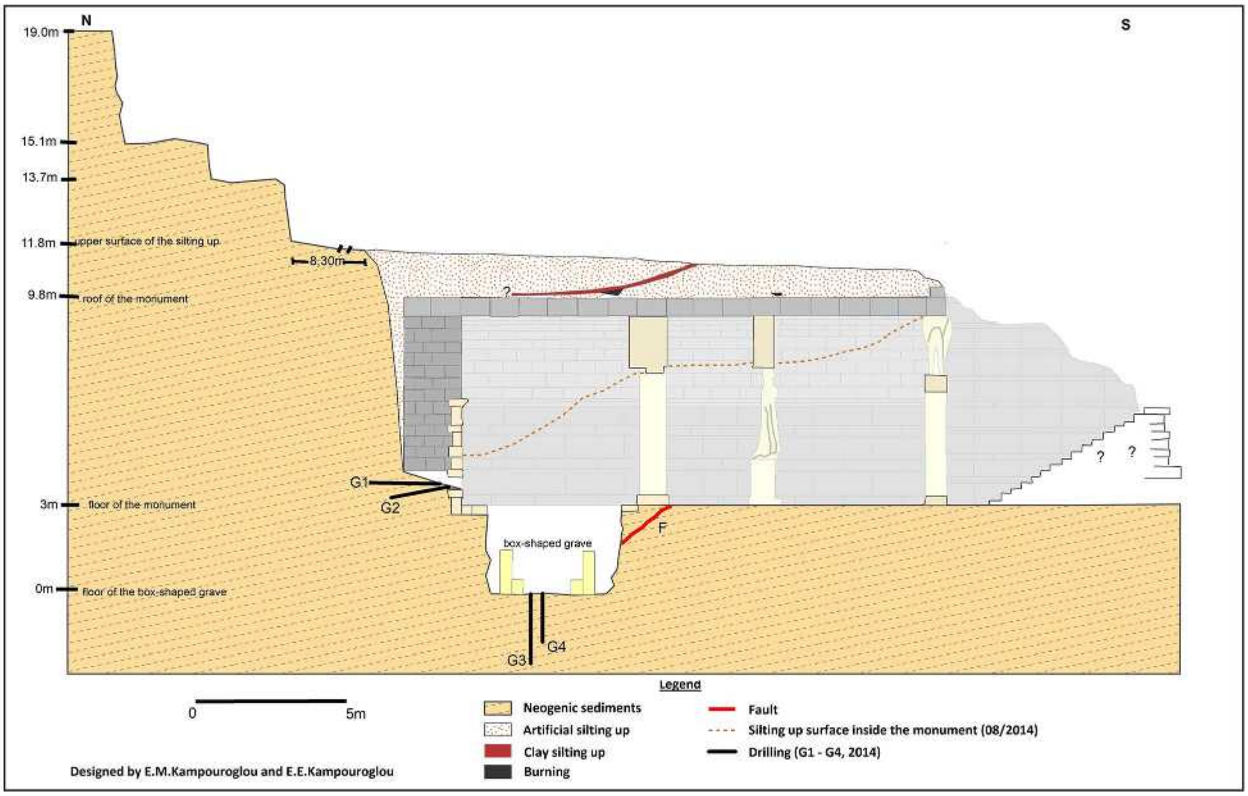

Figure 13. Cross section at length of main axis of the burial monument.

Table 1. Results of the radiocarbon age determination. The samples GX – 124192 – AMS and GX – 33835 – AMS were measured in the Krueger Enterprises Inc. laboratories in Massachusetts, U.S.A., whereas the samples DEM – 3069 (MAMS-31120) and DEM – 3069 (MAMS-31120) with a second MAMS code accelerator (AMS) at the Curt-Engelhorn-Zentrum Archaeometrie gGmbH, Mannheim, Germany.

laboratory code	**sample code**	**type of dated material**	**conventional radiocarbon age ± standard deviation (BP)**	**$\delta^{13}C$ (‰)**	**calendar age within 1 and 2 standard deviation together with their probability distribution**
GX – 124192 – AMS	Kastas 4	charcoal	2570 ± 20	-26.5	620 ± 20 BC
GX – 33835 – AMS	Kastas 1	charcoal	2020 ± 30	-25.1	70 ± 30 BC
DEM – 2565	Kastas 3 (Total mass)	Charred wood	2311 ± 30	-24.83	411 – 357 BC (86,3%) 286 – 235 BC (9,1%)
DEM – 3069 (MAMS-31120)	Kastas 3 (1) (branch, rings: 1-3)	Charred branch	2246 ± 19	-24,50	388 – 350 BC (29,8%) 304 – 209 BC (65,6%)
DEM – 3069 (MAMS-31120)	Kastas 3 (2) (branch, rings: 14-17)	Charred branch	2242 ± 20	-32.70	385 – 350 BC (26,3%) 311 – 209 BC (70,1%)

sand containing ostrea fossils and small fragments of charcoal. The recess was created from the detachment of the structural material towards the interior of the monument due to geostatic thrusts which resulted from an earthquake (Kabouroglou and Mitsis 2020). Our initial view about this particular sand of charcoal was that it had penetrated the interior of the monument from the supernated area of the hill.

These coals were dated by AMS radiocarbon dating in the Krueger Enterprises Inc. laboratories in Massachusetts, U.S.A. (sample No GX – 124192 – AMS). The date is based upon the Libby halflife (5570 years) for ^{14}C. The error is +/-1 s as judged by the analytical data alone. Their modern standard is 95% of the activity of N.B.S. Oxalic Acid. The age is referenced to the year AD 1950. The sample No GX – 124192 – AMS is dated in 2570 ± 20 BP or BC 620 ± 20 (Table 1) during the Archaic period. We know that a necropolis with 98 tombs at various altitudes higher than 10 m from the burial monument dating from the Iron Age, the late Archaic, and the Early Classical period was revealed in the upper part of the hill by D. Lazaridis and C. Peristeri. The result of this dating verifies our initial assessment and agrees with the data of the excavations that this is a hill rather than a tomb.

The sediments that penetrated from the destructive opening created a surface of discontinuity between them and the soil coverage of the burial chamber in the region. (Kabouroglou and Mitsis 2019). On the upper part of the coverage there was a combustion. The combustion material was dated in the same laboratories (sample no GX – 33835 – AMS) in 2020 ± 30 BP or BC 70 ± 30 (Table 1). This dating coincides with the period of the Mithridatic wars.

In August 2014, during the removal of the soil coverage with an excavator above the monument and on the west side (Figure 14), an oblong coating of clay (about 12 – 15 cm thick and 7.5 m in length) and its continuation towards the entrance of the monument covering it, was revealed. Unfortunately, it was destroyed by the excavator, and this resulted in losing important information. We can speculate that the placement of the layer of clay above the arch of the monument, was done so as to protect its roof from the rainwater because of clay's insulating properties.

At the height of the burial chamber and under the layer of the specific clay backfilling, we found part of a combustion point (Figure 15). On the north section and on the west side of the monument, the position of the combustion is located near the dividing surface of the trench that was opened for its construction. In the picture (Figure 15) behind the burial monument, on its north side, Neogene sediments appear. On the combustion point under the clay backfill, the contact of the natural rock of the trench and the backfilling is clear. We designed the transverse geological intersection of the burial chamber with the position of the combustion point (Figure 16). Because the combustion under the clay layer is either later or isochronous to the monument, it gives us a terminus for its construction. For the accuracy of the result, three absolute datings were realized: the first at Democritus and the next two atthe Curt–Engelhorn–Zentrum Archaeometrie gGmbH laboratory of Germany, which has an accelerator.

The samples received the Codes DEM – 2565, DEM – 3069 (MAMS – 31120) and DEM – 3069 (MAMS – 31120). OxCal v.4.2.3 (Bronk-Ramsey 2013) was used for the age calibration with the latest set 2013 data (Reimer *et al.*

Figure 14. Clay silting up overlying the burial monument in a) 2014; b) 2016.

Figure 15. Section in N and W part of the burial monument.

Radiocarbon 55 (4): 1869–1887, 2013). The final results of these three absolute datings gave two ages because of the double fluctuation of the ages in the calibration curve sent to us by Dr G. Maniatis from Democritus: BC 362 – 352 with a probability of 22.4% which refers to the first half of the 4th century BC, the time of Philip II, and BC 271 – 231 with a probability of 73% i.e. between the second and the third quarter of the 3rd century BC. It is obvious that only one of them is valid, and taking into account the geological and other data we can exclude one of the two.

A sample from the same combustion was dated in the Beta Analytic Laboratories (U.S.A.) by Syrides, Pavlides, and Chatzipetros, This gave two ages. The first is BC 300 ± 30 and the second, after further calibration, is BC 360. The researchers do not mention the possibilities for each age (Syrides *et al.* 2017).

In the narrow and broader area of Kastas, Macedonian tombs A, B, and C were revealed. They date back to the 3rd century BC (Lazaridis 1960). Macedonian tomb C is located in Kastas, around 120 m south of the burial

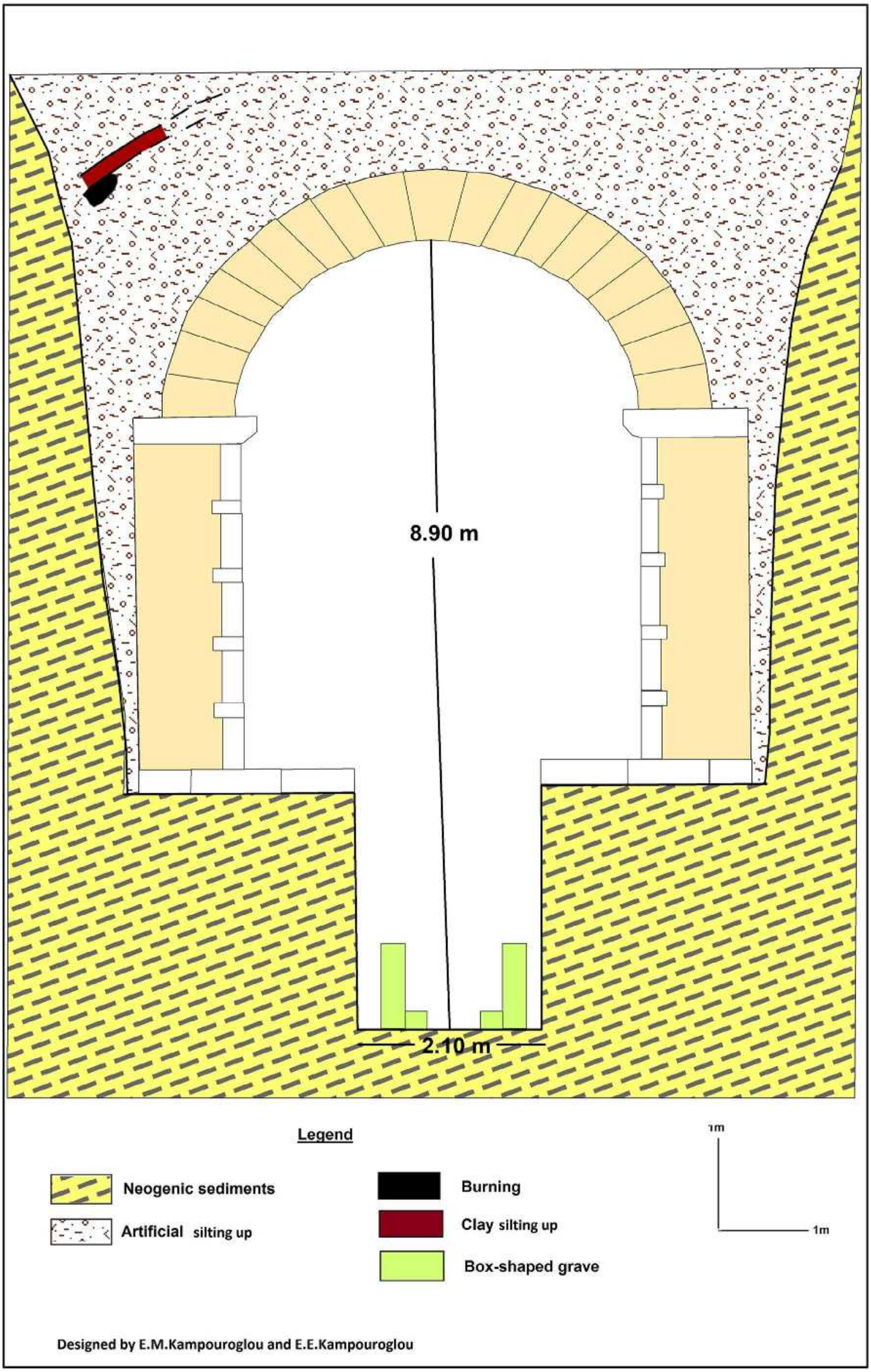

Figure 16. Cross section of the burial chamber.

monument and has common elements with it, namely a trench in the Neogenic sediment and walls covered by porous limestone rock. Its inner sides have mortars that mimic orthomarmarosis, and the floor has a mosaic with the same diamond-shaped multi-coloured decorations as the entrance of the burial monument. The northern part of the floor of the burial chamber, of tomb C was destroyed and another tomb was later constructed in the trench that was createdas in the burial monument. Its axis has the same direction as the axis of the burial monument (parallel axis).

Conclusions

- Based on our research from 2013 to 2017 we are absolutely certain that Kastas is a natural hill with many of diachronic, intense interventions (removal and coverage of soil layers) using excavation machinery. It consists of two sedimentary sequences representing two different dispositive environments. The extensive earthing of 2014 and 2015 created a very large environmental alteration of the natural structure of the hill, and this resulted in the possible deception of its subsequent researchers.
- All interventions on the hill during antiquity—the burial monument, the possible signal on the top, as well as the tombs—were made with a trench on the natural soil.
- The only part of the hill that is a tomb, is bounded by the slopes of the trench that was opened for the construction of the burial monument, whose area occupies about 180 m^2.
- The internal coverage of the soil layers of the burial monument was made with sediments derived from the direct supernatant and surrounding area of Kastas hill. This was carried out during the Roman period, around 70 BC, after all the valuables and artifacts had been removed, obviously not for the protection of the monument, because in its deposits there were only mixed building materials with skeletal remains and scattered architectural members derived from destructive energies.
- The internal coverage of the soil layers of the monument according to the stratification indicates that it was not disturbed by subsequent interventions of tumblers.
- Particularly problematic is the view that the lion of Amphipolis was erected in the place of the possible burial mark of the hill.
- The box-shaped tomb and the burial monument belong to different phases that are very difficult to be dated given their damage and desecration.
- From the horizontal drillings on the northern wall of the monument and the vertical drillings on the floor of the box-shaped tomb, it was discovered that the natural background of the hill was preserved. This means that the monument does not continue further north or in deeper layers.
- From the devastating seismic opening on the northwest end of the burial chamber, the fragments of charcoal along with sand that penetrated inside, are older than the burial monument, and are dated on the first quarter of the 7th BC, that is, in the Archaic period, *c.*620 BC.
- From the temporal removal of accumulated soil, the largest part of the geological background was revealed. This means that no other antiquities of corresponding dimensions with the burial monument are expected.
- The total dimensions of the trench that hosts the burial monument (length 25.30 m, width 7 m and final depth of 12 and more m), as well as the position and dimensions of the box shaped tomb on the north and deepest end of the trench, leads to the conclusion that the box shaped tomb is subsequent to the burial monument.
- The absolute dating of the combustion detected above the arch of the monument and which is contemporary or subsequent to its construction, is more likely to be dated in BC 271 – 231, between the second and the third quarter of the 3rd century BC.
- The burial monument is associated with the Macedonian tomb C of the 3rd century BC, which is located on the southern outskirts of Kastas because of their common elements.

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Progressive Sea Transgression during the Late Holocene in Vatika Bay (Laconia, Peloponnese, Greece): Just When Was the Prehistoric Town of Pavlopetri Drowned by the Sea?

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Abstract: Geomorphological and archaeological sea level indicators, historical evidence and comparison with past sea levels identified along the eastern coast of the Peloponnese enabled us to track the relative sea level changes in Vatika Bay, the consequent sea transgression, and its impact on the coastal landscape during the last 5500 years. Five distinct beachrock generations stretching for 4 km all along the coast of Vatika Bay and now submerged between 5.10 m and 0.80 m below mean sea level (bmsl), a tidal notch, and several marine terraces submerged up to 4.60 m bmsl, formed around the submerged rocky ridge that bounds on the east the prehistoric town of Pavlopetri on the Pounta coast, allowed us to determine five former sea levels. When the sea level was at 5.00 ± 0.25 m bmsl, Elafonisos Island was joined to the Laconic coast by an isthmus. A rocky ridge offered a protected location for the first inhabitants of the Early Bronze Age. The relative sea level rise to 4.50 ± 0.25 m during the Late Bronze Age did not affect the town: only the coastal part of the cemetery and parts of the isthmus were flooded. At this sea level, a tidal notch, today submerged at 4.60 m bmsl, formed along the ridge.

The subsequent sea transgression that occurred between 1190 BC and 700 BC caused further flooding of the isthmus, although Elafonisos was still connected to the mainland, and shifted the sea level to 3.60 ± 0.10 m bmsl. It remained relatively stable until Late Roman times (AD 4th or probably 6th century). At this sea level, the prehistoric town was still protected by the now-lowered ridge. Elafonisos was detached from the Peloponnese by the end of AD 14th century, when the sea level rose to 1.50 ± 0.15 m bmsl, inundating the isthmus, the town, and most of the ridge, by now a reef, with only its higher elevated part now constituting Pavlopetri Island. The sea level remained at this height from 1389 until at least 1840. Over the following 160 years, the sea transgression that gradually shifted the sea level to 0.75 ± 0.05 m bmsl and then to its present stand further inundated the coastal landscape.

KEYWORDS: VATIKA BAY; ELAFONISOS ISLAND; ELAFONISOS STRAIT; POUNTA COAST; PAVLOPETRI; ANCIENT TOWN; EARLY BRONZE AGE; LATE BRONZE AGE; LATE ROMAN TIMES; BEACHROCK; RELATIVE SEA LEVEL CHANGE; SEA TRANSGRESSION; GEOMORPHOLOGICAL INDICATORS; ARCHAEOLOGICAL MARKERS; PALAEOGEOGRAPHIC RECONSTRUCTION; COASTAL LANDSCAPE

Introduction

The Bay of Vatika or Voion is located at the SW edge of the Elos (previously Laconic) Peninsula, NW of Cape Maleas, and belongs to the wider Laconic Gulf (Figures 1A, B). It opens toward the SSW onto the Aegean Sea. In the shape of an inverted 'U', it is approximately 8 km long N-S and 5 km wide E-W in its northernmost narrowest part. The entrance of the bay, approx. 8 km wide, is bounded on the east by Tsoumala Peninsula and on the west by Fragos Peninsula, at the southernmost tip of Elafonisos Island. The main port of the bay is Neapolis, where the ruins of the ancient Laconic polis of *Boeae* are located (Figure 1C).

The northern shore of the bay, at its apex, is fed by the Agioi Apostoloi and Agios Georgios streams. The sandy barrier of coastal dunes that develops all along the northern beach of the bay prevents surface runoff from flowing into the sea and entraps rainwater upstream, thus forming swampy areas parallel to the shoreline. The largest of these is Lake Strongyli, which during high-water periods occupies an area of maximum length and breadth 1200 m and 250 m, respectively (Figure 1C).

A channel, ranging from around 600 m in length in its narrowest part to as much as 1000 m in its widest part, and with a depth of up to 3.50 m, separates Pounta on the Peloponnesian coast from the opposite coast of Elafonisos (Figure 1C). Within Vatika Bay, some 300 m ESE off the Pounta shore and 800 m NE of Elafonisos, the island of Pavlopetri is situated, covering an area of approximately 2500 m^2. At a distance of 380 m NE

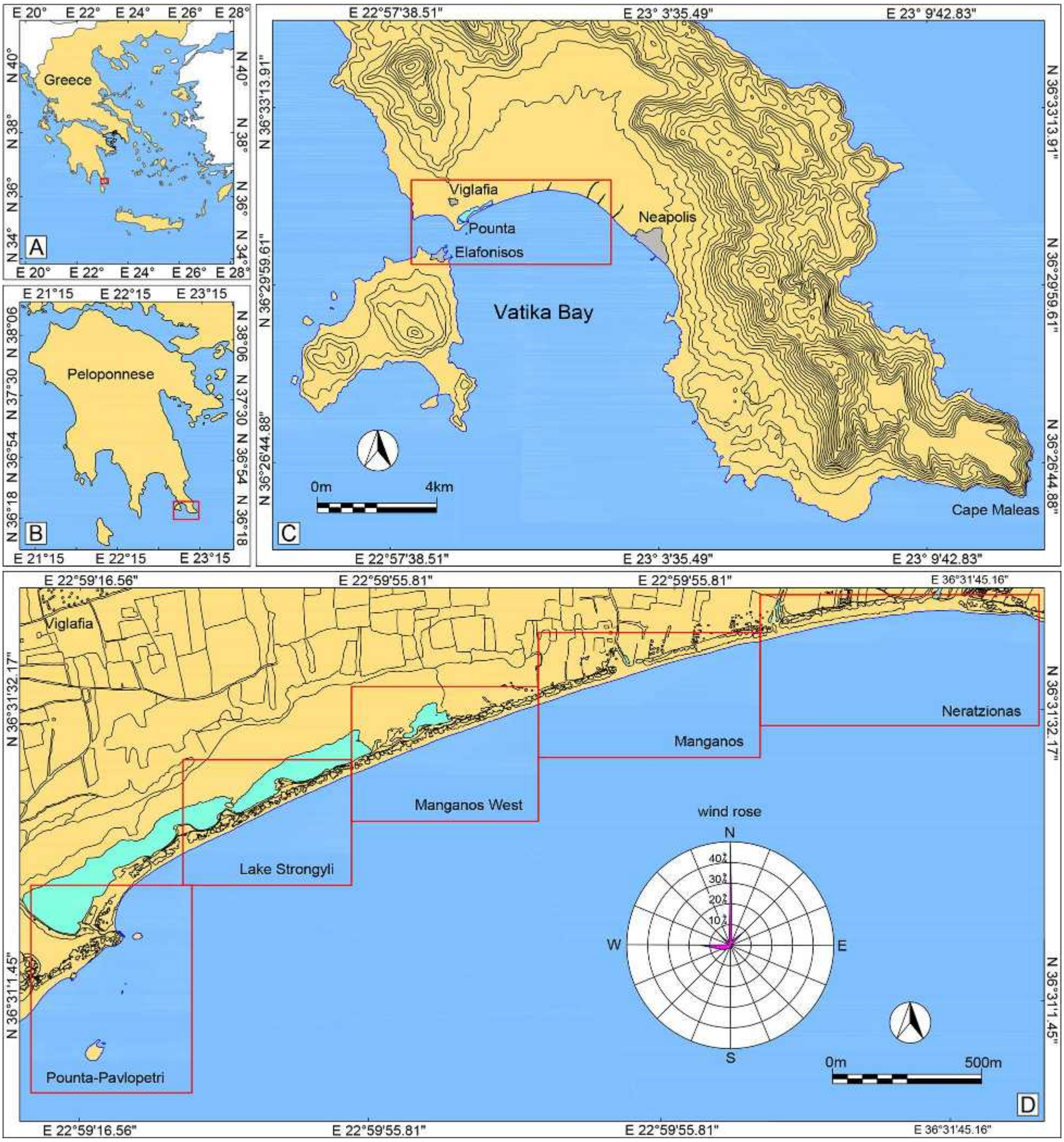

Figure 1. Location maps of: Cape Maleas in the Peloponnese, S Greece **(A)**, Vatika Bay in S Peloponnese **(B)**, the north coast of Vatika Bay and the Elafonisos Strait. **(C)** and the five sections of the north coast of Vatika Bay **(D)** as described in the text. A wind rose diagram showing the average daily wind speed and direction frequencies is presented.

of Pavlopetri Island, and just 30 m off the easternmost tip of Pounta, a second smaller islet (called Chamokelo by the locals) is situated, approximately 500 m^2, henceforth referred to as the 'NE Islet'. Between the two islets, which constitute the NE and SW edges of a submerged sandstone ridge that bounds the submerged prehistoric town of Pavlopetri on the east, two more tiny islets emerge above sea level.

The rocky ridge that apparently protected the prehistoric town, the basin where the town was located, and part of the coastal zone, consists of Upper Pliocene-Pleistocene marine and lacustrine clastic and biogenic sediments, mainly sandstones and calcarenites. These overlay the Jurassic limestone and dolomitic limestone of the Tripolis zone that structure the wider elevated area of Viglafia and the major part of Elafonisos Island.

The extended low area consists of unconsolidated alluvial deposits, eluvial mantle materials, and clastic river and torrent deposits, ending in the coastal zone where coastal dunes and sandy beach deposits also accumulate.

Three active fault zones, the Kountourianika-Viglafia fault zone in the east, the Neapolis-Palaikastro fault zone in the west (both in a N-S direction and dipping to the east and west, respectively), and the Kontrafourianika-Adiakopos fault zone in the north, running NW-SE to WNW-ESE, bound the Neogene basin of Neapolis Voion. The staircase morphology shaped by the successive marine terraces of Viglafia and Elafonisos reflects the long-term uplift of South Laconia during the Late Quaternary (Karymbalis *et al.* 2022).

The first occupation of the site goes back to the Late Neolithic (3500 BC) and continues throughout the Bronze Age until the end of the Mycenaean period and the fall of the Myceanean Palaces (1100 BC), when it was abandoned (Harding *et al.* 1969). Extensive evidence of pottery from the Early to the Late Helladic period with a noticeable Late Minoan IB influence clearly indicates that Pavlopetri had established links with the Cyclades, Crete and mainland Greece since the Early Bronze Age (Henderson *et al.* 2011; Gallou and Henderson 2012). However, its geographical position, in a sheltered bay with sandy beaches east and west of the settlement, favoured the approach of light boats that had already sailed the dangerous Cape Maleas, thus rendering Pavlopetri an important harbour town (Gallou and Henderson 2012). The site was repopulated to a lesser extent, probably during the Geometric and certainly in the Classical and Hellenistic periods (4th-3rd century BC). The Roman and Byzantine pottery at the site is associated with a later, limited occupation of the area mainly related to purple dye production and trading of local stone and iron ore from the nearby haematite mines of Agios Elissaios at the foot of Mount Voion (Henderson *et al.* 2011; Gallou and Henderson 2012).

The submerged remains of the prehistoric town were first reported by Negris (1904), who provided some measurements of depths of the ancient remains, which in his view constituted a town built on the isthmus that connected Elafonisos with the Peloponnese with only two islets protruding from the sea. Over half a century later, in 1967, N.C. Flemming from the National Institute of Oceanography (UK) visited the site in the context of a pioneering geoarchaeological survey in the South Aegean aimed at determining the eustatic and tectonic components of the relative sea level (henceforth 'rsl') change based on archaeological evidence (Flemming 1968; Flemming *et al.* 1973). It was then that the archaeological survey in Pounta-Pavlopetri was begun by the Ephorate of Antiquities of the Peloponnese and the British Archaeological School at Athens (Ministry of Culture – www.culture.gov.gr). In 1968, the "Cambridge Underwater Exploration Group" from the University of Cambridge conducted a more systematic underwater survey and recorded in a first drawing the sunken ruins of the ancient town (Harding *et al.* 1969).

Forty-one years later, in 2009, interest in Pavlopetri resumed and the five-year program "The Pavlopetri Underwater Archaeology Project" was instigated by the University of Nottingham in collaboration with the Ephorate of Underwater Antiquities of the Greek Ministry of Culture. The aim was to conduct digital underwater recording of the site and funerary remains, the architectural remains of both the building complexes originally surveyed in 1968 (Harding *et al.* 1969) over an area of 30,000 m^2, and the new building and rock-cut tombs to the north of the settlement and at the eastern side of the ridge, over an area of more than 9000 m^2 (Mahon *et al.* 2011; Henderson *et al.* 2011).

Flemming (1968) suggested a rsl change of 3 m for Elafonisos during the last 3.5 millenia (with a rate of 0.9 mm/yr). Of this, 0.50 m was attributed to net eustatic change during the last 2000 years, the rest representing a general depression across the margins of the Peloponnese with areas of faulting in the Mani Peninsula. Harding *et al.* (1969, 140), taking into account that the maximum observed depth (3 m) of the ancient remains in the basin was the minimum rsl change, suggested that a "realistic" change was 4 m to 5 m, based on the reasoning that "the buildings are not likely to have stood actually at sea level". They further suggested that the life of the prehistoric town ended in the Late Helladic IIIB period, when it was either destroyed or abandoned, and assumed that Elafonisos was disconnected from the Peloponnese by a local tectonic event in the AD 2nd century. Thereafter, small-scale tectonic events caused the gradual subsidence of the site, as the Elafonisos Strait was fordable until at least AD 1677. They also mentioned the lack of a prehistoric harbour there, while the harbour shown in their plan (Harding *et al.* 1969, *Fig. 11*) on the north side of Pavlopetri Island is actually a quarryscape. In a subsequent study, Flemming *et al.* (1973) argued that the foundations of the Helladic buildings do not exceed the depth of 3 m, thus suggesting a rsl change of 3-3.50 m, with Elafonisos Island having been connected to the Peloponnese until the AD 2nd century and the Elafonisos Strait fordable until the AD 17th century. After his involvement in the 2009 Pavlopetri Project, Flemming reconsidered the theory of the existence of a fordable isthmus in 1677—a theory formulated by the misreading of the diaries of John Covel (1670-1679), first by Bent in 1893, and by subsequent authors. This was briefly presented in a later co-authored publication (Henderson *et al.* 2011, 217 and references therein), but was also explained in detail in a personal communication that we had with him. Henderson *et al.* (2011) suggest a rsl change of 4-5 m during the last 5000 years, and of this attribute 0.50-1 m to eustatic rise and the rest (3-4.50 m) to gradual co-seismic subsidence with a rate of 0.80-1 mm/yr. They do not, however, determine the causative faults or paroxysmal events that caused it. Moreover, they assume a 2-3 m subsidence "by *c.*2000 cal BP" (Henderson *et al.* 2011, 216) and suggest—in the absence of concrete evidence—that the prehistoric town was most likely inundated "by the time of the Roman Empire" (Henderson *et al.* 2011, 217).

The systematic recording of various geomorphological sea level indicators and their dating using archaeological markers, all of which were identified in Vatika Bay, along with their correlation with the past sea levels identified throughout the eastern coast of the Peloponnese, enabled us to track the rsl changes in Vatika Bay, the consequential sea transgression, and its impact on the coastal landscape during the last 5500 years. As a consequence, this study aims to decode the past sea levels in Vatika Bay based on both the analysis of the observed rsl change indicators and their synthesis to reconstruct the palaeogeography of the coast from the Early Bronze Age to the present. The ultimate goal is to answer the question of precisely when the prehistoric town of Pavlopetri was drowned by the sea and whether the sea transgression was the causative factor in its demise.

Methods

The determination of the several sea level stands was based on geomorphological indicators, i.e. marine tidal notches, marine terraces, and various beachrock generations (e.g. Kolaiti and Mourtzas 2023). An underwater geological snorkel survey in Vatika Bay revealed many geomorphological indicators of past sea levels, which were mapped using satellite images (Google Earth Pro, v. 7.3.2) and high-resolution orthophotos at a scale of 1:500 (Ktimatologio SA). During the survey, their features were recorded and depths at selected points were measured. In particular, the morphometric features (opening, inward depth, base width) and elevation of the base of the tidal notch, which represents or is slightly below the mean sea level (e.g. Kelletat 1997, 2005; Antonioli *et al.* 2015; Kolaiti 2019 and references therein), were measured. The length, gradient, and elevations of the inner shoreline angle (landward end) and outer edge (seaward end) of each marine terrace were also measured (e.g. Kolaiti 2019). During snorkel surveys, the length, width and thickness, as well as the depth of the seaward and landward end of the top and base of each beachrock generation, were measured according to the methodology initially suggested by Kolaiti (2019). Correspondingly, the seaward base of a beachrock slab in well-preserved parts that have not undergone erosion or fragmentation, represents the mean low tide of a former sea level. Different sea level stands form distinct beachrock slabs at various elevations that correspond to different generations of a fossilized palaeoshoreline (e.g. Vousdoukas *et al.* 2007; Desruelles *et al.* 2009; Mauz *et al.* 2015 and references therein; Mourtzas and Kolaiti 2023). The loose, unconsolidated, sandy/sandy-gravel sediments on the sea bottom between two different beachrock generations represent a period of rsl change (e.g. Desruelles *et al.* 2009). To determine the former sea level stands, the depth of the seaward base of each beachrock generation representing the low tide of a former sea level is used. Fossils, organic material, or archaeological remains embedded in a beachrock offer a *terminus post quem* for the beachrock formation, which postdates the embedded material (Kolaiti 2019; Kolaiti and Mourtzas 2023).

Various ancient coastal constructions now submerged were related to the sea level at the time they were in use and can therefore be used as precise archaeological indicators for the determination and dating of the former sea level stands inferred along the coast of Vatika Bay. The measurement of the elevations/depths of particular functional features of the ancient structures can lead us to the determination of their functional elevation with sufficient accuracy. The archaeological interpretation and age of ancient structures enable us either to define the time period when the change in sea level occurred or to determine at least a maximum dating limit (*terminus post quem*) after which the structures could not have been in use according to their initial design, or a minimum dating limit (*terminus ante quem*) prior to which the sea level could not have changed since the structures were in use (e.g. Kolaiti and Mourtzas 2023).

All measurements of depths were collected during calm sea conditions using mechanical methods (namely, a tape measure equipped with a stabilizer system on the measurement surface and a circular metallic ranging rod with conical shoe fitted at bottom and fully painted with 10 cm long colour bands in red and white), and repeated during three different survey periods (June 2015, May 2016, October 2017). An accuracy of ±1 cm along the vertical is routinely estimated (e.g. Antonioli *et al.* 2007). To account for tides, observational data were reduced for tide values at the time of the surveys with respect to mean sea level, using tidal data from the Hellenic Navy Hydrographic Service (HNHS) for the closest tide-gauge station, i.e. that at Piraeus. The effect of atmospheric pressure on the sea level was corrected using the meteorological data for the site at the time of the surveys that were retrieved from the web site meteo.gr managed by the National Observatory of

Athens (NOA) or from a portable station measuring the atmospheric pressure in the field. Therefore, all depths reported herein correspond to depths below mean sea level (bmsl).

Wind data were acquired by the website meteo.gr (NOA), for the closest weather station to the study area, at Cape Maleas (LGB5) (Lat: 37°36'00"N Long: 22°06'00'' E, location: Agios Nikolaos Voion, elevation: 161 m). Wind data cover the period from August 2008 to May 2020 sequentially, with only brief interruptions of usually no more than three days, the longest lasting 14 days. Statistical analyses of raw data and the wind rose diagram of average daily wind speed and direction frequencies (Figure 1D, inset) were performed by the authors. The wave parameters were calculated to close approximate by the Sverdrup-Munk-Bretschneider (SMB) empirical model as described in the Shore Protection Manual (CERC, 1977).

Results

Geomorphological indicators of the rsl change in Vatika Bay

The northern shore of Vatika Bay, stretching WSW-ENE for about 4 km from Pounta to Neratzionas, comprises plenty of geomorphological sea level indicators, i.e. five distinct beachrock generations, one tidal notch, and several marine terraces now lying below water, as well as a beachrock formation that is now cementing on the contemporary coastline. By way of illustration, the shore was divided into five sections, namely from E to W (Figure 1D): Neratzionas (length: 940 m), Manganos (length: 720 m), Manganos West (length: 775 m), Lake Strongyli (length: 950 m) and Pounta-Pavlopetri (length: about 600 m). The plan of each section is given in Figure 2, except for Pounta-Pavlopetri, which is given in Figures 3 and 4. The measured depths and the average values are summarized in Table 1. It should be mentioned that for a better understanding of the sequence between sea level stands and geomorphological indicators, the labelling of the beachrock generations, tidal notch, and marine terraces corresponds to that of the sea level stands observed for the eastern Peloponnese (as presented below in the 'Interpretation and Discussion' section).

Neratzionas (Figures 1D and 2A)

On the eastern side of Vatika Bay along the Neratzionas coast, four out of five beachrock generations were recorded. The deepest generation (I), running parallel to and along almost the entire length of the shoreline, has an average width of 15 m (range: 10-38 m). It appears moderately-to-very fragmented, without the blocks having moved from their original position. The seaward top is at 4.30-4.45 m bmsl, its seaward base at 4.90-5.25 m bmsl.

The next beachrock generation (II) develops parallel to (I), at an average distance of 5 m towards the shore, separated from it by a sandy strip. It also appears moderately-to-very fragmented, but with its blocks in the original position. Its breadth varies between 11 m and 33 m, the seaward top is at 3.95-4.10 m bmsl, and its seaward base at 4.60-4.75 m bmsl.

In the central part of the Neratzionas section, after 120 m of sandy bottom from beachrock (II) towards the shore, and 10-15 m offshore, lies the beachrock generation (V). It extends parallel to the shoreline for a length of about 145 m and a total width of 30 m. It is solid to slightly fragmented, with its seaward top and base at 1-1.35 m bmsl and 1.25-1.55 m bmsl, respectively.

Between beachrock (V) and the beach, 5 m offshore, the youngest beachrock generation (VI) runs parallel to the shoreline for 550 m. It is solid, 3-5 m wide and its seaward top is at 0.30-0.45 m and seaward base at 0.85-0.90 m.

Manganos (Figures 1D and 2B)

Along the Manganos coast, the two deepest of five beachrock generations are developing extensively, and only two limited occurrences of beachrock generation (V) were observed at the easternmost side of this section with the seaward top and base at 1.15 m and 1.50 m, respectively. The deepest beachrock generation (I) starts 220 m offshore and runs parallel to it for about 700 m, with an average width of 25 m (range: 12-30 m). It appears moderately-to-very fragmented, without the blocks having moved from their original position. The seaward top is at 3.90-4.30 m bmsl and its seaward base at 4.80-5 m bmsl.

The next beachrock generation (II) develops parallel to (I), at a varying distance of 2-10 m offshore, separated from it by a sandy strip. It also appears moderately-to-very fragmented, but with its blocks in the original position. Its breadth varies between 12 m and 30 m, the seaward top is at 3.95-4.10 m bmsl and its seaward base at 4.80-4.75 m bmsl.

Manganos West (Figures 1D and 2C)

In the central part of the Vatika coast, just after the previous section ends, two out of five beachrock generations are developing westward as far as the area of Lake Strongyli, with the contemporary one now cementing on the beach. The deepest beachrock generation (I) starts 230 m offshore and runs parallel to the shore for about 750 m, with an average width of

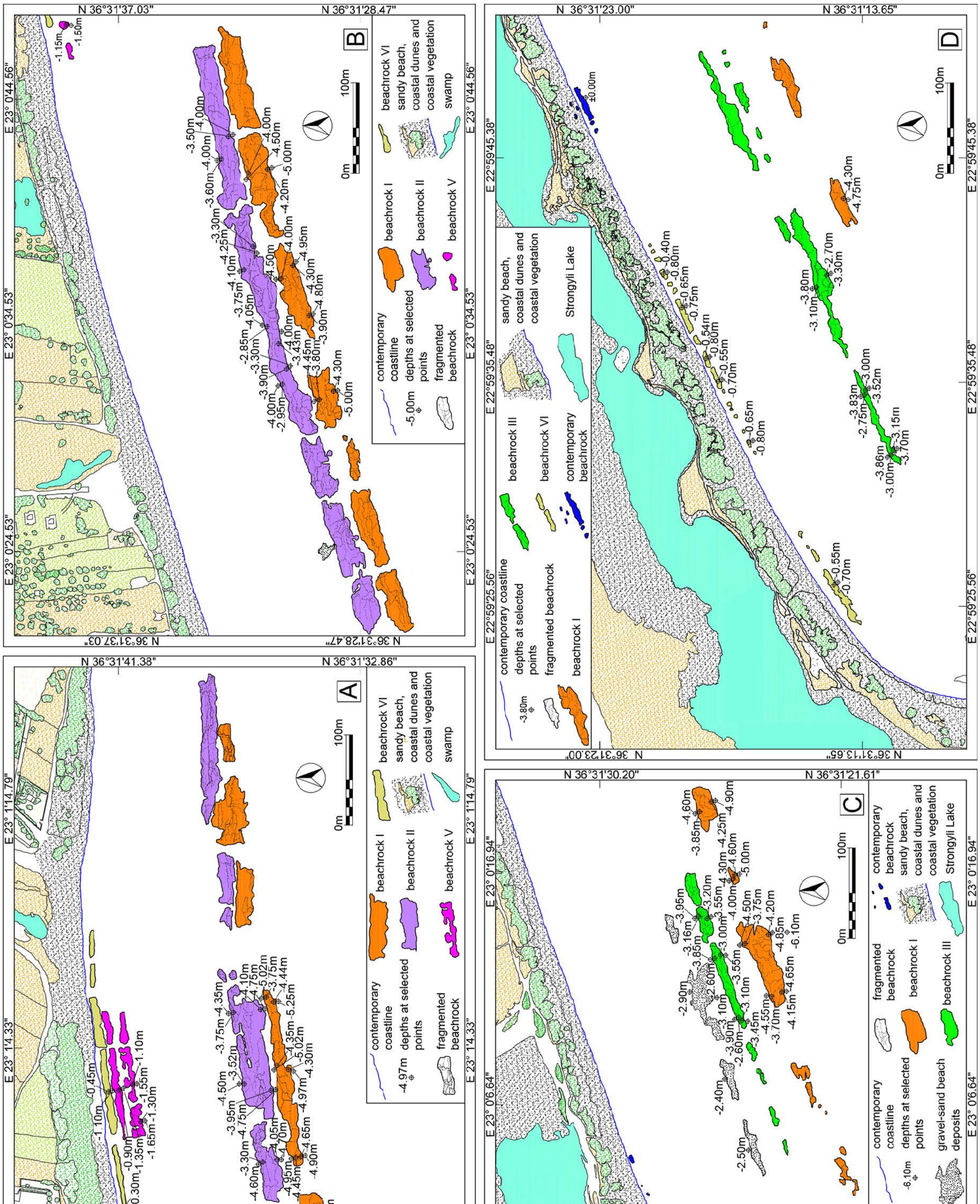

Figure 2. Schematic plans of the various beachrock generations recorded on the coast of Vatika Bay. **(A)** Neratzionas section. **(B)** Manganos section. **(C)** Manganos West section. **(D)** Lake Strongyli section.

Table 1 Depths of the various beachrock generations recorded and measured in Vatika Bay. The locations are shown in Figures 1D, 2 and 3. The depths were measured at the top and base of the seaward end of each beachrock generation (see 'Methods'). All measurements have been corrected for tide and pressure at the time and date of survey and correspond to depths below mean sea level (bmsl) or elevation above mean sea level. In the last row, the average depth of multiple measurements and the depth uncertainty are provided.

Location	depth (m) bmsl										elevation (m)
	beachrock (I)		beachrock (II)		beachrock (III)		beachrock (V)		beachrock (VI)		contemporary beachrock
	top	base	top	base	top	base	top	base	top	base	
Neratzionas	4.50 ± 0.20	5.10 ± 0.15	4.0 ± 0.10	4.65 ± 0.10			1.20 ± 0.10	1.60 ± 0.05	0.35 ± 0.10	0.85 ± 0.05	
Manganos	4.20 ± 0.15	5.00 ± 0.10	3.40 ± 0.10	4.25 ± 0.10			1.15	1.50			
Manganos West	4.30 ± 0.15	4.90 ± 0.10			3.10 ± 0.10	3.55 ± 0.05					±0.00 ÷ +0.50
Lake Strongyli	4.30 ± 0.05	4.75			2.95 ± 0.20	3.60 ± 0.10			0.55 ± 0.10	0.75 ± 0.05	±0.00 ÷ +0.50
Pounta-Pavlopetri								1.50			
average depth (m)	**5.00 ± 0.25**		**4.45 ± 0.30**		**3.60 ± 0.10**		**1.55 ± 0.10**		**0.80 ± 0.10**		**±0.00**

12 m (range: 4-30 m). It appears moderately-to-very fragmented, without the blocks having moved from their original position. The seaward top is at 4.15-4.60 m bmsl and its seaward base at 4.80-5 m bmsl.

At a landward distance of 30-40 m from beachrock (I), separated from it by a sandy strip, beachrock generation (III) is developing for 550 m parallel to it but more sporadically and to a smaller extent than beachrock generation (I). Its breadth varies from 5 m to 12 m and shows a moderate to high fragmentation, but with its blocks, in the well-preserved parts, in their original position. The seaward top of beachrock generation (III) is at 3-3.20 m bmsl, the seaward base at 3.45-3.55 m bmsl. In the central part of this section, and for a length of 300 m toward the west, parallel to, and at a distance of 10-26 m behind beachrock (III) toward the coast, sand-gravel beach deposits are laid on the sandy bottom along the isobath of 2.40 m.

In the swash and backwash zone of the contemporary shoreline, for a length of about 330 m westward, beachrock seems to be cementing. Sporadic occurrences were also found in the spray zone of the modern sandy beach. The average width of the beachrock is 5 m, with a visible trace on the beach extending to a maximum distance of 10 m from the shoreline. These observations clearly demonstrate that the beachrock is cemented concurrently in the intertidal and supratidal zone, and that its seaward end is the most reliable point for measuring the depth as it represents the low tide of the sea level at the time of formation.

Lake Strongyli (Figures 1D and 2D)

This coastal section comprises the coast in front of Lake Strongyli; in its final western part this turns to the south and ends at the Pounta shore. Three out of five beachrock generations were recorded, along with the contemporary beachrock. Two sizeable slabs of the deepest beachrock generation (I) are located 215 m off the coast, growing parallel to it for 72 m in the east and 58 m in the west, with an average width of 10 m and 14 m, respectively. They appear moderately fragmented but have not been dislocated from their original position. The seaward top and base of the western slab are at 4.30 m bmsl and 4.75 m bmsl, respectively.

At a landward distance about 40 m from beachrock (I), separated from it by a sandy strip, beachrock generation (III) runs parallel to the shoreline for 500 m. Its breadth varies from 5 m to 20 m and is slightly-to-moderately fragmented. The seaward top of beachrock generation (III) is at 2.70-3.15 m bmsl and the seaward base at 3.30-3.70 m bmsl. Located at a distance 3-5m off the coast, the younger beachrock generation (VI) is developing parallel to the coast for 480 m from the central part toward the west. It appears solid, with a width of 3-8 m, and its seaward top and base is at 0.40-0.65 m bmsl and 0.70-0.80 m bmsl, respectively.

In the swash and backwash zone of the eastern part of the contemporary shoreline, for a length of about 55 m, beachrock now appears to be cementing. Three sporadic occurrences were also found in the spray zone of the modern sandy beach. The average width of the beachrock is 5 m, with a visible trace on the beach extending to a maximum distance of 8 m from the shoreline.

Pounta-Pavlopetri (Figures 1D, 3 and 4)

At the westernmost final part of the northern coast of Vatika Bay, just opposite the island of Elafonisos, between the 'NE Islet' and Pavlopetri Island to the SW, the prehistoric settlement lies on the seabed. On the rocky Peloponnesian coast bounding the basin of the prehistoric town on the north, there are remains of an ancient quarry in the sandstone bedrock and the terrestrial part of the prehistoric cemetery, while on the north-easternmost side of the coast a channel is cut into the sandstone.

Only a limited occurrence of beachrock generation (V) was observed north of the northernmost edge of the prehistoric town. It lies just 7 m off the Peloponnesian shore and develops for 70 m parallel to it with a maximum width of 20 m. It appears highly fragmented, with most blocks having moved from their original position. In the few intact parts, the seaward base was measured at 1.50 m bmsl.

During the snorkel survey, a now submerged sandstone ridge was observed, with an average width of about 50 m, developing in a NE-SW direction for a length of 600 m, and bounding the prehistoric settlement on the east. The ridge projections from the sea are the 'NE Islet' (about +1 m) and Pavlopetri Island to the SW (+3.60 m). The submerged ridge forms an elongated reef, its upper surface at 0.60-0.80 m bmsl, with sporadic parts reaching the mean sea level. The reef has a stepped morphology, formed by marine terraces underlying and on either sides of the upper surface, from 1.50 m to 30 m wide, separated from each other by small cliffs. The depths of each marine terrace reported below represent the landward and outer seaward edges (see 'Methods' above).

On the east seaward side of the reef, two marine terraces were observed: the higher between 2.40 m and 2.80 m bmsl and the lower from 3.60 m to 4.25 m bmsl, with the seafloor being between 4.20 m and 5.10 m bmsl. On the inner west landward side of the reef, a terrace is formed between 1.50 m and 2 m bmsl with the seafloor at 2.50 m bmsl. The SW part of the reef and its projection above sea level constitutes Pavlopetri Island. Surrounding it, three marine terraces have formed, the highest between 1.80 m and 2.30 m bmsl, the intermediate between 2 m and 2.70 m bmsl, and the deepest between 3.25 m and 3.45 m bmsl. The greatest depths were measured on the seaward side, and the seafloor is at 4.65 m bmsl (Figure 4, cross-section C). The NE part of the reef and its projection above sea level constitutes the 'NE Islet'. Three marine terraces have also formed around it, the highest between 0.25 m and 0.60 m, the second between 1.30 m and 1.90 m, and the deepest between 3.40 m and 3.45 m, with the seabed being at 3.97 m bmsl (Figure 4: cross-section A). The reef section between the two underwater stepped morphologies around the two islets inclines smoothly toward the sea and ends at the seafloor (Figure 4, cross-section B). On this flattened surface, many chamber-tombs were cut into the rock (see below 'Archaeological indicators of the rsl change').

On the seaward side of the reef, east of Pavlopetri Island, a well-preserved tidal notch is incised on the sandstone bedrock and visible for a length of 40 m. Its base is at 4.60 ± 0.05 m bmsl and its opening is 0.30-0.40 m (Figures 3, 4: cross-section C, 5A, B).

Archaeological indicators of the rsl change

The largest depth recorded in 2018 within the basin between the reef and the Pounta coast that once hosted the prehistoric town of Pavlopetri and now hosts its remains is 2.70 m bmsl. The published plans of Harding *et al.* (1968), Flemming *et al.* (1973) and Henderson *et al.* (2011) clearly show that the remains do not extend beyond the isobath of 3 m. Although this depth is indicative of the rsl rise since the Early Bronze Age, it does not suffice to determine its size accurately.

The internal depth of the largest southernmost of two chamber-tombs, carved on the uppermost surface of the ridge and now submerged, is 2.70 m bmsl. An almost equivalent depth (-2.50 m) was provided by Harding *et al.* (1969), who also assigned the tombs to the Late Bronze Age, probably the Mycenaean period. This is clear evidence that, until the late 12th century BC, the sea level was at least 3 m lower than at present.

During the geomorphological snorkel survey, on the surface of the reef between the stepped morphologies of the two islets, at a distance of about 40 m south of the 'NE islet' and a short distance NE of the northernmost edge of the settlement, a large number of man-made circular holes were found. They are carved on the now submerged sandstone bedrock that slopes smoothly toward the sea. Round-shaped, 1.20-1.50 m in diameter, and of an internal depth of 0.50-0.80 m, they resemble the sixty or more chamber-tombs located NE of the prehistoric town on land between Lake Strongyli and

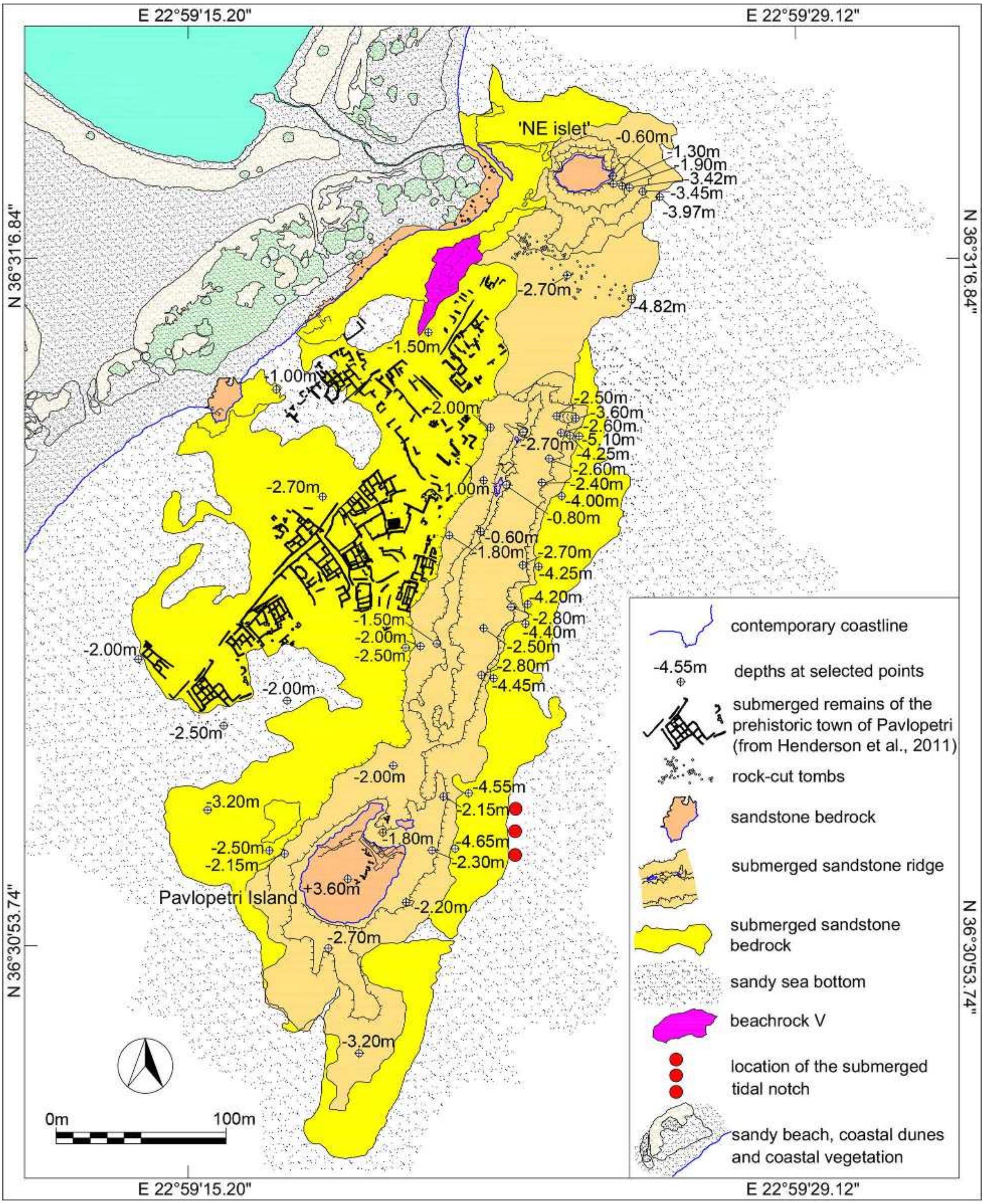

Figure 3. Schematic plan of the Pounta-Pavlopetri section. The outline of the visible submerged ruins of the prehistoric town from Henderson *et al.* (2011).

the sea, which belong to the Early Helladic period (3000-2000 BC) (Harding *et al.* 1969; Henderson *et al.* 2011; Gallou and Henderson 2012). The deepest hole (probably tomb) was found at 4.82 m bmsl (Figure 3). This depth represents a minimum depth limit when this area was occupied and in use, and therefore the coastline would have been at a greater depth than this.

Another archaeological indicator of the rsl change are the carvings found on the eastern seaward side of the

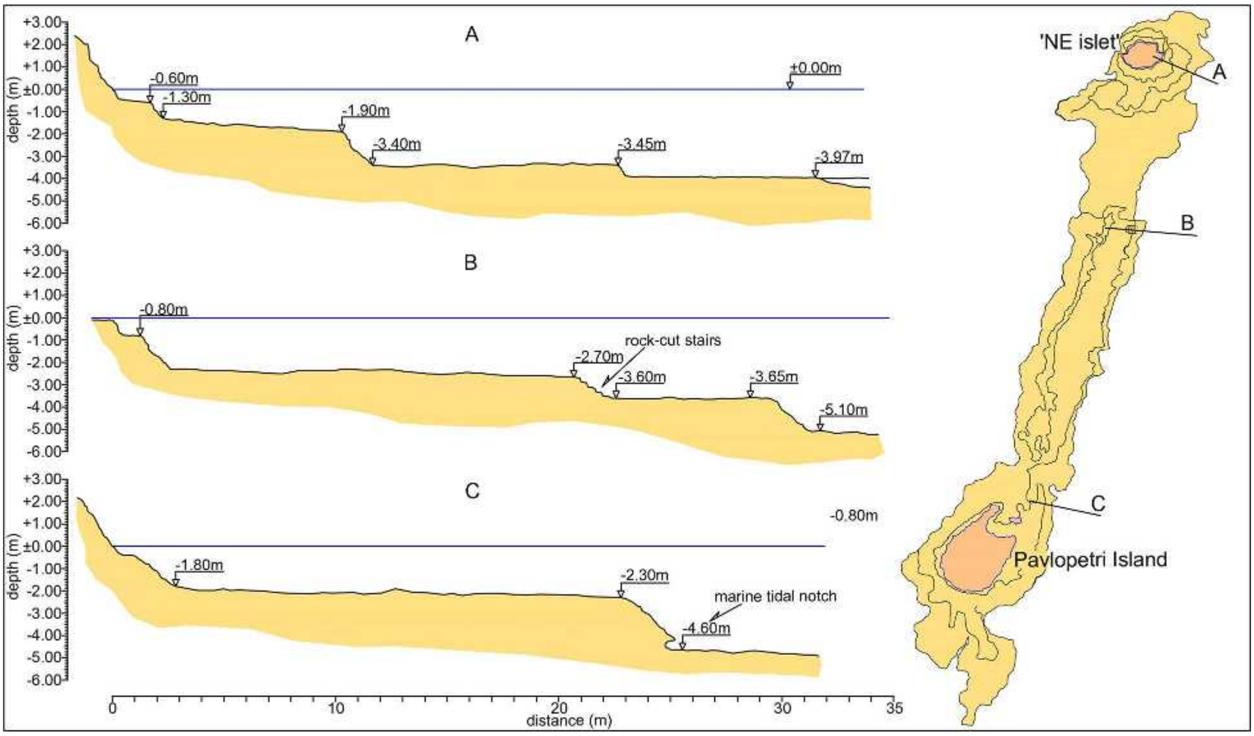

Figure 4. Plan of the ridge bounding on the east the prehistoric town and cross-sections at selected positions along it.

reef, between the depths of 2.70 m and 3.60 m bmsl. They point to a set of five stairs, which lead from the upper marine terrace at 2.50 m bmsl to the underlying terrace at 3.60 m bmsl (Figures 3, 4, 6A). Neither the submerged Early Helladic rock-cut tombs nor the rock-cut stairs were illustrated in the previously published plans of 1968, 1973 and 2011.

The extensive quarrying traces of unidentified age reported by Harding *et al.* (1969), and submerged at 1 m bmsl on the eastern side of Pavlopetri Island, only provide evidence of the rsl rise since the period that the quarry was in use.

During this survey, traces of cart tracks were found incised on the sandstone bedrock along the Peloponnesian coast of the isthmus, at a distance of 440 m west of the modern dock of Pounta (36°31'15.89"N, 22°58'28.25"E). Starting from land at the elevation of +1 m and observed for a length of 27 m up to a depth of 0.80 m bmsl, these are parallel grooves up to 0.20 m deep and 1.30 m to 1.50 m apart (Figure 6B). Two pairs of cart tracks were observed on site, beginning on land 12 m apart and heading towards the sea in a SE and SW direction, respectively. They intersect underwater 21 m off the coast, and then follow a common path toward the south. Apparently, this was the entrance to a road that served the traffic of carriages during the period that the Elafonisos Strait was fordable along its entire length, when the sea level was lower than the greatest observed depth in the strait (now up to 3.50 m in its central part, according to the depths provided by the Hellenic Navy Hydrographic Service, HNHS).

At the eastern end of the sandstone bedrock on Pounta coast, just opposite the 'NE islet', a rectangular channel was cut, with a width of 2.80 m and a visible length of 30 m— today mostly silted. It connected Lake Strongyli with the sea and was probably used to allow seawater to enter the lagoon, although it was also properly blocked to prevent the lagoon from draining into the sea (Harding *et al.* 1969). It was probably built during the Late Roman or Byzantine period and certainly later than the Early Helladic cemetery on the coast, as it has been cut through three tombs (Harding *et al.* 1969). Its current position does not provide evidence of the rsl change.

Was the prehistoric town of Pavlopetri protected from waves?

The prehistoric settlement of Pavlopetri was protected to the N, NE, and NW by the mainland, as is the case today, but it was also protected to the W throughout its occupation and later during the period when the Elafonisos Strait was still land. The only direction in which there is a significant fetch (120-150 km) is SE toward the NW coast of Crete, while in a southerly direction there is a significantly shorter fetch of 25-30 km toward the NE coast of Kythera, and an even shorter fetch in an easterly direction, not exceeding 10 km toward the west coast of the Maleas Peninsula.

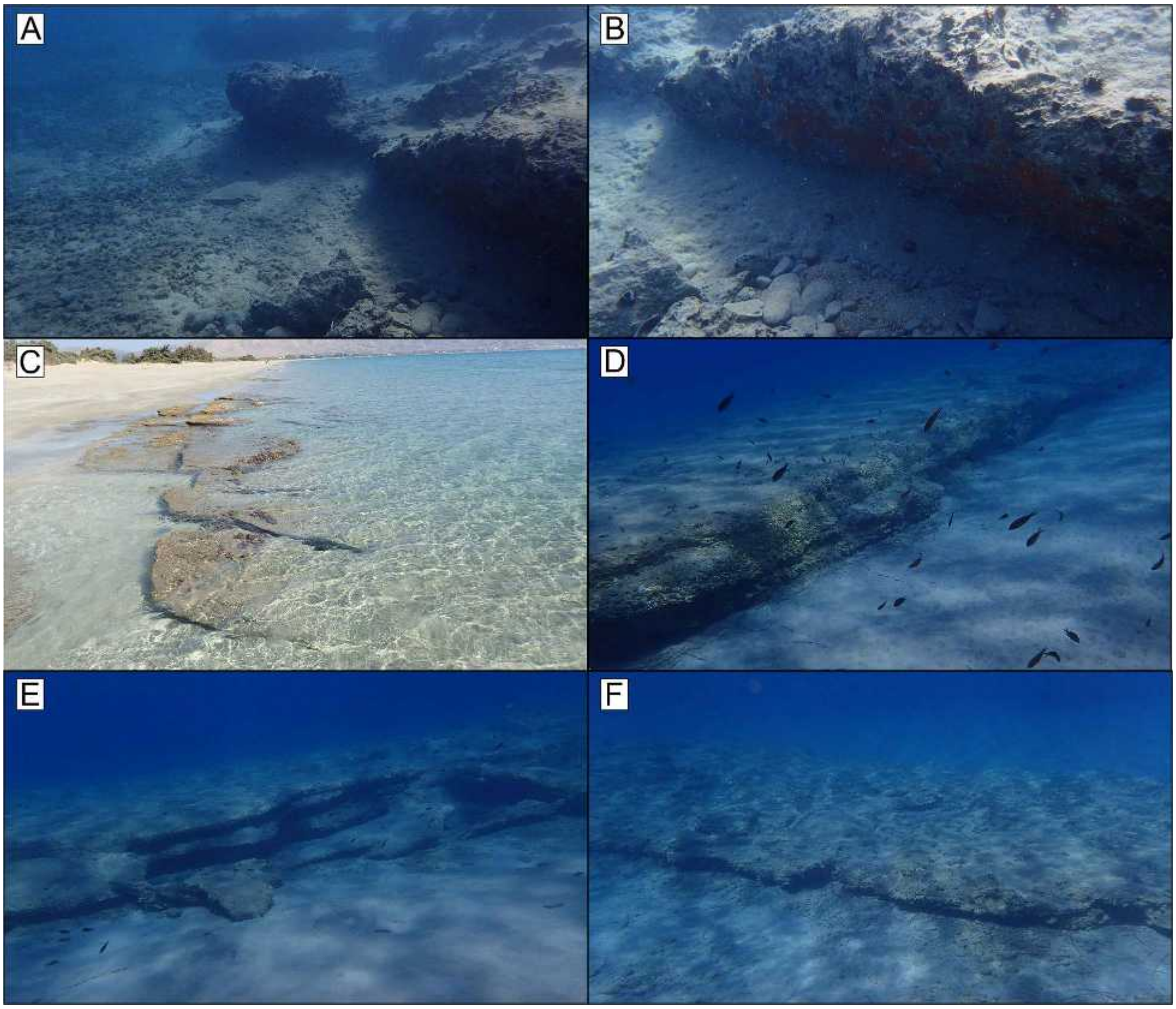

Figure 5. **(A)** Underwater view of the submerged tidal notch to the east of Pavlopetri Island at -4.60 ± 0.05 m bmsl and **(B)** detail of it. **(C)** View of the contemporary beachrock. **(D, E, F)** Underwater views of the submerged beachrock generations (V) **(photo D)**, (III) **(photo E)** and (I) **(photo F)** (photos authors).

The location and orientation of the coast of the prehistoric settlement indicate that the waves are generated by S and SE winds, which create the longest fetch. The wave features generated by E winds were also examined, given the proximity of Pavlopetri to the west coast of the Maleas Peninsula. The analyses of the time series wind data for average and high wind speed and direction along with the corresponding wind rose diagram (Figure 1D, inset) reveal that NW winds are more frequent, representing 68.5% of the total, with the strongest reaching 114 km/h. W winds represent 20.51%, with an observed maximum wind speed of 82.10 km/h. S and E winds are less frequent, with 8.66 % and 2.34%, respectively.

The wind-wave analysis for the study period of 3904 days concluded that SE winds prevailed for 35 days. Of these, there were two days with a maximum wind speed of 91.7 km/h and 83.7 km/h, which generated on the coast of the prehistoric settlement a wave height of 4.20 m and 4 m, respectively, three days with a maximum wind speed of 62.8-69.2 km/h, generating a wave height of 3-3.30 m, twelve days with a maximum wind speed of 43.5-59.5 km/h, generating a wave height of 2.20-2.90 m, and eighteen days with a maximum wind speed of 19.3-59.5 km/h, generating a wave height of 0.30-1.90 m. S and SSE winds were dominant for 106 days with a maximum speed of 20.9-70.8 km/h, generating a wave height of 0.40-1.80 m. Finally, E winds prevailed for 79 days with a maximum speed of 17.70-78.9 km/h, generating a wave height of 0.10-0.90 m.

In conclusion, the wave height very rarely (twice in a twelve year-period) exceeds 4 m, with a maximum observed wave height of 4.20 m produced by SE winds. Therefore, if the ridge that bounded the

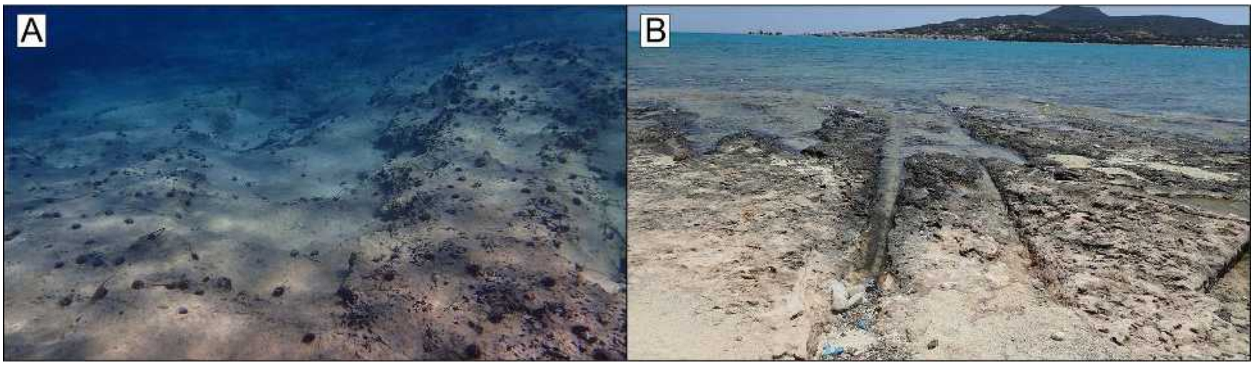

Figure 6. **(A)** Underwater view of the rock-cut stairs at the eastern seaward side of the sandstone reef. **(B)** View of the partly submerged traces of cart tracks on the Viglafia coast, consisting of two pairs of parallel grooves deeply incised on the sandstone (photos authors).

prehistoric town on the east side had a minimum equivalent elevation, then the town would have been fully protected from the waves. Given that the upper surface of the ridge is now at 0.60-0.80 m bmsl—with the exception of Pavlopetri Island (+3.60 m) and the 'NE Islet' (+2 m)—it follows that with a minimum sea level 5 m lower than at present, the town, or even its remains, would not have been affected by waves, even extreme storm waves, whatever the weather conditions.

Interpretation and Discussion

Correlation of the geomorphological indicators in Vatika Bay

Along the entire coast of Vatika Bay, five distinct beachrock generations were observed, mapped and measured, with the average depths of their seaward base at 5.00 ± 0.25 m bmsl (I), 4.45 ± 0.30 m bmsl (II), 3.60 ± 0.10 m bmsl (III), 1.55 ± 0.10 m bmsl (V), 0.80 ± 0.10 bmsl (VI), together with the contemporary beachrock (±0.00). The deepest generations (I) and (II) are developing along almost the entire coast of Vatika Bay, while generations (III), (V), (VI) and the contemporary beachrock appear to a lesser extent. All the beachrock generations distinguished along the coast of Vatika Bay from Neratzionas to the Pounta-Pavlopetri area and the respective coastline during their formation are shown in Figure 7. All depth measurements of the various beachrock generations are presented in Table 1. Depth diagrams of each beachrock generation and the combined depth diagram of all beachrock generations are shown in Figures 8A to 8F. An indicative cross-section of the various beachrock generations is illustrated in Figure 8G. Views of the contemporary and submerged beachrocks (V), (III), and (I) are shown in Figures 5C to 5F.

Comparing the depths of the distinct beachrock generations (seaward base) with those of the marine terraces (inner shoreline angle, landward edge) and the tidal notch (base), a good correlation between them can be deduced. This suggests the same sea level stands during their formation. Beachrock generation (II) at 4.45 ± 0.30 m bmsl is consistent with the tidal notch at 4.60 ± 0.05 m bmsl. The marine terrace between 3.40 m and 4.25 m matches beachrock generation (III) at 3.60 ± 0.10 bmsl. The marine terrace between 1.30 m and 1.90 m agrees with beachrock generation (V) at 1.55 ± 0.10 bmsl. The shallowest marine terrace between 0.60 m and 0.80 m bmsl matches beachrock generation (VI) at 0.80 ± 0.10 m bmsl.

Pizzaro *et al.* (2012) carried out side-scan sonar mapping, sampling, and radiocarbon dating, and used stereo imagery to create a 3D photomosaic of the beachrock formations in a very limited area between the Manganos and Neratzionas sections, of seaward length 140 m and width of 40 m out of 4 km occurrence. They reported that the beachrock bands closest to the shore are 150 m offshore at depths of 3-4 m, provided some depths for three bands (2.50-3 m, 2.60-3.50 m and 3.90-4.80 m)—without defining at which part of the formation they measured depths—and yielded four samples from these bands for preliminary dating. The conventional radiocarbon age of the deepest band is 1850 ± 90 BP (cal. age AD 480-650) while that of the intermediate band is 1520 ± 50 BP (cal. age AD 1030-1150). The shallowest and youngest beachrock band recorded radiocarbon ages older than the two deeper bands. Since these ages do not match the stratigraphic position of the bands, doubt is automatically cast over the ages of the deeper bands.

Rsl change history along the eastern coast of the Peloponnese

The rsl change history along the eastern coast of the Peloponnese (Kolaiti 2019) begins in the Early Bronze Age (3500-2200 BC) with a sea level stand at 5.10 ± 0.20

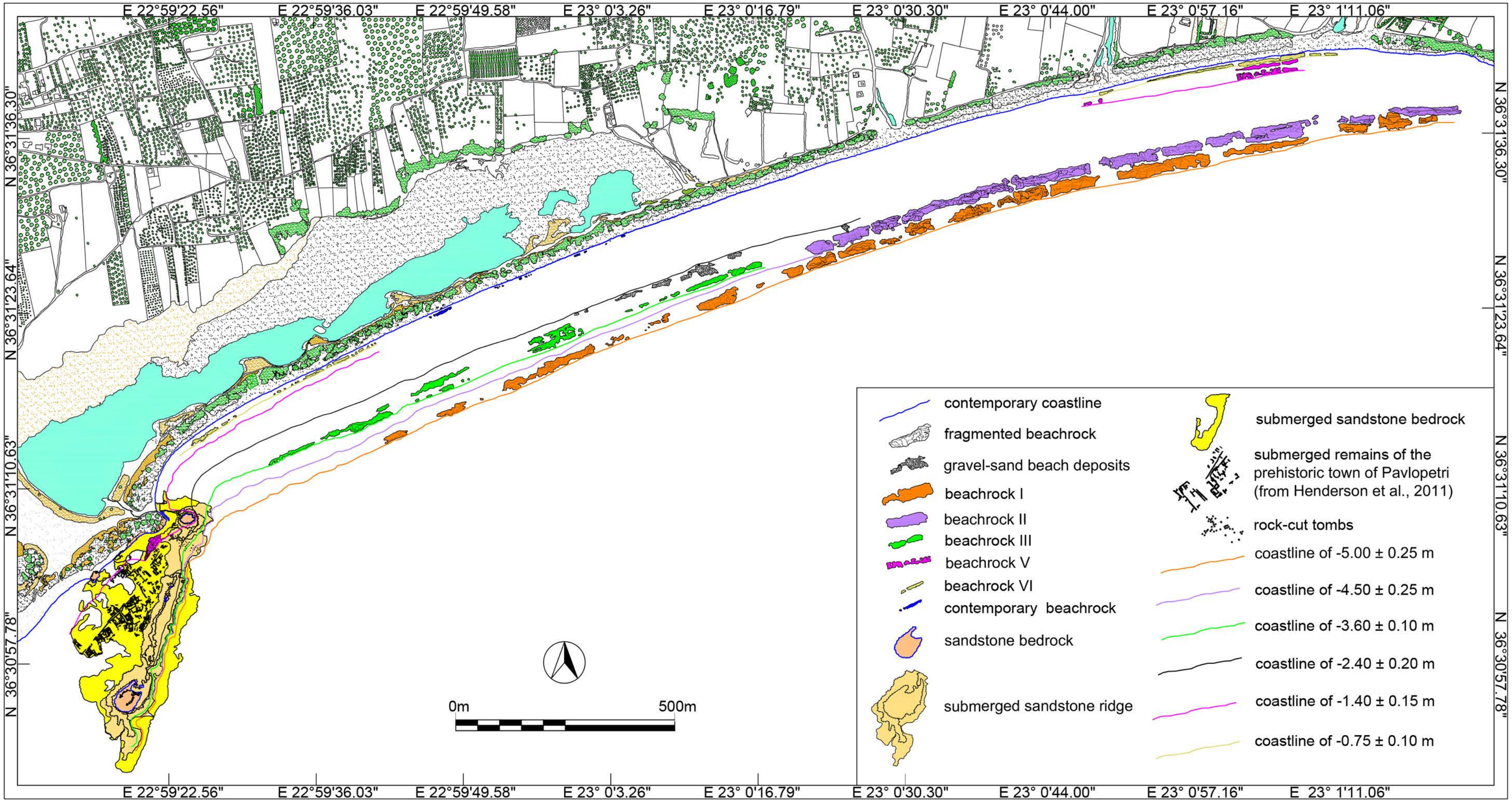

Figure 7. Schematic plan of the entire coast of Vatika Bay from Neratzionas to Pounta-Pavlopetri area. All the beachrock generations and the respective coastline during their formation are distinguished. The 'NE islet', Pavlopetri Island, the submerged ridge and the submerged ruins of the prehistoric town (from Henderson *et al.* 2011) are also shown.

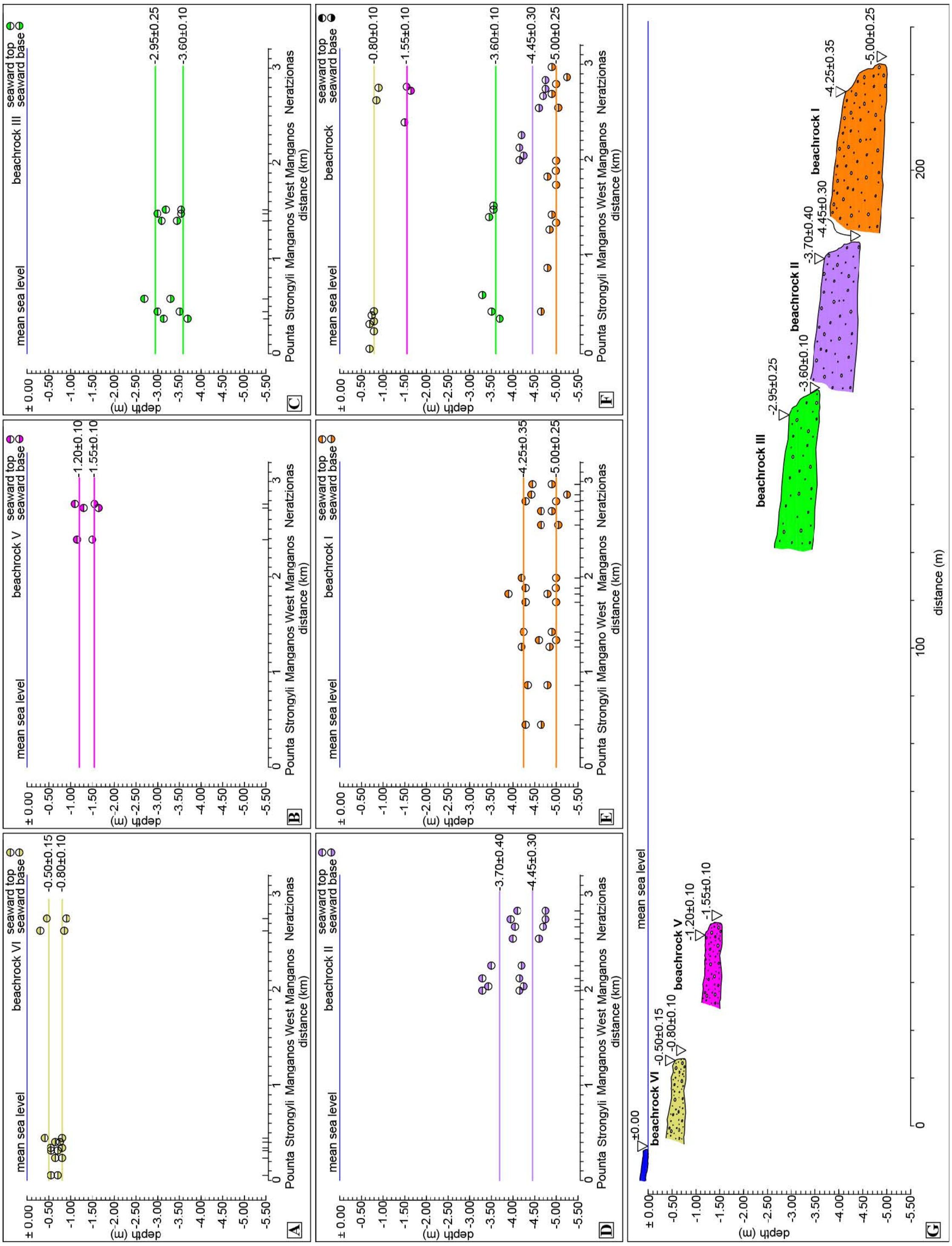

Figure 8. Depth diagrams of each beachrock generation recorded in Vatika Bay. **(A)** beachrock generation (VI). **(B)** beachrock generation (V). **(C)** beachrock generation (III), **(D)** beachrock generation (II) **(E)** beachrock generation (I), **(F)** combined depth diagram of all beachrock generations along the north coast of Vatika Bay. All depth measurements of the various beachrock generations are presented in Table 1. **(G)** Indicative cross-section of the various beachrock generations.

m bmsl (sea level I). The sea level at 4.40 ± 0.20 m bmsl (sea level II) is dated to the Late Bronze Age (1500-1190 BC) and seems to have shifted to the next sea level stand at some time between 1190 BC and 700 BC. Sea level III at 3.60 ± 0.20 m bmsl, repeatedly found to be associated with robust archaeological evidence throughout the eastern coast of the Peloponnese, ranges from the Archaic period to Late Roman times (700 BC to AD 4th or probably 6th century), thus indicating a long period of sea level stability, a period of at least 1000 or 1200 years. Sea level stand IV at 2.40 ± 0.20 m bmsl dates to after AD 13th century and seems to have been short-lived, as its succession by sea level V at 1.45 ± 0.15 m bmsl occurred at some time before the First Venetian occupation. Sea level V dates to between 1389 and *c.*1840. The next sea level stand at 0.80 ± 0.10 m bmsl (sea level VI) dates to Modern times and seems to have lasted for a few decades until the early 20th century, when the sea level rose to 0.35 ± 0.15 m bmsl (sea level VII) and then shifted to its current position. The curve of the mean rsl change during the last 5500 years for the eastern coast of the Peloponnese is illustrated in Figure 9 (red line), along with the inferred periods of the rsl stability and change (Kolaiti 2019).

Determination and dating of former sea level stands in Vatika Bay

On the basis of the geomorphological indicators of the rsl change and their correlation, five distinct sea levels can be determined for Vatika Bay: 5.00 ± 0.25 m (I), 4.50 ± 0.25 m (II), 3.60 ± 0.10 m (III), 1.50 ± 0.15 m (V) and 0.75 ± 0.10 m (VI) bmsl. The sand-gravel beach deposits found in the Manganos West section for a significant length of 300 m at a depth of 2.40 bmsl seem to have accumulated along a former shoreline and might determine a sixth sea level stand at 2.40 m bmsl. The diagram in Figure 9 depicts both the observed mean sea level stands in Vatika Bay and those along the entire eastern coast of the Peloponnese, which are remarkably consistent in terms of depth. In the case of those stands for which evidence of dating is not provided in the study area, we can safely adopt the dating of the respective sea level stands determined for the eastern Peloponnese (Kolaiti 2019) (Figure 9).

The deepest sea level stand (I) at 5.00 ± 0.25 m bmsl is determined by the depth of the seaward base of beachrock (I) at 5.00 ± 0.25, the depth of the reef at its eastern seaward side at 5.10 m, and the deepest trace of the rock-cut Early Helladic tomb at 4.82 bmsl, which certainly dates this sea level stand (I) to the Early Helladic period (3000-2000 BC, 5000 years before present). What is important, the depth and dating of this sea level stand (I), inferred from local rsl change data, is consistent with the predicted rsl 5 ka BP, which is provided by Lambeck (1995) for the Laconic Gulf . In the same diagram, the predicted rsl curve resulting from the Lambeck's (1995) glacio-hydro-isostatic model for the Laconic Gulf since 5 ka BP is also illustrated (Figure 9).

The depth of the seaward base of beachrock (II) at 4.45 ± 0.30 m and tidal notch carved on Pavlopetri Island at 4.60 ± 0.05 m bmsl determines the sea level stand (II) at 4.50 ± 0.25 m bmsl. The tomb of the Late Helladic period carved on the reef, now at a depth of 2.70 m bmsl, as well as the maximum recorded depth of 3 m in the basin of the prehistoric town, reasonably suggest a sea level lower than 3 m during the Late Bronze Age occupation of the area. Moreover, based on evidence of the entire eastern coast of the Peloponnese, the 4.50 ± 0.25 m sea level stand is robustly dated to the Late Bronze Age, between 1500 BC and 1190 BC.

Sea level (III) at 3.60 ± 0.10 m is identified by the seaward base of beachrock (III) at 3.60 ± 0.10 m, the depths of the marine terrace formed around the 'NE Islet', and the marine terrace and the rock-cut stairs on the eastern seaward side of the reef at 3.60 m bmsl. Based on strong evidence pertaining to the entire eastern coast of the Peloponnese, this falls within the range of the Archaic period to Late Roman times, i.e. from 700 BC to AD 4th or probably the 6th century.

Although not adequately documented on the coast of Vatika Bay, sea level (IV) identified on the eastern coast of the Peloponnese at 2.40 ± 0.20 m bmsl also points to a short sea level stand in Vatika Bay, which dates to after AD 13th century and until before the First Venetian occupation (AD 14th century).

The depth of the seaward base of beachrock (V) at 1.55 ± 0.10 and the marine terrace around the 'NE Islet' determine a sea level stand at 1.50 ± 0.15 m, which, based on relevant evidence pertaining to the entire eastern coast of the Peloponnese, dates to the period between the end of AD 14th century (1389) and 1840.

The sea level stand at 0.75 ± 0.05 m is determined by the depth of the seaward base of beachrock (VI) at 0.80 ± 0.05 m, the upper surface of the reef, and the uppermost marine terrace around 'NE Islet', both at 0.60-0.80 m bmsl. It dates to Modern times, after 1840 according to relevant data on the eastern coast of the Peloponnese.

The mean sea level stands observed in Vatika Bay with respect to the curve of the mean rsl change during the last 5500 years for the eastern Peloponnese is shown in Figure 9, along with the inferred periods of the rsl stability and change.

Changes in the coastal anthropogenic landscape

When the sea level was at 5.00 ± 0.25 m lower than at present (Figure 10A), Elafonisos was connected to the Peloponnesian coast by a sandy isthmus about 2.2 km wide, which protruded from the sea by 1.50 m to 4.20 m in its central part. Between the eastern end of the isthmus and the western end of the shore of Vatika Bay, on the coastal zone in front of the westernmost end of Lake Strongyli, sandstone bedrock appears. On its seaward side, an elongated ridge developed in a NE-SW direction, protruding 4.20 m above the sea with occasional local elevations (i.e. the 'NE Islet' +6 m, Pavlopetri Island +8.60 m). On the west side of the ridge towards the isthmus, a depression of the rocky bedrock (+1.80 m to +2.30 m) formed a sheltered basin for the settlement of the first inhabitants of the Early Bronze Age. On the NE side of the settlement, outside its boundaries and at a higher elevation where the bedrock sloped smoothly towards the sea, the chamber-tombs of the Early Helladic period were cut into the rock. The lowermost of these, which is now at 4.82 m bmsl, was

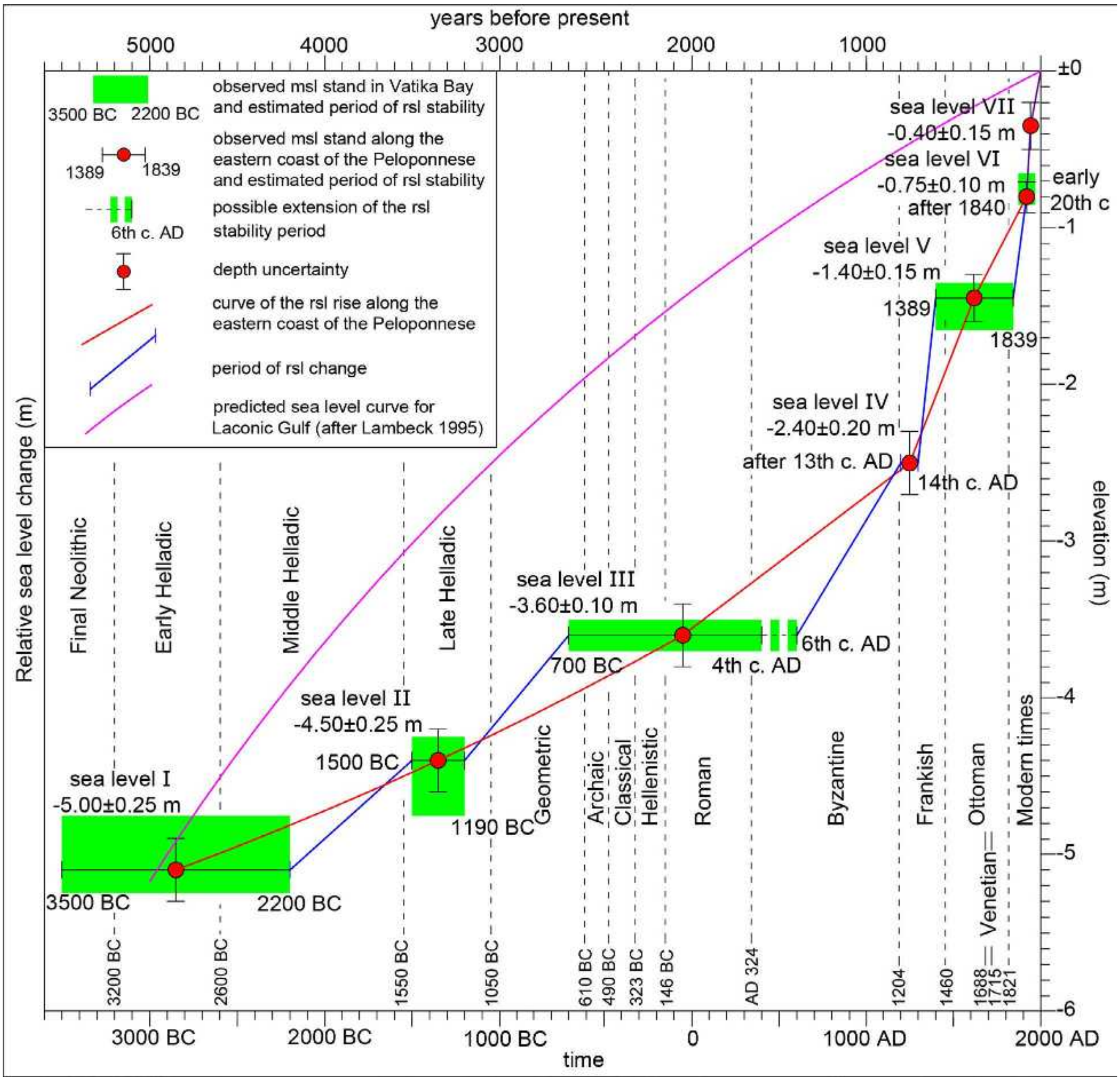

Figure 9. The mean sea level stands observed in Vatika Bay with respect to the curve of the mean rsl change during the last 5500 years for the eastern coast of the Peloponnese and the predicted rsl curve for the Laconic Gulf by Lambeck (1995). The main archaeological periods are shown. (msl: mean sea level, rsl: relative sea level)

at that time just above sea level (+0.50 m). Its position determines the boundary of the usable land area during the Early Bronze Age. At this sea level, the sandy beach deposits were cementing to form beachrock generation (I) on the coast of Vatika Bay. The small boats of that time would have been dragged onto the sandy beach of the bay NE of the settlement or SW onto the sandy beach of the isthmus (Figure 10A, right).

When the sea level was at 4.50 ± 0.25 m lower than at present (Figure 10B), Elafonisos Island was still connected to the mainland by the sandy isthmus, by now inundated on its lower western side up to about 80-100 m inland, yet still protruding from the sea by 1 m to 3.70 m in its central part. The ridge protruded from the sea at least 3.90 m with occasional local elevations (i.e. the 'NE Islet': +5.50 m, Pavlopetri Island: +8.10 m). The life of the Early Bronze Age settlement was not affected by the slight rsl rise, since it was still protected by the rocky ridge in the east. However, the coastal part of the Early Bronze Age cemetery was now inundated. Two chamber-tombs were then carved on the ridge. The internal depth of the southernmost was at an elevation of +1.80 m. Given that the tombs date to the Late Bronze Age, probably to the Mycenaean period (Harding *et al.* 1969), a sea level of 4.50 ± 0.25 m bmsl is assigned to this period. With this sea level, the tidal notch was incised on the ridge (today at 4.60 m bmsl), the beachrock

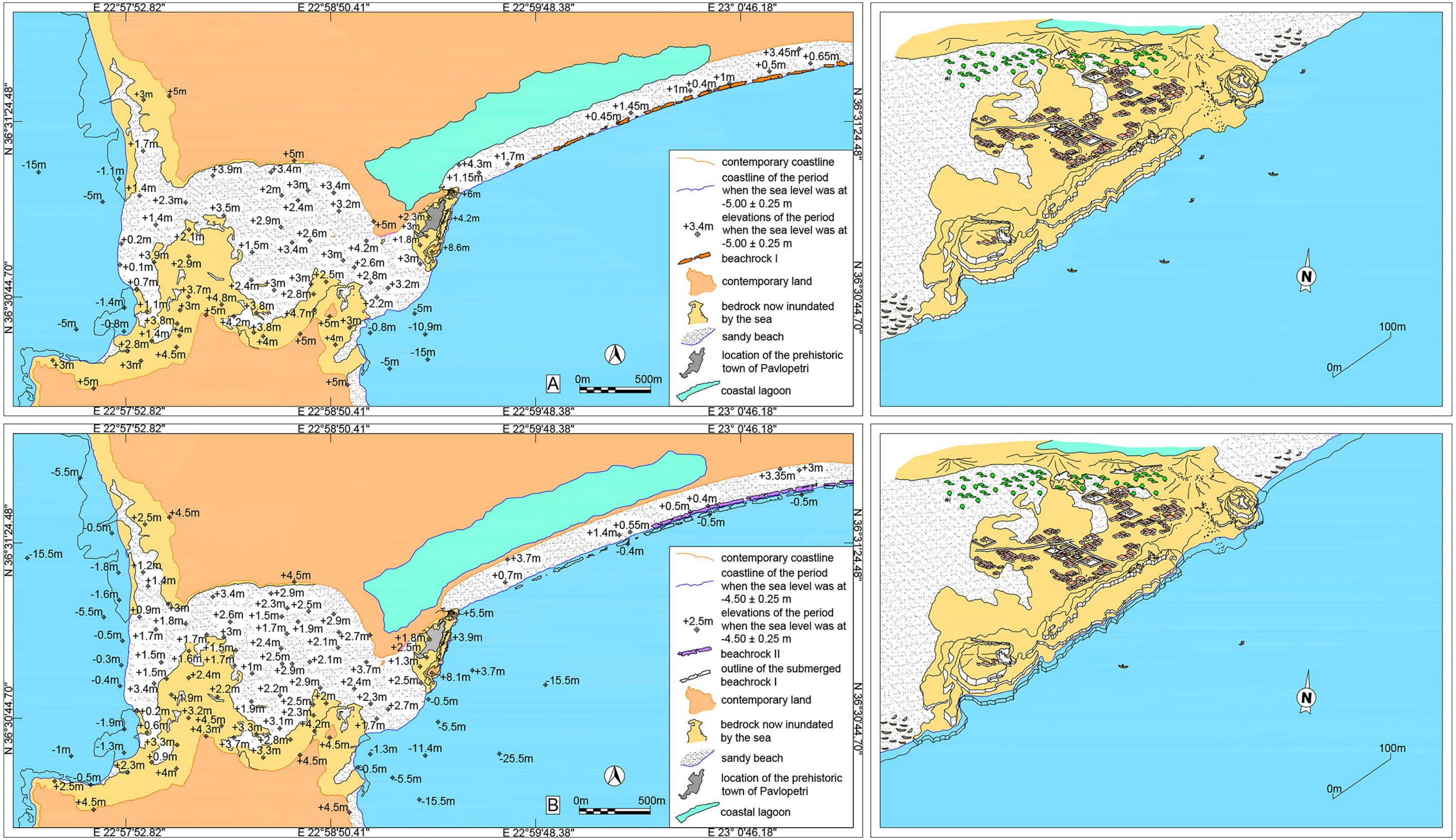

Figure 10. **(A)** Palaeogeographic reconstruction of the shoreline of Elafonisos Strait when the sea level was at 5.00 ± 0.25 m bmsl and a 3D sketch of the prehistoric town of Pavlopetri during the same period (top right). **(B)** Palaeogeographic reconstruction of the shoreline of Elafonisos Strait when the sea level was at 4.50 ± 0.25 m bmsl and a 3D sketch of the prehistoric town of Pavlopetri during the same period (right bottom).

(I) submerged, and a new beachrock generation (II) formed. The small boats of that time would have been dragged onto the sandy beach of the bay NE of the settlement or SW onto the sandy beach of the isthmus (Figure 10B, right).

The rsl rise of 1.10 m that followed shifted the sea level to 3.60 ± 0.10 m bmsl (Figure 11A), further inundating the sandy isthmus up to about 200 m inland. Yet it still protruded from the sea by 0.50 m to 2.80 m in its central part, leaving Elafonisos still connected to the mainland. The ridge protruded from the sea at least 3 m with local occasional elevations (i.e. the 'NE Islet': +4.50 m, Pavlopetri Island: +7.20 m). The Early Bronze Age cemetery was further inundated, although the Late Bronze Age tombs were not affected, since the floor of the southernmost tombs was now at +0.90 m. It was then that the set of five stairs descending to the then shoreline was probably carved on the seaward side of the ridge. At this sea level, the tidal notch and beachrock (II) were submerged, while a new beachrock generation (III) formed on the sandy beach. The boats of that time would have been dragged onto the sandy beach of the bay NE of the settlement or SW onto the sandy beach of the isthmus (Figure 11A, right). The life of the settlement could have continued despite the sea level rise, since it was still protected by the rocky ridge in the east, notwithstanding the rare SE storm waves. After all, the lack of sea defense works on the seafront of the settlement indicates that the habitants never had concerns about the risk of flooding. This sea level stand is evidenced to have lasted from the Archaic period to Late Roman times (700 BC to AD 4th or probably 6th century). Therefore, the assumption of Henderson *et al.* (2011) that the town was inundated during Roman times is open to question. Even if the town had been abandoned during this period, the reasons would have been other than sea transgression. Besides, ancient sources confirm that Elafonisos had not detached from the Peloponnese during the Classical period and in Roman times. It remained connected to the mainland as a low-lying peninsula certainly until the late AD 2nd century (Thucydides, *History of the Peloponnesian War*, VII.26; Strabo, *Geography*, 8.5.1; Pausanias, *Description of Greece*, 3.22.10).

When the sea level rose to 2.40 ± 0.20 m bmsl (Figure 11B), the rocky ridge protruded from the sea by at least 1.80 m with occasional local elevations (i.e. the 'NE Islet': +3.40 m, Pavlopetri Island: +6 m). The isthmus was further inundated leaving only a narrow causeway on its eastern side slightly protruding from the sea by 0.20 m to 1.60 m. The basin where the remains of the prehistoric town was located was partly inundated (Figure 11B, right), while the floor of the tomb carved on the ridge was flooded by sea water to an internal depth of 0.30 m. Beachrock (III) was then submerged and sand-gravel deposits accumulated along the subtidal zone of the then shore of Vatika Bay.

The next rsl rise to 1.50 ± 0.15 m occurred by the end of AD 14th century (after 1389) and caused the flooding of the isthmus with 0.70-1.30 m of water in its eastern part. Elafonisos was cut off from the Peloponnese and now became an island, while on the opposite Laconic coast, the cape of Pounta was shaping. The rocky ridge (along with the tombs on it) was entirely submerged up to a depth of 1 m, with the exception of its SW part, which now protruded from the sea by +5 m, forming Pavlopetri Island, and its elevated NE part that was still connected to the mainland (i.e. the 'NE Islet': +2.5 m). The prehistoric town that had already been abandoned and ruined was now entirely submerged to a maximum depth of 1.50 m. At this sea level, beachrock (V) formed on the eastern coast of Vatika Bay and the eastern side of Cape Pounta (Figure 12A). Therefore, the isthmus of Elafonisos was not fordable by the end of AD 14th century, having become the Elafonisos Strait. This is also attested by historical sources: (a) John Covel in his diaries of 1670-1679 (Covel 1893, as cited in Simopoulos 2007, 115-116) writes that, when English sailors from three warships anchored in Elafonisos, the crew, in search of water and supplies, travelled to the opposite shore in boats. There, people from Mani captured many of them and demanded a ransom for their return. After a meeting of the masters, a fundraiser was held to raise the amount and the Admiral sent his boat to deliver it, while another boat with a white truce flag sailed around the island. (b) W. Leake, who visited the area in 1806 (Leake 1830, as cited in Harding *et al.* 1969) wrote that the strait between Elafonisos and the mainland was 300-400 yd (= 275-365 m) and so shallow that only small boats could pass. Both reports confirm that since at least 1670/1677 Elafonisos had already detached from the Peloponnese and that the strait was not fordable without the use of boats.

The isthmus, the remains of the prehistoric town, and the ridge were further inundated when the sea level shifted to 0.75 ± 0.10 m around 1840. The NE edge of the ridge was now cut off from the mainland and the 'NE Islet' had shaped. At this sea level, beachrock (V) submerged and a new generation (VI) was formed on the coast of Vatika Bay (Figure 12A).

The recent rsl rise of 0.75 m shifted the sea level to its current stand and the remains of a once thriving town lying on the sandy bottom were further covered by the sea (Figure 12B). In the early 20th century, Negris (1904), who showed great interest in the submersion of the Greek coast and the consequential sea level changes, reported the submerged ruins of a town built on the isthmus that connected Elafonisos with the Peloponnese, of which only two islets now protrude

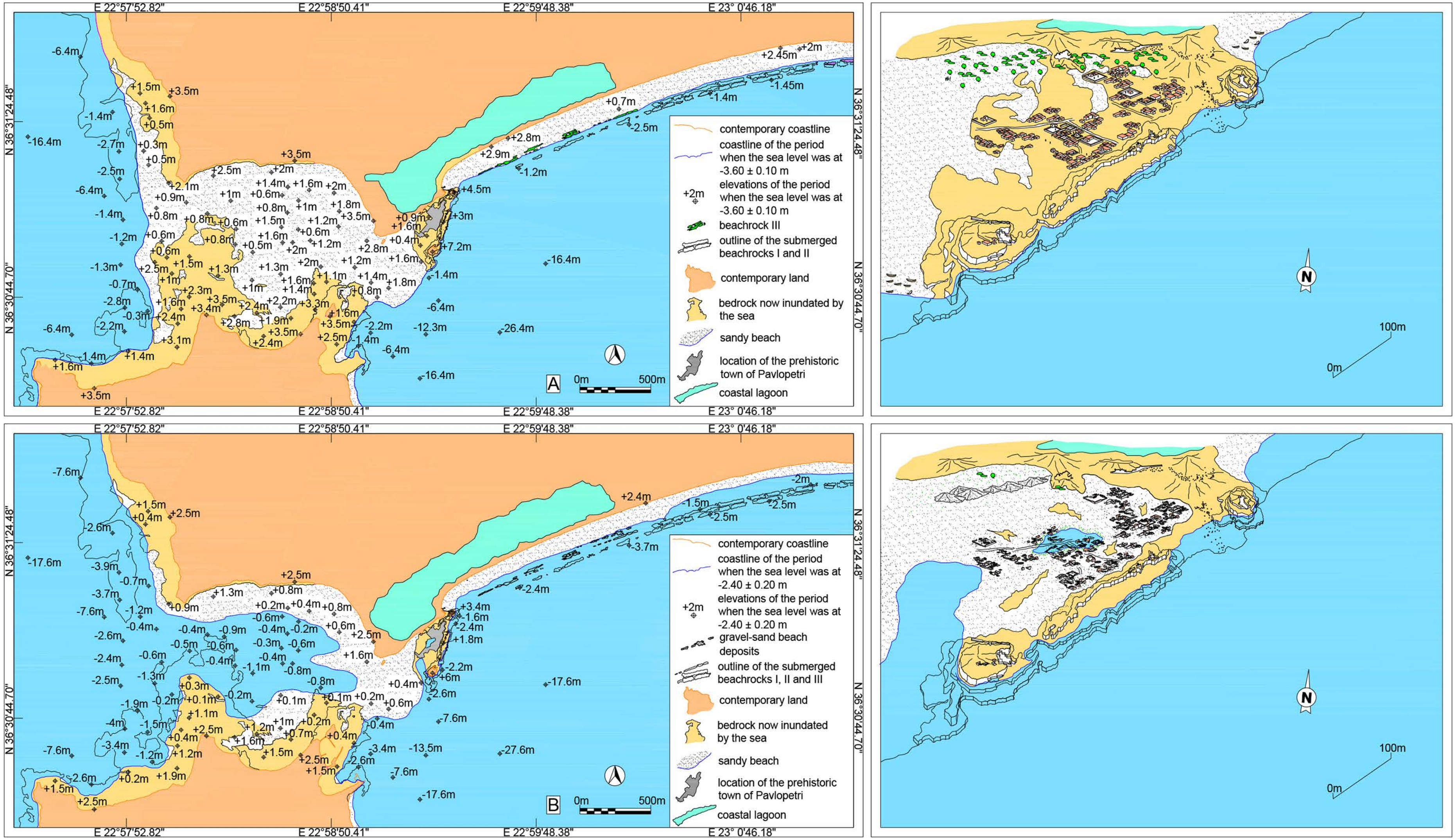

Figure 11. **(A)** Palaeogeographic reconstruction of the shoreline of Elafonisos Strait when the sea level was at 3.60 ± 0.10 m bmsl and a 3D sketch of the prehistoric town of Pavlopetri during the same period (top right). **(B)** Palaeogeographic reconstruction of the shoreline of Elafonisos Strait when the sea level was at 2.40 ± 0.10 m bmsl and a 3D sketch of the prehistoric town of Pavlopetri during the same period (bottom right).

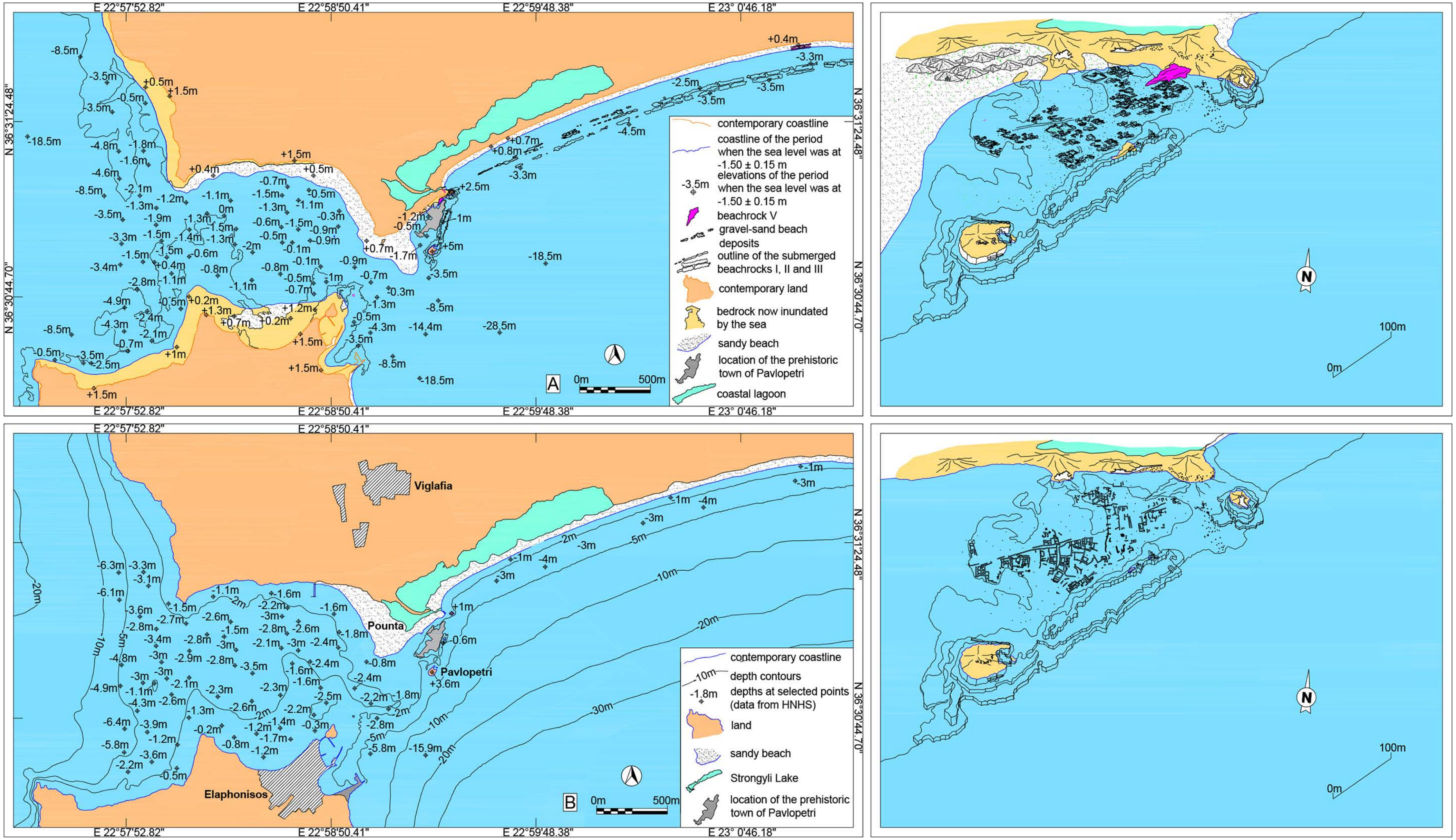

Figure 12. **(A)** Palaeogeographic reconstruction of the shoreline of Elafonisos Strait when the sea level was at 1.50 ± 0.15 m bmsl and a 3D sketch of the prehistoric town of Pavlopetri during the same period (right top). **(B)** The contemporary shoreline of Elafonisos Strait and a 3D sketch of the prehistoric town of Pavlopetri as it now stands (bottom right).

from the sea. In this way, the prehistoric town of Pavlopetri emerges from the shallows into the light.

Acknowlegements

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Defining the Timeframe of a Prehistoric Site near Ioannina, Using OSL Dating Method

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Abstract: A prehistoric site, located on the northern slope of Ayia Marina hill in Pedini, Ioannina, was investigated during the construction of the Egnatia Road. The results of the excavation research testify to the existence of a settlement with huts that would have been constructed with stone foundations and superstructure of perishable materials. During the excavation, a large amount of handmade pottery has been gathered, which is quite homogeneous. Dating pottery in a time context in the past, is difficult in the case of the Epirus handmade one, because of the production of similar vessels for many centuries. The dating of the settlement at the end of the 4th millennium BC is based on the radiocarbon analysis of a single sample of coal.

In the above context, nine sherds of handmade vessels from different depths and strata were chosen to be dated using the Optical Stimulated Luminescence (OSL) method. Paleodoses and radioactivity measurements were conducted at the Archaeometry Centre of the University of Ioannina. Preliminary results show that ages of the sherds are in the time frame from the Final Neolithic to the Bronze Age in Greece.

KEYWORDS: PREHISTORIC SITES, POTTERY OSL DATING, FINAL NEOLITHIC, LATE BRONZE AGE

Introduction

A prehistoric location, a small outdoor site on the north slope of the Ayia Marina hill, Pedini, at the southwest end of the Ioannina basin (Figure 1), was revealed during the construction of the Egnatia Road. During earthworks, sherds of handmade vessels were discovered in two locations in swallow depths and an emergency excavation research was decided and performed under severe weather conditions (freezing temperature, snow and rain). This preliminary work was followed by excavation in two sections A and B, of 4x4 m, at the points of the greatest concentration of findings. These sections were 70 m apart and both point surveys of the same site, where the destruction layer was unearthed (Adam 1998; Siozou 2022).

The excavation's findings relate to parts of foundations, handmade pottery, masses of clay, two clay spindle whorls, a burial and a few animal bones. The findings indicate that a hut settlement had been established on the north slope of the Ayia Marina hill. The huts were constructed with stone foundations and a superstructure of perishable materials such as reeds, branches, skins. (Adam 1998; Adam 1999; Siozou 2022). During the excavation a sample of coal, which was collected from the destruction layer in section B, was sent to NCSR Demokritos. The results of the analysis gave the dating of 3330-3030 BCE (Adam 1999; Adam 2002; Siozou 2022; Vasileiou 2018).

A large quantity of handmade pottery was gathered from both sections. The majority comprises sherds of utilitarian vessels. They are thick-walled sherds of coarse material. Their clay has many inclusions. Many of the sherds have plastic, engraved and inlaid decoration (Figure 2). Together with the sherds of the large utilitarian vessels, more elaborate sherds were also found. They are thinner sherds, with good surface smoothing, cleaner clay and are better fired. They are all small vessel sherds. Few of the sherds have plastic and inlaid decoration (Figure 3). In section A, only in its upper archaeological layer, a few sherds of unpainted orange-red pottery were found. They are small and very thin sherds. Their clay is clean and well fired (Figure 4) (Siozou 2022; Vasileiou 2018).

The results of the ceramics study so far indicate homogeneity between the sherds of section B and the sherds from the deeper layers of section A. Ceramics from the upper layers of section A have different characteristics. In addition to the thin-walled orange-red pottery sherds found only there, differences are also found in the construction, shapes and decoration of the utilitarian vessels (Figure 5).

It is difficult to date the above pottery to a specific prehistoric period. Handmade pottery in Epirus has a relatively small differentiation, with similar categories and shapes for many centuries and therefore cannot be included in a specific period solely on the basis of

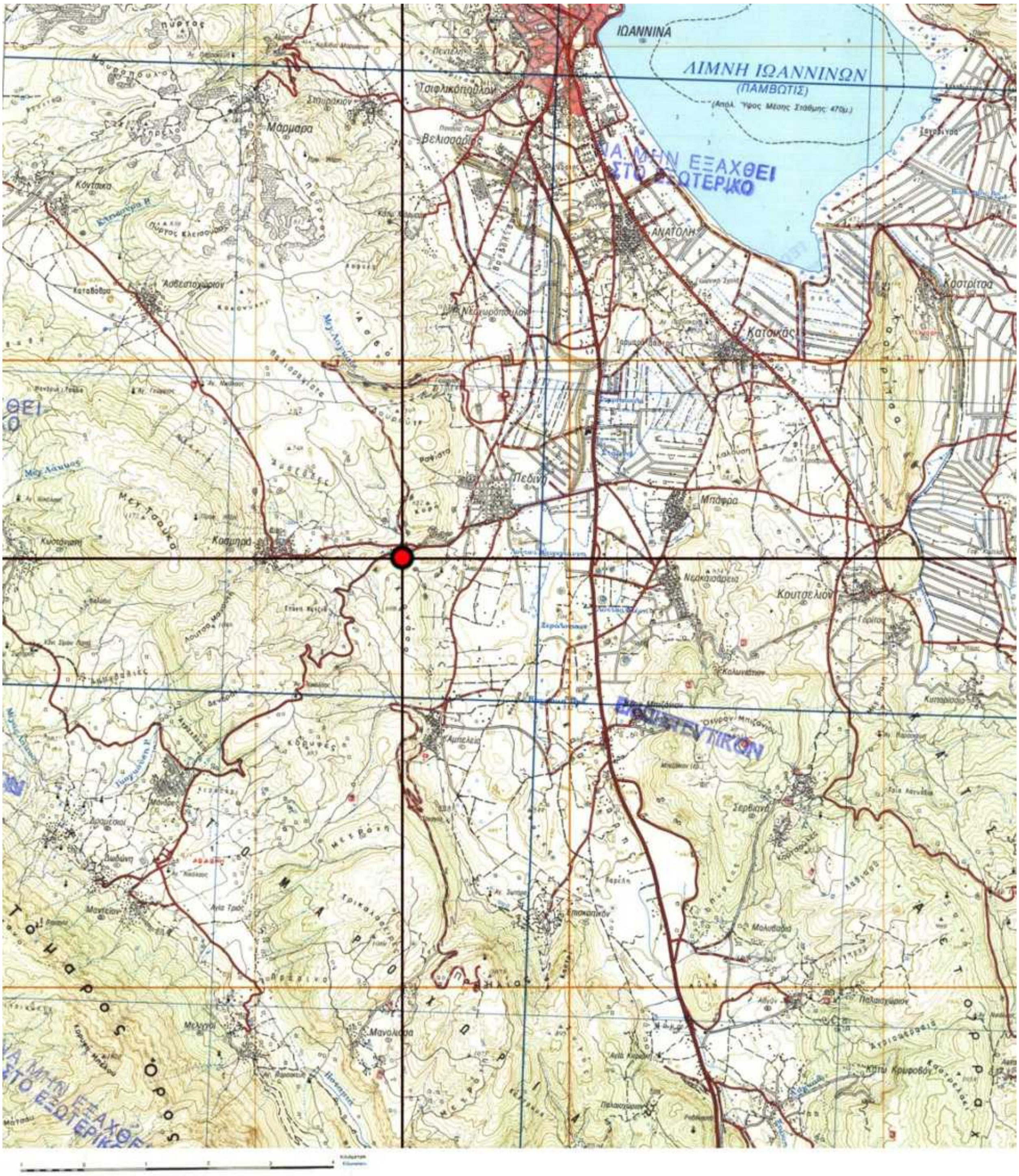

Figure 1. The site of the Ayia Marina settlement

stylistic criteria (Tartaron 2004; Forsén 2016). Findings, at the beginning of the excavation, pointed at the Early Iron age, due to the similarity to the findings of other archaeological sites in the vicinity, like in Kastritsa and Krya, Ioannina (Adam 1998) but the results of the radiocarbon dating, have pushed the time frame of the archaeological remains back to the Early Bronze age. Thus, the OSL dating method was decided to be used, that could give a more precise time context of the prehistoric site.

Materials and methods

In the above context, nine sherds from different depths and layers, were selected from sections A and B. Sherd coded SV-1 was from upper layer of section A,

Figure 2. Thick-walled sherds of utilitarian vessels (section A, B)

Figure 3. Thinner more elaborate sherds (Section A, B)

while sherds SV-2,3 and 4 were from the lower layers of section A. Finally, sherds SV-5,6,7,8 and 9 were collected from section B.

All sherds were brought to the Archaeometry Center of the University of Ioannina in order to be dated with the use of the OSL method. The OSL method involves two steps of measurements and data analysis. The first step is the assessment of the dose absorbed by the quartz grains inside the ceramic sherd induced by the natural radioactivity of the sherd and the surrounding sediments.

This dose is known as equivalent dose D_e or palaeodose. Sherds were treated to obtain pure quartz grains. The 2 mm-thick outer part of the sherds was scratched and discarded and pieces from the inner part were ground to powder. Powder was sieved and grains of 100-150 μm

Figure 4. Sherds of unpainted orange-red pottery from the upper layers of section A

mesh were obtained and treated chemically as follows (Tsodoulos *et al.* 2016).

Few grams of the grains were placed in plastic tubes, and solutions of HCl, H_2O_2 and HF were added successively in order to eliminated carbonates, organic matter and feldspar. Also, during the HF treatment, the ~20 μm outer layer of the quartz grains was etched in order to eliminate the alpha radiation contribution to the luminescence signal. After several water washes between the chemical treatments, the quartz grains were purified. Small quartz aliquots were placed on stainless steel disks and were measured for OSL signal in a TL/OSL-DA-20 reader (Riso), following the SAR protocol (Murray and Wintle 2000). This protocol includes preheat of the aliquots at 240° C, reading of the natural OSL signal with blue LEDs stimulation at 125° C, irradiation with a test dose and finally OSL signal reading under the same conditions with the natural signal. This cycle was repeated after giving increasing doses in order to construct the dose response curve for each aliquot. Analysis of the OSL signals provided the equivalent dose D_e absorbed by the quartz grains of the sherds during their burial period.

The second step is the determination of the annual dose rate of the natural radioactivity of the surrounding environment. Usually, soil from the surroundings is used for the dose rate determination. In the present study, due to the lack of soil, the remaining parts of the sherds were ground and a quantity of 30-70 g depending on the availability of the sample, was placed in a plastic container of 20-50 ml volume, calibrated for radioactivity measurements. All natural radioactivity measurements were performed using a broad energy HPGe γ detector (Canberra) with relative efficiency >26% and energy resolution of 1.8 keV at 1.33 MeV. Natural radioactivity of the decay series of ^{238}U, ^{235}U, ^{232}Th and ^{40}K was transformed to dose rates using updated conversion factors (Liritzis *et al.* 2013), summing up to the total dose rate per sample. Ages of the sherds were calculated by dividing the equivalent dose D_e with the total dose rate.

Results and discussion

Total dose rates in Gy/ky, mean values of the equivalent doses in Gy and the calculated ages for each sherd in years before present (B.P.) and BCE, are presented in Table 1.

Due to fact that the OSL measurements were conducted long time after the collection of the pottery sherds, water content was thought to be negligible since pottery collection was stored in dry store place. Also due to limitation of the shreds availability no water, saturation experiments were performed since this could result in dose alterations. Thus, water content of the sherds was assumed to be 8% and was used for dose rate corrections. For each sherd, 18 aliquots were prepared and measured to determine the equivalent dose D_e. All values are expressed with the associated uncertainties (1σ).

In two cases (SV-2, and SV-6) extreme palaeodose values (very high) were excluded and the rest with a

Table 1. Water content (assumed to be 8%), number of aliquots used to determine the age of the sherd, total dose rate, equivalent dose De and calculated ages. [1] mean values ± 1σ, [2] B.P. = Before present, 3number of aliquots used for the calculation of the mean age values.

	Water content	Number of aliquots	Total dose rate	Equivalent dose D_e	Age (years ± 1σ)[1]	
Sherd code	(%)	#	(Gy/ky ± 1σ)	(Gy ± 1σ)	B.P.[2]	BCE
SV -1	8	18	2.973 ± 0.078	9.9 ± 0.3	3300 ± 100	1300 ± 100
SV -2	8	18	2.412 ± 0.065	14.5 ± 3.1	5600 ± 200	3600 ± 200
SV -3	8	18	2.601 ± 0.048	14.6 ± 0.8	5600 ± 100	3600 ± 100
SV -4	8	18	2.340 ± 0.073	13.8 ± 1.1	5900 ± 300	3900 ± 300
SV -5	8	18	3.067 ± 0.084	16.5 ± 0.7	5100 ± 200	3100 ± 200
SV -6	8	18	2.683 ± 0.087	18.1 ± 14.1	5200 ± 300	3200 ± 300
SV -7	8	18	2.470 ± 0.053	13.2 ± 0.9	5500 ± 100	3500 ± 100
SV -8	8	18	2.345 ± 0.093	14.4 ± 0.7	5900 ± 200	3900 ± 200
SV -9	8	18	2.639 ± 0.085	12.7 ± 0.4	5000 ± 200	3000 ± 200

Figure 5. Sherds of utilitarian vessels from the upper layers of section A

low variation (<8%) were used to calculate mean values. The number of aliquots used to calculate the mean age values are presented in parenthesis, in the 6th column of Table 1. Thus, although in these cases the D_e variation is higher than 8%, up to 80%, the calculated ages are expressed with less than 8% associated error. The equivalent doses in the quartz grains of the sherds were found to vary from 9.9 ± 0.3 Gy to 18.1 ± 14.1 Gy and the total dose rates calculated from the sherd natural radioactivity, varied from 2.340 ± 0.073 to 3.067 ± 0.084 Gy/ky. The values of the calculated dose rates exhibit a medium variation among the sherds, but this could be attributed to the differences of the strata of origin, with ages varying from ~1 ka in section B to up to 2.6 ka in section A.

The sherd from the upper layer of section A (SV-1) dates from the end of the 2nd millennium BCE (1300 ± 100 BCE). The results of the analyses of sherds SV-2 to SV-9, from the lower layers of the section A and the layers of the section B, show that the ages are in the period of the 4th millennium BCE. Sherds SV-2 and SV-3, from the layer of the foundations in section A, have shown similar ages, 3600 ± 300 BCE. Sample SV-4 with the age of 3900 ± 400 BCE was below the foundations also from section A. From the sherds of section B, SV-5 was from the destruction layer with age 3100 ± 200 BCE and agrees with the radiocarbon date of the same layer (3330-3030 BCE). Sherds SV-6,7,8, and 9 were from the layer of the foundations discovered in the section, with ages varying from 3000 ± 200 to 3900 ± 200 BCE.

The results of the analyses place the settlement in the Final Neolithic - Early Bronze Age. However, the settlement also has a newer phase dating to the Late Bronze Age.

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New Evidence for the Timeframe of the Architectural Remains at the Archaeological Site of Vathy, Astypalaia

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Abstract: The archaeological site of Vathy is situated in the northern part of the island of Astypalaia, on the rocky peninsula at the entrance to the Vathy gulf. After preliminary research in 2008, systematic surface survey and investigations since 2012 have revealed an extensive archaeological site that occupies the easternmost part of the Pyrgos / Elliniko promontory. Prehistoric boulder-built walls, a Hellenistic tower complex, an Early Christian basilica and other manmade structures are still visible in the area.

In the present study, five sediment cores and surrounding soil from different depths and strata of recently excavated areas on the promontory were dated using the Optical Stimulated Luminescence (OSL) method. Palaeodoses D_e and radioactivity measurements were conducted at the Archaeometry Centre of the University of Ioannina. Results show a timeframe for human habitation at the site that spans from the Final Neolithic / Early Bronze Age (4th / 3rd mill. BC) to the Early Christian era (5th c. AD).

KEYWORDS: VATHY-ASTYPALAIA, OSL DATING, EARLY BRONZE AGE, FINAL NEOLITHIC, ISLAND CULTURES

Introduction

Vathy, on the island of Astypalaia, is a naturally protected peninsula controlling the narrow access from the open sea to the gulf of the same name, thus ensuring full monitoring of a wide area of sea and land (Figure 1a-b). Continuous human habitation (Figure 1c) over the millennia indicates that Vathy was an important harbor and surveillance point for sea routes in the central Aegean (Vlachopoulos 2017; Vlachopoulos and Angelopoulou 2019).

At the easternmost tip of the peninsula, on Cape Pyrgos / Elliniko, an acropolis was founded in the late 4th/ early 3rd millennium BCE, the boulder-built circuit walls and megalithic retaining walls of which are visible today. Numerous rock engravings, several Π-shaped constructions along the coasts with pot burials of newly-born infants, large quantities of pottery dated to the late 4th and 3rd millennia BCE, marble figurines, obsidian artefacts, stone tools and vessels brought to light in systematic excavations at the site, redefine the geographical horizon of Early Cycladic culture, in which Astypalaia evidently participated.

On the upper level of the headland, a guard tower with surrounding ancillary facilities was erected in the second half of the 4th century BCE. At some time, the tower complex was demolished and probably in the 5th century AD it was transformed into a three-aisled Christian basilica with a narthex. Another church was erected on top of the basilica, after a severe earthquake, and some Christian graves mark the continuity of faith in Medieval times.

As briefly described above, human activity has been uninterrupted at Vathy since the Prehistoric times, continuing onto Classical and Christian times, offering to research an island-site palimpsest of great importance. Earlier OSL studies, dating stones of boulder-built walls and soil, point to human activity at the site from the Final Neolithic / Early Bronze Age (*ca* 4th / 3rd millennium BCE) up to Middle Byzantine times (11th c. CE) (Vlachopoulos *et al.* 2016), verifying the chronological phases that resulted from the study of the archaeological findings. In order to strengthen these previous findings regarding the various phases of habitancy or use of the site, further OSL dating studies were decided to be conducted. For this, sediments were collected from different archaeological strata during the excavation season of September 2018 (Figure 1c) at the site, and OSL dating of the samples was conducted in late 2018.

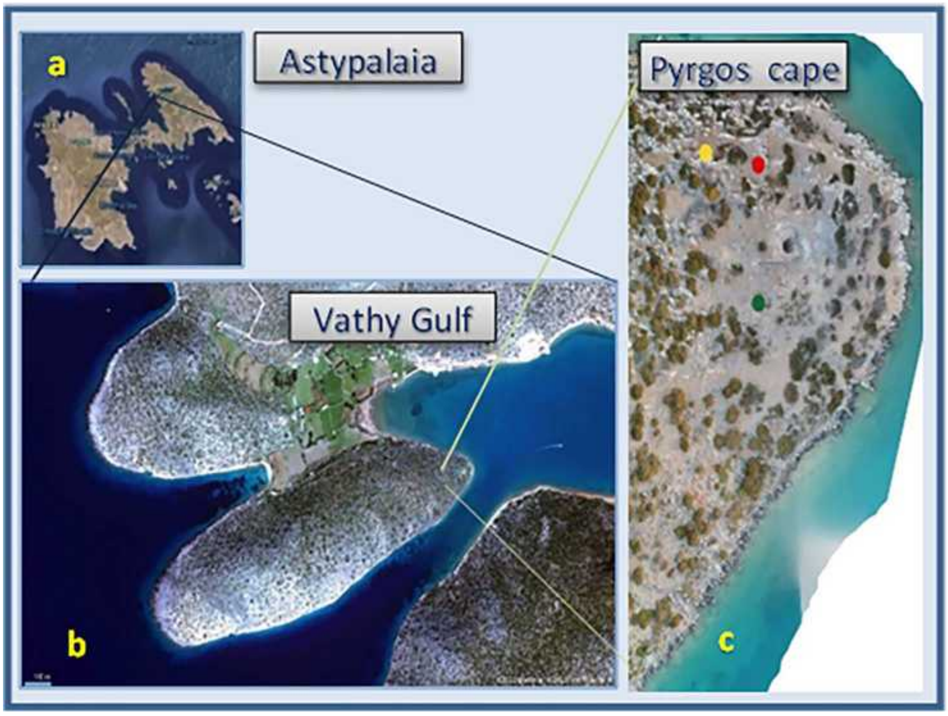

Figure 1. Astypalaia. Pyrgos promontory in the gulf of Vathy. The red bullet indicates the sampling site of AST-D1 and AST-D2 (Trench 7); the yellow bullet indicates the sampling site of AST-D3 and AST-D4 (Trench 6); and the green bullet indicates the sampling site of AST-D5 (Trench 5).

Materials and methods

Although we had the opportunity to collect stone samples from the inner parts of the wall remains of the site, to date the walls from the quartz grains of the outer layers of the stones, as we did in earlier studies (Vlachopoulos *et al.* 2016), we have chosen to date sediments from different strata of the site, since this method is more accurate and well established.

Five sediment cores and surrounding soil samples collected during the excavation campaign of 2018, were brought to the Archaeometry Center of the University of Ioannina in order to be dated by the method of Optical Stimulated Luminescence (OSL). Sediment cores coded AST-D1 and AST-D2 were collected in Trench 7 from two distinct layers underneath a thick boulder-built wall (K14) running N-S on the upper level of the acropolis. This wall joins the Great Retaining Wall oriented E-W, creating a rectangular terrace to which the rock-engraved gates lead (Figure 1c, red dot). Wall K14 is founded partly on the bedrock and partly on accumulated fill (epichosis), the two stratigraphic horizons of which were sampled (Figure 2). Sediment cores coded AST-D3 and AST-D4 were collected from the stratigraphic horizons of the nearby Trench 6 (Figure 1c, yellow dot). Finally, one sediment core, coded AST-D5, was collected from Trench 5 and corresponds to the destruction horizon of the Early Christian basilica of Vathy (Figure 1c, green dot).

The OSL method involves two steps of measurements and data analysis. The first step is to assess the equivalent dose or palaeodose D_e absorbed by the quartz grains inside the sediments induced by the natural radioactivity of the surrounding soil. To obtain pure quartz grains, sediments were treated as follows. Sediment soils were dried at 50° C, ground and passed through sieves in dark room. Grains of 100-150 μm mesh from soil powder were obtained and chemically treated with dissolution in 8% HCl and 30% H_2O_2 to eliminate carbonates and organic material and finally in 45% HF to eliminate feldspars (Tsodoulos *et al.* 2016). The purified quartz grains were measured for OSL signal following the SAR protocol (Murray and Wintle 2000). Up to fifteen aliquots of each sample were preheated at 240° C and OSL signal derived from blue LEDs stimulation, was acquired at 125° C for 40 sec. Afterwards a test dose ~5 Gy, was delivered, and the measuring protocol with a cut heat at 160° C was repeated. Finally, a cycle of increasing delivered doses up to 50 Gy (regeneration doses) and test doses was repeated to acquire the dose response curve and calculate with interpolation the equivalent dose of each aliquot. The assessed equivalent doses varied widely from 10 to 47%, which may be attributed to partially bleached quartz grains.

Thus, the outliers were excluded from the calculation of the mean equivalent doses for each sample. All OSL measurements were performed in a TL/OSL-DA-20 reader (Riso). Analysis of the OSL signals provided the equivalent dose D_e absorbed by the quartz grains.

The second step of the OSL method is to determine the annual dose rate from the natural radioactivity of the surrounding environment. Soil from the surroundings was used for the dose rate determination. Each sample was dried at constant weight at 105° C, sieved and a fraction of <500 μm grains (50-70 g) was placed in a plastic container of 50 ml volume, calibrated for radioactivity measurements.

Figure 2. Excavation of Trench 7. Under the foundations of boulder-built wall K14 two sediment cores AST-D1 and AST-D2 were obtained. Calculated ages are also presented.

Natural radioactivity measurements were conducted using a broad energy HPGe γ detector (Canberra) with relative efficiency >26% and energy resolution of 1.8 keV at 1.33 MeV. Natural radioactivity of the decay series of ^{238}U, ^{235}U, ^{232}Th and ^{40}K was transformed to dose rates using updated conversion factors (Liritzis *et al.* 2013), summing up to the total dose rate per sample. Ages of the sediments were calculated by dividing the equivalent dose D_e with the total dose rate.

Results and discussion

For each sample up to 15 aliquots were prepared and measured to determine the equivalent dose D_e. As mentioned above, due to the high variation of the assessed equivalent dose, the mean values were calculated from fewer aliquots (10-14) excluding the aliquots that seem to be outliers due to partial bleaching. Total dose rates in Gy/ky, mean values of the equivalent doses in Gy from the total of the aliquots and from

Figure 3. Excavation of Trench 6 near the boulder-built wall K14 where two distinct layers were sampled providing samples AST-D3 and AST-D4. Calculated ages are also presented.

Figure 4. Excavation of Trench 5 at the narthex of the Early Christian basilica where sediment AST-D5 was collected. Calculated age is also presented.

Figure 5. a) Early Bronze Age pyxis fragment with incised decoration, b) Early Bronze Age handle of stamnos.

Table 1. Sample description, number of aliquots used to determine the age of the sample, total dose rate, equivalent dose and calculated ages. [1] mean values ± 1σ , [2] B.P. = Before present, [3]Number of aliquots used for mean age calculations excluding outliers.

	Number of aliquots	Total dose rate	Equivalent dose, D_e	D_e, excluding outliers	Age (years ± 1σ)[1]	
Sample code	#	(Gy/ky ± 1σ)	(Gy ± 1σ)	(Gy ± 1σ)	BP[2]	BCE-CE
AST-D1	15	2.578 ± 0.059	12.4 ± 5.5	10.9 ± 2.2 (13)[3]	4200 ± 850	2200 ± 850 BCE
AST-D2	12	2.396 ± 0.044	10.4 ± 1.9	10.4 ± 1.7 (10)[3]	4400 ± 800	2400 ± 800 BCE
AST-D3	15	2.996 ± 0.064	10.7 ± 5.1	9.1 ± 0.7 (14)[3]	3050 ± 250	1050 ± 250 BCE
AST-D4	15	2.989 ± 0.063	13.4 ± 1.3	13.2 ± 1.0 (14)[3]	4500 ± 400	2500 ± 400 BCE
AST-D5	15	1.792 ± 0.045	3.4 ± 0.7	3.2 ± 0.5 (14)[3]	1800 ± 300	200 ± 300 CE

those after excluding outliers (4th and 5th columns), and calculated ages for each sediment, in years before present (BP) and BCE (6th and 7th columns), are presented in Table 1. All values are expressed with the associated uncertainties (1σ). Total dose rates varied from 1.792 ± 0.045 to 2.996 ± 0.064 Gy/ky while mean values of assessed equivalent doses (excluding outliers) varied from 3.2 ± 0.5 to 13.2 ± 1.0 Gy.

Sediment AST-D1 shows an age of 2200 ± 850 BCE while sediment AST-D2, below AST-D1, shows an age of 2400 ± 800 BCE. Both OSL dates given to these stratigraphic levels, i.e. *ca* 2200 BCE for the upper layer (D1) and *ca* 2400 BCE (D2) for the lower (Figure 2), match satisfactorily with phases of the Early Bronze Age pottery (Figure 5a, 5b) unearthed in Trench 7.

Sediments AST-D3 and AST-D4 from the nearby Trench 6 show ages 1050 ± 250 BCE and 2500 ± 400 BCE, respectively, which are consistent with their stratigraphical sequence. The OSL date (*ca* 2500 BCE) for the lower stratigraphic horizon (D4) of the trench (Figure 3), also matches to the Early Bronze Age pottery found here.

Finally, sediment AST-D5 collected from Trench 6 and the destruction horizon of the Early Christian basilica of the promontory (Figure 4), which show age 200 ± 300 CE, likewise matches, in the margin of the error, to the date of the monument (*ca* 400 CE).

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Journey to Mystras: The Digital Narrative of the Urban Development of the Castle City

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Summary: A map is a static representation of a physical space. Respectively, the study of human activity through time is in turn the subject of the science of archaeology. Combining and comparing the spatial and temporal evolution of human activity in an environment is an exciting aspect of the study of human history. This study aims to provide a visualization and projection of the temporal evolution of the Byzantine Castle of Mystras using modern spatial technologies.

The city of Mystras is the best-preserved Byzantine state in Greece also known as the "Castle City of Mystras" (Ministry of Culture, n.d.). Located in western Laconia, 6km southwest of Sparta, it was founded by the Frank commander William II of Villehardouin in 1249. Villehardouin built a castle fortress on top of Myzithra Hill to control the Valley of Evrota. The castle expanded and its surrounding area was populated creating the city of Mystras which eventually developed into the powerhouse of the Peloponnese, capital of the Despotate of Morea. Mystras came under Byzantine rule in 1259 and then flourished through a significant number of phases, different rulers and population changes (Sinos 2009). These changes are reflected in the city's urban fabric (Arvanitopoulos 2004). This study aims to tell the story of Mystras through a digital depiction of the different phases of the city using a digital spatial application.

KEYWORDS: GIS, UAV PHOTOGRAMMETRY, MYSTRAS, CULTURAL HERITAGE MANAGEMENT, DIGITAL APPLICATIONS

Introduction

After the first fall of Constantinople in 1204 during the Fourth Crusade, the Franks and Latins divided the territories of the Empire along with the Peloponnese which was granted as a Feud to the Villehardouin house. The Franks conquered Lacedaemonia, Medieval Sparta, in 1207, and continued to subjugate a significant part of the Laconia prefecture excluding Monemvasia, the lands of the Tsakonians in Parnon and the Slavic Milingans in the Taygetos mountain range. The city and castle of Monemvasia were conquered by the Frankish Prince of Achaia in 1246, after a three-year long siege. On his return from Monemvasia in 1249, William II built, in a key position to control the valley of Evrotas, six kilometers southwest of Sparta, an emblematic fortress at the top of Myzithra Hill. Following the natural morphology of the land, it occupies the entire rocky peak. Structurally, the fortress is divided into three sections, the exterior wall, the interior wall and a large building within the second enclosure. The castle has only a single gate ensuring the control of the entrance to the outer fortification, of the exterior wall. The sections correspond to defense zones, the exterior wall or outer enclosure, a second enclosure internally significantly smaller than the outer one and a rectangular two-storey building (Arvanitopoulos 2004) located at the south east of the interior wall. The Frankish citadel is the main defense complex in the overall organization of the city (Georgiadis 2002).

Mystras soon came under Byzantine rule when in 1259 William II was captured by the Byzantine forces during the Battle of Pelagonia. He negotiated his release, during which he bestowed the castles of the Great Maina, Monemvasia and Mystras to the Byzantine Emperor Michael VIII Palaiologos (Kalonaros 1940). In 1262 the Franks finally surrendered Mystras to the Byzantine forces. Despite their agreement with the Byzantines, William II later continued to claim Mystras, prolonging the tension in the area, leading part of the population of Lacedaemonia to flee under the shadow of the castle where they felt more secure (Chatzidakis 1992).

This generalized insecurity and impending population growth in the area under the castle led to the actual "genesis of Mystras" between 1262 and 1264 (Arvanitopoulos 2004). At the same time, the Metropolis of Lacedaemonia was transferred to Mystras with the construction of the Metropolitan Church of Agios Dimitrios. During the period 1259 to 1349, Mystras became the seat of the Byzantine general, "Sevastocrator", who ruled the entire Peloponnese and was replaced yearly. The new city, Chora, was created in the area below the Frankish Castle summit and was fortified after 1262 (Ministry of Culture, n.d.).

In 1349 Mystras was upgraded to a Despotate, becoming one of the most important provinces of the weakened Byzantine Empire. The Emperor Ioannis Katakouzinos VI appointed his second son Manouel Despot of Mystra, thus founding the Despotate of Morea with Mystras as its capital. What followed was an important period of prosperity for the city, which played an important role in Byzantium until the fall of the Empire (Sinos 2009). The city's expansion and evolution into the Despotate of Mystras made it the epicenter of Byzantine power in the Peloponnese strengthening its bond with the empire's capital Constantinople.

After the fall of Constantinople in 1453, the Turks occupied the northern Peloponnese and in 1460, under the suffocating pressure from the Ottomans the besieged surrendered Mystras to the Turks. Under Ottoman rule, Mystras held an important position in the Ottoman Empire and was one of the most important silk production centers in the Eastern Mediterranean (Sinos 2009; Runciman 1986).

In 1687 and until 1715 Mystras was for a short period under the reign of the Venetians who occupied the Peloponnese and went back to Ottoman rule in 1715 during which a significant part of the Greek population was killed or forced to leave (Arvanitopoulos 2004). Following the commencement of the Greek Revolution in 1821 and the establishment of the Greek State in 1834, the new city of Sparta was founded and a large part of the inhabitants of Mystras left the Castle City, which was declared in 1921 a prominent Byzantine monument. The last inhabitants finally left Mystras in 1953. In 1989 the archeological site was included by UNESCO in the list of World Cultural Heritage sites (UNESCO), being the best-preserved Byzantine state of Greece (Ministry of Culture, n.d.).

Methodology

The historical development of the Castle of Mystras is multidimensional, including political, economic and spatial parameters. This multifaceted development is distinguished based on the political situation of the city into seven periods. Chronologically the periods correspond to,

I. 1249 - 1259 From the establishment of Mystras by William II to the surrender to the Byzantines
II. 1259 - 1349 Late Byzantine I - First Byzantine rule occupation of Mystras
III. 1349 - 1460 Late Byzantine II - Second period of Byzantine domination where the city is politically upgraded to Despotate.
IV. 1460 - 1687 Post-Byzantine I - First period of Ottoman rule
V. 1687 - 1715 Venetian period
VI. 1715 - 1821 Post-Byzantine II - Second period of Ottoman rule
VII. 1821 - 1953 From the commencement of the Greek Revolution until the Castle City is abandoned by its last inhabitants.

The declared by UNESCO archeological site of Mystras covers more than 540 acres (54.43 hectares), which in combination with the extensive vegetation and the morphology of the area, extending on a sharp slope in some parts, means that detailed mapping of the entire archaeological site should be carried out using advanced technological equipment (Forte *et al.* 2020). In this study the Acropolis, where the Castle of Mystras is located, is examined. The equipment used to map the acropolis area includes a DJI Mavic 2 Pro unmanned aerial vehicle (UAV) and a Top Con GR5 geodetic station GPS. The resulting images are processed using Agisoft Metashape Pro photogrammetry software and the digital maps are developed using a Geographic Information System (GIS), ArcGIS 10.4.

The necessary images for the photographic overview of the castle and the surrounding area of 5,000 sq.m., were shot using the UAV at two different heights from the ground, 150m. and 90m. The study area of the citadel was divided into two parts and Ground Control Points (GCPs) were placed on site in order to be visible from the UAV. GCPs, Akr1, Akr2, Akr3 and Akr4 were first placed in the northern part of the castle during the first flight. For the second flight and image collection on the south side GCPs, Akr5, Akr6, Akr7 keeping the Akr4 point constant were placed. A double grid flight pattern (Figure 1) was implemented with two passes, west to east and north to south using the UAV navigation application DJI Go and maintaining 75% overlapping images (Gutiérrez 2016). For the relevant geo-reference, 7 GPCs were placed, the exact coordinates of which were measured using the

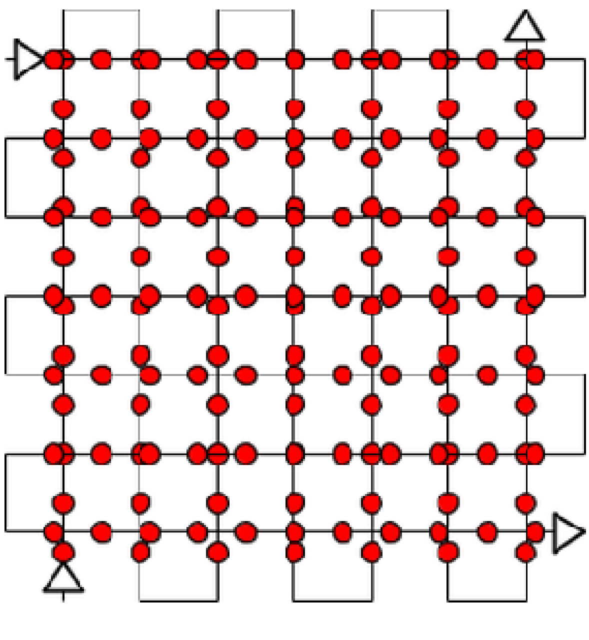

Figure 1. Double grid UAV flight plan

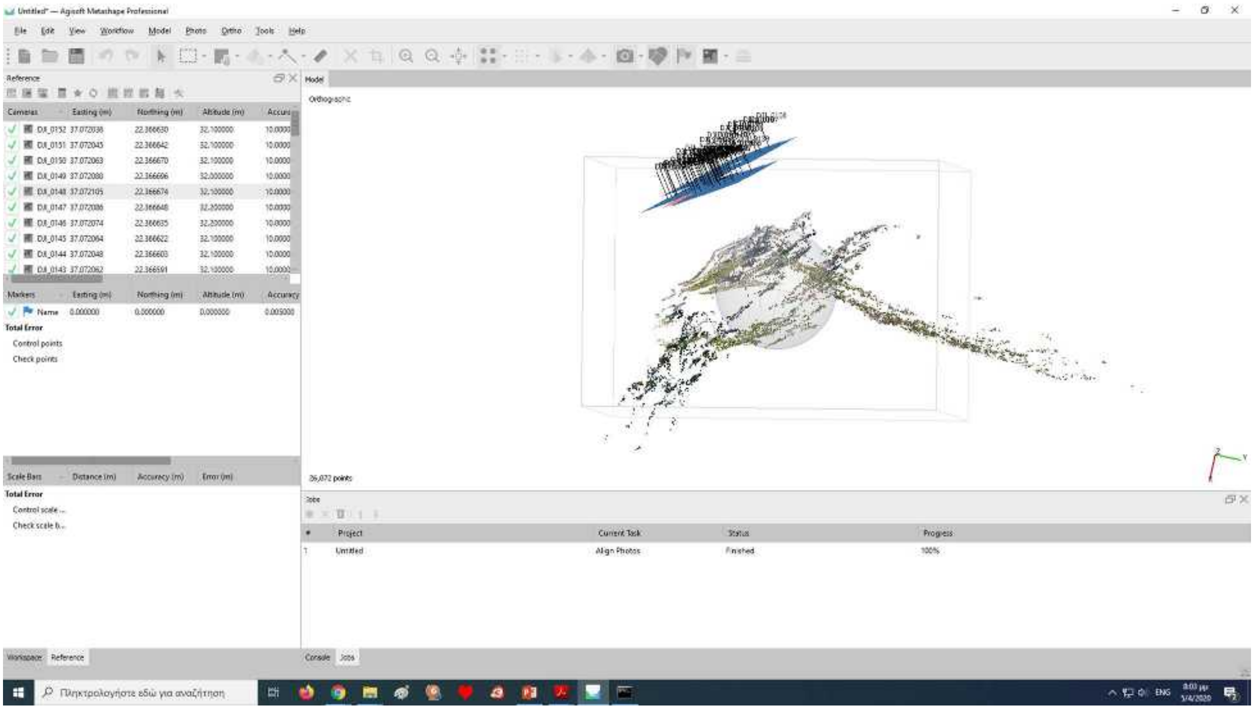

Figure 2. Camera positions, alignment and sparse point cloud

GPS Top Con GR5 GNSS receiver. All data was collected in the Greek coordinate system EGSA '87.

Overall, in order to record the Acropolis photographically 294 photos from the UAV with a resolution of 5472 X 3648 pixels and seven GPCs were required. The images were then transferred via computer to the Agisoft Metashape photogrammetric analysis program. The process of creating an orthophoto map of the entire acropolis of Mystras from multiple photographs of individual parts is a complex computational process. Following image (cameras) alignment, a rough three-dimensional model of the space is obtained in the form of a sparse point cloud (Figure 2). Markers are then added in the workplace of the model to the respected GCPs directly to the images where they are visible using the recorded coordinates from the GPS during the survey.

The position of the markers in each image must be adjusted separately to confirm the correct placement in the images and the model. With this process the model is georeferenced minimizing relevant errors. Based on the above data, a dense point cloud of the acropolis develops (Figure 3).

Upon completion of model's dense point cloud, the detailed three-dimensional model of the examined area is created (Figure 4) as well as the digital elevation model (DEM). The final product is the high-resolution georeferenced image of the acropolis, its orthophoto (Meouche *et al.* 2016).

Comparing and presenting temporal changes spatially requires the digitization of historical maps, the availability of which for this region is very limited. To create a dynamic map, the historical maps are digitized through scanning and transferred to the GIS by recognizing elements of the current landscape as reference points and scale matching. The orthophoto created by the photogrammetry software composes the basemap of the area on which the historical maps will be transferred, using reference points and building different layers of information. Separate layers in the ArcGIS environment contain different elements of information, thus composing an important database of historical information (Anagnostakis *et al.* 2014).

In the case of this study the historical topographic plan of the Myzithra hill during the 2nd Venetian Empire was used, F. Levasseur (Gnmani, Racolta, αρ. XXXIV. Forteza e Borgo di Mestra) (Figure 5) as well as topographical plans from the Archaeological Ephorate of Laconia.

The digital scan of the topographic plan is placed to scale and aligned over the orthophoto basemap with and georeferenced using reference points. The overlapping layer with the historical topographical plan will give results compared to Levasseur's record in relation to the archaeological study and the remains.

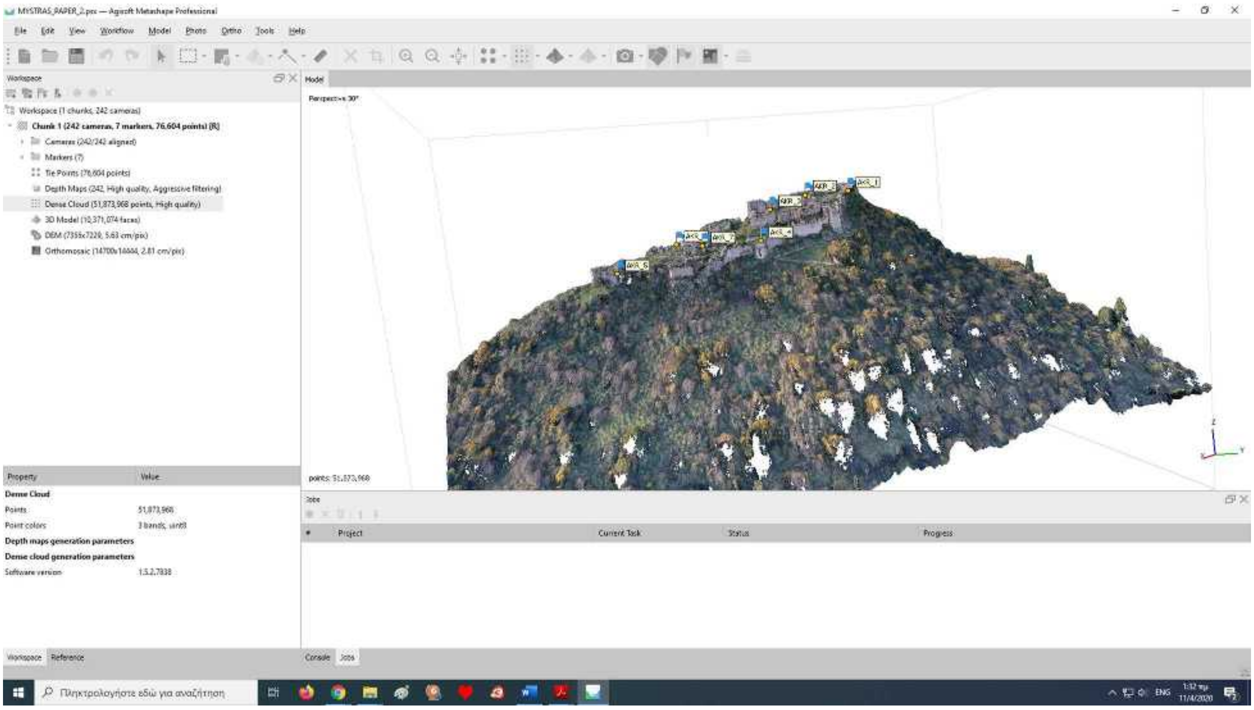

Figure 3. Dense point cloud with markers

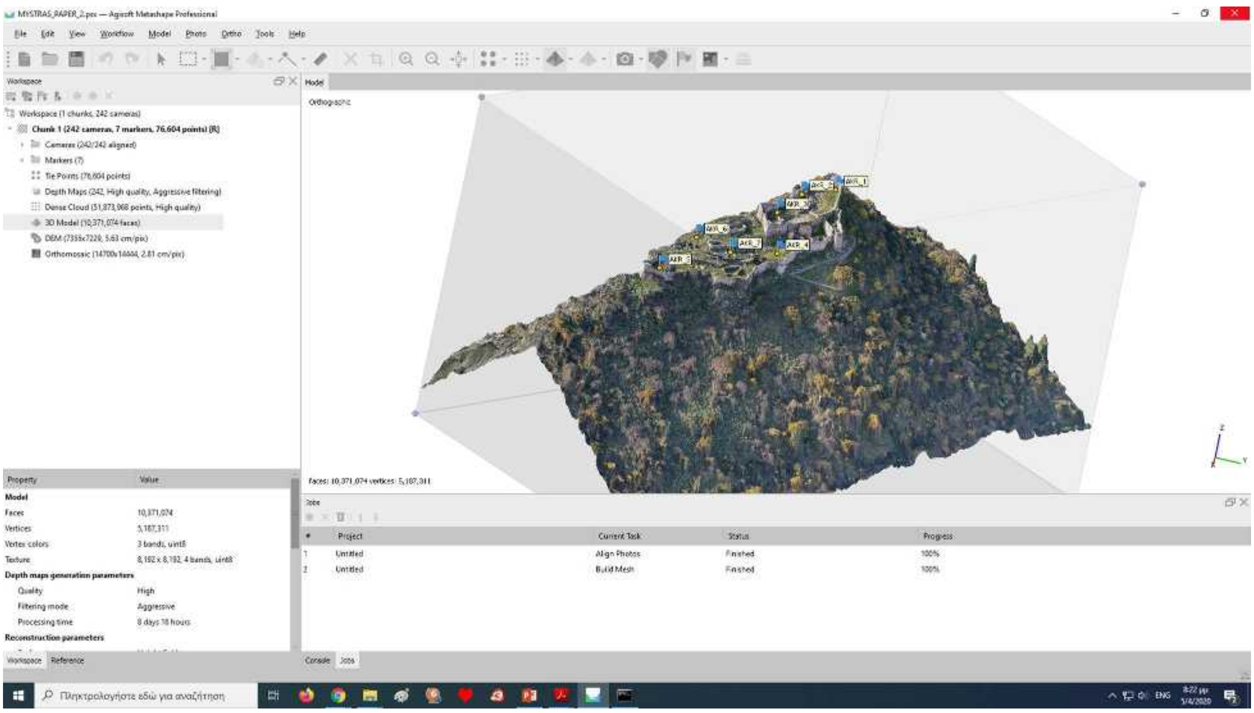

Figure 4. 3D model of Acropolis

To visualize the phases of the citadel, different shapefiles are created for each period and the respective buildings are located according to the archaeological documentation. Specifically, in the citadel there are structural remains and fortification remains mainly from the first period when William II built the citadel and the post-Byzantine period of Ottoman rule (IV and VI). during the short Venetian occupation (period V) there is no intense activity in the citadel. Following the Greek Revolution and the establishment of the modern

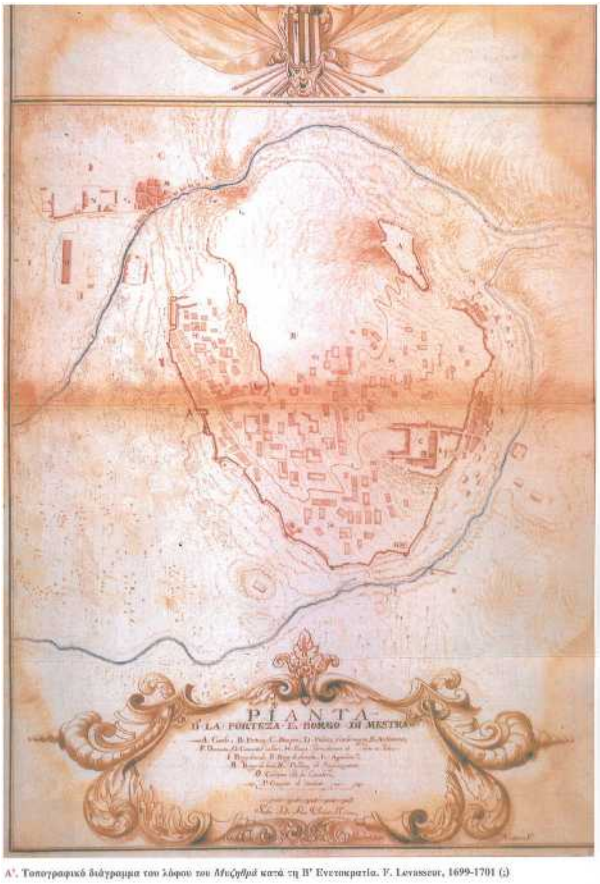

Figure 5. Topographical Site Plan of Mystras. F. Levasseur (Gnmani, Racolta, αρ. XXXIV. Forteza e Borgo di Mestra)

Figure 6. Digital map of Latin occupation of Mystras

Greek state Mystras is gradually abandoned for the modern city of Sparta in the valley.

Results

From the available bibliography and archaeological study of the castle of Mystras the general categorization of the remains within the Acropolis by time period is shown in Table 1 (Arvanitopoulos 2004; Sinos 2009; Chatzidakis 1992; Georgiades 2002; Runciman 1986). During the short period of Venetian rule of the city there was no reconstruction or intervention work regarding the fortifications (Arvanitopoulos 2004) therefore the specific period, 1687 – 1715, is excluded from the timeframe.

During the first period of the city of Mystras the castle fortress is built. The initial structures of William II include the exterior and interior fortification walls, the main tower Φ1 and main gate (Π), the commander's housing (K), cisterns and towers on the exterior wall, Φ4 and Φ5 (Figure 6).

Following the unrest and hostilities in the region the population of Lacedemonia gradually moves to the area of the north east slope of Myzithra under the shadow and security of the castle fortress above (Sinos 2009). As the population continuously grows, residences are established even further from the Acropolis creating the area of Kato Chora (Lower City) which too is eventually fortified. During the Late-Byzantine period the ramparts of the castle were reinforced, the main tower Φ1 is reconstructed and additional buildings are added (Figure 7).

The Ottoman period is the most active in regard to interventions to the Castle of Mystras. A number of building remains found in the area of the outer enclosure are from this period. The west tower Φ5 is reconstructed from guard watch to tower (Arvanitopoulos 2004). The exterior wall directly west to the south west corner of the main tower is extended (T3). The activity is visible in the digital map of the period (Figure 8).

It is not always clear where the Acropolis remains can be accounted to. For example, the vaulted chambers east of the Chapels are mentioned in the plan from the Venetian occupation of Mystras, providing usage of the structures, gunpowder storages. On the other hand, reference to when they were constructed cannot be found. Taking under account that gun powder was

Table *1 Acropolis remains categorization*

Remains	Code	Time Period	Era
Exterior Fortification Wall	EFW	1249 - 1259	Latin Occupation
the second fortification wall within the exterior	IFW	1249 - 1259	Latin Occupation
Garrison commander's housing	K	1249 - 1259	Latin Occupation
enclosed cistern beneath K	K7	1249 - 1259	Latin Occupation
Gate to the exterior fortification wall	ΠΛ	1249 - 1259	Latin Occupation
Main Tower above gate	Φ1	1249 - 1259	Latin Occupation
South east watch tower	Φ4	1249 - 1259	Latin Occupation
Cistern adjacent to Φ4	K4	1249 - 1259	Latin Occupation
North west guard watch	Φ5	1249 - 1259	Latin Occupation
Greek Christian chapel	Ch	1249 - 1259	Latin Occupation
Chapel	Ch2	1249 - 1259	Latin Occupation
Tower west of main gate	Φ6	1249 - 1259	Latin Occupation
Small building	M1	1259 – 1460	Late Byzantine
Small building	M2	1259 – 1460	Late Byzantine
Small building	M3	1259 – 1460	Late Byzantine
Reconstructed main tower	Φ1	1349 – 1460	Late Byzantine
Vaulted chambers gunpowder deposits	Θ1	1259 - 1460	Late Byzantine
Vaulted chambers gunpowder deposits	Θ2	1259 - 1460	Late Byzantine
Northern semi-circular tower	Φ2	1460 – 1821	Ottoman Period
North east cistern	K3	1460 – 1821	Ottoman Period
Housing within exterior wall	E2	1460 – 1821	Ottoman Period
Housing within exterior wall	E3	1460 – 1821	Ottoman Period
Housing within exterior wall	E4	1460 – 1821	Ottoman Period
Housing within exterior wall	E5	1460 – 1821	Ottoman Period
Housing within exterior wall	E6	1460 – 1821	Ottoman Period
Housing within exterior wall	E8	1460 – 1821	Ottoman Period
Housing within exterior wall	E9	1460 – 1821	Ottoman Period
Housing within exterior wall	E10	1460 – 1821	Ottoman Period
Housing within exterior wall	E11	1460 – 1821	Ottoman Period
Western expansion of exterior wall to main gate	T3	1460 – 1821	Ottoman Period
Construction western watch tower	Φ5	1460 – 1821	Ottoman Period
South watch tower adjacent to commander's housing	Φ7	1460 – 1821	Ottoman Period
Garrison commander quarters	EG	1460 – 1821	Ottoman Period

developed in Europe after the mid-13th century (Chase 2003) it is quite likely the buildings where constructed during the Late – Byzantine period. The overall categorization of the acropolis remains result in an image with three layers of information for periods I, II, III, IV and VI (Figure 9).

These layered images can be contrasted with the castle's layout from the Archaeological Ephorate of Laconia (Figure 10). A number of structures can be identified from the UAV survey that correlate to the layout. In this case the inner and outer fortification walls are clearly displayed along with the cisterns K4, the Garrison commander's housing K and the adjacent cistern K7, the main gate ΠΛ, the main tower Φ1, watch towers Φ4 and Φ5 as well as a the remains of 6 smaller structures, labeled 5, used for housing. These housing structures are associated to, E6, E2, E3 and EG. Cistern K3 is E and E (Figure 11).

Figure 7. Depiction of interventions to the acropolis during the Late-Byzantine period

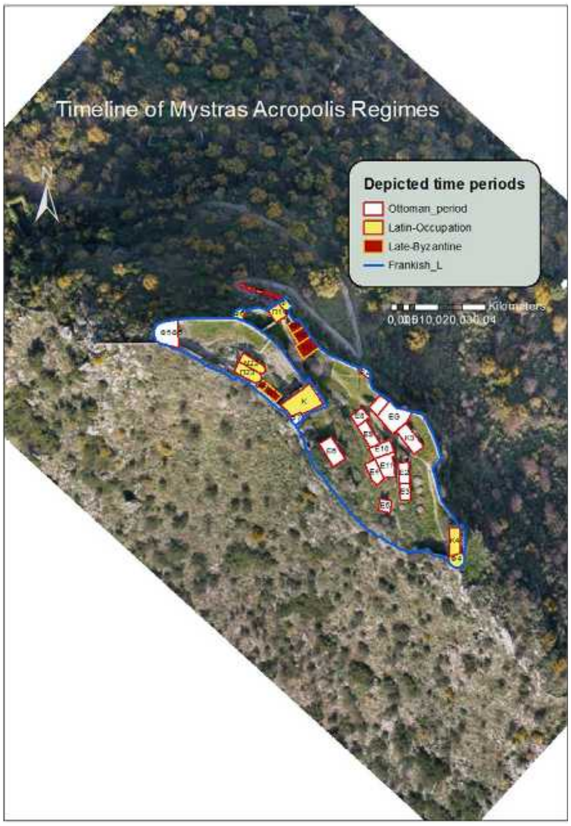

Figure 9. Timeline of Mystras Acropolis evolution

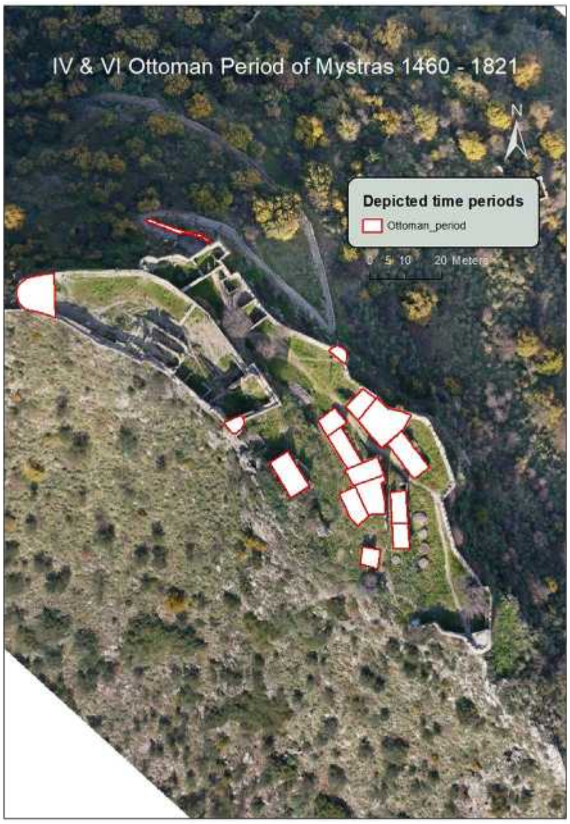

Figure 8. Depiction of development of acropolis during the Ottoman period

Finally, the overlapping layer of the historical topographical plan offers a view of Levasseur's record in relation to the archaeological study and the remains that exist today (Figure 12). Levasseur's map clearly presents the outer fortification wall which overlaps to a large degree with that from the survey result. In addition, structures are visible within the castle outer walls. These can be identified through the comparison with the developed digital map of the Acropolis. Specifically, the south east watch tower Φ4, the north west guard watch Φ5 and the gate ΠΛ as well as the main tower Φ1. South of the rectangular structure on Levasseur's map that can be identified as the two Chapels Ch and Ch2, another structure is presented, most likely the vaulted gunpowder deposits Θ1 and Θ2, taking under account the size of the depicted structure, the scale and its proximity to the Chapel without ruling out that it may be however the Garrison commander's housing K which is located south of the Chapels.

Conclusions – future goals

This survey is the first part of the study of the total area of the city of Mystras. Due to concentrated vegetation, dense construction in the Acropolis, Chora and Kato Chora its recording requires segmented mapping and synthesis of orthophoto maps, digital elevation models and 3D models of the different parts. The

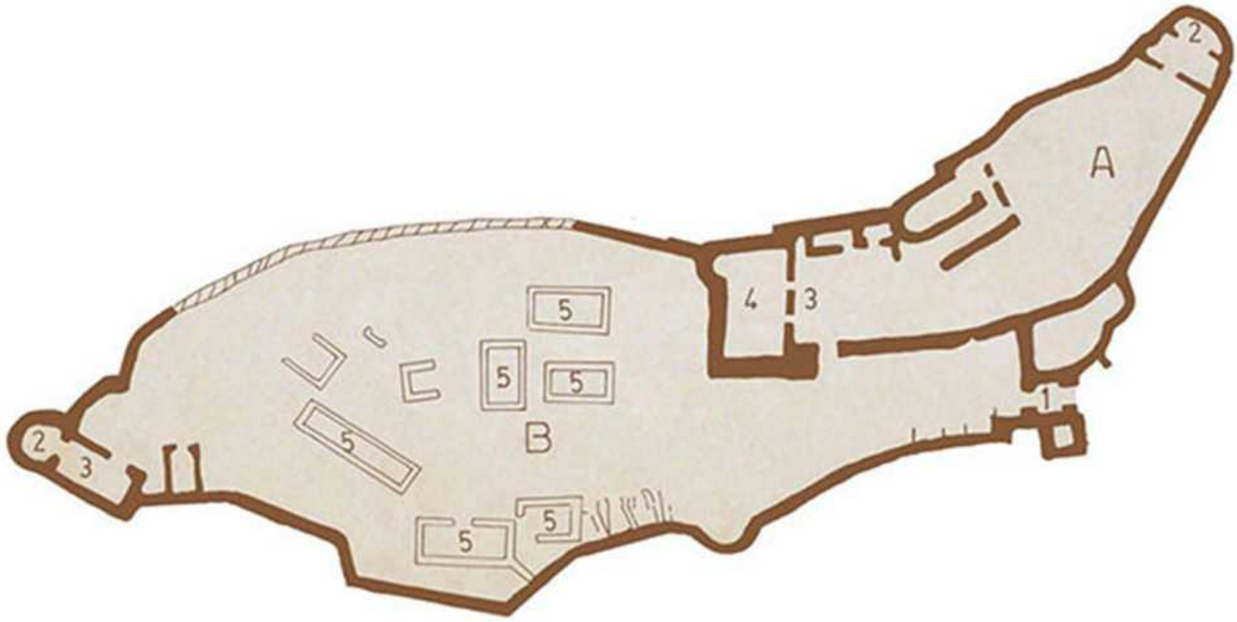

Figure 10. Castle Layout (A Internal Precinct, B Extenal
Precinct, 1 Castle Gate, 2 Towers, 3 Cisterns, 4 Commanders Quarter's, 5 Housing [courtesy of the Archaeologicasl Ephorate of Laconia]

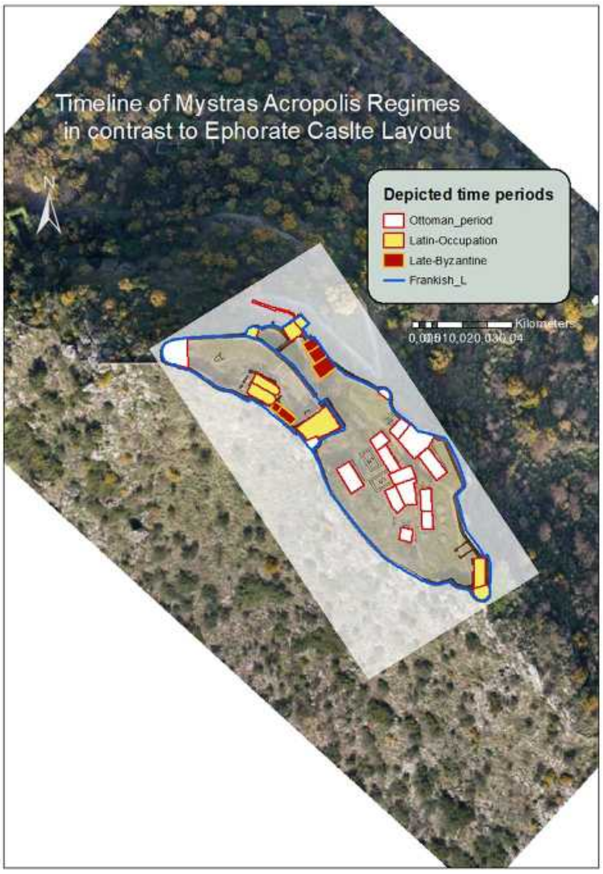

Figure 11. Timeline of Mystras Acropolis Regimes Evolution over Archaeological Ephorate of Laconia Castle Layout

aim is to record with the described methodology and present the temporal and spatial evolution of the city while providing additional data such as population fluctuations, structural elements, ecclesiastical and secular buildings as well as fortifications (Arvanitopoulos 2004; Sinos 2009; Georgiadis 2002).

With the digital depiction of the evolution of the urban fabric, the narration of the history of the city itself begins. The material is the first example of the possibility of visual presentation of spatial information. Combining infrastructure with additional information such as environmental characteristics, population data and comparison with the modern environment creates a complete picture of the characteristics of the city in terms of location, population and property development.

The ultimate goal of this work is to create a dynamic map with different layers of information available to the general public as an alternative means of information. In other words create a visual tool to understanding the evolution of Mystras from its establishment by William II Villehardouin in 1259 until its abandonment in 1953, highlighting the contribution of digital technologies in Cultural Heritage Management (Panagiotidis *et al.* 2019).

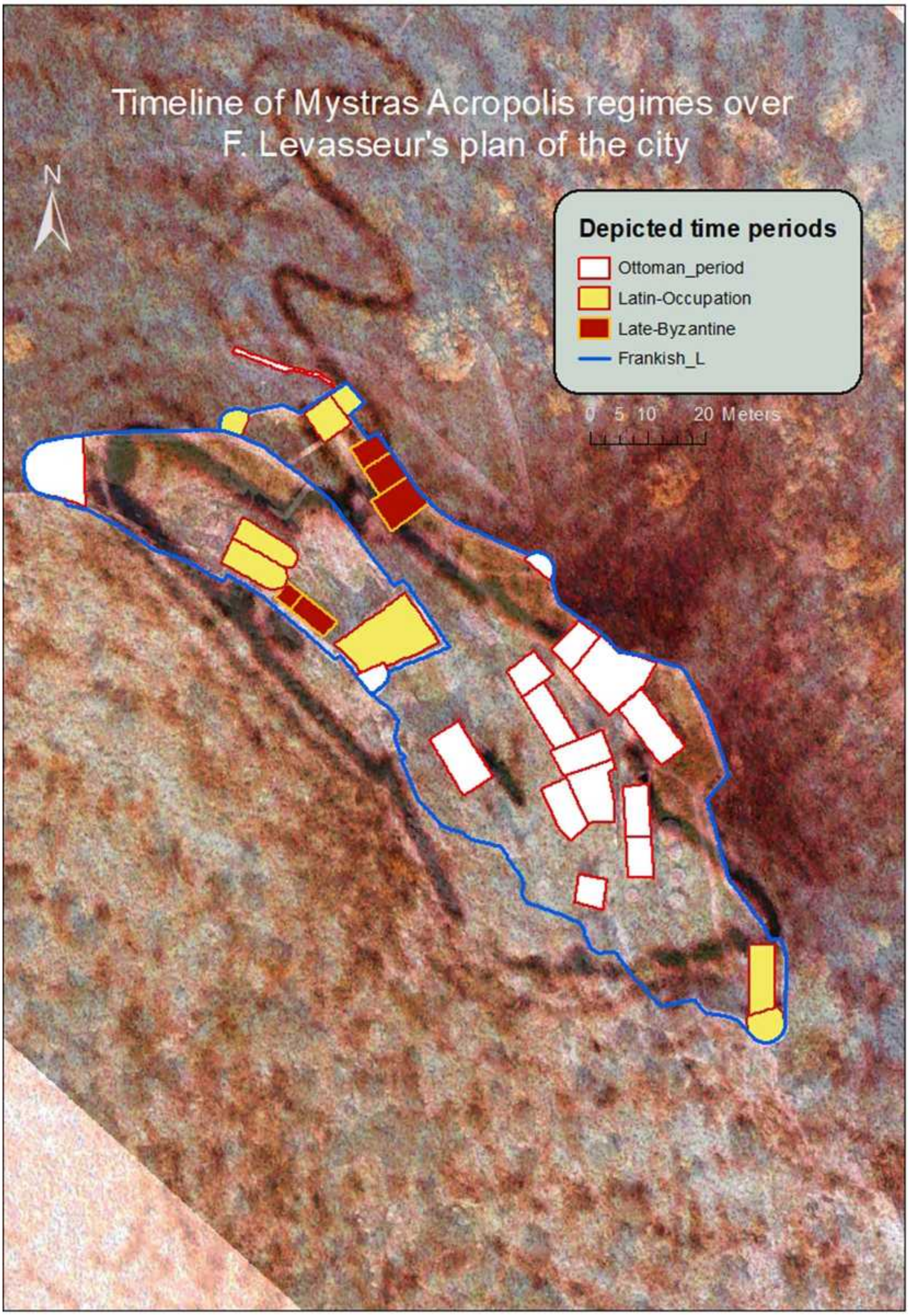

Figure 12. Timeline of Mystras Acropolis over F. Levasseur's plan

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Photointerpretation-Remote Sensing and Geophysical Prospection Voidokilia Bay, Messenia Prefecture, Peloponnesus, Greece: Detection of Buried Archaeological Relics

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Abstract: Recently, a new methodology for the detection and identification of new archaeological sites has begun to prevail (Allen *et al.* 1990; Chroni 2012; 2013; 2014; 2015; Campana 2002; Estes 1992): this supports and recommends a more extensive use of photointerpretation, remote sensing, and GIS methods (Argialas 1999; Ebert and Gutierrez 1981; Estes 1992; Jensen, P. 2016; Koutsopoulos 2003; Parmegiani and Poscolieri 1993; Rokos 1988; Seidl Da Fonseca and Klammer 2018) combined, in many cases, with the procedure of ground survey (Ammerman 1981; Horobik 2007; Schiffer *et al.* 1978) as well as with geophysical prospection (Cross 1988; Hesse and Tabbagh 1986; McNeill 1994; Noel and Walker 1989; Papadopoulos 2010; Papamarinopoulos *et al.* 1985; Piro and Finzi 2000; Reynolds 1998; Sharma 1994; Tsokas *et al.* 2006; Weymouth and Huggins 1985).

The study area of the specific Doctoral Research Project has been Voidokilia Bay at the western coast of Messenia Prefecture, Greece, an area with a very long history and a wealth of archaeological sites and relics. In this context, all the available bibliographic and archaeological data have been collected, analyzed, cross-examined, and evaluated leading thus to the strong likelihood that, most probably, the Middle Helladic I settlement, not yet located, lies on the plateau (*possibly-archaeological area*) to the north of the excavated Early Helladic II settlement/Middle Helladic I tumulus/Late Helladic vaulted tomb (*trial research area*)[1] of the northern arm of Voidokilia Bay (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Hassiakou 2003; Zangger *et al.* 1997). In this context, geological data of the greater area of Voidokilia Bay have also been analyzed and evaluated, both for the modern era and antiquity (Bintliff 1977; Brackman and Goossens 1991; Charalambous, D. 1959; Higgins and Reynolds 1996; Katsikatsos 1992; Kiskyras 1938; Kraft *et al.* 1980; Fytrolakis 1973; Zachos 1991; Zelilidis *et al.* 1988), while, at the same time, the correlation of geology-geomorphology types with the development of settlements has also been taken in consideration (Bintliff 1977; Kraft *et al.* 1980; Lagopoulos 2009; Zachos 1991).

The methodology applied for the specific project, proposed as the most effective and accurate, resulted from the application of remote sensing and photointerpretation methods for both the *trial research area* and the *possibly-archaeological plateau*. Subsequently, cartographic data, six stereoscopic pairs of aerial photographs[2] and two sets of *IKONOS* satellite imagery[3] have been extensively studied in a GIS (Jensen 2016; Seidl Da Fonseca and Klammer 2018), thus rendering possible their systematic, inter-related, and comparative study. The respective digital image processing products led to the detection of *linear traces* and *microtopographic relief shadow marks* on the northern plateau that have been studied in relation to the architectural typology of habitation sites for the specific periods, as well as to the archaeological excavation data of the area where the EH II settlement-MH I tumulus-LH vaulted tomb to the south, had been already excavated.

The traces detected have been furthermore cross-examined with the results derived after ground surveying the northern plateau, a procedure that has strengthened the aforementioned digital research products. Moreover, part of the plateau has been geophysically prospected by applying electric tomography and geo-radar methods (Gaviano *et al.* 2000-01): The integration of the respective electric tomography and geo-radar resistivity maps in the aforementioned GIS, has further strengthened the probability of buried structures for similar depths, spatially coinciding with the traces already detected by applying digital image processing and the photointerpretation methods for the remotely sensed imagery.

KEYWORDS: PHOTOINTERPRETATION, REMOTE SENSING, GEOPHYSICAL PROSPECTION, VOIDOKILIA BAY, ARCHAEOLOGICAL RELICS

[1] *EH* for Early Helladic, *MH* for Middle Helladic, *LH* for Late Helladic.
[2] Hellenic Military Geographical Service. https://www.gys.gr/index_en.html
[3] Satellite Imaging Corporation. https://www.satimagingcorp.com/satellite-sensors/ikonos/; Space Imaging Europe. https://www.euspaceimaging.com/

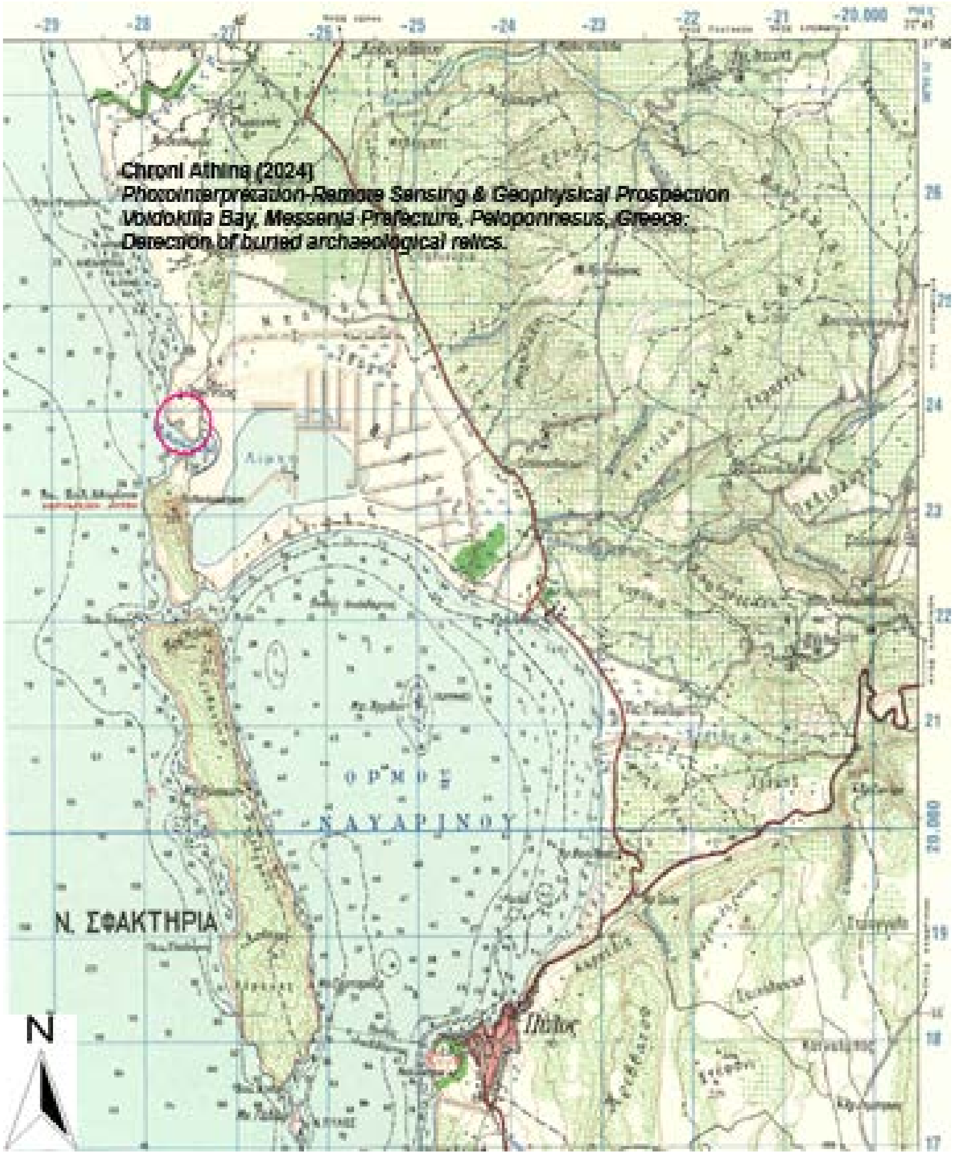

Figure 1. Part of the topographic map, scale 1:50,000, of the greater area of Voidokilia Bay and Navarino Bay: *Pylos* Charter, edited in 1977. The vector layer defines the area of the northern arm of Voidokilia Bay (also called *Prophet Elias*). In Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 191. Original cartographic datum source: The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html.

Archaeological profile of the research area

Messenia Prefecture is an area where most of the archaeological sites mentioned by ancient writers and travelers (Chroni 2012; Davis *et al.* 1997; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Zangger *et al.* 1997), have already been identified and partially excavated as a result of extensive and systematic study of bibliographic data. However, there is still a small percentage of sites not yet identified, although their spatial location is suspected, as evidenced by cross-examining bibliographic and archaeological data (Chroni 2012).

One of the aspects of a related research project implemented by the *Minnesota Messenia Expedition* scientific team (McDonald *et al.* 1972) has been the statistical approach of ancient settlements already located in the greater area of Messenia. Concerning our research project, this has proved to be very helpful for tracing the profile of a site most probably inhabited. More precisely, concerning the Bronze Age and for approximately 300 archaeological sites registered in

Messenia Prefecture, the statistical data derived (as previously mentioned) are as follows (McDonald *et al.* 1972):

Neolithic period (*c.*7000 BC - *c.*2800 BC): Only 18 sites are Neolithic, out of which only one is likely to be earlier than the Late Neolithic. Of these, 5 are located on high hills, while 8 are caves or crypts with finds.

Early Helladic period (EH) (*c.*2800 BC - *c.*2000 BC): 35 sites. 2/3 of the sites are located on natural low hills or on artificial highlands. About half of the sites are located on the coast or very close to it.

Middle Helladic period (MH) (*c.*2000 BC - *c.*1580 BC): 107 sites. 82 sites were first established during this period (indicating a high population growth): about 77% are located on high to moderate hills or ridges. For 10 sites, it is certain that the same location was used during the EH period (7 out of 10 are located on hills). Most of the sites are located inland, while only 15% remains on coastal locations. The *hill-fort* becomes a rule during this period.

Late Helladic period (LH) (*c.*1580 BC - *c.*1100 BC): 195 sites. About 2/3 of the LH sites are located again on high to medium hills or ridges. Only one location, dated as MH, did not provide any data proving re-use during the LH period. The ratio of coastal to non-coastal sites follows approximately the same standards as those of the MH period.

As derived from the evidence, the geomorphology of Voidokilia Bay's northern arm meets all the geomorphological characteristics as pointed out in the aforementioned statistics.

The excavated EH II settlement of the northern arm of Voidokilia Bay, constitutes one of the two most important coastal centers of Pylia.[4] At the end of the EH II period, the settlement had been destroyed. Later on, at the beginning of the MH I period, a tumulus was created, in which, during the Early Mycenaean era, a vaulted tomb was formed, the so-called *Thrasymedes Tomb* (Archaeological Bulletin (Archaelogikon Deltion), 1960, 1983; Chroni 2012; McDonald *et al.* 1972; Proceedings of the Archaeological Society of Athens 1956, 1975, 1979, 1981, 1982, 1983).

[4] The other is the adjacent settlement of Romanos. At Romanos, Viglitsa, archaeological relics of a settlement and a cemetery were located. The related archaeological finds include statuettes from the Classical and Hellenistic periods, Roman tombs, and a medieval column. The excavations in progress, for the year 2012, outside Romanos and at a distance of 1-2 km from the bay of Voidokilia revealed the archaeological remains of a very important, extensive EH settlement.: Archaeological Bulletin (Archaeologikon Deltion), 1961-62; Bulletin de Correspondance Hellenique 1962; Chroni 2012; McDonald *et al.* 1972; Rambach 2011; Valmin 1930.

Focusing on the excavated area (trial research area) of the northern arm of Voidokilia Bay and for an area of about 35X35 meters, the archaeological data derived, so far, are as following (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Hassiakou 2003; Zangger *et al.* 1997):

Use of the area and of the large natural cavities of the rock in the late Neolithic years (BC 3000 - BC 2700), as well as in the EH period (c 2600 BC).

Buildings with at least 6 residential and construction phases of the EH II period (BC 2500 - BC 2400).

An enclosed tomb made of raw stones and founded on the wall of a previous EH II period residential structure.

A burial tumulus (EH II - MH I) with a conical shape, stone mantle, retaining enclosure and burials in pits placed radially with the opening outwards: it is assumed that it must have been the cemetery of a family or a genus of the beginning of the 2nd millennium BC, which probably had its settlement on the plateau of the hill, at about 100 meters to the north of the excavated area (the potentially archaeological area). The tumulus was formed on the ruins of the EH II settlement, covering most of its area, a reason for which the EH II settlement remained and will probably remain unexcavated.

A vaulted tomb constructed by the Mycenaeans of the Early Mycenaean period (16th century BC) by intervenions in the MH I tumulus: the largest central and southern part of the tumulus was dismantled and an enclosure with massive stones, removed from the ruins of the EH II settlement, was added around it as a support. This family tomb, integrated in the tumulus, had been located by Sp. Marinatos looted; however, it gave some important finds, like sherds from all of the Mycenean sub-periods that prove the long use of the tomb, as well as arrowheads, a gold ribbon with spirals, and semi-precious stones.

Small semicircular or irregular enclosures (niches) of limestone full of clay tiles and figurines with relief representations dated in the Hellenistic times and a modern small thanksgiving house.

Consequently, Voidokilia Bay has been chosen to be the project's research area under the following reasoning (Chroni 2012):

It constitutes an important link for figuring out the evolution of cultural periods in antiquity, as derived from the above.

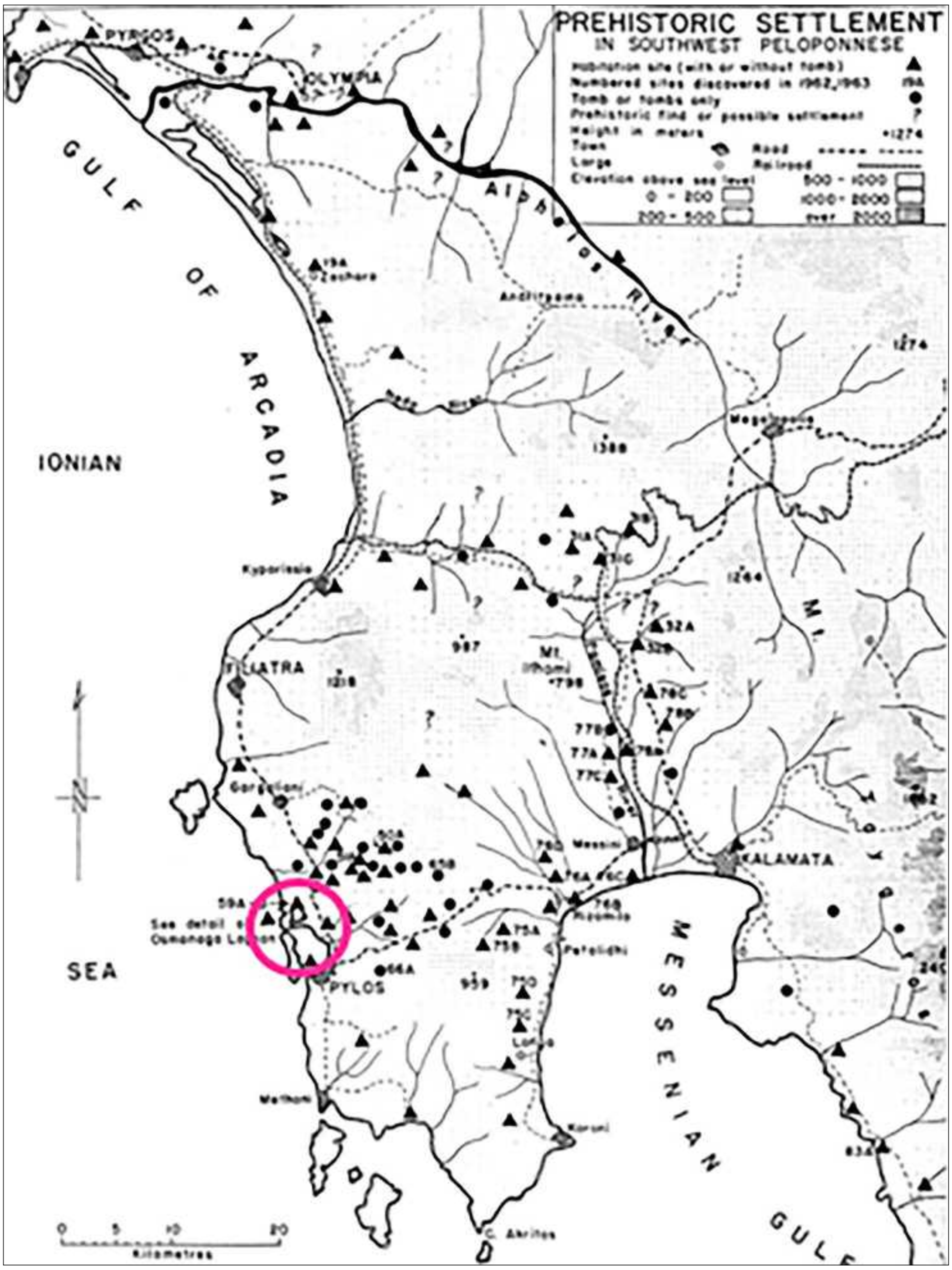

Figure 2. Prehistoric settlements in southwestern Peloponnese. The vector layer defines the area of the northern arm of Voidokilia Bay (also called *Prophet Elias*). Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 125. Original cartographic datum source: Mc Donald W. A., Rapp G.R. *et al.* 1972, *The Minnesota Messenia Expedition: Reconstructing a bronze Age Regional Environment*, The University of Minnesota Press, Minneapolis.

It can be easily identified and located in remotely sensed imagery of various scales due to its geographical position.

It has not been inhabited in recent years, so it has suffered the least damage and alterations due to human action.

It is not adjacent to or surrounded by a modern settlement, a fact that reduces the possibility of visual confusion of probable archaeological traces with modern structures.

Excavations have been carried out in this area with long intermediate time intervals, a fact that renders

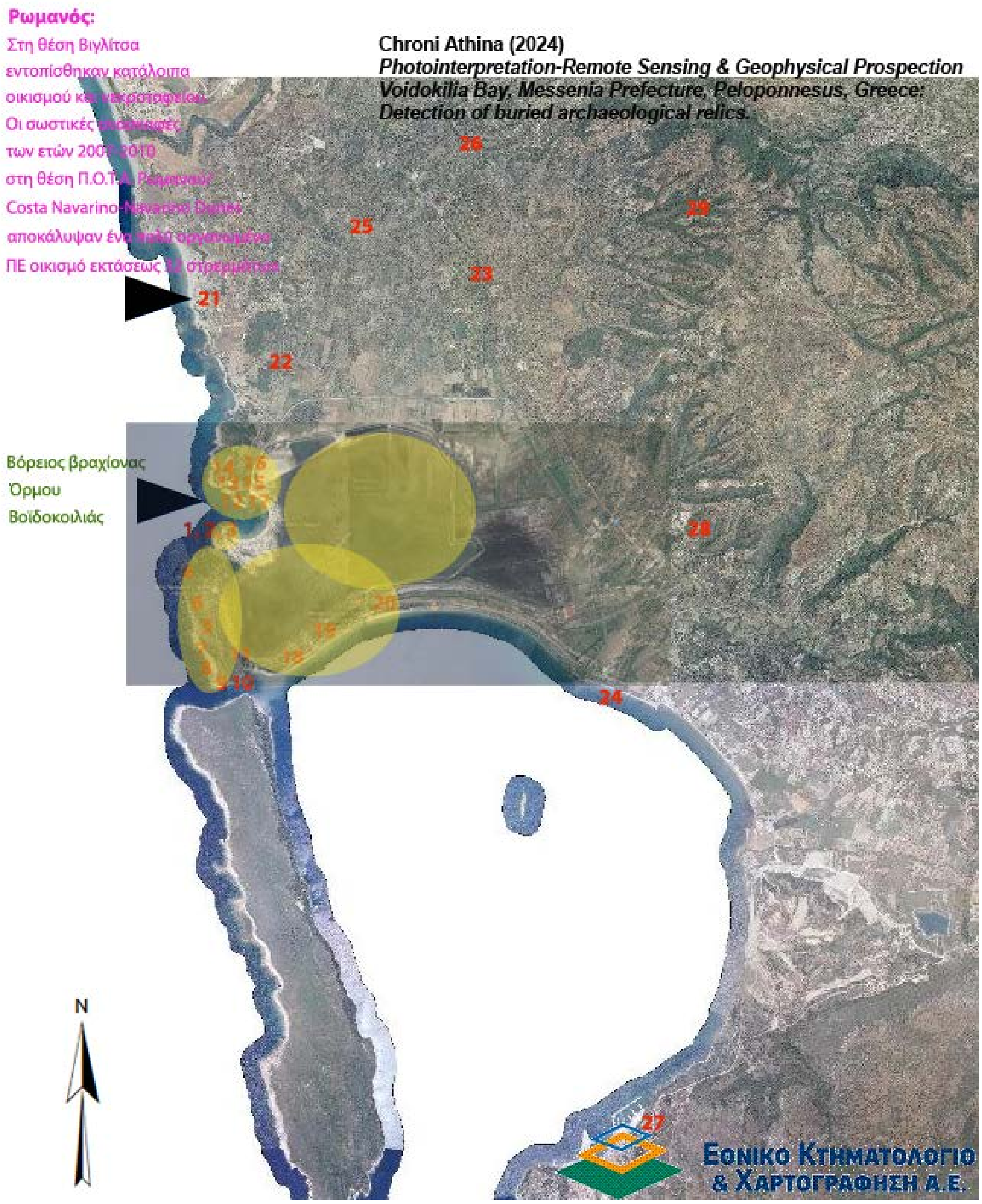

Figure 3. The greater area of Voidokilia Bay on a remotely sensed imagery dated in the year 2015-2016. Citation of the archaeological relics already located and most of them excavated. Yellow coloured areas: The areas of archaeological interest, excavated or not, of the wider area of Voidokilia Bay and the related buffer zones. Original imagery source: The Hellenic Cadastre. https://www.ktimatologio.gr/en

possible the comparative study of remotely sensed imagery of various dates, before and after any human intervention.[5]

The greater area of the northern arm can function both as a *trial research area* (the excavated area) as well as a *model area* (the possibly-archaeological plateau) for applying the photointerpretation scientific methodology derived.

The same geological data apply for both the sub-areas of the northern plateau: limestone rocks of the Eocene, one of the most characteristic types in Greece.

The specific rocks are characterized by low erosion rates, at least related to the rest of the wider area's coast.

[5] Excavational timeline of Voidokoilia Bay northern arm:
- 1956–1958: Location and excavation of the LH vaulted tomb called *Thrasymedes Tomb*.
- 1976–1983: Excavation of the MH I tumulus (*Tumulus Á of Voidokoilia*) around the aforementioned LH vaulted tomb.

The area derived to be *possibly-archaeological* is not inhabited in modern times: consequently, an archaeological excavation in the future might be feasible in relation to probable negative reactions from the local community.

Consequently, the archaeological profile of the northern arm of Voidokilia Bay should be organized as following:

- The ***trial research area*** of about 800 m^2, where archaeological relics of the following periods have come to light after long-term excavation procedure (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Hassiakou 2003; Zangger *et al.* 1997):[6]
  - an EH II settlement
  - a MH I tumulus (*Tumulus A' of Voidokilia*)
  - a LH vaulted tomb
  - Hellenistic period vessels, figurines and worship tiles
- The ***possible archaeological plateau*** of about 5000 m^2, where there is a high degree of probability of buried archaeological relics. It is located to the north of the excavated area, at a distance of 100 m. Taking into account similar spatial arrangement types of other sites in Greece, where a settlement and the related cemetery are closely located,[7] we can assume that an EH II-MH I settlement,[8] or even a LH settlement[9] might have been located at the northern plateau, close to its respective, already excavated, burial site. Given that the EH II cemetery has not been located so far, one might also take into consideration the probable location of the EH II settlement's respective burial site at the northern plateau, at a stratigraphic level lower than the one of the supposed MH I settlement.[10]
- The ***area around Prophet Elias chapel*** where (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Hassiakou 2003; Zangger *et al.* 1997):
  - In the 1970s McDonald had located ground elevations on the eastern, relatively flat slope of Prophet Elias hill, which are considered to be potential witnesses of archaeological relics of the EH period (possibly an EH cemetery or part of the EH settlement).
  - In the year 1980, illicit excavations gave cause for rescue excavations[11] on the top of Prophet Elias hill: a MH vessel, with a burial partially disturbed was brought to light, apparently belonging to a MH tumulus (*Tumulus B́ of Voidokilia*).
  - EH II sherds were found in the vessel's backfilling. Hellenistic sherds were also found during the aforementioned rescue excavations. Subsequently, the image resembles the one of the excavated MH I tumulus to the south (*Tumulus A' of Voidokilia*), since, at the specific site, as well, evidence of an EH settlement, of a MH tumulus, and of Hellenistic vases, figurines and worship tiles,[12] were also located.

The distance between the *possible-archaeological plateau*[13] and the *trial research area* is about 100 meters.

Most of the buildings of the EH II settlement are located at a lower level to the one of the MH I tumulus, while significant sections were destroyed in the center of the tumulus when the LH vaulted tomb (Thrasimedes Tomb) was constructed later on, chronologically, the last of the burial monuments of the specific site. A large EH II building has also come to light. In total, the settlement extended at least 20 meters from north to south and about 24 m from east to west (≈ 800 m^2) (Chroni 2012; Korres 1980).

The diameter of the MH I tumulus (considering the variations it suffered during its long-lasting use) is 13.70 m SSE-NNW and 15.20 m SSW-NNE: there is, namely, a clear asymmetry. The final enclosure of the tumulus has been estimated to have a circumference of 42.40 m, but it would certainly have been larger if the damaged section to the south was also taken

[6] As already mentioned.

[7] As are the cases of several Bronze Age settlements and their adjacent cemeteries, such as the ones of Hagia Irini-Kea island-The Cyclades, Hagios Kosmas-Attica, Askitario-Rafina-Attica, Lithares and Lake Yliki-Thebes, Grota-Aplomata-Naxos island-The Cyclades, Chalandriani-Kastri-Syros island-The Cyclades.: Chroni 2012.

[8] Considered as the most probable version: the MH I settlement corresponding to the MH I tumulus (*Tumulus A' of Voidokoilia*), developed at the site where part of the EH II settlement might have also extended.

[9] Not a strongly supported version, as, taking into account related archaeological data, a vaulted tomb of the LH period should be expected to be located at a longer distance of the respective settlement.: Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972; Papahatzis 1991; Papathanassopoulos and Papathanassopoulos 2000; Themelis 1984; Valmin 1930; Hassiakou 2003; Zangger *et al.* 1997.

[10] Alternatively, one might also assume that part of the EH II settlement might have extended to the plateau to the north.

[11] Implemented by the Hellenic Ministry of Culture.

[12] Apparently related to the deceased's tomb, thus confirming ancestor worship: Chroni 2012; Korres 1980.

[13] Where probably the settlement corresponding to the Early Helladic II - Middle Helladic I burial tumulus was already excavated, located at a distance of 100 m to the south of the plateau.

Figure 4. 1: The *trial research* area
2: The *possibly-archaeological* plateau
3: The area around Prophet Elias chapel.
Original imagery source: Google Maps. https://www.google.com/maps/@36.9672472,21.6622467,727m/data=!3m1!1e3

into account. Therefore, the enclosure would have had an overall circumference of about 46 m (Chroni 2012; Korres 1980).

The diameter of the burial chamber of the LH vaulted tomb is slightly over 5 m and its height should be slightly smaller, while its circumference is 15.59 m. The western semicircle is larger than the eastern semicircle. Accordingly, the upper half of the dome would stand out in relation to the surrounding tumulus (the maximum preserved height of the dome lies in its E.S.E. section and reaches 1.95 m). It is very possible that the top of the new LH vaulted tomb would rise freely, in a certain way, in the middle of the MH I tumulus. The outer width of the entrance at the present level is 1.33 m, while the interior is 1.30-1.31 m. The outer width at the top of the entrance is 1.27 m (Chroni 2012; Korres 1980).

Remotely sensed imagery

The selection of the stereoscopic pairs of panchromatic aerial photographs of 6 different dates was based on the timeline program of the archaeological excavations at the northern arm of Voidokilia. This renders possible the comparative study of the traces revealing the archaeological relics before and after each excavational phase as evolved upon the following timeline:

- 1956–1958: Location and excavation of the LH vaulted tomb, the so-called *Thrasymedes tomb*.
- 1976–1983: Excavation of the MH I tumulus (*Tumulus Á of Voidokilia*) around the aforementioned LH vaulted tomb.

Consequently, concerning remotely sensed imagery, three distinct study-periods are derived:

- Before the year 1956: a period during which the site was intact, not having undergone any human, excavation-type intervention.
- Between the years 1958-1976: a period during which only the LH vaulted tomb was excavated, while the MH I tumulus area remained intact.
- After the year 1983: when the MH I tumulus was excavated.

As a result, aerial photographs of the following dates have been digitally processed and photo-interpreted:

- August 24, 1945, before 11:30 am (oblique lighting), scale 1:42.000, the Hellenic Military Geographical Service.[14]
- Year 1964, during summertime (from mid-May to early September), during the morning (unknown lighting axis), scale 1:15.000, the Hellenic Military Geographical Service.
- Year 1965, during summertime (from mid-May to early September), during the morning

[14] The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html

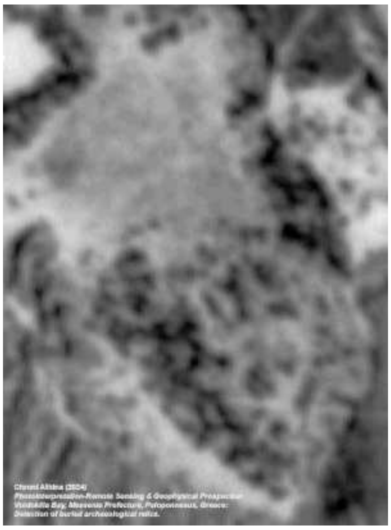

Figure 5a
- Part of aerial photograph from the stereoscopic pair Nrs 002 90582 1 and 003 90582 1
- Date: August 24, 1945
- Time: before 11:30 am
- Scale: 1:42.000
- Relation to the area's excavational timeline: before 1956, i.e., the period during which the site has not undergone any human, excavation-type intervention.

Chroni 2012: 292, 342

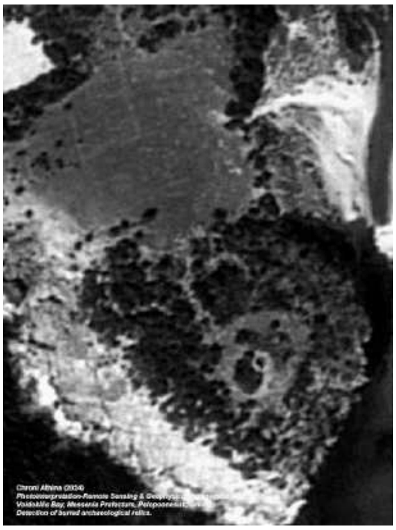

Figure 5b
- Part of aerial photograph from the stereoscopic pair Nrs 7532 and 7533
- Date: mid-May to early-September 1964
- Time: Morning time
- Scale: 1:15.000
- Relation to the area's excavational timeline: between 1958-1976, i.e., the period during which only the LH vaulted tomb has been excavated, while the MH I tumulus area remains still intact.

Chroni 2012: 292, 347

Figure 5c
- Part of aerial photograph from the stereoscopic pair Nrs 218494 and 218495
- Date: July 30, 1992
- Time: 11:30 am
- Scale: 1: 8.000
- Relation to the area's excavational timeline: after 1983, i.e., the period during which the MH I tumulus, as well, has been excavated.

Chroni 2012: 292, 372

Figures 5a–c. Analogue remotely sensed imagery of the northern arm of Voidokilia Bay. The archaeological relics of the EH II settlement, the MH I tumulus and the LH vaulted tomb are clearly distinguished. Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 292, 342, 347, 372. Original imagery source for aerial photographs: The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html

(unknown lighting axis), scale 1:15.000, the Hellenic Military Geographical Service.
- September 26, 1975, before 11:30 am (oblique lighting), scale 1: 8000, the Hellenic ex-Ministry of Environment, Planning, and Public Works.
- June 29, 1989, 12:30 pm (vertical lighting), scale 1:30:000, the Hellenic Military Geographical Service.
- July 30, 1992, 11:30 am (vertical lighting), scale 1: 8000, the Hellenic Military Geographical Service.

Digital remotely sensed imagery: The *IKONOS* satellite sensor was successfully launched as the first commercially available high-resolution satellite sensor on September 24, 1999 at Vandenberg Air Force Base, California, USA. *IKONOS* imagery began being sold on January 1, 2000, and the spacecraft was retired in 2015.[15]

Subsequently, concerning high-resolution satellite imagery of the present research project, there was availability of high-resolution satellite imagery data only for the years after the excavation of the specific site and only from the *IKONOS* satellite.

Concerning *IKONOS* satellite high resolution imagery (i.e., 1 m for the panchromatic, 4 m for the multi-spectral), acquired for the present research: two sets of panchromatic and two sets of multispectral in four channels (red, green, blue, near infrared), 8 bits per pixel for each channel, 0% cloud cover and geometrically corrected in a U.T.M. projection, have been ordered.[16]

The multispectral *IKONOS* satellite color imagery can be merged with the panchromatic to produce 1m-resolution digital color imagery of natural or false

[15] Satellite Imaging Corporation. https://www.satimagingcorp.com/satellite-sensors/ikonos/; Space Imaging Europe. https://www.euspaceimaging.com/

[16] Space Imaging Europe provided *IKONOS* satellite imagery free of charge, in the context of assisting and contributing to the development and advance of scientific research.

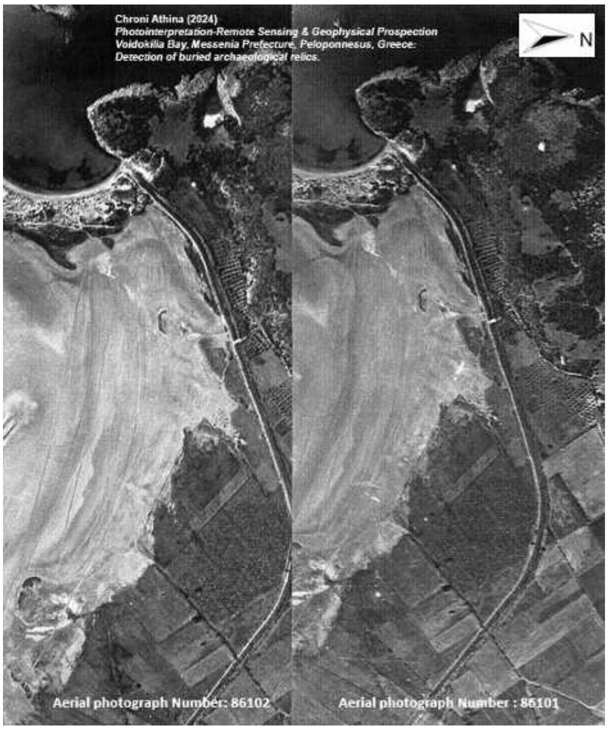

Figure 6. Stereoscopic pair of panchromatic aerial photographs. Date: September 26, 1975. Scale 1:8.000. Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 296. Original imagery source for aerial photographs: The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html

color display, according to the composite. The specific resolution is suitable for the study of archaeological relics at the size of the ones already excavated, as well as for those under investigation, that is, the northern arm of Voidokilia Bay.

More specifically, *IKONOS* satellite imagery of the following dates has been studied:

- A set dated May 23, 2000, 9:16 am (oblique lighting).
- A set dated June 3, 2000, 9:18 am (oblique lighting).

The excavated area, clearly distinguished in all the available remotely sensed imagery of the present study for all the excavational phases, indicates and confirms the adequacy of the specific scale range of imagery for detecting archaeological relics of the specific size and type, also constituting a comparative model for similar cases.

Analog and digital processing of the imagery-aerial photographs

The aerial photographs were at first studied and photo-interpreted by making use of different types of stereoscopic equipment and evaluating basic imagery identification elements, focusing on tone, texture, shadow, patterns, location, and relationship with the environment. After the implementation of the analog photointerpretation stage, they were digitized, integrated in the GIS developed in the framework of the specific Doctoral Research Project, geometrically corrected according to *IKONOS* June 3, 2000 satellite imagery, and digitally processed by applying the *ER Mapper* software (Estes 1992; Jensen 2016; Jensen 1996; Parmegiani and Poscolieri 1993).

The digital image processing techniques applied consisted of:

- Contrast enhancement (i.e. linear contrast stretching, histogram equalization, Gaussian equalization, density slicing, exponential transform, logarithmic transform)
- Filters (i.e. low pass filter, high pass filter, edge enhancement)
- Ratios

The digital processing resulted in the enhancement of the traces detected after the analog-stereoscopic processing, more specifically:

- 1945: Linear traces in the area of the northern plateau and microtopographic relief shadow marks in the area of the LH vaulted tomb excavated since the year 1958, as well as at the area of the MH I tumulus excavated since the year 1983.
- 1964: Linear traces in the area of the northern plateau and microtopographic relief shadow marks in the area of the MH I tumulus excavated since the year 1983 and surrounding the LH vaulted tomb already excavated since 1958, clearly distinguished in the specific remotely sensed imagery.
- 1965: Linear traces in the area of the northern plateau and microtopographic relief shadow marks in the area of the MH I tumulus excavated since the year 1983 and surrounding the LH vaulted tomb already excavated since 1958, clearly distinguished in the specific remotely sensed imagery.
- 1975: Microtopographic relief shadow marks in the area of the northern plateau, as well as in the area of the MH I tumulus excavated since the year 1983, surrounding the LH vaulted tomb already excavated since 1958, clearly distinguished in the

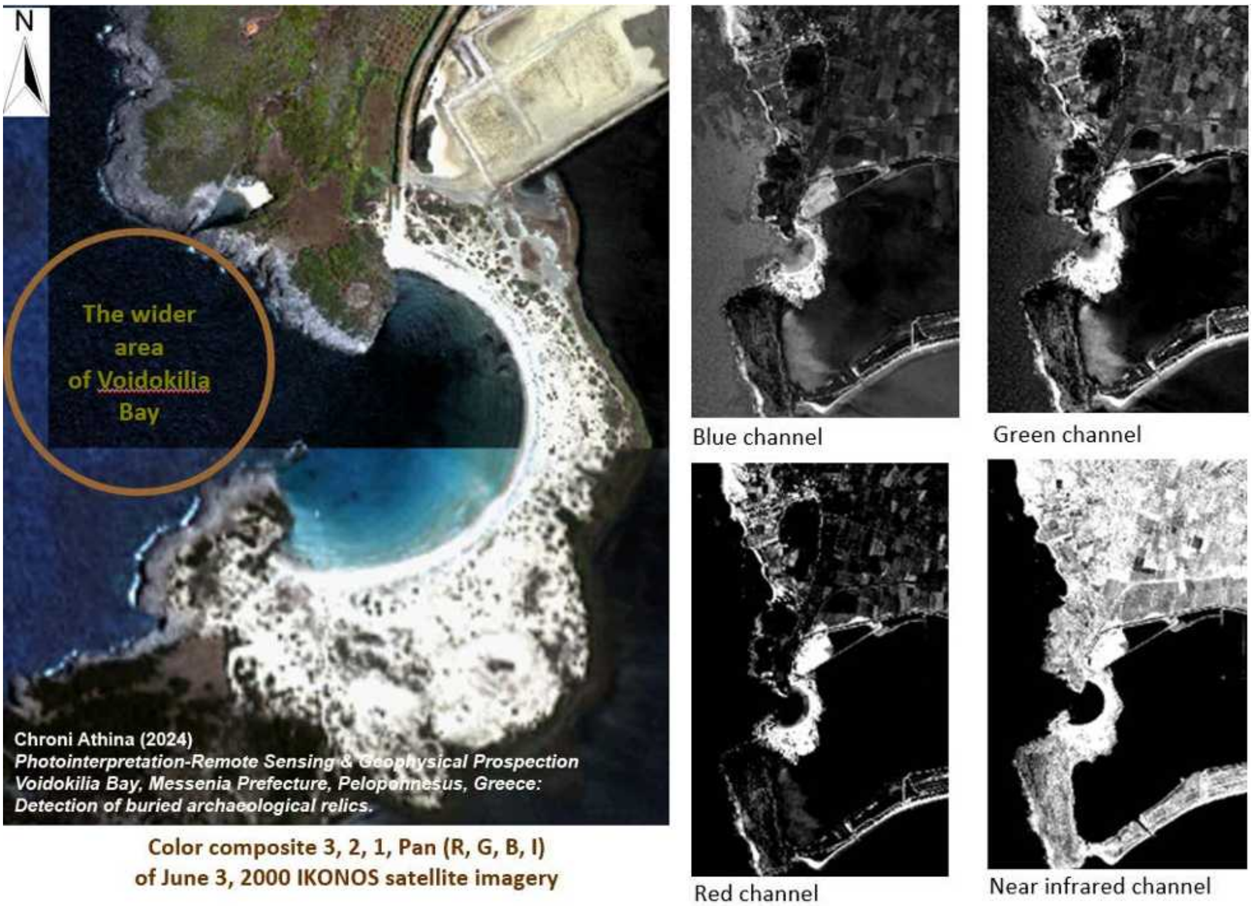

Figure 7. *IKONOS* multispectral satellite imagery. Left: Color composite 3, 2, 1, Pan (R, G, B, I) of June 3, 2000. Right: The four different channels of *IKONOS* satellite imagery dated June 3, 2000. Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 321-322. Original *IKONOS* imagery source: Space Imaging Europe. https://www.euspaceimaging.com/

specific remotely sensed imagery. Especially for the northern plateau, microtopographic relief shadow marks enhanced two linear formations, in the same locations with the ones detected in the afore-mentioned imagery.

- 1989: Microtopographic relief shadow marks in the area of the northern plateau. Unfortunately, the quality of these images is extremely poor due to the poor quality of the original negatives of the respective aerial photographic shots. Therefore, we should be particularly cautious about drawing conclusions when photo-interpreting the specific aerial photographs. Moreover, due to the poor quality of these aerial photographs, neither the MH I tumulus nor the LH vaulted tomb can be clearly distinguished.
- 1992: Linear traces in the area of the northern plateau. Concerning the excavated area, both the MH I tumulus and the LH vaulted tomb can be clearly distinguished.

Digital processing of the imagery-IKONOS satellite imagery

The following *IKONOS* digital products have been chosen for photointerpretation:

- The monochromatic representations of the case study area as represented in each channel separately: red, blue, green, near infrared.
- The false color composites as derived from different combinations of the visible spectrum's three channels with the near infrared integrated in the image composite.
- The false color displays as derived from the integration of aerial photographs in the multispectral imagery composites.

The photointerpretation is based on the evaluation of basic imagery identification elements, focusing on tone, texture, shadow, patterns, location, and relationship with the environment.

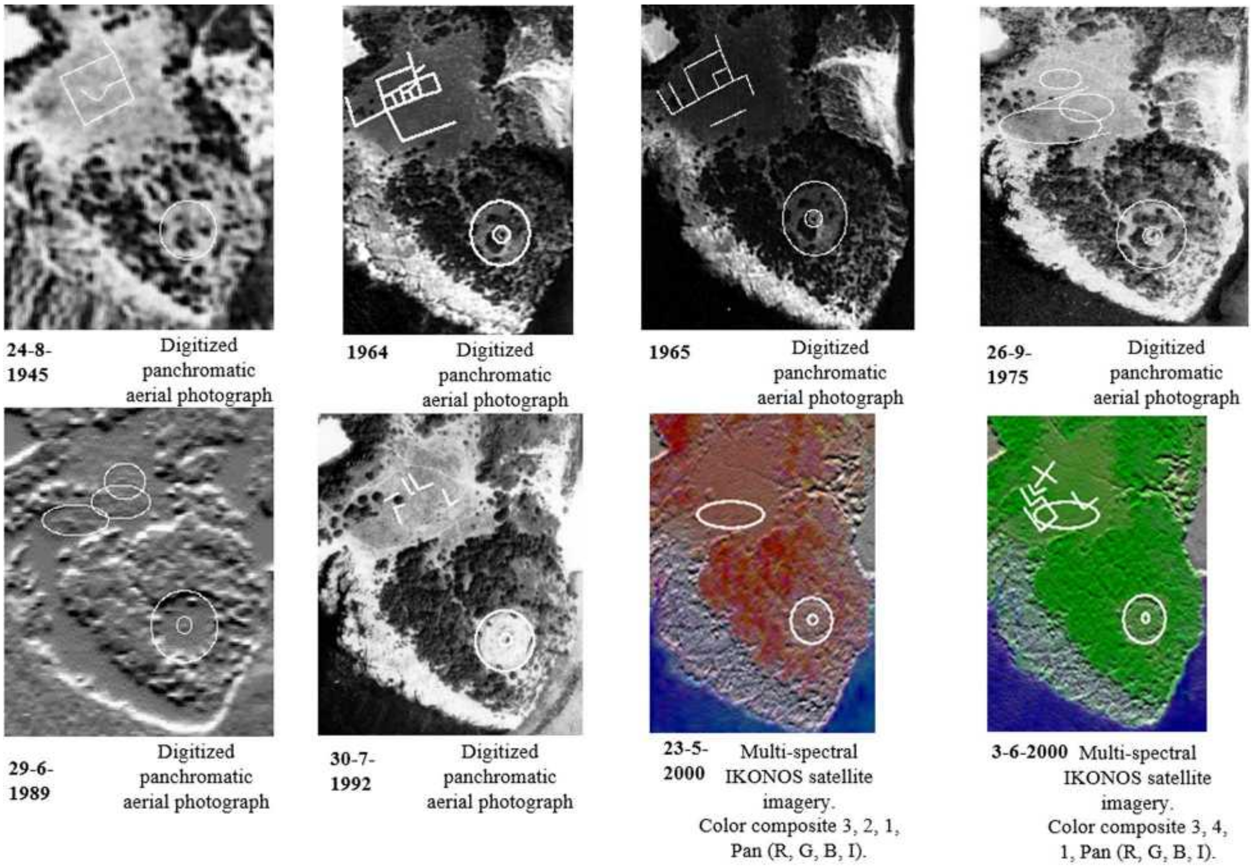

Figure 8. Aerial photographs and *IKONOS* satellite imagery: laboratory results after digital image processing and photointerpretation. After the application of digital image processing for the enhancement of the linear traces and the microtopographic relief shadows detected on the remotely sensed imagery, both analog and digital, the laboratory photointerpretation results have been digitized and depicted by additional vector layers overlayed on the respective digitally processed imagery. Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 445-447. Original imagery source for aerial photographs: The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html Original *IKONOS* imagery source: Space Imaging Europe. https://www.euspaceimaging.com/

Concerning the multi-spectral 4m-resolution imagery, the channels chosen for the color composites are:

- The red channel: it is the area of the spectrum absorbed by the chlorophyll of healthy vegetation and thus constitutes one of the main channels for distinguishing vegetation types. It is also useful for detecting soil and geological boundaries. In addition, it may be more gradual in tone due to the reduced effect of atmospheric diffusion in this channel.
- The blue channel: it has increased penetration into water bodies, while also being suitable for the study of land uses, soils and vegetation characteristics.
- The near infrared channel: due to its high absorption by aquatic bodies, whether as a lake, sea or river or as a component of vegetation and soil, it renders land-water contrast more intense.

The channel of green yields the absorbance of the specific region of the spectrum from healthy vegetation. As a result, it has not been considered particularly useful for the purpose of the specific research. Priority has also been given to natural color composites, which are considered to be more effective for the photointerpretation procedure due to the naturalistic rendering of reality (the panchromatic imagery is incorporated in one of the layers of the digital image). This has increased the resolution of the final digital image to 1 meter (i.e. similar to the panchromatic resolution) that is deemed necessary for the study of the traces detected of sizes similar to the ones already described. Actually, the procedure of merging the panchromatic (1m-resolution) with the respective date's multi-spectral imagery (4m-resolution) turned out to be particularly effective.

As a result, linear traces were detected only in the imagery of June 3, 2000.

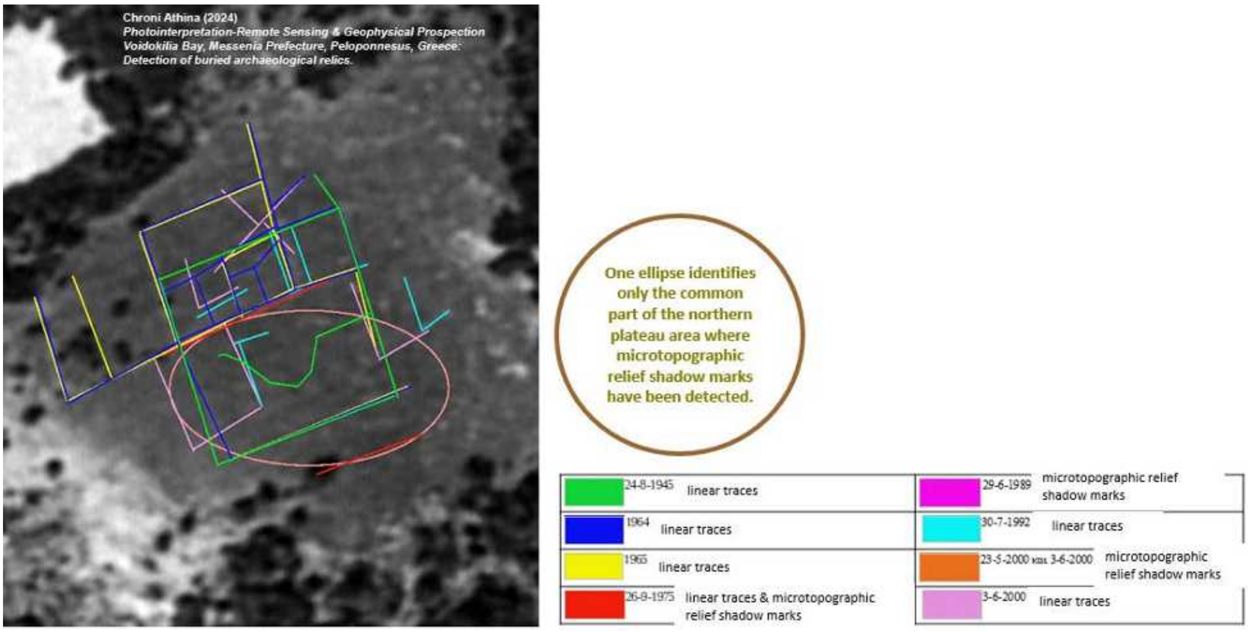

Figure 9. Overlaying of all the detected traces on the northern plateau (linear traces and microtopographic relief shadow marks) on the panchromatic aerial photograph of the year 1964. Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 454. Original imagery source for aerial photographs: The Hellenic Military Geographical Service. https://www.gys.gr/index_en.html

Subsequently, further digital image processing was applied to *IKONOS* satellite imagery by making use of the *ER Mapper* software, giving priority to natural color composites, and having the panchromatic imagery integrated in one of the layers of the digital image.

The digital image processing techniques applied were identical to the ones applied for the digitized aerial photographs, plus a combination of different spectral zones and data fusion (*merging*) (Estes 1992; Jensen 2016; Jensen 1996; Parmegiani and Poscolieri 1993) resulting in:

- The enhancement of the traces detected after the first processing phase of *IKONOS* June 3, 2000.
- The detection of microtopographic relief shadow marks on both May 23, 2000 and June 3, 2000 satellite imagery, in the same ellipsoid area, spatially identical to the one where the same type of traces were detected in the aerial photographs of September 26, 1975 and June 29, 1989.

Results processing

An overall view of the traces and the microtopographic relief shadow marks detected in all of the remotely sensed imagery as well as their comparative study was indispensable, decisive and effective for the study.

The spatial identification of the traces and the microtopographic relief shadow marks detected is confirmed when overlaying the relative vector layers in the GIS developed, a fact strengthening the probability that they actually reveal archaeological relics (Chroni 2012).

Moreover, the foregoing conclusion becomes even stronger when correlated with the following types of data (Chroni 2012):

- Meteorological data prevailing on the day the imagery was shot-A/P/received-*IKONOS* as well as on the two previous days. Furthermore, the average monthly humidity during the years 1964 and 1965 fluctuated in similar, very high levels, a fact that must have contributed substantially to the very strong appearance of the detected linear traces, which show up in a more “integrated” form as shapes than in any other year’s imagery (Chroni 2012).
- Flora of the region at the present time: the area is covered with a few shrubs, a fact that renders safe the conclusion that the shadow marks are due to the microtopographic relief (Chroni 2012).
- Climatic and microclimatic conditions of the area during the specific period in antiquity in which the archaeological relics are probably

dated: the contemporary Mediterranean climate was prevalent throughout Greece during the Holocene (from 10.000 BC onwards), a fact that confirms the favorable climatic conditions for inhabiting the specific site (Bintliff 1977; McDonald *et al.* 1972; Kraft *et al.* 1980).

- Geological data of the area: the study area of the northern arm of Voidokilia Bay is covered by limestone: in limestone soils the traces are not sufficiently clear and rather restricted. This might probably result from the fact that the limestone rock beneath the surface in most places made it particularly difficult for the first inhabitants of the area to dig ditches and pit. As a result, most of the ancient structures of the site were made of stone walls that were later destroyed and removed by subsequent natural or man-made causes (Bintliff 1977; Brackman and Goossens 1991; Charalambous, D. 1959; Higgins and Reynolds 1996; McDonald *et al.* 1972; Katsikatsos 1992; Kiskyras 1938; Kraft *et al.* 1980; Fytrolakis 1973; Zachos 1991; Zelilidis *et al.* 1988). Specific regional and local settings concerning the geological and geomorphological data of the greater Voidokilia Bay area that prevailed during the specific period in antiquity[17] lead to the conclusion that more fertile, though less extensive, lands extended on the hills and foothills of the mountains, soils derived mainly from tertiary marl, sand and flysch. For this reason, most prehistoric and early historical settlements were set on or adjacent to hills, or even between rocky areas rather than in the center of a plain. There are few exceptions and there are usually observed in the case of a port or of a key position for fishing (Bintliff 1977; Brackman and Goossens 1991; Charalambous, D. 1959; Higgins and Reynolds 1996; McDonald *et al.* 1972; Katsikatsos 1992; Kiskyras 1938; Kraft *et al.* 1980; Fytrolakis 1973; Zachos 1991; Zelilidis *et al.* 1988).
- Flora of the region that prevailed during the specific period in antiquity in which the archaeological relics are probably dated. Data resulted from the study of pollen sequence based on samples from Divari lagoon (revealing oaks, olive trees, and cereals) and Pylos tablets (referring to agricultural products such as cereals, olives, grapes, figs and domesticated animals, such as cattle, sheep, goats and pigs, as well as hunting and fish) confirms the sufficiency of food and cultivation land for the Bronze Age inhabitants of the greater region (Bintliff 1977; McDonald *et al.* 1972; Kraft *et al.* 1980).
- Form of the buildings and of the burial monuments of the chronological periods involved (Chroni 2012): studying the plan-views of LH-MH settlements, the resemblance to the linear traces detected is quite obvious.
  (Chroni 2012): studying the plan-views of LH-MH settlements, the resemblance to the linear traces detected is quite obvious.
- Model of proximity or not of a source of drinking water to a settlement, and water supply systems during the specific period in antiquity in which the archaeological relics are probably dated: proximity to drinking water is not always the primary or decisive factor in choosing a habitation site, and no places have ever been found with plenty of drinking water but without arable land or a good port. During the Mycenaean period, water systems were complex in order to supply water over long distances, e.g. between the settlement and the drinking water source, as derived from the related Minnesota Messenia Expedition research project (Chroni 2012; McDonald *et al.* 1972).
- Form of activities (agriculture, livestock, trade) and type of organization and control of the economy during the specific period in antiquity in which the archaeological relics are probably dated. According to the economic, social, and political relations of the different regions and the ways of communication that prevailed during the LH period, Eglianos (i.e., the Palace of Nestor) served as a safe-warehouse and commodity exchange for most products that came from both the Palace workshops and the provincial towns and settlements, which were under its economic control. It is probable that a family or group of elites possessed an area in the form of individual properties and had developed activities similar to those of the Palace, though in an area of a smaller scale. Perhaps most settlements were loosely organized into small independent satellites around a fortified center, with each settlement subordinate to the local lord and obliged to pay taxes, but self-governing in economic and commercial activities (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972).
- Road network of the area during the specific period in antiquity in which the archaeological relics are probably dated: intensive research of the area by the University of Minnesota interdisciplinary scientific team in 1963 highlighted that the specific period's road network was quite complex and was developed right next to the contemporary highway, a conclusion that supports the version of Voidokilia bay constituting a satellite-settlement

[17] Taking also into consideration that the terrain is mostly formed by hard limestone mountains.

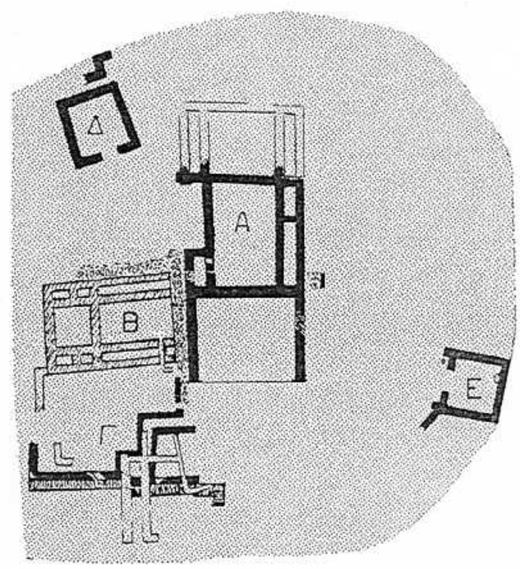

Figure 10a. Akovitika, Messenia. Plan view of mansions A and B. Source: Themelis P. 1984, *Early Helladic Monumental Architecture*, Sonderdruck aus den Mitteilungen des Deutschen Archaologischen Instituts Atheniche Abteilung, Band 99: 345.

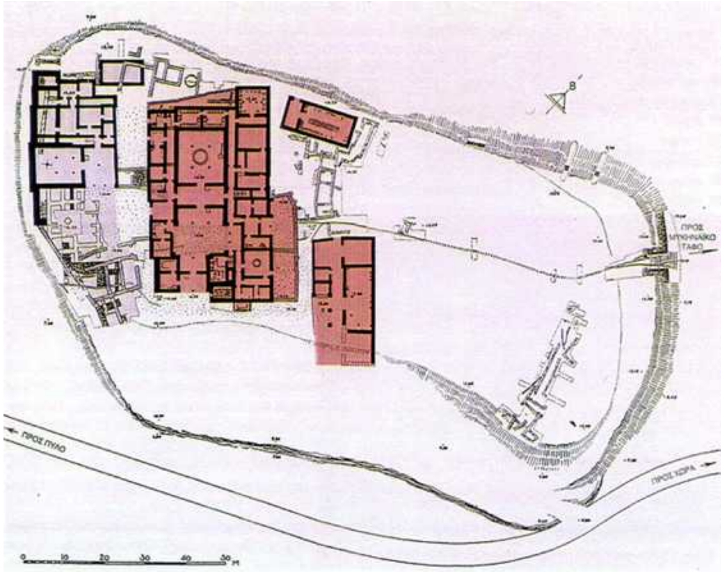

Figure 10b. Acropolis on the hill of Epano Englianos, Messenia. Papathanassopoulos G. and Papathanassopoulos Th. 2000, *Pylos, Pylia-Travel in space and time*, Organization for the Management and Development of Cultural Resources (ex Fund for Archaeological Resources and Expropriations), Athens: 19.

of Eglianos central settlement site (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972).

- Model of settlements and cemeteries and their interconnection (Chroni 2012; Davis *et al.* 1997; Korres 1980; Korres 1987; Korres 1993; Korres 2008; Korres and Hassiakou 2006; McDonald *et al.* 1972):
  - The largest settlement-centers in each region during the Mycenaean period were located at a walking distance of 1–1.5 hours between them.
  - Cases of settlements operating separately in different zones from their sphere of influence (i.e., soil quality suitable for crop development or coastal area suitable for fishing and navigation) is very common for the precise chronological periods.
  - The burial site is always located near the respective settlement.
  - The location of a Mycenaean vaulted tomb, which usually accompanies larger centers, is often found at a certain distance. In this case, the LH vaulted tomb should be connected to the Palace of Nestor.
- Throughout the Bronze Age shipping had been developed to handle trade and product exchanges: at the specific site archaeological relics of an ancient port have been located at the northern corner of Voidokilia bay (Chroni 2012; Korres and Hassiakou 2006; McDonald *et al.* 1972).
- The import of obsidian in the Peloponnese for the purpose of processing it in local workshops (Chroni 2012; Korres 1980; Korres and Hassiakou 2006).

Ground survey

A ground survey of the northern plateau took place on the 3rd of December 2000 and confirmed the digital image processing and photointerpretation results (Chroni 2012). More precisely:

- There were no indications of use of the area in modern times, a fact confirmed by the information collected from the present inhabitants of the wider region.
- No linear structures or relics were located, a fact confirming that the linear traces detected in *IKONOS* satellite imagery of June 3, 2000, are traces revealed due to reasons of soil moisture. The light tones under which they appear, further confirm the specific hypothesis.
- The initial analysis, based on photointerpretation, highlighted two different types of linear traces that have been confirmed after ground surveying the area:
  - linear traces indicating archaeological relics and
  - linear traces indicating paths.

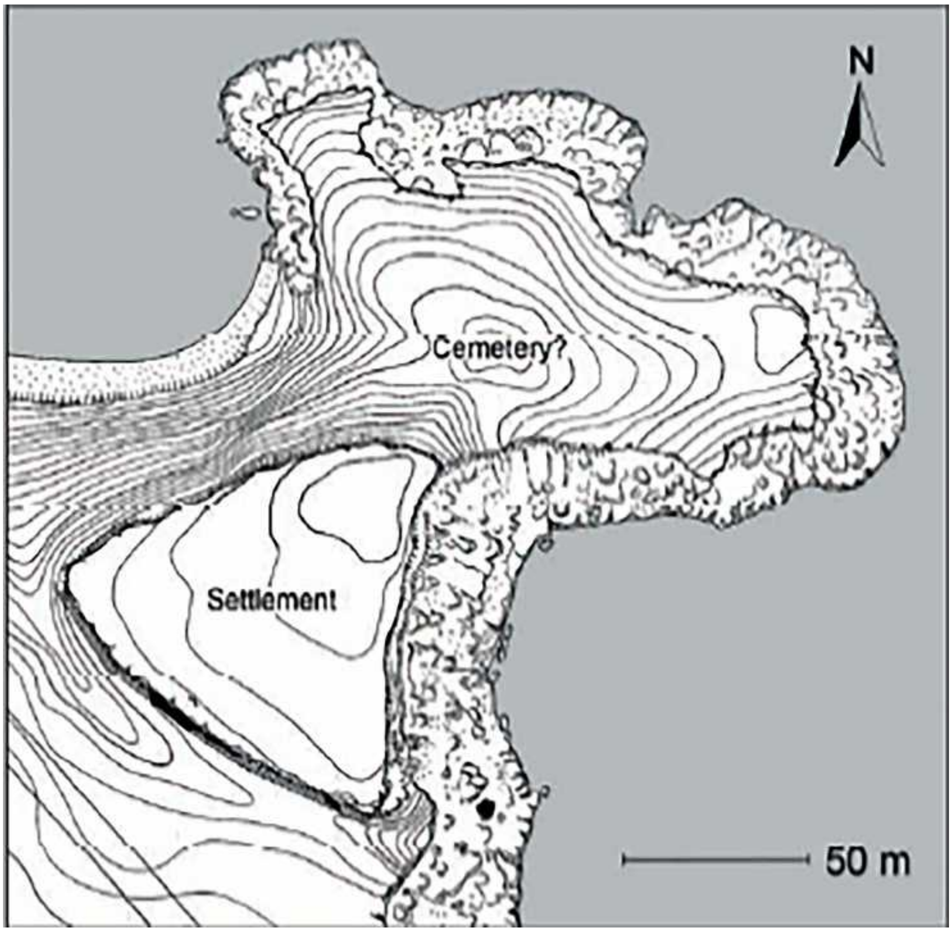

Figure 11. Askitario, Rafina, Attica. EH-MH settlement and adjacent cemetery. Source: Travlos J., *Bildlexikon zur Topographie des antiken Attika*, Tubingen 1988.

The foregoing reinforces our hypothesis regarding linear traces detected in the aerial photos of 24-8-1945, summer 1964, summer 1965 and 30-7-1992 — traces which are identical to those of *IKONOS* imagery of June 3, 2000.

- The two linear formations detected by microtopographic relief shadow marks in the aerial photographs of September 26, 1975 have been located. The fact that these two linear formations are revealed in only one set of remotely sensed imagery out of 8 different sets, confirms the need for imagery of various dates for the same area.
- The observation of the surface of the ground from a very low height (about 20 cm) confirmed the shape of the microtopographic relief as revealed in our remotely sensed imagery even before the application of a spatial filter of edge enhancement (26-9-1975, 29-6 -1989), as well as after the respective digital image processing (23-5-2000, 3-6-2000).
- The vegetation on this plateau is confined only to grass and low shrubs. In places where micro-shadows were observed, there were no bushes except grass.
- The area to the north of the plateau is scattered with stones similar in shape and type to those discovered during the excavation of the MH I tumulus and the LH vaulted tomb, which constituted the structural material of the archaeological relics already excavated.
- The location, at about the center of the plateau, of a circular ditch of about 1 meter in diameter, may indicate a dwelling pit or the foundation of the main building of the sought EH II-ME I settlement.

Geophysical prospection

The geophysical prospection by Prof. Gaetano Ranieri's scientific team[18] took place on the 10th and the 11th of

[18] Geophysical prospection by Prof. Gaetano Ranieri, Dipartimento Ingegneria del Territorio, Universita di Cagliari, Sardegna. Technical assistants: Luigi Noli and Mario Sitzia. Students: Silvia Gaviano and

April 2001 and was applied for only part of the northern plateau, specifically for an area of approximately 1200 m^2 due to the extremely adverse weather conditions (heavy rain) during the process. The area chosen for the prospection was the one that, after applying the photointerpretation methodology, revealed the highest concentration of traces and microtopographic relief shadow marks. Electric tomography and geo-radar methods were each applied at parallel routes of prospection of 1-meter distance between them. However, the specific distance reduced the resolution of the results. Thus, it is likely that archaeological relics at a size smaller than 1 meter have not been detected. Moreover, the excessively high humidity adversely affected the results of the geo-radar. Subsequently, the resistivity maps derived from the electric tomography and the geo-radar were integrated in the Doctoral Research Project GIS and were georeferenced.

Electric tomography

The area of the northern plateau geophysically prospected by the electric tomography method has been divided in three sub-areas (Gaviano *et al.* 2000-01):

- Area A1: 12 parallel routes, one meter apart, along a 47-meter length, in a north-south direction. The two Syscal Switch cables were connected with 48 electrodes one meter apart, according to Wenner's layout, thereby achieving a signal penetration to a depth of approximately 8 m.
- Area A2: 13 parallel routes, one meter apart, along a 35-meter length, in a north-south direction. The two Syscal Switch cables were connected with 36 electrodes one meter apart, according to Wenner's layout, thereby achieving a signal penetration to a depth of approximately 6 m.
- Area B: 3 parallel routes, one meter apart, along a 23-meter length, in an east to west direction, perpendicular to the routes of sub-area A.

Analyzing the electric tomography vertical sections (*profili verticali*),[19] an extensive resistivity band across sub-region A1 is evident, with higher values in routes 6-7-8 (900-2100 ohm*m) and especially route Nr 7,

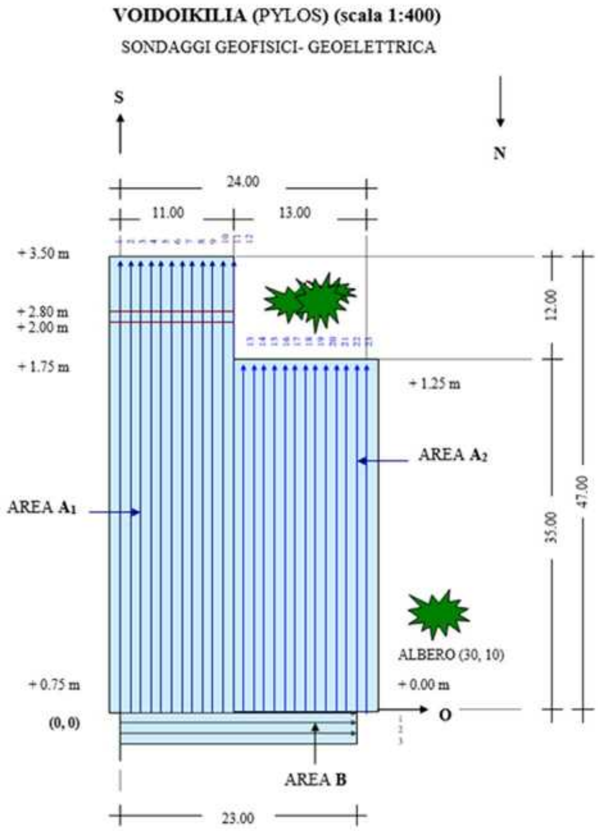

Figure 12. Plan of the area of the northern plateau geophysically prospected by the electric tomography method. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari, in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 487.

where the resistivity has the highest value, reaching 2180 ohm*m, to be followed by lower values. However, by observing the color gradation, they can be considered as promising (600-800 ohm*m). Sub-region B exhibits moderate-specific resistivity bands with values ranging from 825 to 645 ohm * m, for a route length of 7 to 12 m.

Studying the six different resistivity maps[20] that have been rendered by the electric tomography prospection in relation to the photointerpretation laboratory results, the following conclusions arise:

Carla Olivas. Related results publication: Gaviano, S. Olivas, C. and Ranieri G. 2000-01, Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari.

[19] Concerning the resistivity profiles and the respective resistivity maps for both methods applied, "cold" colors, such as blue or violet, represent areas with high conductivity and therefore high absorption of the transmitted signal, while "warm" colors, such as red or orange, represent areas with low conductivity, and thus high resistivity and response to the transmitted signal, that is, high reflection of the transmitted signal indicating the existence of "abnormalities" in the subsoil.

[20] The six different electric tomography resistivity maps corresponding to six different levels of depth: 0,00 m, -1,00 m, -2,00 m, -3,00 m, -4,00 m, -5,00 m.

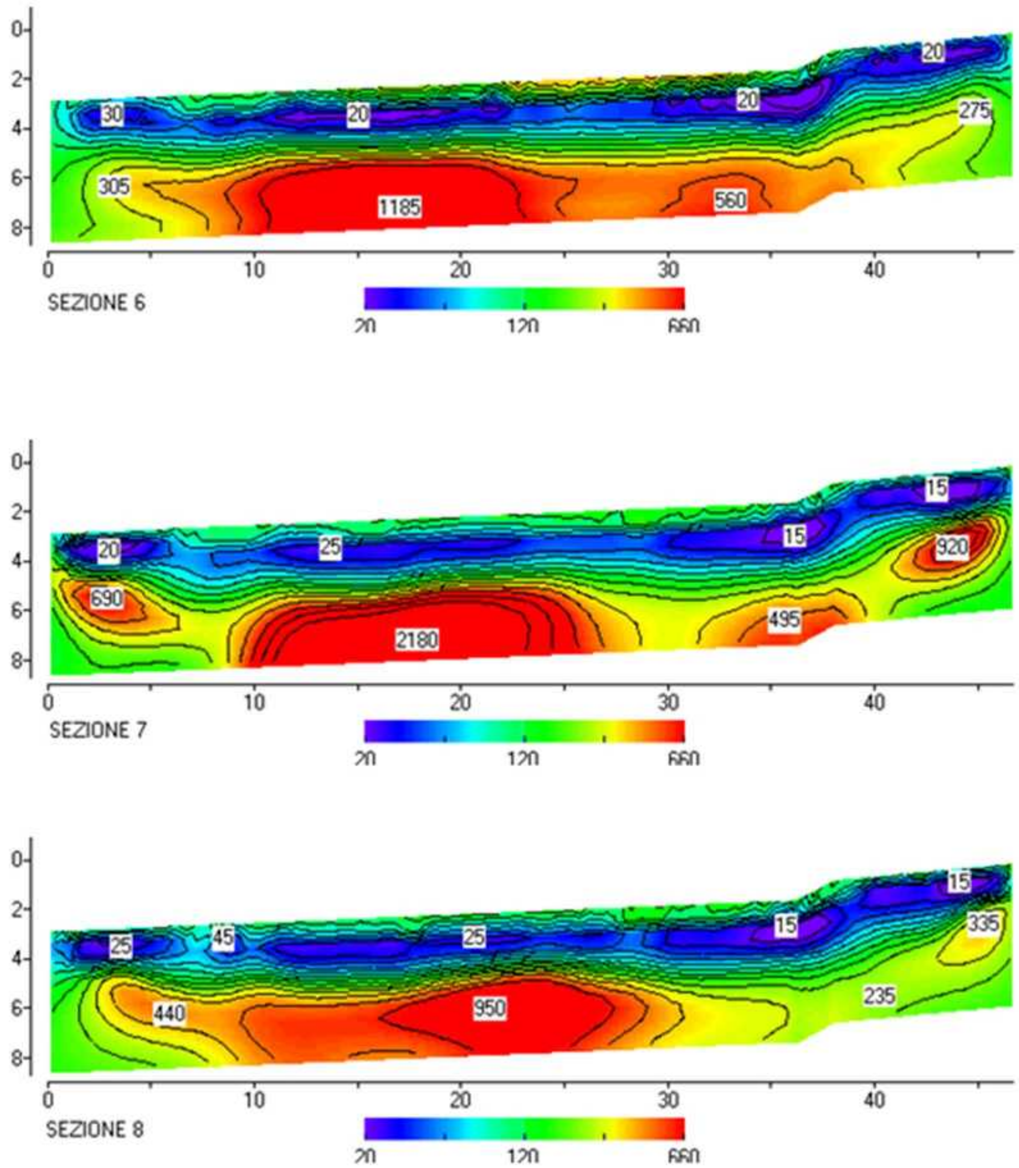

Figure 13. Electric tomography profiles of the routes 6-7-8. Warm colours indicate high resistivity. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari, in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 489.

- Higher values (warmer colors) on the parts of the plateau where traces were detected.
- Remarkable are the higher values of ground resistance of the map of 2,00 m depth, in areas where detected linear traces overlap, a fact that reinforces the view that these traces do not relate to relics of modern structures (if they did, they would not be detected at the specific depths).
- Extensive high resistance area on maps of 3,00, 4,00 and 5,00 m.: this probably indicates the limestone slab of the subsoil on which human structures were probably founded in ancient times.

No specific linear features were clearly identified to subsurface architecture, but considering the extremely adverse weather conditions that reduced the sharpness

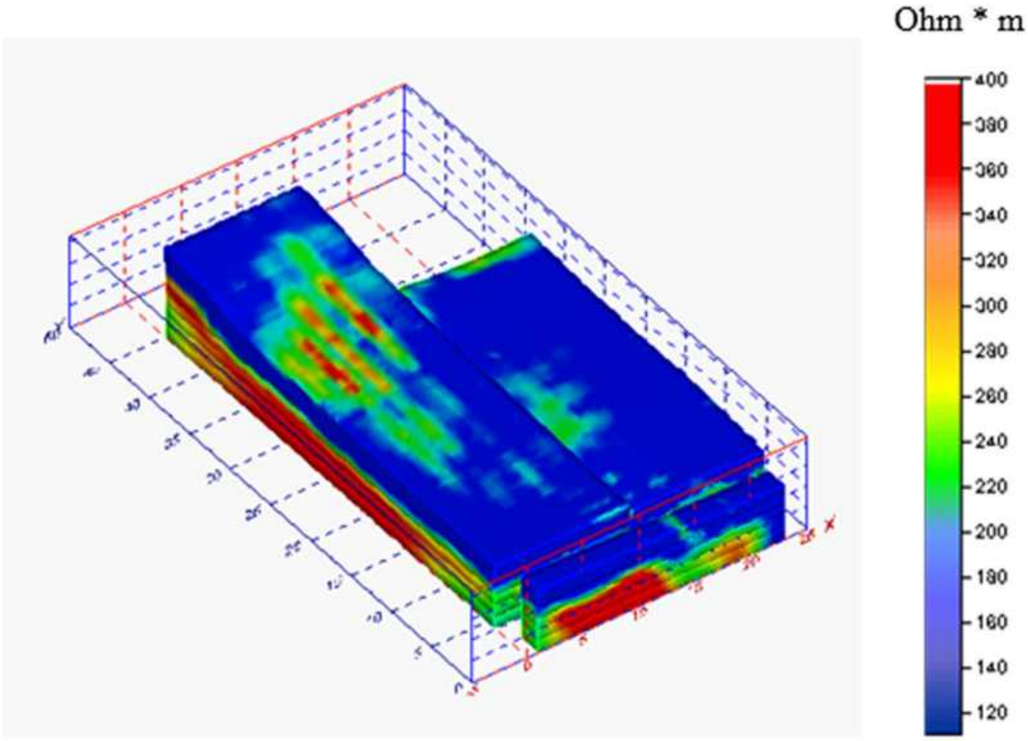

Figure 14. Electric tomography: 3D rendering of ground resistivity of the area prospected. Warm colours indicate high resistivity. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari, in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 499.

and effectiveness of the geophysical prospection implemented, "one has to consider the strong possibility that something "suspicious" is actually hidden in the subsoil" as Prof. Ranieri noted (Gaviano *et al.* 2000-2001: 165).[21]

Geo-radar

The area of the northern plateau geophysically prospected by the geo-radar method was divided in two sub-areas (Gaviano *et al.* 2000-01):

- Area C1: 9 routes, one meter apart, along a 50-meter length, in a north-south direction.
- Area C2: 13 routes, one meter apart, along a 40-meter length, in a north-south direction.

The GPR-Georadar SIR 2/GSSI USA, transmitter 400 Mhz, was dragged on the ground surface along each route, rendering it possible to obtain values for each point.

Sub-region B was not geophysically prospected.

Studying the ten different resistivity maps[22] that were rendered by the geo-radar prospection in relation to the photointerpretation laboratory results, the following conclusions were derived:

- Higher values (warmer colors) in the areas of the plateau where traces were detected.
- Depth 0,00-0,27m: extremely high return signal (red throughout the area under detection) due to the transmitter's very short distance from the detected depth: almost no radar wave propagation occured; as a result, the signal returned almost unaltered.
- Depth 0,27-0,55m: increased return signal in approximately the same area where increased ground resistance was detected by electric tomography (0.00-1.00 m).
- Depth 1,09-2,19m: an extremely strong return signal, the rectangular shape of which was kept

[21] Gaviano *et al.* 2000-2001, p. 165: «...nella parte A...deve essere analizzata la possibilita reale que "qualcosa di sospetto" effettivamente si nasconda al disotto del terreno.»

[22] The ten different geo-radar resistivity maps corresponding to ten different levels of depth: -0,27 m, -0,27 to -0,55 m, -0,55 to -0,82 m, -0,82 to -1,09 m, -1,09 to -1,37 m, -1,37 to -1,64 m, -1,64 to -1,91 m, -1,91 to -2,19 m, -2,19 to -2,46 m, -2,46 to -2,73 m.

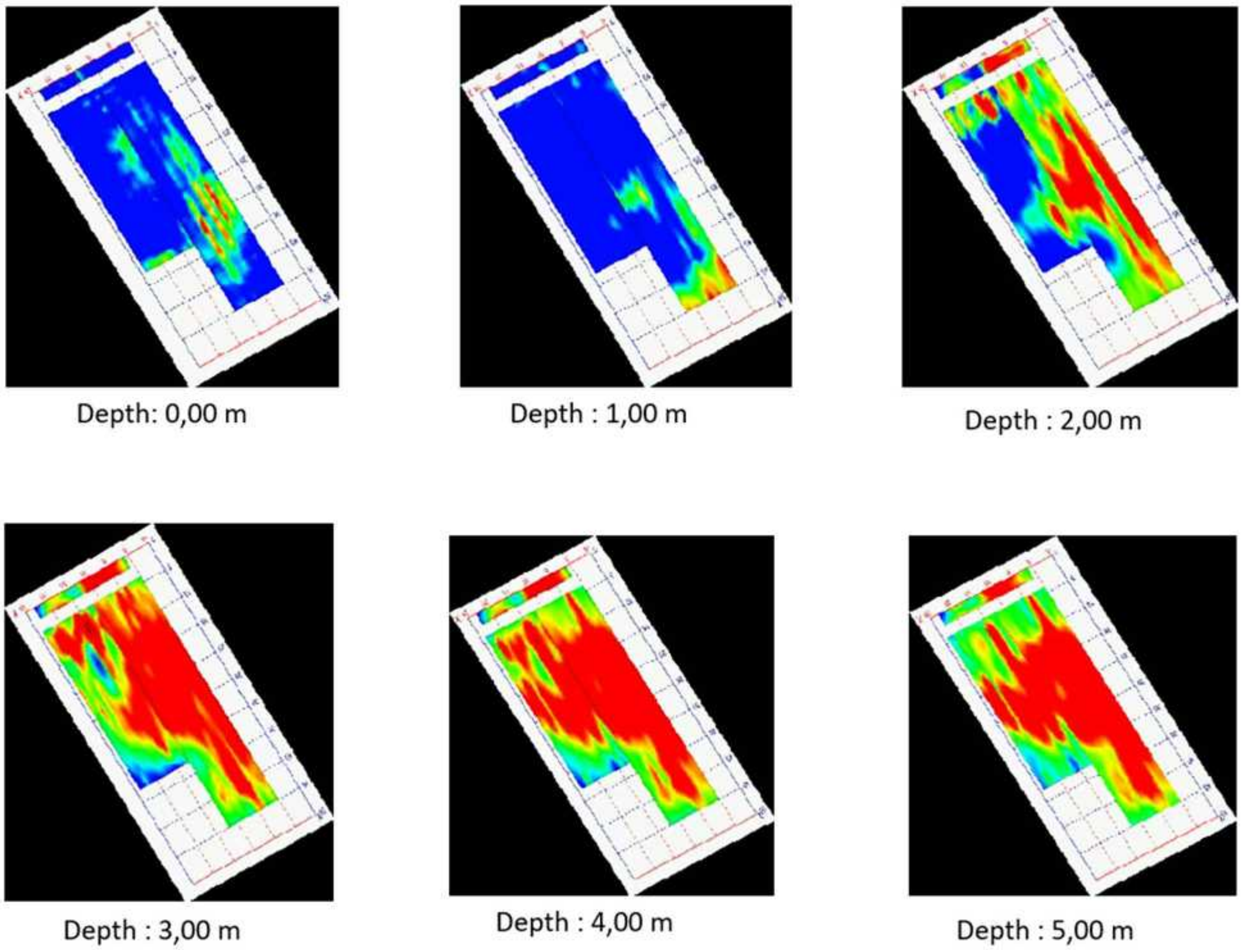

Figure 15. Electric tomography: the six different resistivity maps. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 497-498.

almost unaltered for a width of 7 meters from the S-axis of the reference system. Apart from this rectangular structure formed by the values of the return signal, there was also a remarkable return signal on specific spots on the rest of the area geophysically prospected. It is noteworthy that for these depths there was a spatial coincidence with the electric tomography results.

- Depth 2,73m: the signal was completely lost, a fact justified by the adverse for the geo-radar method weather conditions prevailing both on the day of the survey and on the previous ones. Thus, the contradictory, at first glance, nature of the geo-radar and electric tomography resistivity maps concerning the specific depths, was negated.

Consequently, according to Prof. Ranieri "the zones with warm colors evoke our interest, suggesting the possible existence of structures" (Gaviano *et al.* 2000-2001: 166),[23] although no specific linear features were clearly identified with subsurface architecture, as the extremely adverse weather conditions reduced the sharpness and effectiveness of the geophysical prospection implemented.

Photointerpretation and geophysical prospection

As already mentioned, all of the data applied in the framework of the specific Doctoral Research Project, i.e. cartographic data, remotely sensed imagery, and geophysical prospection resistivity maps, were integrated in a GIS and georeferenced to *IKONOS*

[23] Gaviano *et al.* 2000-2001, p. 166: «Sono quindi le zone ad intensita di colori caldi a destare maggiore preoccupazione, lasciando supporre la probabile esistenza di strutture murarie.»

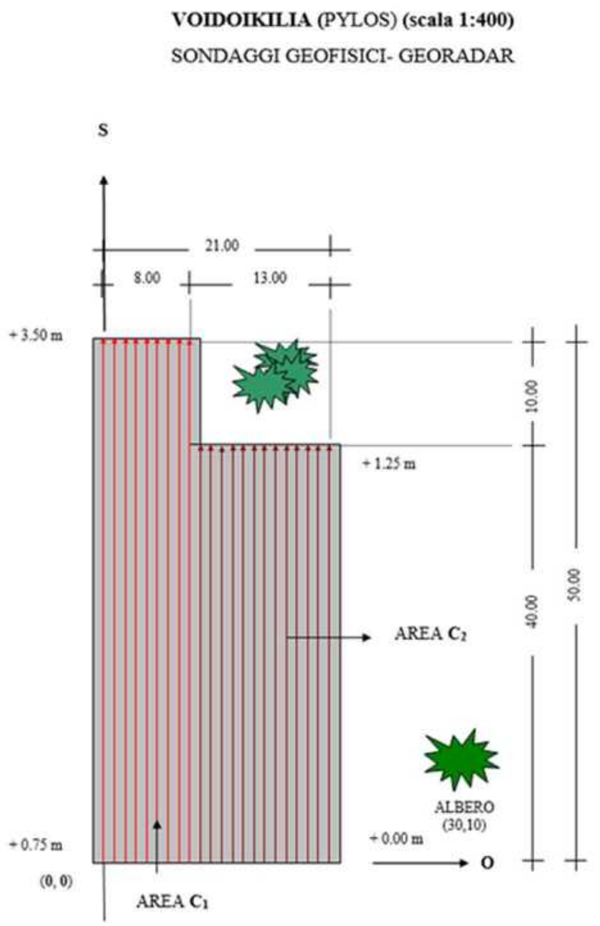

Figure 16. Plan of the area of the northern plateau geophysically prospected by the geo-radar method. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari, in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 503.

satellite imagery.[24] Overlaying the traces detected after the digital image processing and the related photointerpretation procedure of the remotely sensed imagery on the electric tomography and the geo-radar resistivity maps was considered as the most effective methodology for cross-examining the results derived from the application of the aforementioned scientific methods.

The overlaying procedure was organized in two subsequent stages:

- 1st Stage: Overlaying of the electric tomography and the geo-radar resistivity maps for similar depths, specifically the electric tomography, depth -2,00 m resistivity map, and the geo-radar, depth -1,37 m to -1,64 m resistivity map: the overlaying technique confirmed the spatial coincidence for similar depths of possible buried structures detected by the electric tomography and the geo-radar prospection.
- 2nd Stage: Overlaying of the aforementioned electric tomography and geo-radar resistivity maps together with the traces detected by the photointerpretation procedure: the overlaying of the data confirmed the spatial coincidence of possible buried structures detected by the electric tomography and the geo-radar prospection, as aforementioned, with the traces already detected by the digital image processing and the photointerpretation procedure of the remotely sensed imagery.

Conclusion

Having already accepted as the most probable scenario that the traces detected by the digital image processing and the photointerpretation procedure of the remotely sensed imagery reveal archaeological relics of a habitation site, we can therefore assume that the electric tomography and the geo-radar resistivity maps are very likely to indicate archaeological relics of residential structures, probably of the EH II-MH I settlement corresponding to the MH I tumulus already excavated, and located at a distance of 100 m to the south of the plateau, if we consider that:

- The photointerpretation-remote sensing methodology results have a high degree of reliability since multiple dates of remotely sensed imagery, stereoscopically studied and digitally processed, revealed a variety of traces (linear traces and microtopographic relief shadow marks) spatially coinciding.
- The photointerpretation-remote sensing methodology results were confirmed by ground surveying the area.
- The fact that, for similar depths, there is a spatial identification of the location of probable buried structures revealed by the electric tomography and the geo-radar resistivity maps.[25]

[24] *IKONOS* satellite imagery was received under conditions of 0% cloud cover and geometrically corrected according to the Universal Transverse Mercator-UTM projection. The panchromatic channel has a pixel size of 1 meter, while each monochrome of the multispectral channel has a pixel size of 4 meters. The satellite received data from a height of 681 km, moving in a solar-synchronized orbit at a speed of 7 km per second.: Chroni 2012.

[25] Although no clear linear features were identified by the geophysical techniques, the geophysical prospection scientific team estimated

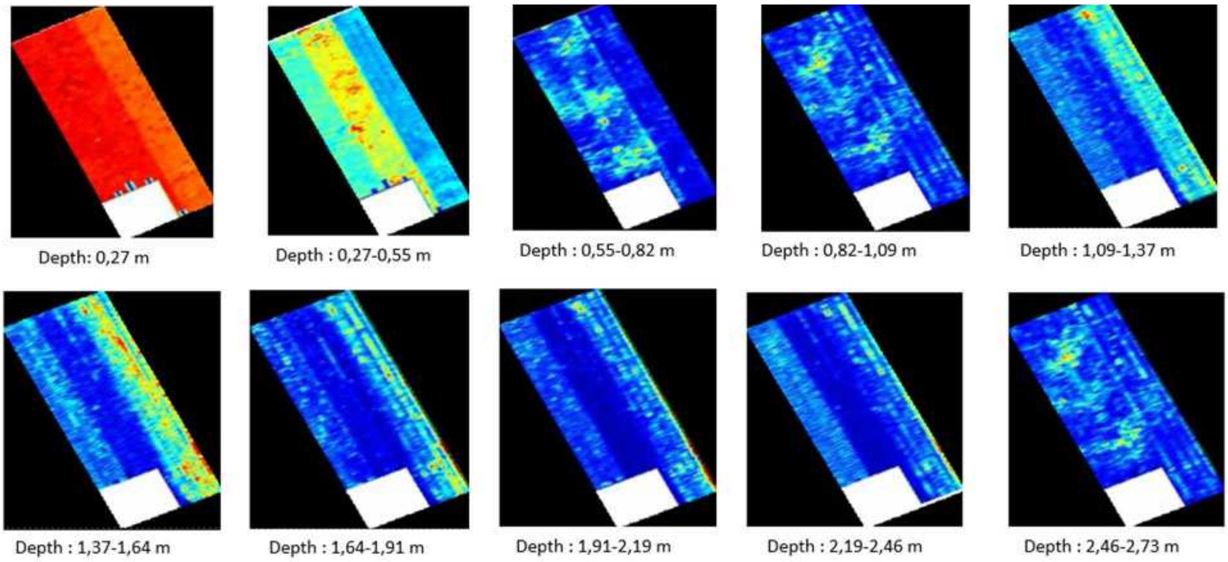

Figure 17. Geo-radar: the ten different resistivity maps. Gaviano, S. Olivas, C. and Ranieri G. 2000-01, *Riduzione del rischio archeologico con metodi geofisici. Casi di studio nel sud-ovest del Peloponneso, Grecia*, Anno Academico 2000-01, Universita degli Studi di Cagliari, Facolta di Ingegneria, Cagliari, in Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 507-509.

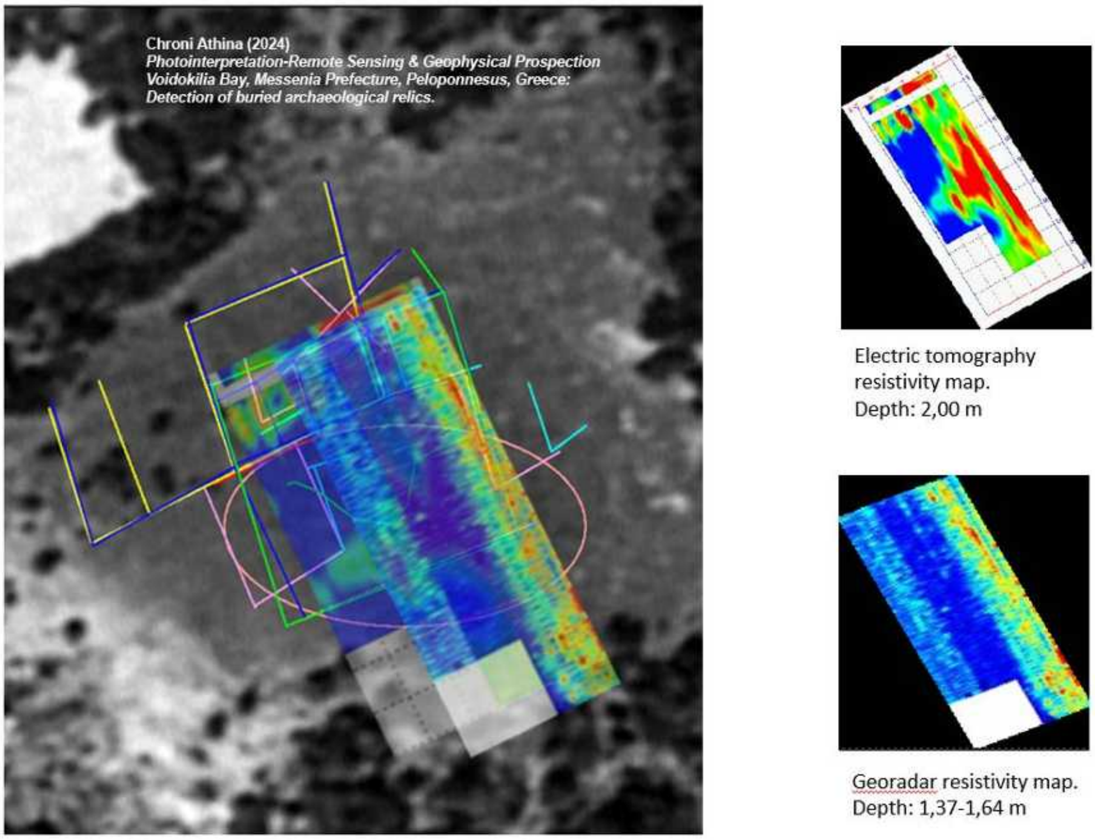

Figure 18. Overlaying of the electric tomography, depth -2,00 m resistivity map, and the geo-radar, depth -1,37 m to -1,64 m resistivity map, together with the vector layers of the traces detected by the photointerpretation methodologyin Chroni, A. 2012, *Applications of Photointerpretation and Remote Sensing in Archaeology*, Doctoral Thesis, Advisory Board Professors Rokos D., Korres G. and Koutsopoulos K., National Technical University of Athens-School of Rural, Surveying and Geoinformatics Engineering-Department of Topography-Laboratory of Remote Sensing, July 6, 2012, Athens, Greece: 449.

- The depth at which probable archaeological relics are detected by applying the electric tomography and the geo-radar prospection, is the most expected one, considering:
  - the size (mainly the height) of the houses[26] and the quality of their construction during the specific chronological periods (EH II-ME I),
  - the possible landfills from antiquity to the present day on this plateau by the hillside where the chapel of Prophet Elias stands today.

The interdisciplinary scientific approach of the specific Doctoral Research Project and the combined study of the results of the remotely sensed imagery's digital processing and photointerpretation, the ground survey, and the geophysical prospection, renders highly probable the existence of archaeological relics in the plateau of the northern arm of Voidokilia Bay.

The specific paper, part of the related Doctoral Research Project, published in 2012 (Chroni 2012), constituted one of the first case studies in which *IKONOS* satellite imagery was integrated as an additional layer in the related GIS project in order to be cross-examined with analog remotely sensed imagery of various dates and scales, thus highlighting the fundamental value of the diachronic study of remotely sensed imagery for a specific area.[27] In recent years, GIS has been accepted and implemented as a documentation methodology that mirrors analog documentation principles and constitutes a methodical challenge strongly related to general digital and technical developments (Jensen, P. 2016). This paper, then, contributes to the aforementioned scientific field while also cross-examining research results with geophysical prospection methodology. Consequently, the northern plateau is strongly considered to be a *possible-archaeological site* and also constitutes a *model area* for applying the derived methodology in other regions of a similar profile, as well, from the point of view of archaeological, climatic, and geological data types under the perspective of an *integrated cultural heritage management,* for *protecting*, *preserving,* and *highlighting* cultural assets.

that the weak character of the traces detected was due to the extremely adverse weather conditions.

[26] Most probably the traces reveal an EH II-MH I settlement.

[27] Under the reasoning that certain traces of buried archaeological relics may be revealed or not, according to the climate conditions prevailing at the time of the imagery's reception dates, as well as to the light axis differentiated during day-time: Argialas 1999; Chroni 2012; Rokos 1988.

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Towards a Dialogic Perpetuation of Cultural Heritage

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Abstract: The exponential integration of current information and communication technology (ICT) theories reveals a paradigm shift in the way we approach cultural heritage, from the concept of preservation to that of perpetuation. The perpetuation of both tangible and intangible cultural artworks is an increasing domain in digital heritage. The main objective is to study and benefit from the digitization framework in cultural heritage with the aim of transforming our perceptions to a different paradigm, that of dialogic perpetuation. We will propose the concept of perpetuation through a framework of dialogism. The goals of the current ongoing research are, on the one hand, to theoretically and methodologically approach an overlapping multi-disciplinary field of cultural heritage's perpetuation as a result of archaeometric methods and augmented reality approaches in order to reveal the collective and cultural memory. On the other hand, to discuss the capabilities and potential of Augmented Reality in expressing aspects of collective and cultural memory of heritage and enhancing the role of archaeometric quantitative and qualitative knowledge towards the individual's engagement with cultural heritage works and events. Cultural heritage perpetuation could encourage a palimpsest of multi-creative layering of divergent interpretations and finally a dialogic approach to tangible and intangible objects and sites.

KEYWORDS: DIALOGISM; PERPETUATION; CULTURAL HERITAGE; AUGMENTED REALITY; THREE-DIMENSIONAL MODELS.

Introduction

The exponential integration of current information and communication technology (ICT) theories and methodologies reveals a paradigm shift in the way the scientific community and stakeholders' approach cultural heritage from the concept of preservation to that of perpetuation (Cormier 2017). The perpetuation of cultural tangible and intangible artworks is an increasing domain in digital heritage populated by scientific fields such as three-dimensional acquisition, three-dimensional documentation and semantic modeling, building information modeling, generative modeling, and augmented reality (Georgopoulos 2017), (Ioannides *et al.* 2017). The overall digital framework is based on a series of multi-layer workflows that in turn integrate implicit and explicit knowledge from diverse scientific disciplines, such as archaeometry, archaeology, conservation, architecture, museology, computer graphics, digital humanities, and digital entertainment (Liritzis *et al.* 2019; Makris *et al.* 2018a, 2018b; Münster *et al.* 2019). It is worth noting that the disciplines involved were concerned, in a broader sense, with the creation and consumption of works and events of cultural heritage. Digitally reproduced items (as enriched with various scientific quantitative information and knowledge) alone could, in general, narrow towards a standard understanding of the artifact. Each cultural heritage piece carries a volume of interrelated, unique qualities as a result and expression of interwoven meanings and contexts. How is it possible to avoid narrowing the study to items only based on their digitally reproducible qualities? Based on the abovementioned question, our approach concerns a specific point of view that focuses on the digital three-dimensional model and attempts to study three initial concerns: a) What ultimately appears as a result of a digitization process?; b) What appears (in what condition-levels of detail, information, knowledge?); and c) Why appears, inherent in or not in a frame of reference in what kind of context? As regards the first, a thorough study (from a specific point of view) of the current situation reveals a triptych of issues, problems, and concerns. In principle, it has been documented by scholars that a majority of three-dimensional files that accompany scientific publications (articles, press releases, magazines, conferences) are not available not only to the rest of the scientific community, but in particular to the public concerned (Champion, Rahaman 2019). In terms of the second, integrating the framework of scientific studies and research with geometrically and topologically based reproduced artwork – site is often limited and represented within specific scientific software and hardware. The use of a specific digital environment has the potential to reveal the richness and impressiveness of scientific results. However, the case is the same for the individuals. As a result, very important aspects of the digitally acquired artwork—site and relative levels of detail remain distant from study and admiration. What is the ease with which you can incorporate data and knowledge from archaeometry ? As for the third, all current efforts posted via digital repositories are mainly related to the hegemony of the visualization of information based on three-dimensional digital reconstruction processes. The majority of cultural institutions and museums are following a typical scenario which involves the scope (but is not limited) to, allowing guests to recreate the original artwork visually. However, visitors could only rebuild their original frame due to the latter's apparent loss. Given the availability of the collected and existing knowledge, many doubts about the artwork itself are avoided.

The main question here is how to recreate and perpetuate the contextual memory (collective memory, cultural memory, historical, social, and aesthetic context) that accompanies the exhibited object or site (or the digital object or site itself) (either by real or digital means composed). The majority of institutions (due to limitations in funding and staff) repeat their physical exhibition approaches in a digital repository. Understanding and interpreting knowledge of cultural heritage based on data and models, and further communicating with immersive reality (Bekele and Champion 2019) based on media such as Augmented Reality (Gherardinia 2019; Papagiannakis *et al.* 2018), Extended Reality (Banfi *et al.* 2019), and Mixed Reality (Leach *et al.* 2018; Rahaman *et al.* 2019), requires profound interaction with the natural and built environments in which they co-exist with the explicit context (collective, cultural memory, social contexts, political situations). The synthesis of knowledge about such a multidisciplinary field, is an important activity to support both interdisciplinary teams and public audiences (individuals, visitors, etc.). Three-dimensional, four-dimensional, and five-dimensional (Moropoulou *et al.* 2017) representations generated by current trends in digital image processing, computational imaging, three-dimensional digitization, geographical information systems, digital multi-dimensional, multi-sensorial immersive environments (augmented reality; extended reality), computer vision, and image recognition provide individuals with a powerful agency to engage with the tangible and intangible.

Three-dimensional models: analytical and compositional virtues

Digital reconstruction was invented and utilized for single artworks, objects, and sites with the advent of computer graphics in the 1960s, and specifically since the 1990s (Messemer 2016). Three decades after its popularization, we consider that three-dimensional modeling and simulation are used mainly in the form of environmental condition-based simulation, temporal analyses, digital conservation, digital color restoration, and storytelling-based video derivatives products. The various potentials of three-dimensional computing are fully exploited in scientific documentation and the presentation of results.

Due to anthropogenic factors such as wars, urbanization, tourism, accidents, and abandonment, numerous non-existent objects and sites are retro-digitized and reappear, having a second life as digital and real surrogates (Denker 2016), while they could reveal new research cases for archeology, painting, sculpture, architecture, and urban history. Two conditions apply to three-dimensional models' excellent capabilities. First, they allow the accurate digital reproduction of materials (based on simulations) and geometric properties of a cultural heritage item. Second, the in-depth interpretation of sources, as well as the incorporation of the various dimensions of collective and cultural memory, enables hypothetical-interpretive-reproductions of the artifact, allowing multiple understandings and approaches to emerge not only for scholars, but also for researchers, artists, designers, and architects. Morphological memory could enable the extraction of divergent aspects for the enhancement of documentation, diagnosis, physical and digital conservation, monitoring, promotion, valorization, and enhancement.

The generated digital three-dimensional models of Digital Heritage provide wealth preservation, perpetuation, and communication purposes with occasional, specialized, and general audiences. It is necessary to refer to cultural elements and events in a spatiotemporal context in order to gain a deeper and better understanding of them. Space and time create a direct (sensory and mental) orientation of users and thus successfully influence the utilization of cultural heritage sites. Furthermore, the creation of a four-dimensional (including digital acquisition at different times of geometries, shapes, and constructive and formal conditions), and five-dimensional (including the future states–conditions of the curated–stored cultural heritage item) could make it possible to describe artefact–site growth (as a time-life biography) and various phases or previous interventions, including the temporal dimension in the three-dimensional modeling development. We would like to reveal the need for individuals' experience through a holistic spatiotemporal and highly bodily sensorial engagement with the artworks and sites of interest and study. Within the first axis, we want to reflect on a holistic approach to accomplishing a high level of qualitative and quantitative dissemination of knowledge. Our framework is based on historic-building information modelling, museum-building information modelling, and generative-building information modelling. On a second axis, we discuss the capabilities and potential of Augmented Reality in expressing aspects of collective and cultural memory of heritage (Halbwachs 1980), and enhancing the role of archaeometric quantitative and qualitative knowledge towards both scholars' and individuals' engagement with cultural heritage works and events.

Three-dimensional digitization of any scale of artwork provides a fundamental and robust analytical tool for researchers, historians, archeologists, conservators, and curators. A tool like this could pave the way for the emergence of new and distinct types of knowledge that would otherwise be impossible to obtain using traditional methods. On the other hand, high-resolution three-dimensional models, fully completed with all possible extracted and acquired information and knowledge from the collaborative scientific teams, could enable numerous and divergent synthetical practices based on creative synthesis. The latter could involve – but is not limited to – the design of three-dimensional and four-dimensional environments of virtual reality museum spaces, augmented reality location-based applications, serious games, etc. (Gherardini *et al.* 2019). Within a two-dimensional framework, they could be embedded into a video as multisensorial approaches. Last, three-dimensional models could aid in supporting a vast area of stakeholders, such as individuals with visual or kinetic disabilities. Therefore, all creative synthesis approaches are directed towards the creation of reachable conceptual and aesthetic provocations.

Aims and scope

In this effort, we will restrict ourselves to the conceptual challenges for the cultural heritage aided by three-dimensional digital reconstruction in scholars' research and the public interest. We mainly emphasize the impact on cultural heritage perpetuation processes that result in digital conservation and reconstruction, or utilize digital reconstructions as, frequently, the only source. Our focus is on one fundamental aspect: dialogic perpetuation. First, three-dimensional digital acquisition and dissemination of real cultural heritage items – sites; second, digital concrete perpetuation – interpretation based on three main directions, the preservation of its denotations, like visual depiction (structure, color, material), and of its connotations (meanings – sense), both in its socio-historical and everyday context. Reconstruction of meaning, that is primarily based on the object's or site's visual surrogate reconstruction, its spatial-temporal, socio-historical context, and its behavior while in usage. The main situation is: in which ways could cultural heritage perpetuation move towards in order to ensure individuals' experiences that present a world always becoming. On a wider approach, we would like to confront questions and hypotheses concerning individuals' engagement with cultural heritage environments and events (caves, landscapes, museums). Digital humanities provide rich methodologies for linking and integrating large and embodied cultures into the physical world for new exploitation and interpretation of cultural heritage chronotopes. Bakhtin has defined the concept of chronotope as a constitutive frame of narrative (Bakhtin 1981). We approach the concept of chronotopes, on the one hand, as the inner biography and contextual references of any cultural heritage item or site. On the other hand, all relevant archaeometry-based approaches are confronted as mutually interwoven chronotopes.

The main objective is to study and benefit from the digitization framework in cultural heritage with the aim of transforming our perceptions to a different example, that of dialogic perpetuation. We will propose the concept of perpetuation through a framework of dialogism (Bakhtin 1981). In order to satisfy the dialogic perpetuation paradigm, we should ensure that cultural heritage is experienced from a particular position, as an event, as a situation. The concept of dialogism could ensure the multiplicity of individual human perception. Dialogism could function as a synthesis of various scientific approaches (archeology, geophysics, geology, astronomy, mathematics, biology, physics, chemistry, informatics, etc.) expressed through various forms of building information modelling and Augmented Reality. In particular, the perpetuation of tangible and intangible knowledge during the life of the object of cultural heritage. We propose that chronotopes could become the common foundation and the vital connecting tissue for the creation and development of relative protocols for cultural heritage optimized three-dimensional documentation. Based on an inclusive approach, all tangible (geometry, materials, etc.) and intangible (meaning, importance, etc.) are entangled. Accordingly, and based on a dialogism approach, the proposed chronotropic framework encapsulates a spatial model within its diachronic and synchronic dimensions. The interactions between the divergent chronotopes are fundamentally dialogical (Bakhtin 1981). We draw three levels of dialogism. First, the dialogism between the contextual chronotopes of the cultural heritage object and site. Second, the dialogism between the divergent frames of reference in archaeometry approaches and studies. Third, the dialogism between the chronotopes of visitors, individuals, locals, etc. A framework presented here is grounded in chronotopes that can enable individuals (and scholars) to experience and engage with the many and diverse dimensions of cultural heritage. All digital environments (and not simply tools) like Building Information Modelling, while they enable the organization of diverse categories of knowledge, but the relative framework within which they are deployed is characterized by a low expression of the qualitative diversity of digitized artworks. Specifically, the goals of the current research are, on the one hand, to theoretically and methodologically approach an overlapping multi-disciplinary field of cultural heritage's perpetuation as a result of archaeometric methods and augmented reality approaches in order to reveal the collective and cultural memory of places and peoples, (Moira Makris 2018). On the other hand, to discuss the capabilities and potential of Augmented Reality in expressing aspects of collective and cultural memory of heritage and enhancing the role of archaeometric quantitative and qualitative knowledge towards the individual's engagement with cultural heritage works and events, body: sensory perception of the digital as a creator of aesthetic emotional experiences, knowledge, and memories.

Building Information Modeling and cultural heritage

Reliable digital three-dimensional models that allow for the design and management of these projects in a remote and decentralized manner are now a growing necessity. There are different and varied computer-aided design software tools for modeling and completing the three-dimensional documentation of the inserted monuments. However, in recent decades, due to advances in software and hardware properties and capabilities, the Architecture, Engineering, and Construction (AEC) sector has rapidly adopted the Building Information Modeling (BIM) standard. The multilayer and multidimensional modeling of cultural heritage through commercial or open-source BIM software leads to the concept of Heritage-BIM (H-BIM) (Jouan, Hallot 2019). This rapidly evolving approach seeks to model architectural, structural, and decorative elements in accordance with structural, historical, stylistic, and artistic expressions and typologies. In addition, H-BIM is considered to be an emerging framework that enables us, firstly, to document, understand, diagnose, make decisions, and substantially restore the structured heritage. And secondly, it feeds new directions like Museum-BIM (based on data bases) (Tucci, *et al.* 2019), and Generative-BIM based on parametric modelling (Brumana *et al.* 2018). The different BIM approaches have encompassed particular cultural heritage fields, such as documentation, studies, and management. They can provide a virtual building for the representation of the different reconstruction phases of the building environment (scale independent) under inspection and conservation. Many researchers have faced particular limitations during possible virtual reconstruction paths because of the inherent difficulty of cultural heritage objects, which are, in the majority of cases, complex, heterogeneous, singular in character, and consist of irregular features. Hence, it is necessary to integrate historical, social and technical approaches within a multifaceted BIM environment, as well as digital derivatives (point clouds, three-dimensional meshes from three-dimensional laser scanning and photogrammetry acquisition methodologies) and semantic data to model diverse simulated parametric elements (based on geometrical, topological, material and colorimetric information) and to achieve a definite BIM model of architectural heritage that has been analyzed.

Via immersive three-dimensional modeling, the artwork and archeological sites regain integrity and a purpose aimed at capturing, maintaining and culturally disseminating cultural heritage inside museums, enabling the computational methods to recreate captured reality in a condensed form in order to enable the emergence of opportunities for visualization, interpretation and teaching, through energetic, structural, acoustic and luminous studies, creating serious games, applications and digital printing of surrogates.

Recontextualize the lost spatiotemporal landscape – ecosystem through BIM and AR

If a cultural heritage item is an encrypted text, a hermetically palatable one, how can individuals and scholars communicate with multiple layers of fragments of historical memory and fragments of unrecognized topographies clustered together in one? So that they can discover the special nature of the cultural heritage element? The dialogic perpetuation proposed framework integrates two main poles. The first includes historic building information modelling and museum building information modelling, with a new approach called "generative building information modelling." The latter could explore possible assumptions and hypotheses on morphological continuity and relations based on artificial intelligence evolutionary algorithms. All such methodologies rely on both three-dimensional geometric and semantic acquirement. The second pole is augmented reality, as state-of-the-art technological methodologies that, in many cases, have overcome the borders of technological approaches and have appeared as theoretical and philosophical questions.

Understanding, interpreting, preserving and perpetuating the elements of cultural heritage beyond any scale, as well as any three-dimensional models as a result of digitization, requires consideration and study of the frame of reference within which they exist and the context they reveal as digital objects (Lloyd 2016)). A frame of reference can consist of historical and archaeological references, geo-temporal references, its collective, cultural setting, role, or function. The set of information and knowledge about all its intertwined dimensions is essential to make it accessible to scholars, experts, and the general public. Developing hybrid environments Historic-Building Information Modelling, Museum-Building Information Modelling and can gather and organize a variety of situations, including the relevant reference information of the object during the entire investigation and maintenance and perpetuation of related objects of cultural heritage. The Generative Building Information Modelling framework can help researchers in the following cases: a) study of the interconnection of space (based on morphometric - syntactic features) with its temporal dimension in order to achieve expression of multiple extracts of collective and cultural memory (automatic creation - production of spatial bridging scenarios of different historical - social phases of the monument); b) study of the dynamic characteristics of the space (architectural, urban, natural and built environment) to draw conclusions (or context) of the particular cultural period; c) Investigate the complexity of the space-site in relation to its various levels of representation based on its emerging multifunctionality.

The three-dimensional model is a powerful capacitor not only of basic geometric and topologic information - data, but much more semantic knowledge. Generally, the different technologies and three-dimensional data collection methodologies could capture and acquire different types of primary quantitative data (point-clouds, reflectance, colorimetric value, etc.), which must be interpreted so as to become important. Conversely, qualitative data cannot, in general, be expressed as numbers, but they do determine the key to understanding the digital description provided by the received three-dimensional data. Quantitative data represents the whole of the object that has been researched, and which must be interpreted qualitatively to understand the elements that determine the object (materials, etc.). Accordingly, the main challenge in three-dimensional digital data management in historic building information modeling, museum-building information modeling, and historic digital environments relates to the ability of models to create and combine, quantitative and qualitative knowledge in a three-dimensional, semantically integrated model.

Beyond the widely referenced applied approaches of three-dimensional digitization, of great importance are the theoretical implications for cultural heritage. The main question that is raised herein is the obvious danger of losing the tangible dimension of artworks and, consequently, an increasing impact on the resultant interpretations that scholars may draw. There is no longer a phenomenon of a decline in real cultural heritage items over their digital curation environments. The unavoidable enrichment with a variety of potential inputs from archaeometry greatly supports the significance of the three-dimensional model and its growing importance in new ways of evaluating and operating. The adoption of three-dimensional digitization in the wider area of the cultural heritage field is fast spreading new approaches—like digital conservation, restoration, digital curation, and digital museum exhibitions.

Cultural heritage is inherently unseparated from context. The multifaceted digital measuring of all acquired three-dimensional knowledge could allow meaning and interpretation to evolve into new socio-historical theories. The implementation of three-dimensional digitizing in cultural heritage focuses on the semantic and symbolic dialogical transfer between divergent contexts (scientific, social, collective, historic, anthropologic). Bakhtin supports the importance of dialogic understanding as a result of understanding the given related context as an approach between times, and active-dialogic understanding (Bakhtin 1986). Three-dimensional cultural heritage models could become a privileged space for thinking about and combining many realities and imaginaries of cultural heritage items and environments. The AR-BIM integration could accomplish a role as a palimpsestic layering through the life-time of CH environments. We approach a cultural heritage context expressed as space that enables the emergence of multidimensional cultural fragments, social overdeterminations, and historical layers (Friedman 2007).

A dialogic perpetuation that is based on the advances of three-dimensional digitized methodologies and the resulted three-dimensional digitized models. But rather, it is based on the potential of a more spatial narration that is influenced by the capabilities of the diverge and numerous scientific layers of documentation of the material and immaterial dimensions of cultural heritage objects. In this way, new spaces, as interwoven chronotopes, could emerge as commonly interrelated, interweaved, interwoven continuities of study, understanding, and interpretation. We are focusing on the visitors - individuals in dialogic and evocative interaction between individuals and artworks - items of a scale, and between individuals and the cultural heritage world, and between individuals and the contemporary world. Can we argue that the distinction between reality and the digital could somewhat be suspended? At the meeting of two different worlds, reality and the digital, is approached dialogically. Meanings, ideas, and materiality (beyond the materiality of real matter, there exists the materiality of scientific analysis) collide.

Augmented Reality and chronotopes' amalgamation

The Augmented Reality framework is an immersive process that could redefine individuals from preconceived observers to progressive active participants. An important aspect of Augmented Reality is that individuals remain in the physical environment and, in combination and relationship with Augmented Reality, have the inherent potential to enable viewing of such surrounding realities through the imaginative worlds of another person. Augmented Reality could be added to the traditional four categories of spatial proximities scales (Montello 1993): figural, vista, environmental, and geographical space. with the advent of hardware improvements and widespread Augmented Reality in areas like cultural heritage, entertainment, tourism, retail, advertising, etc. (Jung, tom Dieck 2018). Augmented Reality, Mixed Reality, and Extended Reality represent state-of-the-art technological methodologies, that, in many cases, have overcome the borders of technological approaches and have appeared as theoretical and philosophical questions. The Augmented Reality medium presents a challenge to multi–domain and multi–discipline synthesis in the context of cultural heritage because it can function as dialogic mediation, mediations of participation and reciprocity, through which individuals, visitors, and scholars can be dynamically and openly engaged with the specific cultural heritage item and environment.

Augmented Reality is a state-of-the-art technology that aims to bridge the real world with its virtual and indirect aspects. The result is the creation of a “new reality” that is improved, expanded, and enriched. In one of the first definitions, “augmented reality” is referred to as a system that fulfills three key features: a combination of real and virtual worlds, real-time interaction, and accurate three-dimensional recording of virtual and real objects (Azuma 1997: 356). Klopfer defines it as “a situation in which a real environment is dynamically overlaid with coherent virtual information,” which allows the user to engage and interact (Klopfer and Squire 2008: 205). In recent years, it has become widely accepted that augmented reality creates richer and more exciting content, resulting in improved interaction, perception, and experience of real-world environments by different users (Jung, tom Dieck 2018). Individuals, by providing customized and personalized information based on their current location, can experience a site physically and realistically even if they have limited knowledge of it, or discover and reveal its views that no longer exist. Users are able to discover the world by adding new levels to their perception of reality and space. As users know in advance that they are moving into the surrounding world and understand its physical effects (MacIntyre *et al.* 2001), the sense of immersion is further enhanced. As a result, augmented reality’s emerging technology profoundly changes the underlying and perceived objects as it introduces new objects (tangible and/or intangible) into our world (Liberati, Nagataki 2015). Augmenting the real world through digital data pads can create a new entity with its own characteristics and dynamics.

Augmented Reality can be used to assist in archaeological and architectural research, enhancing features in the modern landscape, allowing the researcher to formulate conclusions regarding the placement and configuration of the site or allow users to understand what they are seeing. Computer-generated models can be placed in real life to rebuild ruins, buildings, landscapes, or even ancient characters as they used to be. This technology can only be useful in the real field, the physical environment, – the surrounding space, because it needs a real environment and objects that need to be augmented. The expression of augmented spaces, appropriately shaped both in form and dimension, will allow navigation, introduction and export of real and qualitative features (measurements, colors, materials, historical documentation, maintenance phases). At the same time, it will be able to express and highlight qualitative characteristics of the frame of reference, such as atmosphere, psychogeography, emotional horizons, etc. Augmented Reality could be added to the traditional four spatial proximities scales: figural, vista, environmental, and geographical space (Montello 1993), where we impose four strategies that underpin a storytelling Augmented Reality typology: reinforcing, recontextualization, remembering, and re-embodiment (Moira Makris 2018). Montello has defined four basic categories of spatial scales, (Montello 1993). The first scale is that of figural space, which can be defined as a scale projectively smaller than the body. Perception of objects’ perception in this space does not involve any body movement. The second scale refers to the vista space, which is projectively close to the body volume or relatively larger under the condition that it can be observed physically from a single spatial point without any prior movement of the perceiver. Such spaces involve room interiors, town squares, and close horizons. The third scale, the environmental space, encompasses the human body and it is not possible to be experienced on the perceiver’s side, without human movement (locomotion). Such a category concerns spaces that contain large edifices and urban and landscape environments. Although not explicitly perceptible within a short period of time, it is claimed that with simple access, this scale of space is nevertheless perceptible. The fourth category, that of geographical space, is again on a larger scale, and it is not perceptible by direct personal experience or navigation. Such space’s scale can only be understood by symbolic representations, like multilayered maps, that are capable of reducing geographical space to geometric and iconographic space.

The preceding lead to the interweaving of Augmented Reality media based on four strategies: reinforcing, recontextualization, remembering, and re-embodiment. The reinforcing strategy works when overlapping digital spatial objects are presented as ‘real’ to the interested individuals during the reported time frame.

For example, three-dimensional augments consist of three-dimensional digital representations of good but absent artifacts, either fragmented reconstructions or partially damaged or destroyed buildings and artworks, which show the corrupted or disappearing part of a city. The recontextualization strategy aims to transform the physical and semantic properties of places, which in the context of a time-based narrative acquire new significance and meaning. The main objective is to reveal the different aspects of cultural heritage environments. The re-enactment of reality is based on an intertextual narrative that allows different signals to appear. Based on the events of the fictional plot, places are articulated and spaces are digitally recreated. Next, the related cultural heritage context timeline aligns the narrative sequences with the real and digitally reshaped surrounding environment. Intertextual narration is superimposed digitally in such a way that historical, social, and cultural interrelations can be experienced alongside the plot's developmental timeline. The result of this strategy is that the image of cities changes according to the atmosphere and historical era of the cultural heritage contextual narration. In this way, residents and visitors perceive the overall character of the city, which blends in with its historical, social, and cultural parameters. The strategy of remembering allows for the simultaneous appearance of different mnemonic fragments from the same urban site (Azuma 2015). Certain temporal narratives provide mnemonic content from the urban area (specific frame of reference) because they have different plots and ideological targeting. Thus, it is possible to discover, individually, for each user, the different social, cultural, and aesthetic content of the sites through the same set path. Cultural heritage narratives lead individuals to approach locations in the light of the emotional context of the characters in the stories and to engage both mentally and physically. Users, based on their personality or interests, record individual emotional states during their visit, and as they interact, their personal experiences and memories from the site they visit relate to and contrast with the events of the fiction. The re-embodiment strategy allows scholars and the public to engage with environments that they aim and desire to understand and experience as they navigate through a transformed or unfamiliar environment. Such an approach allows individuals to discover the endless layers of matter and meaning of the sites they visit, enabling them to gain renewed interest and increase participation. This process leads users and stakeholders to a deeper spatial, emotional, and cognitive understanding of the particularities and differences between places and events. Finally, and in reconnecting them with the spirit of place. In the broadest sense, residents can gain deeper spatial, emotional, and cognitive engagement with the different aspects of their urban areas that they are unaware of (Forte 2016). Individuals and visitors can also connect organically, rather than superficially, with local communities and effectively become familiar with social, collective, and cultural memory.

Augmented reality goes beyond the typical behavior of other visual media, which allows the visual hegemony to dominate in the representation of the cultural heritage landscape. It thus differs greatly from such visual approaches, allowing the user to experience cultural heritage objects and sites space rather than merely visualizing them. Users are immersed in an augmented reality of the place they are exploring. Augmented reality provides an environment in which the disclosure is introduced as part of its development (Gould 2014). In this way, neither the digital media nor the body of cultural memory dominate one another. The experience of invisible cultural heritage values promotes simultaneous perception of both media and memory. The museum theory's contemporary threads redefine the visitors' concepts from a passive recipient of content as an emancipated (Ranciere 2011) actor in a multisensory dialogic framework of approaching with the surrounding exhibits environment wherein they are entirely immersed.

Discussion and conclusions

One of the most important objectives in the field of digital cultural heritage is the dissemination of the tangible and intangible values of heritage artworks. When the three-dimensional digitized cultural heritage spaces, artefacts, and events are based on archaeological and conservation scholarly and ethical norms and guides, when they are combined with particular augmented reality strategies, they result in many fruitful spatiotemporal experiences. From the three-dimensional models, it is possible to process and analyze new ways of assessing complex factual relationships and implicit knowledge, including other resources connected to data networks. In addition, documentation of creative, resource-based reconstruction ensures that the results are scientific because the process is verifiable. The three-dimensional digital model as a new creation of a complex sequence of situations - contents - of realities, such as those caused by digital "recordings" and "surveys".

Developments in, Augmented Reality and Mixed Reality technologies allow for exciting new interactive experiences, which in turn bring new experiences in seeking and communicating the results of scientific research. We are now in the early days of a technological process. In terms of both content and methods, digital reconstruction (DR) is gradually being established as a proven research methodology. Augmented Reality as a digital medium can provide an interpretive environment, which in turn acts as an experiential environment that contributes to the emergence of a new mixed reality by creating multiple spatial narratives. Augmented Reality allows for a multifaceted perspective on cultural memory, as a walk through different historical and social contexts. It is a digital medium that allows one to explore, critique, compare, etc., the multiple collective aspects of an urban palimpsest, such as a central square. It reveals new connections between digital media and the ideas that shape and synthesize collective and cultural memory.

Augmented reality experiential environments invite both users and stakeholders to choose and, at the same time, create different spatial locations, while at the same time offering many ways of approaching and examining the various aspects of cultural heritage. We strongly argue that the introduction of Augmented Reality can restore collective and cultural memory to new spatial and contextual relationships between urban areas and their residents and visitors. Augmented Reality is an immersive process that could redefine individuals from preconceived observers to progressive active participants. We emphasize a model of immersive experience that is focused on meaning, feelings, values, and connotations as a result of associative cultural heritage works and events. The overlaid layers of augmented chronotopes have the ability to re-establish new aesthetic-social-collective related spaces within the fluid cultural heritage body, while at the same moment, revealing the transcendence of tangible or intangible heritage borderlines. The development of dialogic augmented spaces properly set up in terms of both shape and measurements would allow the qualities (such as atmospheres, psychogeography, etc.) and requirements (measures, colors, materials, historical documents, environmental records) to be navigated, accessed, and retrieved in real time, composed in a moment. Cultural heritage perpetuation could encourage a palimpsest of multi-creative layering of divergent interpretations and finally a dialogic approach of tangible and intangible objects and sites. Therefore, new meanings, ideas, voices, could be added in many alternative ways through creative, artistic, and dissemination processes, recreating explicit and implicit qualities (Hindmarch *et al.*2019).

Heritage sites can be dialogically experienced and engaged based on an intelligent, dynamic combination of scientific methods and spatial narratives. The dialogic potential of augmented reality amalgamates cultural heritage narratives and individuals' personal approaches and experiences with the dynamic potential of the digital and the implicit authority of material form. The dialogicality and the unfinalizability of cultural heritage experiences are rendered visible as we perceive the past and future in present objects, events, and situations.

The emotionally engaging fusion of the un-observable and observable, emotion and cognition, external and internal, tangible and intangible, forces the steam of individuals and scholars participating in a variety of experiences. The concept of perpetuation, which is aided by deep digital methodologies, enables the cultural heritage's emergence as a consonant field of significance and meaning that is capable of tolerating multiple interpretations. Especially now, when anthropogenic and natural disasters threaten the survival of our ancestors' civilization.

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Strontium Isotope Ratio Research on Residential Mobility and Provenance in Aegean Archaeology: A Review

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Abstract: Provenance, residential mobility and migration are recurrent themes in archaeological research, particularly in relation to questions of cultural change and discontinuity. Since the 1980s, initially in America and Northern Europe, strontium isotope ratio analysis of archaeological skeletal remains has generated substantial new data on the lives of past people and revolutionized research on provenance and mobility. In Aegean Archaeology, nearly ten years following the first ever announcement of strontium isotope results from Greece at the 10th Cretological Congress in 2006 and the first publications using this methodology, new to this context research teams have started to contribute into an ongoing scholarship in the field. Given the growing interest in this type of research, it is high time that we critically reviewed the data in hand. To this end, the author uses the case study of EBA Manika on Euboea to describe the potential and limitations of strontium isotope ratio research with a particular focus on the Aegean context. She also identifies major shortcomings in published research in the field and discusses best practices for sampling, data analysis and data interpretation to avoid potential pitfalls and thus enhance strontium isotopic research in Aegean Archaeology.

KEYWORDS: STRONTIUM ISOTOPE RATIO, ^{87}SR/^{86}SR, TOOTH ENAMEL, RESIDENTIAL MOBILITY, PROVENANCE, MANIKA, AEGEAN.

Introduction

Provenance, mobility and migration are recurrent themes in archaeological research, particularly in relation to questions of cultural change and discontinuity. This largely stems from a cultural-historical approach that equates certain material culture characteristics, archaeologically inferred practices and ideologies with certain people, and considers any inter-regional stylistic and ideological similarities and imports to be the results of population influx (Kossina 1911, Montelius 1903). More recent research, however, has shown that equating the presence of pots, other material culture, or inferred ideologies with the physical long-term presence of the people who are suggested to be the first to create them, and viewing population residential mobility as the exclusive determinant of cultural history, can be highly problematic (Binford 1965; Bintliff 1994; Lyons and Papadopoulos 2002: 5; Renfrew 1972; Tournavitou 1990; Wilson 1987). It is equally possible, for example, that culture change and inter-regional cultural similarities may reflect inter-regional contacts and the transfer of goods, ideas or technologies without significant population influx. Since the 1980s, initially in America and Northern Europe, and later in the rest of the globe, biogeochemical analysis of archaeological skeletal remains has generated substantial new data on the lives of past people and fertilized research on provenance, mobility, and migration.

In essence, isotope ratio analysis of archaeological skeletal remains measures a chemical ‘fingerprint’ within human or animal bones or teeth, which can be directly linked to food and water ingested by the individual. This is based on the principle that ‘you are what you eat’ (Kohn 1999: 335), which describes the processes by which molecules consumed as food or water are incorporated into consumers’ body tissues, and therefore a chemical signal passed either unchanged or altered in a quantifiable fashion from dietary intake into the body can be linked back to the intake (Nafplioti 2016: 44). Isotope ratios of strontium in particular, which this paper will examine, largely relate to local bedrock geology, and can thus provide information on an individual’s geographical origin and track residential mobility between geologically and isotopically different regions/sites (Price *et al.* 2002; Bentley 2006). Since tooth enamel for most of the permanent human dentition largely forms by the age of eight and does not remodel afterwards, human tooth enamel strontium isotope signatures reflect childhood diet and the respective local food web at the place where an individual spent those years; hence their provenance. By contrast, human bone continuously remodels so isotope signatures of cortical bone largely reflect the last 10-15 years of one’s life (Hedges, *et al.* 2007; Hillson 2002; Sealy *et al.* 1995). Thus strontium isotope analyses of tooth enamel and bone can help reconstruct dietary-life records over different periods

Figure 1. Map of the Aegean; marked on it is the site of Manika on Euboea.

of people's lives and potentially trace mobility between geologically different contexts.

In Aegean archaeology, nearly ten years following the first ever announcement of strontium isotope ratio results from Greece at the Tenth Cretological Congress in 2006 and the first publications using this methodology (Nafplioti 2006, 2007, 2008; Richards *et al.* 2008), research teams (Isaakidou *et al.* 2019; Panagiotopoulou *et al.* 2018; Triantaphyllou *et al.* 2015; Wang *et al.* 2019; Whelton *et al.* 2019) have started to contribute to ongoing scholarship in the field (e.g. Nafplioti 2009, 2010, 2011, 2012a, 2012b, 2015, 2018; Nafplioti *et al.* 2021). Given the growing interest in this type of research, it is high time that we critically reviewed the data in hand. This paper is thus timely, while the Symposium "Archaeology - Archaeometry: 30 years later" and the associated volume offers a most appopriate venue for it. Drawing an example from my own work in this context, and taking into account all relevant literature for the Aegean region, I will assess the potential and limitations of strontium isotope ratio research with a particular focus on the Aegean context, identify potential pitfalls and suggest best practices for sampling, data analysis, and data interpretation to avoid them.

Archaeological background

The archaeological case study discussed here concerns to the Early Bronze Age (EBA) site of Manika on Euboea (Figure 1) dating to EH II: 2900/2850-2450/2400 BC and EH III: 2450/2400-2350/2300 BC.[1] The site serves as a very good example of an EBA site in mainland Greece, that, in its early phase, shows material culture characteristics that are most typical in the Cyclades. The presence of imports from and cultural affinities with the Cyclades during this period, led to inferences

[1] EHII=Early Helladic II, EHIII=Early Helladic III.

that this was a Cycladic colony. In its later phase (EHIII), links with Anatolia and the north-eastern Aegean have been interpreted in a similar fashion.

EBA Manika comprised of a well-designed urban coastal settlement of approximately 50 hectares or more, situated about 5km from the modern city of Chalkis, and a nearby contemporary cemetery (Sampson 1988). Its wealth was to a great extent linked to its access to two major valleys of central Euboea, Psachna and Lelandion, and also to its strategic position over the north and south Euboean Gulf, which probably facilitated control of the commerce in the region (e.g. obsidian, metals, and agricultural products) (Sampson 1986, 1988).

Although excavations at Manika revealed 189 tombs, the cemetery probably contained a total of more than 5000 tombs extending over an area of five to six hectares. They were chamber tombs that in most cases comprised of a corridor (i.e. "dromos") and usually one chamber only (Sampson 1988). Many were probably re-used in later periods for new interments. Of the two chronological phases identified, EH II was the main phase of use, while EH III is represented only by a few graves (Sampson 1985, 1988). Affinities with both the Cyclades (EHII) and Anatolia (EHIII) were abundant in the ceramic and metal repertoire, while links with the Cyclades were further evident from the stone vessels and figurines (Sampson and Hadji 2019: 164).

Interpretations of cultural affinities between sites of the broader Aegean region during the Early Bronze Age (i.e. sites on Attica and Euboea in the mainland, the Cyclades, the north-eastern Aegean islands and western Anatolia) are not unequivocal: some scholars associate them with the physical long-term presence in the mainland of Cycladic people and/or people from western Anatolia (e.g. Childe 1957: 51-52; Doumas 1976: 77, 1977: 68; Koronakis 2003; Mylonas 1959: 162-3; Papavasileiou 1910; Sapouna-Sakellarakis 1987: 264), while others emphasize local variation and differences between these contexts and argue for local developments under external influence/s (e.g. Sampson 1988: 126; Theocharis 1959: 300).

In relation to the above, Sampson argued that the available archaeological evidence is not conclusive for the identification of Cycladic colonies in the mainland and agreed with Coleman's theory of the parallel development of the mainland (Attica and Euboea) and Cycladic burial customs (Coleman 1992; Sampson 1988). As regards Manika, in particular, Sampson and Hadji argued that despite the extra-regional influences from the Cyclades and Anatolia during the EHII and EHIII phases, respectively, the character of the settlement was mostly Helladic, and that the presence of objects of non-local origin in the Manika tombs does not say anything conclusive about the long-term settlement of the people who created them or colonised the region?. Rather, they link the imported Cycladic objects or those of Anatolian origin discovered in a few tombs in the Manika cemetery to the wealth/status of the deceased, and to contact and movement of people between the respective regions for trade purposes (Sampson and Hadji 2019: 164).

In this context, the present paper discusses for the first time selected results of strontium isotope ratio analyses applied to burials from the Manika cemetery and thus uses evidence from the people themselves to determine their provenance, track any inter-regional residential mobility, and shed new light on the nature of the site, i.e. colony versus indigenous settlement with occasional, if any, gene flow. It uses this case study as an example to briefly discuss major methodological and interpretational issues in strontium isotope ratio applications. Taking also into consideration shortcomings in relevant work published for the Aegean region, it concludes with best practices in strontium isotope ratio research on provenance and mobility.

Principles of 87Sr/86Sr analysis

Strontium ($^{87}Sr/^{86}Sr$) isotope ratio analysis of skeletal remains is the most popular isotopic application in research on past population residential mobility and provenance. It uses $^{87}Sr/^{86}Sr$ signatures as a proxy for local geology in order to determine the geographical origins of the individuals examined and distinguish between locals and non-locals at the sites investigated. The principles of $^{87}Sr/^{86}Sr$ analysis are well documented (e.g. Bentley 2006; Evans *et al.* 2009; Price *et al.* 2002), and they have also been discussed in detail in earlier relevant work of the present author (e.g. Nafplioti 2008, 2011, 2012b).

In nature, strontium occurs in the form of four stable isotopes, ^{87}Sr (comprises *c.*7.04% of total strontium), ^{88}Sr (*c.*82.53%), ^{86}Sr (*c.*9.87%) and ^{84}Sr (*c.*0.56%). Strontium isotope ^{87}Sr is radiogenic and is the product of the radioactive decay of the rubidium isotope ^{87}Rb, which has a half-life of approximately 47 billion years. All other three strontium isotopes are non-radiogenic (Faure 1986). Therefore, in any geology the ratio of strontium isotope ^{87}Sr to ^{86}Sr depends on the relative abundance of rubidium and strontium at the time the rock crystallised and on the age of the rocks (Rogers and Hawkesworth 1989). Although other factors, for instance, proximity to marine environments and $^{87}Sr/^{86}Sr$ in sea spray (Veizer 1989), atmospheric deposition (Miller *et al.* 1993) and in modern contexts fertilizers too, can also impact local $^{87}Sr/^{86}Sr$ signatures, the latter largely reflect local bedrock geology and mineral weathering (Bentley 2006).

$^{87}Sr/^{86}Sr$ passes from the bedrock into the soil, the groundwater and the food chain, and reaches the human skeletal tissues largely from the food and water consumed with no fractionation related to biological processes (Blum *et al.* 2000; Faure 1986; Graustein 1989). Thus $^{87}Sr/^{86}Sr$ signatures in skeletal tissues of local people largely match the $^{87}Sr/^{86}Sr$ values in local soils, plants, animals and waters at the sites of their residence (e.g. Bentley *et al.* 2004; Nafplioti 2012, Price *et al.* 2002; Wright 2005). In particular, because $^{87}Sr/^{86}Sr$ signatures from tooth enamel reflect childhood diet (Hillson 2002; Ubelaker 1989), whilst bone signatures reflect the dietary intake of one's last 10-15 years, if an individual was born and raised in the local area, the $^{87}Sr/^{86}Sr$ values measured from his/her tooth enamel should be similar to his/her bone $^{87}Sr/^{86}Sr$ and the local bioavailable $^{87}Sr/^{86}Sr$ signatures. Furthermore, they will be in overall agreement to comparable data from local geological material(s). Otherwise, if tooth enamel $^{87}Sr/^{86}Sr$ is found to be significantly different from the local bioavailable $^{87}Sr/^{86}Sr$ signatures, we may conclude that the respective individual spent his/her childhood at a location geologically and isotopically different from his/her residence prior to death (Sealy *et al.* 1991; Steele and Bramblett 1988).

In order to determine the local bioavailable $^{87}Sr/^{86}Sr$ and to distinguish between locals and non-locals at the site/s under investigation, studies of this kind largely use archaeological and modern animal remains (Bentley 2006; Price *et al.* 2002), modern plants and/or water samples (Evans *et al.* 2009; Evans *et al.* 2010). Nevertheless, plants and water strontium signatures can be too 'local' and also susceptible to contamination by fertilizers and/or atmospheric pollution. Samples from archaeological animal skeletal tissues can thus offer a more accurate measure of the range of local $^{87}Sr/^{86}Sr$ values in soils, plants, animals and waters in the areas under investigation as they provide an average of the bioavailable $^{87}Sr/^{86}Sr$ signatures of the feeding territories that these animals occupied in life (e.g. Bentley *et al.* 2004; Nafplioti 2012b; Price *et al.* 2002; Wright 2005). Tooth enamel in particular is more resistant to post-depositional chemical and physical modifications compared to bone and dentine because it is denser, harder, and more inert (Bentley 2006; Kohn *et al.* 1999). In the case study presented here we use tooth enamel isotopic signatures from archaeological animals from the site to characterize local bioavailable $^{87}Sr/^{86}Sr$.

Strontium isotope ratio variability in the Aegean

A prerequisite for the successful application of strontium isotope ratio analysis to track residential mobility is that there is adequate variation in the bioavailable strontium signatures between the specific sites/regions under investigation and alleged origin places for the newcomers. If variation is too low, strontium isotope ratio analysis alone cannot be of any use to the questions explored and we need to combine it with analyses of other isotope systems that are more appropriate for the specific context.

Evidence for the potential of strontium isotope ratio research for tracking mobility in the Aegean region in particular, comes from relevant published work, including the first map of such signatures generated for Greece by the present author (Nafplioti 2011; Wang *et al.* 2019). This evidence is corroborated by further, ongoing research by the author (Nafplioti 2021). Variation in bioavailable strontium signatures in the Aegean follows a clear geographical patterning that suggests a marked difference between the Argolid and eastern Corinthia in the Greek mainland, and the islands of Kos and Rhodes in the south-eastern Aegean, where mean $^{87}Sr/^{86}Sr$ values range between 0.7082 and 0.7087, and the central Cyclades and the north-eastern Aegean, which exhibit values ranging between 0.7093 to 0.7115. Ratios from central Euboea, south-eastern Attica, the western Cyclades, and central Crete range between 0.7089 and 0.7091 and fall within the two ends of the range of variation of the local biologically available $^{87}Sr/^{86}Sr$ in the South Aegean described above (Nafplioti 2011: 1569). As regards the regions concerned in this paper, there is a marked difference between central Euboea, the Cyclades, and the northeastern Aegean, where the newcomers are said to have originated from.

Materials and methods

Strontium isotope ratio was measured in tooth enamel samples from 65 human individuals from EBA Manika. First molars were preferentially sampled to investigate diet and provenance in early childhood (at the age of two to four) for the respective individuals. Specific burials were selected based on their chronology so as to sample from both EHII and EHIII burials the presence/absence of non-local material culture in the tombs, and on their spatial distribution within the cemetery. An additional five $^{87}Sr/^{86}Sr$ signatures were measured from archaeological animals (three sheep/goats, two cows) from the site to characterize the local Manika bioavailable $^{87}Sr/^{86}Sr$ signatures.

The author analysed all samples at the National Oceanography Centre at Southampton. The procedures of sample extraction, sample preparation prior to analysis, as well as measurement of the actual $^{87}Sr/^{86}Sr$ values have been described in earlier publications (Nafplioti 2008, 2009, 2011). $^{87}Sr/^{86}Sr$ signatures were measured to the sixth decimal digit by a VG-Micromass Sector 54 thermal ionization mass spectrometer (TIMS). Repeated measurements of the NBS 987

($^{87}Sr/^{86}Sr$=0.710250) during the period when the samples were analysed yielded an average $^{87}Sr/^{86}Sr$ value of 0.710265 ±0.000024 (2 s.d., n=101).

Results

The mean human enamel $^{87}Sr/^{86}Sr$ was calculated as 0.70932 ±0.00065, while the actual $^{87}Sr/^{86}Sr$ values range between 0.70862 and 0.71286. Thus, intra-group variation for the Manika population is high, evidenced by the large standard deviation and range (Table 1). It is also higher than other Bronze Age human skeletal collections in the South Aegean, viz. Grave Circle A at Mycenae (SD=0.00002), Chora of Naxos (SD=0.00044), Ailias (SD=0.00010), Gypsades (SD=0.00003), Sellopoulo (SD=0.00015) and the Knossos South of the Palace collections from Knossos on Crete (SD=0.00025) (Nafplioti 2007, 2008, 2009, 2012a). The mean animal tooth enamel $^{87}Sr/^{86}Sr$ was calculated as 0.70897 ± 0.00021, while the actual values range between 0.70869 and 0.70927.

The graph in Figure 2 shows human tooth enamel $^{87}Sr/^{86}Sr$ signatures for the Manika cemetery. Each bar on the graph represents a single $^{87}Sr/^{86}Sr$ signature, while the grey horizontal band represents the range of the mean local bioavailable $^{87}Sr/^{86}Sr$ at Manika as determined from the five archaeological animal tooth enamel samples, plus/minus 2 standard deviations. It is used here to mark the confidence limit for characterizing the local population at the site. Based on this criterion, any values that fall below or above this range can be identified as non-locals at the site (Price *et al.* 2002).

On the graph the bars are grouped according to the dating of the burials into EHII, EHII-III and EHIII groups, respectively. Each of these groups is further divided into subgroups according to the material culture associated with the deceased, and bars of different pattern or color are used to differentiate between burials associated with different types of material culture: a) non-local Cycladic pottery (lines oriented to left), b) non-local Anatolian pottery (hatched lines), c) both non-local Cycladic and Anatolian pottery (brick), d) local imitations of Cycladic and/or Anatolian pottery (lines oriented to the right), e) local or not preserved material culture (grey), f) metal objects of Anatolian type(s) (grey), and g) unpublished tombs (black).

Table 1. Descriptive statistics for human enamel $^{87}Sr/^{86}Sr$ values from the EBA cemetery at Manika.

Statistic	Values
Mean $^{87}Sr/^{86}Sr$	0.70932
Median $^{87}Sr/^{86}Sr$	0.70920
Standard Deviation	0.00065
Minimum	0.70862
Maximum	0.71286
Range	0.00424
Skewness (standard error)	4.496 (0.297)
Kurtosis (standard error)	21.871 (0.586)

$^{87}Sr/^{86}Sr$ signatures from ten out of the 65 individuals analysed gave values that fall above the range for the local at Manika bioavailable $^{87}Sr/^{86}Sr$ signatures. Based on the animal dental enamel criterion, therefore, 15% of the people analyzed can be identified as non-locals at Manika. Out of these, four were buried in tombs with non-locally produced Cycladic (two) or Anatolian pottery (two), three were associated with local imitations of Cycladic/Anatolian pottery, while the remaining three represent burials with local or no material culture. The results suggest that less than half of the non-local individuals at Manika could be associated with non-local material culture. Moreover, out of the thirteen individuals from tombs where non-local pottery was found, only four (31%) can be identified as non-locals at Manika, based on the strontium isotope results.

Discussion and conclusions

Human strontium isotope ratio signatures from the cemetery of EBA Manika confirm the presence of non-locals among the population. They also offer unique insights into the relationship between the non-local provenance of objects inside the tombs and that of the people associated with them. The $^{87}Sr/^{86}Sr$ results suggest that in the cemetery of EBA Manika non-local pottery was not strictly associated with burials of non-locals, meaning that one did not need to be non-local to be buried with non-local material culture. This finding thus seems to corroborate Sampson and Hadji's interpretation of objects of Cycladic and Anatolian origins in the cemetery as manifestations of wealth rather than provenance of the respective individuals (Sampson and Hadji 2019: 164). Based on bioavailable $^{87}Sr/^{86}Sr$ signatures from the Aegean region (Nafplioti 2011), those identified as non-locals at Manika probably originated from the Cyclades or the north-eastern Aegean. Their proportional representation, however, is too low to lend support to hypotheses of colonization or large-scale population movements.

The influence that the Cyclades appear to have exercised over the rest of the Aegean in the 3rd millenium BC and the presence of Cycladic objects or their possible local imitations at the cemetery of Manika on Euboea in particular, can better be explained by the operating networks for trade and intermarriage (Broodbank 2000; Renfrew 1991; Sampson and Hadji 2019). Population

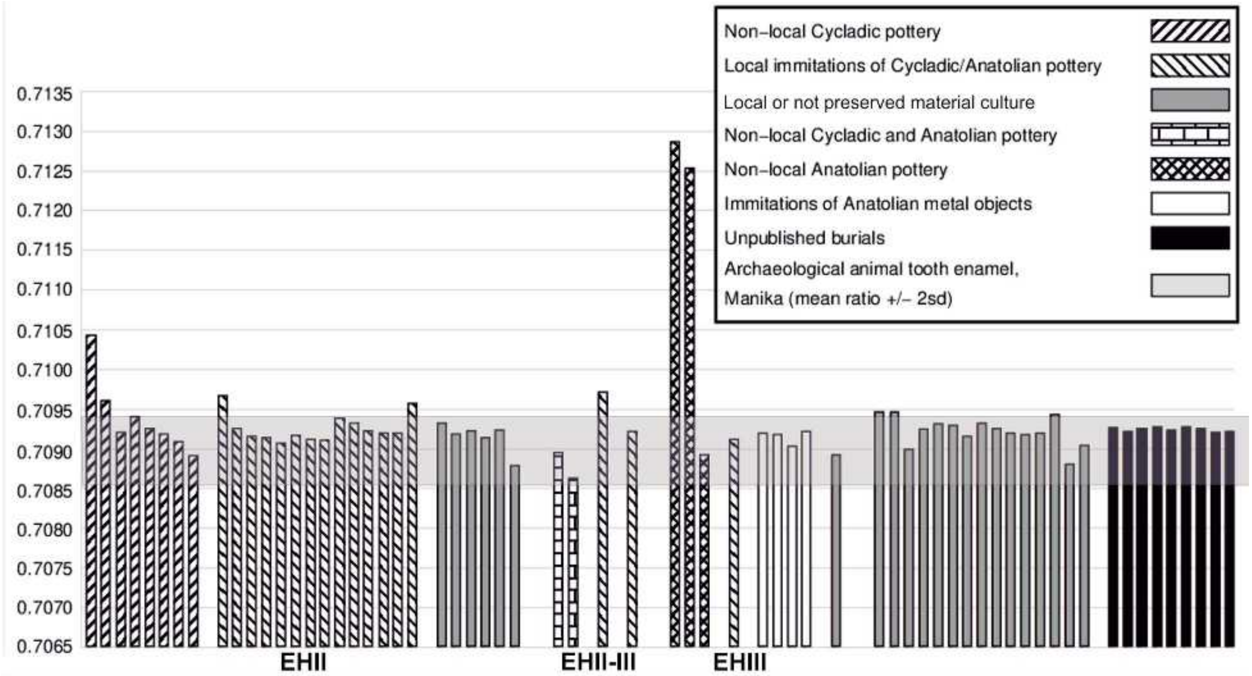

Figure 2. Strontium isotope ratios measured in tooth enamel from Manika individuals.

movement and the establishment of social interactions is a prerequisite for the movement of goods and inter-regional cultural assimilation (Manning 1994). People were moving, but not necessarily for the purpose of colonization. They were moving along with goods, ideas, practices, and technologies, resulting in the development of a more or less homogeneous culture in this region that transcended the boundaries of the various geographical units (Wilson 1987: 43). In a similar fashion, the EHIII archaeological record suggests similar contacts between Manika, the northern Aegean, and Asia Minor (Sampson and Hadji 2019: 164).

The case study of Manika presented here helped demonstrate the potential of strontium isotope ratio applications for tracking past residential mobility and provenance in the Aegean and the benefits to archaeological research from the contextual analysis of isotopic data from skeletal remains. At the same time, the paper also drew attention to inherent limitations associated with such applications, which if overlooked, can lead to serious shortcomings in archaeological interpretation. Drawing examples from the published strontium isotope research in the Aegean, we can make the following concluding remarks with the intent of identifying pitfalls and enhancing strontium isotopic research in Aegean Archaeology.

Although the potential of strontium isotopic analysis for tracking mobility in the Aegean has been adequately described in relation to the geographical patterning of bioavailable strontium isotope signatures (Nafplioti 2011, 2021), a major shortcoming in published research in this field concern the interpretation of what appear to be 'local' strontium values as evidence for the absence of mobility. Unless there is a clearly defined hypothesis in which the specific individuals tested are thought to be non-locals—based, for instance, on material culture, mortuary architecture or other evidence—and unless the sites/regions under investigation are clearly diverse? in terms of their local bioavailable strontium signatures, to simply show that the human signatures are compatible with local strontium isotope values does not say anything conclusive about the origins of the people tested. If the sites/regions investigated are not diverse? in terms of the locally bioavailable strontium signatures, it is possible that at least some of the individuals that appear to be 'locals' may in fact be non-locals, coming from different regions that are geologically and isotopically similar to the site where they were buried. A strontium isotope ratio study is meaningful only when it investigates movement between geologically and isotopically different sites/regions. If there is not sufficient variation, any mobility will go unnoticed and the strontium isotopic results will be erroneously interpreted as evidence for either insignificant mobility or no mobility at all. Similarly, high intra-regional geological and strontium isotopic variation, if not adequately characterised, can lead to false interpretations of mobility. It is therefore evident that a deep knowledge of the bioavailable strontium isotope ratio variation for any region under investigation, and a clear understanding of what 'local' signatures actually stand for, is a prerequisite for a successful strontium study.

Sample size is also critical and often overlooked in data interpretation. For instance, samples in the order of a couple of dozen are simply not large enough to characterize mobility from mortuary contexts that were used for over a few hundred or even 1000 years, such as the tholos tomb on EBA Crete. Not to mention that statistical analyses may be unable to adequately describe differences in such contexts.

Commingled assemblages are even more problematic as it is difficult, if not impossible to confidently identify and sample individuals that may represent first generation immigrants. In multiple burials, lack of consistency in sampling the same skeletal element from all individuals may result in the duplication of certain people in the analyses. Finally, in cases where there is not enough variation in the strontium isotope ratios between the sites under investigation, the potential of this analysis is compromised. In such cases, different isotopes, and preferably a combination of more than one isotope system, for instance, oxygen, sulphur and hydrogen isotope ratios, in addition to strontium can prove to be more informative in relation to past people's provenance and residential mobility, than strontium isotopes alone.

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The Exact Dating of the Trojan War with Zero Uncertainty Error

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Abstract: The gradual darkening of the sun on the day Patroclus died during the Trojan War has been identified, thanks to NASA's catalogue of solar eclipses as a partial solar eclipse. In accordance with the Homeric text, three days after the hero's death, Venus appeared in the sky on the Eastern Horizon. The three particular mornings between Patroclus' death and Venus' appearance have been identified too. After the examination of all types of solar eclipses visible in Troy between 1400-1130 BC., that is, between the height of Achaean civilization and its fall, the solar eclipse on 6 June 1218 BC with significant obscuration of 75.2 % of the sun's discus fits fully with the Homeric description. The application of the Starry Night software allowed us to project the sky of 1218 BC above Troy, and to demonstrate Venus's appearance after the third ceremonial night in which Patroclus' body, Achilles' beloved friend, was consumed by fire exactly as Homer narrated.

KEYWORDS: HOMER, ILIAD, SOLAR ECLIPSE, TROJAN WAR, ACHILLES SHIELD, PATROCLUS

Introduction

Many scholars attempted to date the Trojan War in the past. Two groups produced dates. The first is that of the ancient Greek historians and the second is that of archaeologists. In this paper a new archaeometric trans-scientific methodology is added. In TABLE 1 the list of the ancient Greek historians is presented. In TABLE 2 the list of archaeologists and historians is presented.

Homer and the archaeologists

It is well known that Homer was not a historian. He was neither Herodotus nor Thucydides. It is also well known that the Homeric text contains anachronisms and exaggerations. Could a scientist attempt to examine if the Homeric text contains testable textual information by an acceptable scientific methodology in spite of the negative views of reliable archaeologists such as Sherrat (1990) for instance? The answer is yes! Kraft *et al.* (2003) demonstrated with geoscientific techniques, in a twenty year period that the Homeric text, in terms of historical topography, is explicitly exact. The paradoxical narrations that undoubtedly exist can be understood, firstly by defining what the term "myth" meant for Homer, since he used it 147 times in the *Iliad* and 151 times in the *Odyssey* in contrast to the term *logos*, which he only used twice (in plural). Analysis of these textual statements has deduced that "myth" meant truth, not fiction, and that the terms *mythos* and *logos* were interchangeable for Homer. Cline (2013) showed that there is enough archaeological evidence to illustrate that there was a war between the defenders of the city and their attackers. Figure 1 shows arrow heads thrown by the attackers and a group of ballistic stones used by the defenders. Both are associated with the burnt TROYIIa stratum. In Figure 2 a part of Troy's stratigraphy is shown (Wagner G.A. *et al.* 2003).

The astronomical dating

It is known that some astronomical events are described in the Homeric epics (Theodossiou *et al.* 2011). Among them, a solar eclipse was mentioned by Heraclitus of Pontus (*Allegories*, 75, 1, 1-9, 3). This same solar eclipse was described in the Odyssey during the killing of the suitors (Od. 20. 356-357). We note that Homer described a *gradual increase in darkness* during late noon. Indeed the solar eclipse of the 6 June 1218 BC with a maximum obscuration (over 75%) occurred at 15.45 LT. After Sarpedon's death, a *destructive night* ('*ολοήν νύκτα*') occurred. After Patroclus' death, the *destructive night* became *much darker* ('*ηέρα πολλήν*'), translated by an interpreter as *thick darkness.* It is a very *careful* and *detailed* description of a progressing partial solar eclipse. It is well known that an *absolute darkness* is exhibited when a total solar eclipse occurs. However, the latter did not occur because the battle continued. In other words the increasing darkness never reached total darkness.

Homer, in Il.11.84-90, describes a battle scene, indicating that the time had reached *noon,* and connecting it with the time during which a woodman has his meal. During this time, Patroclus was engaged in fighting against Sarpedon whom he eventually killed. After Sarpedon's death (Il.16.567-568) Zeus covered the battlefield with a *destructive night ('ολοήν νύκτα'):* 'Ζευς δ' *επί νυκτ' ολοήν* τάνυσε κρατερή υσμίνη όφρα φίλω περί παιδί μάχης ολοός πόνος είη—Zeus drew *destructive darkness* over the mighty combat so that around his dear son might be waged the *destructive toil of war*'. This particular darkness was interpreted by astronomer Knut Lundmark in 1940

Figure 1. Projectiles of the attackers and a group of defensive rocks against the attackers associated with Troy the seventh the Homeric Troy and especially with the burnt stratum TROYIIa, after Cline. H.Eric, 2013.

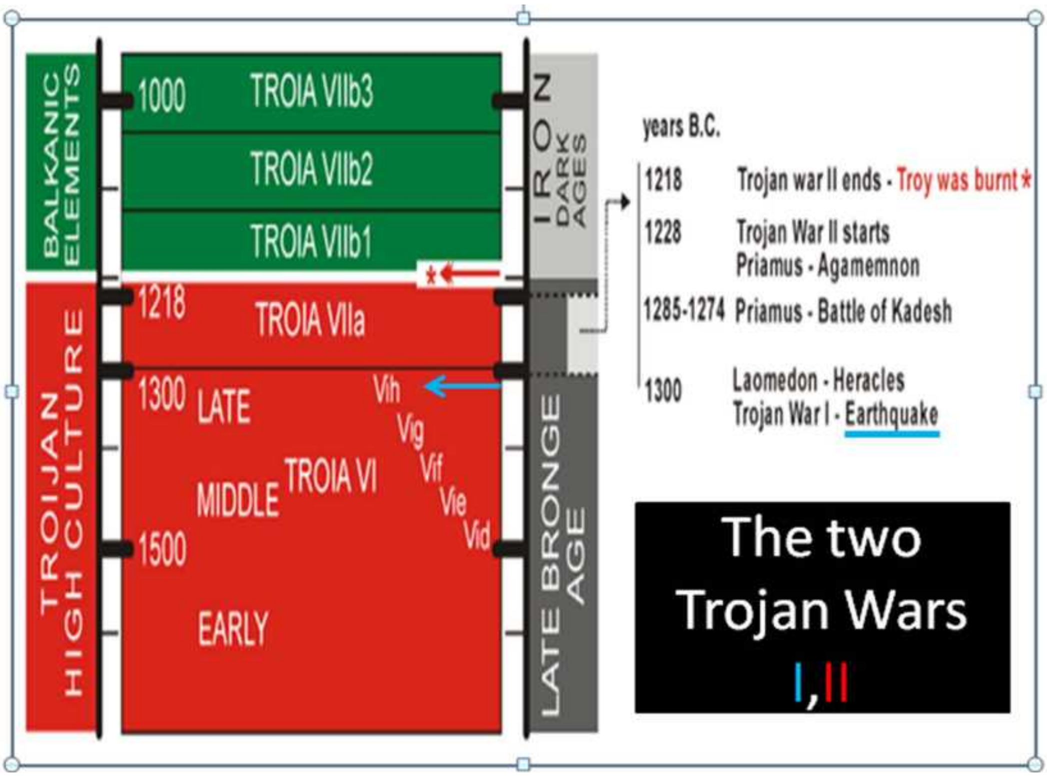

Figure 2. Part of Troy's stratigraphy illustrating the catastrophe layer TROYIIa (through fire) shown by an arrow, and the catastrophe layer TROYVih (through a seismic event) dated to middle-to-late 13th century BC. The stratigraphy is after Wagner, Gunther A, Pernicka, E and Uerpmann, Hans-Peter (2003) the arrows and the legend to the right of the stratigraphy are by the author.

as a solar eclipse. He was quoted by astronomer Goran Henriksson (2012). The latter interpreted the same darkness as a total solar eclipse visible in the Troad too.

However, the Homeric narration does not fit a total solar eclipse. The text says: Il.17.366-376 *'πέπτατο δ' αυγή ηελίου οξεία, νέφος δ' ου φαίνετο πάσης γαίης ουδ' ορέων'*—'the piercing brightness of the sun, and on all the earth and the mountains was no cloud seen' The 'piercing sunlight' in a cloudless sky is present in spite of the impressive imposed darkness on the ground caused by the partial solar eclipse. That piercing light was transmitted by the remaining uncovered part of the sun's discus. Consequently, we had to search for a partial solar eclipse visible in the Troad and not

Figure 3. The coexistence of darkness piercing sun light in the sky as produced by a partial solar visible at the Gobi desert. The photo was taken by astronomer Kosmas Gazeas of the University of Athens. It fits fully with the Homeric description.

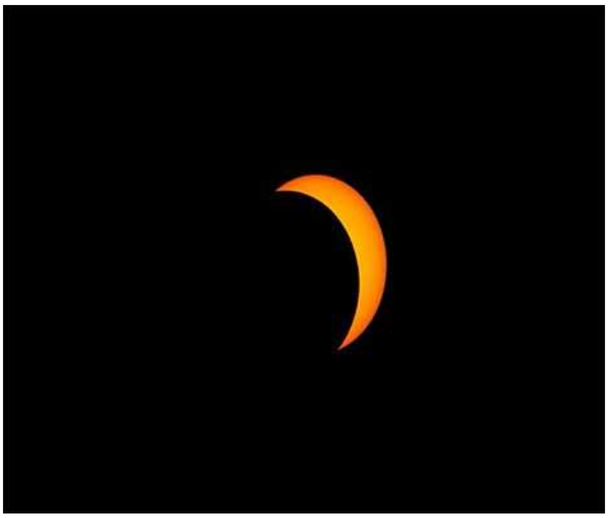

Figure 4. A common partial solar eclipse with significant obscuration of the sun's disc.

a total one. NASA's catalogues were utilized for this purpose. Such a solar eclipse has been found. It is that which occurred on the 6 June 1218 BC with significant obscuration of the sun's discus (75.2 %). The starting time for the gradual and progressive darkness was at 14.10 LT. In another part of the Homeric text it says: Il.17.269-270 *'ηέρα πολλήν χεύ'*—'shed thick darkness'. This thick *darkness* was characterized by Homer as *'night—νύκτα' at noon.* We note that this 'night' did not prevent the battle's continuation. Patroclus tried four times to overtake the wall of Troy (Il.16.702-709).

In Figure 3 and Figure 4 a case of a partial solar eclipse with significant obscuration from the Gobi desert is illustrated by way of example (Astronomer Kosmas Gazeas University of Athens).

The solar eclipse in Figure 5—reproduced here thanks to NASA's catalogue from which the dating was deduced, and the software Starry Night from which the picture of the ancient sky above Troy was deduced—can be coupled with the appearance of Venus in Figure 6 at dawn in the East as Homer narrates. *Venus'* appearance on the *eastern horizon* three days after Patroclus' death is indicated by the Homeric text as follows in Il.23,226-228: ‶Ημος δ' *εωσφόρος* είσι φόως ερέων επί γαίαν,όν τε μέτα κροκόπεπλος υπείρ άλα κίδναται *ηώς*, τήμος πυρκαιή εμαραίνετο, παύσατο δε φλόξ—but at the hour when *the star of morning* goeth forth to herald light over the face of the earth—*the star after* which followeth saffron-robed *Dawn* and spreadeth over the sea—even then grew the burning faint, and the flame died down. Indeed, the planet Venus was visible in the Trojan sky *before dawn* on 9 June 1218 BC because it rose at 3:12 LT, while sunrise occurred at 4:48 LT according to Starry Night program. In other words two astronomical events offer the exact date of the year in which Troy fell. About two months later, from the partial solar eclipse, Troy VII was captured for second time and it was burnt. The first time was some decades earlier by a much smaller army. The latter took advantage of a damaged Troy VI due to a destructive earthquake. Troy was not burnt then as the reader can see in Figure 2.

Conclusions

The proposed new dating for the Homeric Trojan War to 1218 BC by its nature allows for no ambiguity in constrast to the archaeometric techniques used by Papamarinopoulos *et al.* (2012 and 2014). It satisfies fully the Homeric text and as the reader can see, some of the ancient Greek authors (TABLE 1) offer dates compatible with the year 1218 BC. Similarly, the reader can see in TABLE 2 the dates for the burnt layer TROYIIa associated with Homeric Troy, and dated by some of archaeologists pretty close to our dating of 1218 BC. Our dating of a significant astronomical event—the partial solar eclipse of 6 June 1218 BC—is coupled with

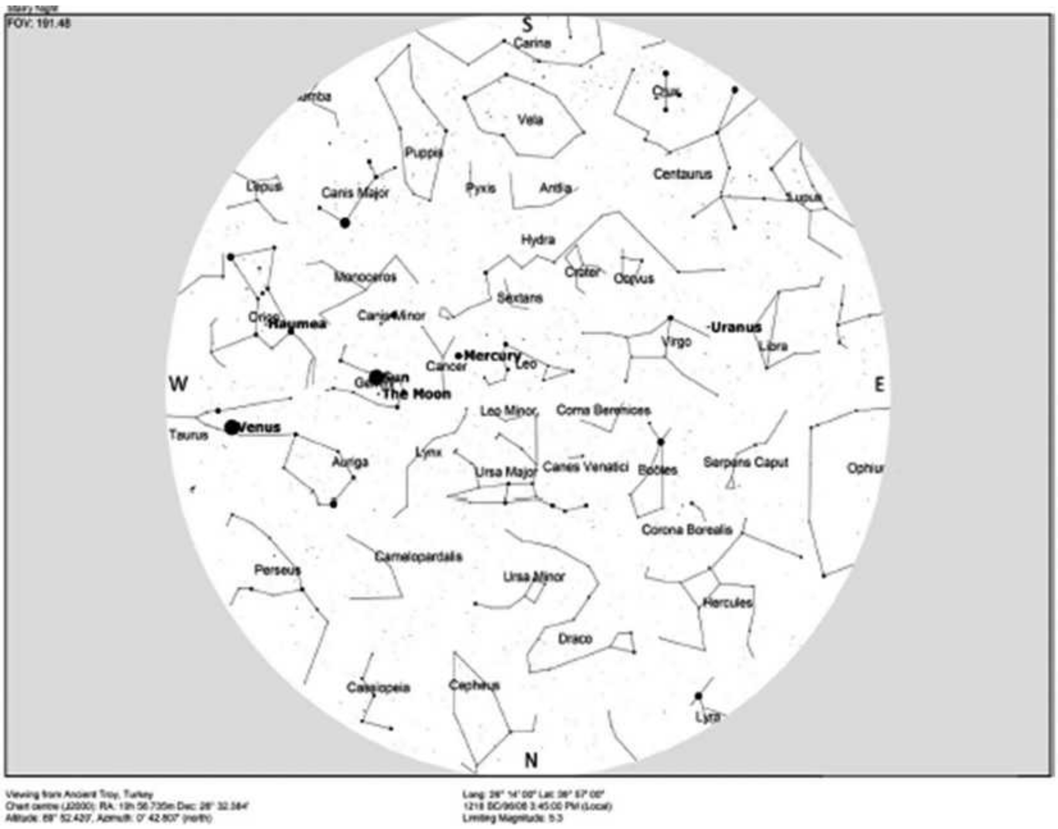

Figure 5. The position in Troy's sky of the solar eclipse of 1218BC as illustrated through NASA's catalogue with the assistance of Starry Night software.

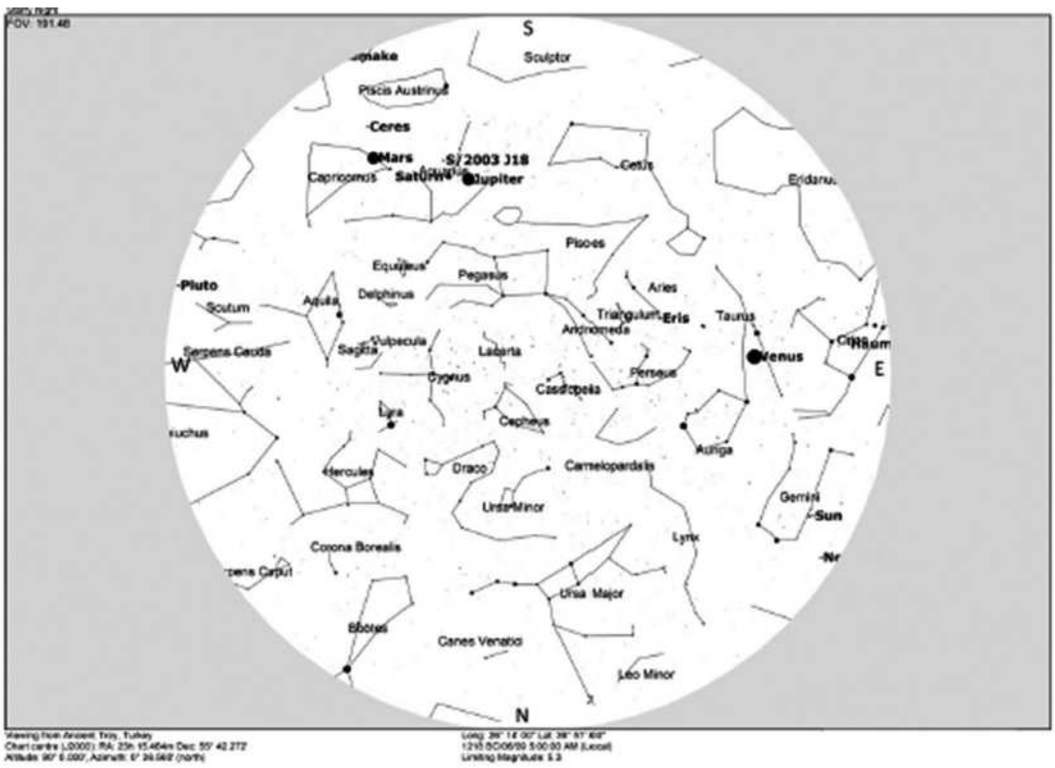

Figure 6. The second astronomical event, coupled with the solar eclipse that was shown in Figure 6, illustrates Venus appearing in the East prior to the sunrise three days after Patroclus' death as Homer described.

another astronomical event, that of Venus' appearance on 9 June in the ancient sky of Troy in the eastern horizon, and prior to the sunrise in accordance with the Homeric text. In other words, our dating satisfies the views of some of the ancient historians and some of the modern archaeologists. Both scientific teams, that of Kraft *et al.* and the present study illustrate beyond any doubt that the Homeric text can offer valuable evidence when approached with trans-scientific methods whose results can be tested with the rules of natural sciences.

In the bibliography the reader can find all the opinions of both the ancient Greek historians and modern archaeologists, and can deduce her/or his own way of thinking for the valitidy of our dating and the tools we have used like, for instance, the NASA catalogue and the software Starry Night which allows us to present the ancient sky anywhere on the planet and at any time:

Espenak F., Meeus J. (2006) Five Millennium Canon of Solar Eclipses: -1999 to +3000, NASA Technical Publication TP-2006-214141.

Espenak F., Meeus J. (2009a) Five Millennium Canon of Lunar Eclipses: -1999 to +3000, NASA Technical Publication TP-2009-214172.

Espenak F., Meeus J. (2009b) Five Millennium Catalog of Lunar Eclipses: -1999 to +3000, NASA Technical Publication TP-2009-214173.

Espenak F., Meeus J. (2009c) *Five Millennium Catalog of Solar Eclipses: -1999 to +3000*, NASA Technical Publication TP-2009-214174.

Note

There is plenty of information in the remaining 5% of ancient Greek texts from which several archaeometric approaches can be realized for the dating of cataclysmic events through trans-scientific studies in Greece within the geoscientific, the astroscientific, the astrogeodaetic and above all the bioscientific domain, while taking into account advances in philological, historical and archaeological publications. Elias Mariolakos in his book *Hellenic Geomythology* (2018) describes many cases of geomyths that can be explained with clarity using archaeometric techniques. Similarly, Cindy Clendenon in her book *Hydromythology and the ancient Greek world* (2009) explains several geomyths. This is important for the next generation of archaeometrists, since I was one of the founding members of the Hellenic Society for Archaeometry when the decision was taken on a wonderful and memorable day thirty years ago at 'Demokritos' the Hellenic Nuclear Center in Athens in Greece.

Dedication

This paper is devoted to the people who worked on archaeometric issues at 'Demokritos' and advanced archaometry together with several others who are active in Research Institutes or Universities all over Greece.

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The Origins of Archaeometry in Greece: A Narrative from the Recent Past

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Abstract: Amongst the aims of the research that lead to this paper, was to trace the origins of archaeometry in Greece and to narrate its infant steps through the work of the first scientists that applied it in the country, with a focus on the Bavarian Xavier Landerer who acted after the establishment of the Greek nation-state and a reference to the Greeks Othon Rousopoulos a "museums' chemist" whose career is linked with the National Archaeological Museum, and the chemist Konstantinos Zengelis who acted between the Wars. The results of the research contribute to an eventual understanding of this relatively new scientific field, which is very closely linked with and has a tremendous impact on other scientific fields such as archaeology, heritage conservation and anthropological and sociological sciences. The methodological process of the research comprised extensive mining and synthesis of archival and bibliographic records, in particular Greek periodicals, and a thorough analysis of published and unpublished material. The research has brought to light the archaeological findings and the monuments that constituted the core of the scientists' work and the multi-dimensional scientific concerns that motivated them while carrying out their work in the, unknown at that time, scientific field of archaeometry. Although limited information is revealed on the technical processes and methods adopted by the scientists, their contributions on ancient technologies and the interpretation of the ancient world, set the basis and initial setting of the field of archaeometry in Greece. Further research on the two scientists' exact methodological approaches, the potential linkage between each other's work and their impact on 45the work of scientists that followed, will eventually enable us to follow the evolutionary road of archaeometry in Greece.

KEYWORDS: LANDERER, ROUSOPOULOS, ZENGELIS, PARTHENON, ANTIKYTHERA, DELOS, ARCHAEOMETRY.

Introduction

In 1990 the First Symposium of the Hellenic Society for Archaeometry was organized in Athens and the correlations between archaeology and archaeometry, two scientific fields that had seemingly little in common, were then discussed (Figure 1).

Archaeologist Nikos Gialouris stated at the time: *"Until the first half of the 20th century Greek archaeologists and professors of archaeology in greek and other Universities had such unconditional faith in the self-sufficiency of the archaeological methodologies that regarded science to be irrelevant to the archaeological research… "* (Γιαλούρης 1992: 27), and then he added: *"…This sense of self-sufficiency proved to be deceptive…"* (Γιαλούρης 1992: 28). Gialouris also referred to the experiences that gradually lead to the realization for interdisciplinary collaboration, and to the first steps towards its implementation on behalf of officials of the Hellenic Archaeological Service, such as the archaeologist Spyridon Marinatos in 1965 (Γιαλούρης 1992: 29).

At the same Symposium, it was stated by the archaeologist Michalis Andronikos that: *"Although archaeometry is a recent scientific discipline it serves purposes of a long tradition…"* (Ανδρόνικος 1992: 23). Recent research has indeed proved this. Research in the historic archives of key institutions of the Hellenic

Figure 1. First Symposium of the Hellenic Society for Archaeometry in 1990

Archaeological Service, such as that of the Directorate for the Management of the National Monuments Archive and several peripheral Archaeological Ephorates and Museums, as well as study of publications dating between 1834 and 1939, has brought to light evidence of early collaborations which outline the awkward, yet systematic development and finally, the establishment of archaeometry in Greece.

This paper aims at presenting a chronicle of the early steps of archaeometric research in Greece, with a focus on the first ever scientist who practised it, and a reference to the scientists that followed, in an attempt to contribute to the evaluation of the progress in this scientific discipline.

Early steps in archeometry in the newly founded hellenic state. The work of Xavier Landerer (1809-1885)

Archaeometric research in Greece was affected by equivalent research that had preceded in Europe, as the first scientist who practised it was European and had been educated in Europe.

In 19th century Europe along with archaeology archaeometry emerges[1], in order for issues of provenance, technology and dating of archaeological material to be addressed (Tite 2007, 139). Archaeometry represents the timeless connection between archaeology and science and for most of the 19th century, it was also related to the scientific application of monumental conservation[2].

European scientists such as the French Jean-Antoine Chaptal (1756-1832) who analysed ancient pigments from Pompey and Ercolano as early as 1809 in order to define their chemical composition[3], and the British scientists Humphrey Davy (1778-1829)[4] and Michael Faraday (1791-1867), who had long term collaborations with institutions such as the National Gallery and the British Museum for archaeometric studies (Δελή, 2019, 47-48), are some indicative examples of scientists who devoted part of their scientific careers to archaeometry.

The Hellenic State was founded in 1830. In 1833 with the establishment of the Bavarian monarchy under prince Otto, European scientists arrive in the newly founded state to assist the organization of its structures. Among those, arrives the Bavarian chemist, royal doctor and chief pharmacist Xavier Landerer (1809-1885)[5] (Figure 2).

Figure 2. Xavier Landerer (1809-1885) (Source: Athens University History Museum)

Landerer's scientific and literary work was multi-dimensional. It included research of medical, pharmaceutical and geophysical nature[6]. He was the author of the first teaching chemistry books in Greece[7] and the first scientist to conduct consistent archaeometric research (Figure 3).

Landerer's activity in the field was accelerated by the archaeologist and General Ephor of Antiquities Kyriakos Pittakis (1798-1863) (Figure 4), who seems to have had foreseen the inevitable link between archaeology and science.

[1] The term 'archaeometry' appears in 1958 as the title of the English magazine *"Archaeometry"* (Maggetti 1996, 65)

[2] The linkage between archaeometry and conservation was the design and development of effective yet compatible materials and methods used for archaeological and art conservation, through the application of science (Tite 2007, 141)

[3] Chaptal analyzed a specific pigment for which he concluded that it was derived from the plant 'rubiatinctorum', (Merimee 1839).

[4] Humphrey Davy was Chairman of the Royal Society. He invented electrolysis and the miners' safety lamp, he isolated Sulphur and proved in collaboration with Michael Faraday, that diamonds are pure carbon [online] https://e.wikipedia.org/wiki/Penzance, accessed 02/11/2015)

[5] Xavier Landerer was born in Munich in 1809. He had a PhD in Sciences and Medicine, he was among the first professors of chemistry at the University of Athens (1837-1875) (Στεφάνου 1948: 7-8), and also taught pro-Bono at the School of Arts (later Technical University) (Κανδήλης 2009)

[6] Some of Landerer's newspapers articles of a geophysical context: Landerer, X., (1874) «Ἱστορία τῶν Μεθάνων», *Μέριμνα,* N. 1320, 08 Οκτωβρίου, 4; Landerer, X., (1868) «Περὶ τοῦ ὕδατος τῆς Ἑλένης ἐν Κεγχρεαῖς», *Ἀλήθεια* N. 659, 11 Ιουλίου, 4.

[7] Some of Landerer's publications on chemistry and pharmacology: *Αναλυτική Χημεία* (1842); *Χημεία Ανόργανος* (1840); *Χημεία Οργανική* (1842); *Ὁδηγίαι πρὸς παρασκευὴν χημικῶν καὶ φαρμακευτικῶν σκευασμάτων* (1857); *Ἐγχειρίδιον Ζωολογίας* (1844); *Ἐγχειρίδιον Συνταγολογίας* (1845); *Ἐγχειρίδιον Τοξικολογίας* (1843), http://argolikivivliothiki.gr/2009/09/11/1809-1885, accessed 26/07/2017.

Figure 3. Landerer with his assistants at the University
(Source: Athens University History Museum)

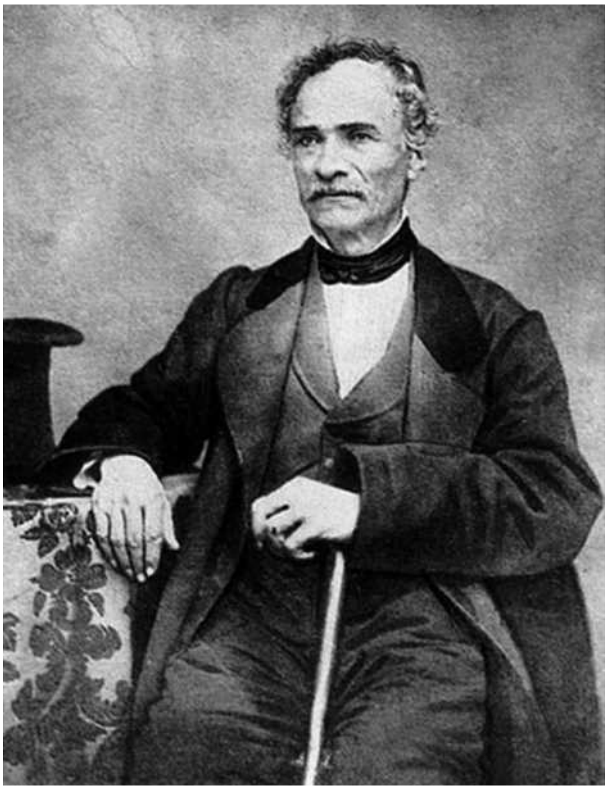


Figure 4. Kyriakos Pittakis (1798-1863)
(Source: http://www.arcchetai.gr accessed 09/02/2022)

In this spirit, Pittakis made available to Landerer archaeological findings from the General Ephorate's excavations for study[8]. The collaboration seems to have started as early as 1838, date of the first publications in the Archaeological Journal (A.J.)[9], and its agenda was "dictated" by the demands of archaeological research: the improvement of the findings' legibility as they were regarded the bearers of multi-dimensional information about the ancient world, and an urgent and immediate need for their life to be prolonged It is indeed an early, productive collaboration among scientists with different scientific backgrounds, which evolved in the vast field of archaeologic research.

Analysis of grave offerings

The analysis of grave offerings constituted a crucial part of Landerer's archaeometric work due to the wealth of sociological, anthropological and technological information they could potentially provide. Between 1839 and 1840 he analyses surgical equipment and the content of a ceramic vessel (Λάνδερερ 1839a, 144)

[8] Kyriakos Pittakis as the General Ephor was in charge of the excavations conducted by the General Ephorate (Δελή, 2019, 105)
[9] Landerer's last publication in the Archaeological Journal was in 1855 (Δελή, 2019, 105)

- a therapeutic mastic-based mixture-all found in a sarcophagus that, as he clarified, belonged to a doctor (Λάνδερερ 1840a, 429) in order to reach conclusions on their technology and their preservation state (Λάνδερερ 1839a, 144).

Women in antiquity were often buried with their beauty products and Landerer analyses soaps (Λάνδερερ 1839b, 143) and pigments comprised in make-up products known as "*entrimmata*" (εντρίμματα), all of which came from women's burials. The white and soft powder that gave the female skin a white shine was clay-based, while the red pigment was nothing but the white powder and an addition of ferrous clay. The new information on the red pigment composition, would add to the up to that date knowledge according to which, the red pigments were made of murex (πορφύρα) and sea plants (Λάνδερερ 1839c, 211). In a similar way the chemical composition of other beauty products was defined[10], such as that of the black pigment used for colouring the eye-brows and the eye-lashes. Its powder contained shiny particles and once heated, a sulphate odor emerged, which indicated a presence of Sulphur and antimonite[11].

Landerer's conclusions on the provenance and use of a black glass-like substance contained in a vessel from a sarcophagus on the island of Kea are overwhelming for modern societies. Analysis confirmed that it was a narcotic substance, specifically hemlock, the poison given to the old citizens of Kea during the ceremony of a voluntary euthanasia (Λάνδερερ 1842: 5537) known as "*Keion Nomimon*" (Κείων Νόμιμον).

Pigment analysis

In 1839 Landerer analysed the sample of a unique blue-shaded pigment traced on a marble sculpture, so unique that it did not resemble any other blue pigment that he had analysed until then. After analysis Landerer traces cobalt, a mineral well known for its colouring properties and its exceptional stability as a pigment agent. This confirmation by Landerer of cobalt's use in ancient Greece indicated that the ancient Greek artists were aware of the mineral's properties and had developed the technology to exploit them. This was quite a turn-over as until then (1839) the earliest use of cobalt as a colouring agent was documented in 1540 Europe for the colouring of glass (Λάνδερερ 1839d, 70).

Analysis of the protective patina on metal artefacts

Through his archaeometric work Landerer also contributed to an understanding of the complex deterioration processes of metal objects, which did not allow an empirical approach and conservation policy; on the contrary they imposed a scientific approach.

In this context Landerer studied a set of copper coins, on the surfaces of which he had traced a green-blue shaded layer that resembled enamel-glaze, but was exfoliating causing the inscriptions to vanish (Λάνδερερ 1855a, 1227). Landerer assumed that it was a manmade, protective layer, created by the ancient craftsmen who had developed the technology to create it. In order to prove it scientifically, he implemented a time consuming experimental process, initiated long before the final publication of its results: coins were buried in various subterranean environments (i.e. sandy, clay, dry, high salt content, in immediate contact with the earth or not etc) for a six year period. Then they were removed and any superficial alterations were observed and recorded According to the observations he had made, Landerer reburied the coins for another two years having prior coated some with a mixture of bees-wax and mastic-resin (known since antiquity), the so-called "*kiromastichin*" (κηρομαστίχην), and some with a mixture of mastic-resin and turpentine oil. The experiment's outcome allowed Landerer to confirm his theory and to define the technology of the protective patina of the metal objects (Λάνδερερ 1855a, 1227).

Archaeometric studies on architectural monuments

Landerer's work on architectural monuments was motivated by alterations traced by himself and other scientists on monumental surfaces, which needed interpretation as far as the deterioration mechanisms and the conditions that accelerated them.

The yellow shade on the surfaces of ancient marbles was a constant challenge for Landerer's contemporary scientists: archaeologists considered it to constitute a deliberately applied protective layer, part of the original structure, while botanists who had microscopically traced plant seeds in the marble's pores, attributed it to these[12]. Landerer questioned the two theories[13] as he believed that the yellow colouring was due to the presence of iron. To prove his theory, he submitted iron from the marble samples he had received by abrasion, to microscopic analysis, and to a test with reagents (Λάνδερερ 1840c, 430). It was a successful attempt

[10] The base of all beauty pigments was white lead (lead carbonate known as "psimithion"-ψιμμύθιον) with the addition of a small quantity of silver and a mixture of water and gum-a resin that worked as a binding agent-was also added Landerer had also traced in all the pigments an animal substance that could be egg white or animal gel, possibly used to improve the consistency of the final product (Λάνδερερ 1840b, 330)

[11] Antimonite: sulfide antimonite mineral, used in antiquity as a make-up product for eye-lashes (Dana, J.D., 2008)

[12] Λάνδερερ 1839e, 187.

[13] He actually rejected the archaeologists; Theory due to absolute lack of even a single trace of any potentially protective substance from the marble surfaces and only partly accepted the botanists' theory for which he believed that it was affected by several other factors (Λάνδερερ 1839d, 187).

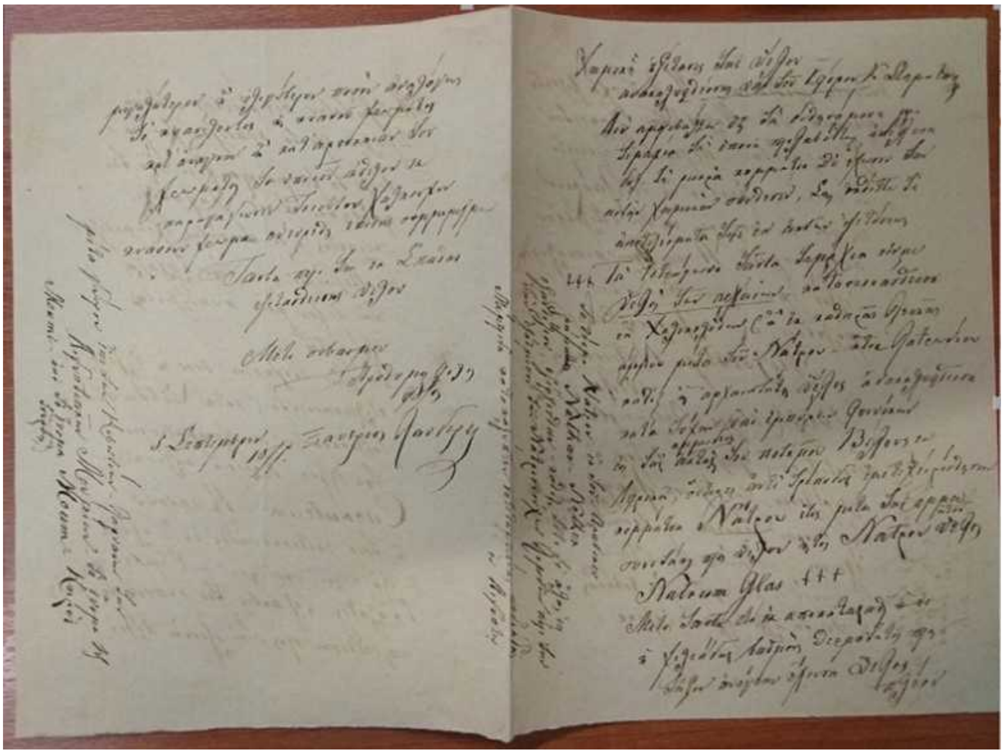


Figure 5. Document with the analysis results of ancient glass samples from the region of Spata signed by Xavier Landerer (Without Protocol number, 03/09/1877) (Source: Directorate for the Management of the National Archive of Monuments-Department for the Management of the Historical Archive of Antiquities and Restoration, BOX:430)

to prove that the oxidation of iron in the presence of oxygen and water and its subsequent colour alteration, caused discolouring of the marble surfaces (Λάνδερερ 1839e, 187). He conducted the experiment on samples from the temples form the Acropolis, the temple of Olympion and the temple of Poseidon in Sounio (Λάνδερερ 1840c, 430).

The columns of the Poikile Stoa (or Painted Porch) were also studied by Landerer. This time he worked towards the comprehension of the formation process of a black shaded discolouration on marble monuments. The layer was in immediate contact with the marble surface which excluded the possibility of it being artificial (Λάνδερερ 1840d, 338). Analysis of the samples taken by abrasion, indicated a content of organic and inorganic substances and soot, which was the actual colouring agent. It is quite possible that this was an early identification by Landerer of the so-called "black crust" phenomenon met in urban environments and attributed to a combined action of soot, atmospheric pollutants and environmental agents (Λάνδερερ 1840d, 338).

Study of ancient technologies: Artefacts, sculpture and utilities

Landerer's study of ancient technologies, concerned the processing of wood in the context of artefacts and furniture making (Λάνδερερ 1855b, 1225), marble and stone sculpture, the use of gypsum mortars and the use of wax in sculpture (Λάνδερερ 1855b, 1224), the use of clay in construction[14], the processing of bronze[15] and its colouring techniques[16] and the processing of lead, in antiquity (Λάνδερερ 1855b, 1226)[17]. Also, as part of his collaboration with K. Pittakis, Landerer did research on the manufacture technology of ancient mirrors (Λάνδερερ 1840d, 331).

In this context, archival research has brought to light a unique, and the only one so far, manuscript signed by Landerer himself. It is dated in 1877 and in it Landerer refers to the method of glass-making in antiquity, linking the results of archaeometric analysis of samples from ancient glass from Spata, with historic information (Figure 5).[18]

[14] The mixture known as *"chori"* (χωρί) in Landerer's time was quite possibly a filling mortar for the composition of which he does not provide any information (Λάνδερερ, Ξ., 1855b,1224)

[15] Cadmium was an ore that contained zinc (Λάνδερερ, Ξ., 1855b,1224)

[16] Such as a statue with an ochre face and another one with a red face and a relief with coloured details (Λάνδερερ, Ξ., 1855b, 1224)

[17] Λάνδερερ, Ξ., 1855b, 1226

[18] Αρχείο /Archive της Διεύθυνσης Διαχείρισης Εθνικού Αρχείου Μνημείων, Τεκμηρίωσης και Προστασίας Πολιτιστικών Αγαθών-Archive of the Directorate for the Management of the National Monuments Archive, for the Documentation and the Protection of Cultural Objects (ΔΔΕΑΜΤΠΠΑ), Κιβώτιο/Box 430, *Ακρόπολη και ανασκαφαί Ακροπόλεως και περίπαρθεν 1888-1877-Τάφοι Σπάτων*

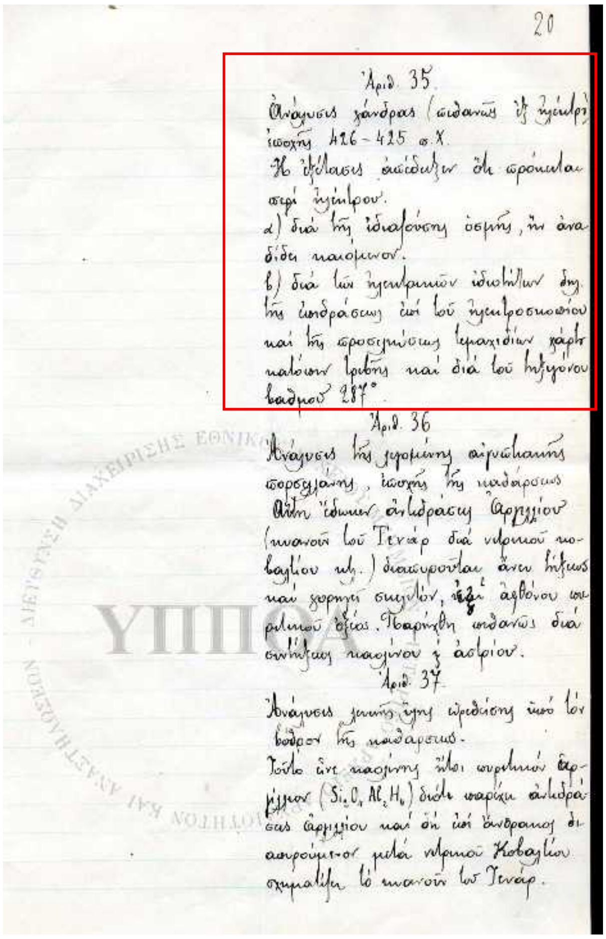
The contribution of the 'museums' chemist' Othon Rousopoulos to archaeometry

Chemist Othon Rousopoulos's (1856-1922)[19] (Figure 6) work in the field of conservation in Greece has only recently been studied upon and published.[20]

It must be emphasized that Rousopoulos was the first Greek scientist with a career focus in archaeological conservation, Μωραΐτου 2016 a career closely related to the National Archaeological Museum where he worked under the job title: Museums' Chemist[21]. His involvement in conservation began as early as 1888 with the conservation of bronze findings from the excavations at the Acropolis[22]. He had also undertaken the conservation of great archaeological revelations of his time, such as the "Stelai of Dimitrias" (Στήλαι Δημητριάδος)[23], archaeological findings from the Antikythera shipwreck, the marble architectural elements of the Acropolis monuments, material from the excavations in Delos etc.

Figure 6. Othon Rousopoulos (1856-1922) (Source: National Hellenic Research Foundation)

The majority of his work in archaeometry was conducted in conjunction with his work in conservation. An indicative example of this fact is his report addressed to the Archaeological Service dated 1913, which includes the conservation program he proposed for the archaeological material from Delos 1 (Figure 7).[24]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Αριθ. 35

Αριθ. 36

Αριθ. 37

Figure 7. Analysis of archaeological material form Delos documents (P.N: 1151, 13/9/1913) (Source: Directorate for the Management of the National Archive of Monuments-Department for the Management of the Historical Archive of Antiquities and Restoration, BOX 794)

Although in the report conservation issues are mainly raised, Rousopoulos also points out the need for archaeometric analysis, with specific references such as metal artefacts, glass beads, artefacts made of the

[19] Othon Rousopoulos was born in Athens in 1856. He studied Physics in the National University of Athens and Chemistry in Germany. In 1894 he founded the Industrial and Commercial Academy and he worked at the Ministry of Economics while in 1915 he was elected as a Parliament Member. Finally he was a lecturer at the University of Athens (Στεφάνου 1948: 7-8).

[20] More on Othon Rousopoulos in: Δελή, Μ., (2016) "Οι γραπτές στήλες της Δημητριάδος: ένα χρονικό συντήρησης από τις αρχές του 20ου αιώνα", στο: *Πρακτικά ΠΕΣΑ 2017*, 3 Δεκεμβρίου (υπό έκδοση) (Deli, M., (2016) «The painted Stelae of Demetrias: a conservation chronicle from the early 20th century», in: *Proceedings of the 2017 Annual Meeting of the Panhellenic Union of Conservators of Antiquities,* December 03 (in print); Μωραΐτου, Γ., (2016) «Η «Οδύσσεια» της συντήρησης και της φυσικοχημικής έρευνας των αρχαιοτήτων στο Εθνικό Αρχαιολογικό Μουσείο», στο: Λαγογιάννη-Γεωργκαράκου, Μ., (επιμ.) *Κατάλογος Έκθεσης: Οδύσσειες*, εκδ. Εθνικό Αρχαιολογικό Μουσείο-Ταμείο Αρχαιολογικών Πόρων και Απαλλοτριώσεων (ΤΑΠΑ), Αθήνα, 237-260 (Moraitou, G., "The Odyssey of conservation and physicochemical research of antiquities at the National Archaeological Museum", in: Lagogianni- Georgakarakou, M., (ed) *Catalogue of the exhibition: Odysseys*, National Archaeological Museum-Fund of Archaeological Proceeds, Athens 2016, 237-260);

[21] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 27, Γ́ Αρχ/κη Περιφέρεια (Θεσσαλία), 1912-1916 (1899-1916), 1912: *Έγγραφα Ρουσόπουλου*, 28/06/1910

[22] Μωραΐτου, Γ., (2019) «Πότε αρχίσαμε να συντηρούμε τις αρχαιότητες στην Ελλάδα;»[online], Accessed 08/02/2019.

[23] Δελή, 2016 (in print)

[24] Under the supervision of which the Greek Archaeological Service was at the time.

so-called at the time Egyptian porcelain[25], a fragment of fabric and pigments from wall-paintings[26]. The material is submitted to microscopic analysis and tested with reagents such as acids. Also Rousopoulos refers to the use of the electroscope[27], an early scientific instrument for the measuring of electricity in a body (invented by the British physicist William Gilbert (1504-1603) around 1600) (Fleming 1911, 239).

Rousopoulos's contribution in archaeometry is also demonstrated through his participation in committees specially appointed by the A. S. for the addressing of complicated preservation issues related to the natural properties of the ancient fabric, the chemical composition of alloys and others, for which an interdisciplinary approach was necessary. Prominent scientists such as: the chemists Anastasios Damvergis (1857-1920)[28] (Figure 8), Anastasios Christomanos (1841-1906)[29] (Figure 9) (Petros Zalokostas (1855-1941)[30], Georgios Krinos (1850-1935) and Skintzopoulos Angelos[31], the geologist-mineralogist Konstantinos Mitsopoulos (1844 ή 1946-1911)[32] the mineralogist and crystallographer Friedrich Wilhelm Berthold Rinne (1863-1933)[33] and the botanist Theodor von Heldreich (1822-1902)[34] participated in such committees with him.

Figure 8. Anastasios Damvergis (1857-1920)
Source: Elia.org (Terms of use: CC BY 4.0, creator's quotation)
Picture by: Boehringer, Carl

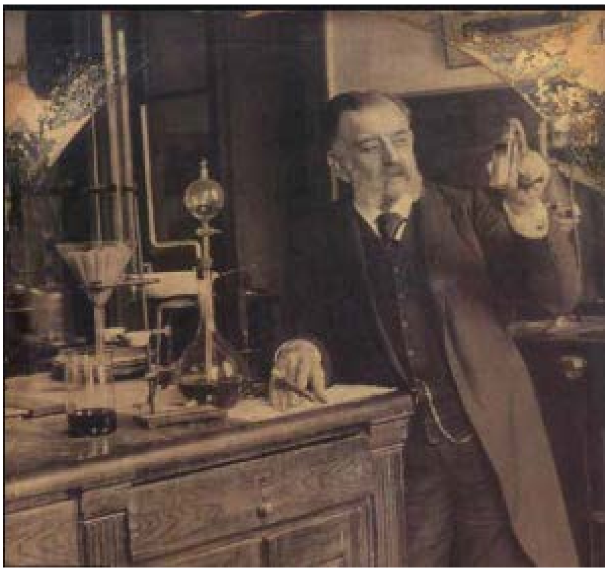


Figure 9. Anastasios Christomanos (1841-1906) (Source: Athens University History Museum)

[25] The Egyptians enameled stone. One half at least of the scarabei, cylinders, and amulets contained in the museums are of limestone or schist covered with a coloured glaze. The common clay seemed to be inappropriate to this kind of decoration, for they substituted in its place various sorts of earth-some white some sandy. Another sort, brown and fine which they obtained by the pulverization of a particular kind of limestone found in the area of Keneh, Luxor and Asuan. And a third sort, reddish in tone and mixed with powdered sandstone and brick dust. These substances are known by the inexact names Egyptian porcelain and Egyptian faience (Maspero, G., (2009) *Manual of Egyptian archaeology. A guide to the studies of antiquities in Egypt*, Salzwasser Verlag, 237).

[26] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 384, *Μυκόνου, Δήλου ανασκαφαί κλπ, 1873-1916*.

[27] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 384, *Μυκόνου, Δήλου ανασκαφαί κλπ, 1873-1916*.

[28] Anastasios Damvergis was born in Mykonos in 1857. He studied Pharmaceutics at the University of Athens and he also studied chemistry by scholarship. He got his PhD from the University of Heidelberg (Στεφανίδης 1948: 10)

[29] Anastasios Christomanos was born in Vienna in 1841. He graduated from the University of Heidelberg in 1861 and he taught chemistry at the University of Athens until 1906. He died in1906. (Κανδήλης 1981: 565)

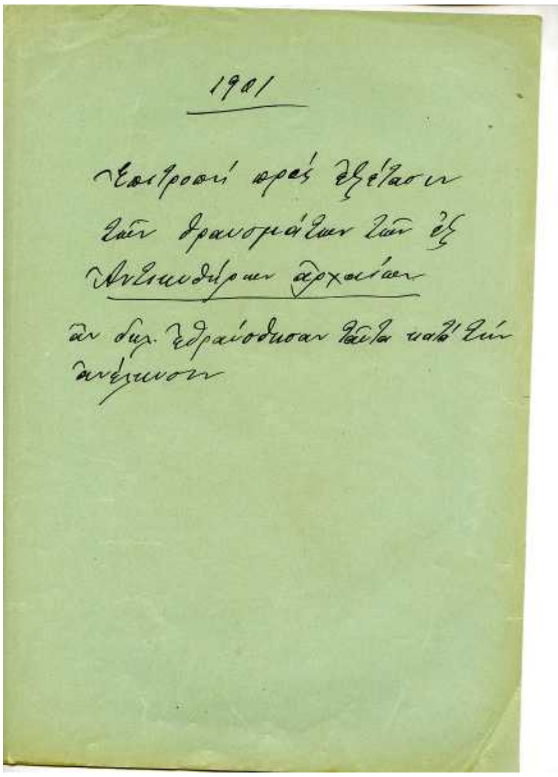
[30] http://pandektis.ekt.gr accessed 01/10/2019.

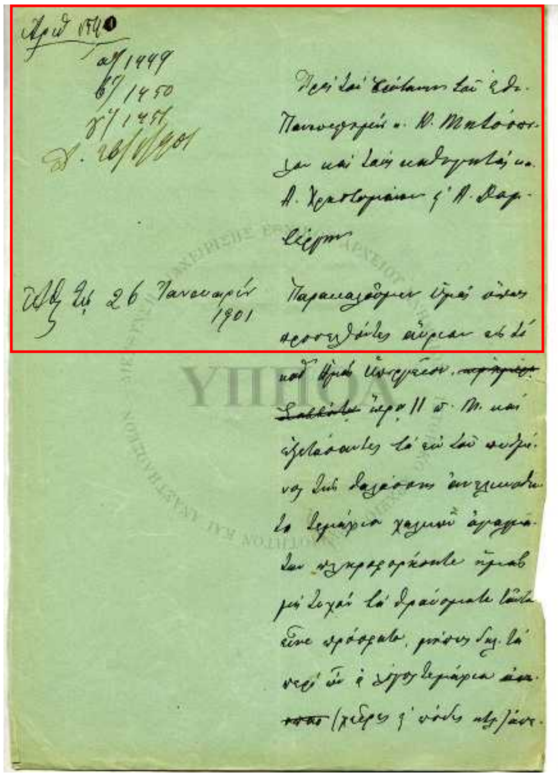
[31] *Κατάλογος των Ελλήνων Χημικών*, (1924) Ένωσις Ελλήνων Χημικών, Αθήναι, 14.

[32] Konstantinos Mitsopoulos was a physicist and mathematician born in Patra in 1844 or in 1846. He was the first PhD graduate of the University of Athens (1888). He studied physics, chemistry, geology, geodesy, metallurgy, mining, mining law and mechanical engineering at the Freiberg Bergakademie in Saxony, with a six year scholarship from the Greek government. He started teaching at the National University and at the Technical University in Athens in 1875. He was the first geologist and mineralogist in Greece (Κρητικός 2003: 753)

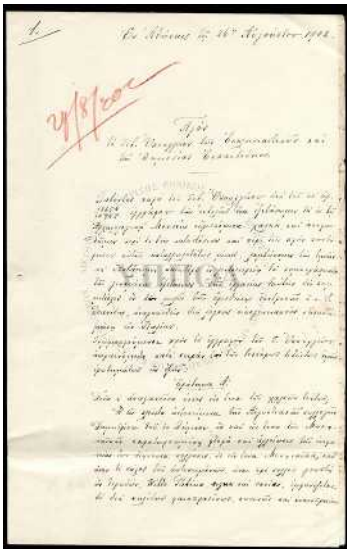
[33] http://www.uni-leipzig.de/unigeschichte/professorenkatalog/leipzig/Rinne_124/(accessed 08/12/2019)

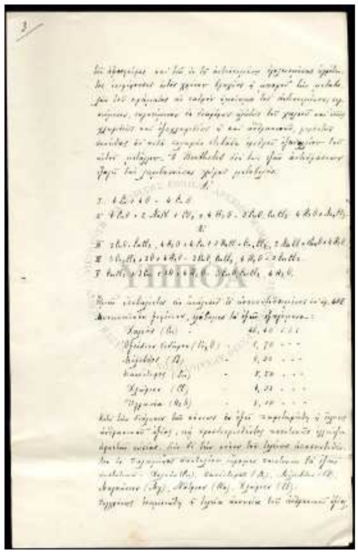
[34] http://www.deutsche-biographie.de/sfz29463.html#we (accessed 08/12/2019)





Figures 10 and 11. Analysis of artefacts from the Antikythera shipwreck documents (P.N.: 154, 26/11901) (Source: Directorate for the Management of the National Archive of Monuments-Department for the Management of the Historical Archive of Antiquities and Restoration, BOX: B438)





Figures 12, 13 and 14. Analysis of artefacts from the National Archaeological Museum documents (P.N.: 154, 26/8/1902) (Source: Directorate for the Management of the National Archive of Monuments-Department for the Management of the Historical Archive of Antiquities and Restoration, BOX: B438)

Metal fragments from statues and silver decorative elements from objects of an elite provenance[35] from the shipwreck of Antikythera[36] (Figures 10–11), copper axes, swords and metal statues from the National Archaeological Museum[37] (Figures 12–14).

[35] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 438, *Αντικυθηραϊκά, Διάφοραι Αναλύσεις και γνωματεύσεις*, 62/β, 09/02/1901

[36] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 438, *Αντικυθηραϊκά, Διάφοραι Αναλύσεις και γνωματεύσεις*

[37] Αρχείο/Archive ΔΔΕΑΜΤΠΠΑ, Κιβώτιο/Box 438, *Περί καθαρισμού και συντηρήσεως των εν Εθνικώ Μουσείω χαλκών αρχαίων. Σχηματισμός επιτροπής και γνωμάτευσις-1902*, Α.Π. 144, 09/08/1902 και Archive ΔΔΕΑΜΤΠΠΑ, Box 438, *Ανάλυσις χαλκών πελέκεων εν τω Εθνικώ Αρχαιολογικώ Μουσείω*, Α.Π. 2076, 1904

as well as marble powder samples from the temples of Parthenon and Erechtheion from the Acropolis (Ρουσόπουλος 1912: 121) were analysed and studied by the scientists mentioned earlier.

As far as the analysis of marble samples from the Acropolis monuments is concerned towards the formation of their conservation strategy, Rousopoulos participated in a committee with An. Damvergis and the mineralogist Friedrich Rinne. The reports of the two scientists are remarkable in terms of their scientific documentation and detailed description, as it derives from their publication in the A.J. Damvergis's analysis in particular, lead him to reject his initial hypothesis according to which sodium chloride was the main cause for marble deterioration, as it proved that the vulnerable mica inclusion was actually the main deterioration factor (Ρουσόπουλος 1912: 121) The research is completed by Rinne's report in which he includes information on the properties of mica, that under certain conditions, triggered deterioration mechanisms[38].

Archaeometry between the two wars. Konstantinos Zengelis (1870-1957)

Contemporary to Rousopoulos was the scientist Konstantinos Zengelis (Figure 15).[39]

Figure 15. Konstantinos Zengelis (1870-1957)
(Source: Digital Repository of the Academy of Athens)

He acted in Greece in the interwar period and after WWII, primarily in the field of monumental conservation which, like in the case of Rousopoulos, triggered his activity in the field of archaeometry too. He was part of a scientific elite and a great supporter of the Greek scientific community, an informal institution which brought scientists together for an exchange of views and knowledge related to sciences[40]. Zengelis's interest in the roots of science in antiquity and the ancient world in general, becomes evident in his very early publications[41]. One of the very first archaeometric researches that he conducted was in 1907 on coins from the collection of the Monetary Museum in Athens[42].

In 1905 Zengelis took part in the Á International Archaeology Conference in Athens, with a paper of an archaeometric context titled: *"About Prehistoric*

[38] He refers to mechanical erosion caused by the action of water, and to chemical erosion caused by chemical substances detected in the atmosphere and also, mechanical and chemical erosion caused by biological action (Ρουσόπουλος 1912: 122).

[39] He was born in Athens in 1870, he had studied at the Physics and Mathematics School of the National University in Athens and he received a PhD in Sciences in 1891. He also studied at the Universities of Heidelberg, and Leipzig and Geneva and Paris and in 1895 he was appointed lecturer of General Chemistry at the National University in Athens and in 1904 a professor of Physics and Chemistry. He taught until 1912 but remained at the University until 1938 («Πρυτάνεις Πανεπιστημίου Αθηνών», *Επετηρίδα Πανεπιστημιακών Ετών,* 2010-2012, 2013, 28, [online] https://www.uoa.gr accessed 06/09/2016). He was also an ordinary member of the International Union of Chemistry and the author of many scientific papers on chemistry (Κανδύλης 1981: 30). The results of his research were published in Greek periodicals such as Χημικά Χρονικά and Προμηθεύς, but also in foreign ones (Μωραΐτου 2013)

[40] The scientific elite consisted of about thirty scientists who had regular meetings and developed scientific dialogue, between 1932 and 1938. They would meet once a week in the Chemistry Lab from November to may από Νοέμβριο every year. Amongst the scientists were: G. Karagounis (1904-1990), L. Zervas (1902-1980), M. Stefanidis (1868-1957), A. Papapetrou (1907-1997), K. Alexopoulos (1909-2010), Th. Kougioumtzelis (1906-2001), P. Zervos (1878-1952) and the only woman who was a graduate of the Physics Department E. Agalidou, (Βλαχάκης, Γ., (2014) «Επιστήμονες του Μεσοπολέμου: Ο άγνωστος κύκλος του τριάντα», στο: *Fractal: η γεωμετρία των ιδεών*, [online] www.fractalart.gr, accessed 26/07/2017).

[41] Konstantinos' Zengelis Thesis: *Ἡ ἐπιστήμη τῆς φύσεως παρ' Ὁμήρῳ* (1891) and his journal papers: Zengelis, K., (1891) «Η παρ' Ὁμήρῳ μεταλλουργία», *Προμηθεύς*, Α, 270-271; Zengelis, K., (1930) «Τὶς ἤτο ἡ ἀρχαία κηροτακὶς», *Πρακτικά της Ακαδημίας Αθηνών*, 5, 127-133); Zengelis, K., (1941) «Ἡ Αἴγυπτος λίκνο τῶν θετικῶν ἐπιστημῶν», *Πρακτικά της Ακαδημίας Αθηνών,* 16, 27-38).

[42] Λυκιαρδοπούλου-Πέτρου, Μ., (2012). «Η συμβολή των μεθόδων ανάλυσης και εξέτασης στην εξέλιξη της συντήρησης», Ομιλία στο σεμινάριο με θέμα: *Διαγνωστικές Τεχνικές στην επιστήμη της συντήρησης έργων τέχνης,* Θεσσαλονίκη 17-19 Φεβρουαρίου [online] http://www.typologos.com τελευταία επίσκεψη 20/08/ 2016 (Lykiardopoulou-Petrou, M., (2012) "The contribution of the analytical and diagnostic methods in the development of conservation", Speech at the seminar titled: *Diagnostic techniques in the scientific field of conservation of works of art*, Thessaloniki, February 17-19 [online] http://www.typologos.com accessed 20/08/ 2016)

copper" (*«Περὶ τοῦ χαλκοῦ τῆς Προϊστορικῆς ἐποχῆς»*), on the technology of alloys from the Bronze Age in Greece, based on archaeometric data from prehistoric findings from Naxos and Sesklo. At the conference he also presented an innovative analytical colourimetric technique which was guaranteed to provide accurate results only with a small quantity of sample (Ζέγγελης 1905: 226)

Zengelis's published work is highly scientific and analytical, as indicated by the illustrative introduction on nomenclature and on the proper use of the terms *patina* and *bronze*, to a paper on the preservation state and conservation of the bronze statue of the *Marathon Boy* (Ζέγγελης 1924a, 86).

The provenance of the patina of bronze artefacts and statues troubled Zengelis at an early stage[43] and over time[44], as indicated by his publications in *A.J. (1924)* and the *Abstracts of the Academy of Athens (1926)*[45]. They are indeed two archaeometric publications of great value for Greek bibliography on historic terms, as they demonstrate the scientist's approach for the differences between a protective and a harmful patina on ancient metal artefacts. The experimental part of his research aimed at the reproduction of the protective patina and simultaneously to the development of a simple method for identifying it. The identification method in particular would be quite a breakthrough and exceptionally useful on a practical level (Μωραΐτου 2013). Indeed through his archaeometric work Zengelis was able to define the manufacture technology and the exact composition of the artificial patina, while at the same time he distinguished a protective from a harmful patina. Moreover, he developed identification methods for the harmful patina and suggested alternative ways for its treatment (Ζέγγελης 1924b, 98).

Zengelis addressed his contemporary archaeologists, the professionals who would come in systematic and immediate contact with the archaeological material and he presented to them a simple method based on the reaction of copper salts and fire, which would allow them to detect and confirm the presence of copper chloride salts, the main constituents of the harmful patina[46]. It must be emphasized that the theory on the manmade, protective patina was not easily "digested" by the archaeological arena, as its accuracy was questioned (Ζέγγελης 1929: 244). It was finally accepted by archaeologists in 1929, when Zengelis further analysed samples from findings from Artemisio and compared the results with those from past analysis from the 'Marathon Boy' (Ζέγγελης 1929: 244).

Conclusions

Xavier Landerer was the scientist who introduced archaeometric research in Greece from Europe. Scientific accuracy and a rigid documentation of his theories characterized his work in the field and an integral academic background was his main asset.

His contribution to the evolution of archaeometry in our country is indisputable even though it is possible that archaeometry did not constitute one of his personal scientific objectives. Nevertheless, his desire to contribute to K. Pittakis' struggle for a thorough understanding of antiquity, was a powerful motive for his activity in the field. A gap in the research so far is the lack of more detail on the exact experimental and analytical procedures that he applied and also the degree to which his work affected if at all, of the scientists that followed

Othon Rousopoulos developed his work in archaeometry according to the current needs of archaeological research for study and interpretation of the archaeological findings, in a similar way that Xavier Landerer had done before him. As far as potential interaction between the two scientists is concerned, there is no evidence so far that would even imply it. Rousopoulos practised archaeometry in almost every case, in conjunction with the monuments' preservation state and their conservation, providing limited, yet more information than Landerer did on the archaeometric methodologies that he had adopted, (i.e. the use of reagents and the subjection of samples to microscopic analysis). Finally, at the time of Rousopoulos interdisciplinary collaboration is encouraged and in fact established

Through his archaeometric research Konstantinos Zengelis developed a modern approach towards the study and the conservation of archaeological findings which was based on scientific accuracy, something the three scientists had in common, and on respect of the monuments' inherent values. A lot of his work focused on prolonging the life of ancient monuments. Furthermore, Zengelis chose to communicate his work with remarkable extroversion through publications of a high standard.

Having looked into only a moment of archaeometry' s course in Greece through the work of the three scientists and their collaborators, one notices that this

[43] Zengelis refers to a speculation that was triggered by some bronze findings from Dodoni and by a statuette of Athina. In time the concern evolved into a conflict between French archeeologists (Ζέγγελης 1926: 49). In Greece the first person to deal with this issue in a scientific manner was Xavier Landerer το 1854 and the case study of his work was a set of ancient coins (For Landerer's work on the metal coins see here, pages 4-5: Analysis of the protective patina of metal artefacts)

[44] Vrounzos (Βρούνζος)-Bronze = an ore of copper and tin (Ζέγγελης 1924a, 86)

[45] Ζέγγελης, Κ., (1924b) «Περὶ τῆς πατίνας τῶν ἀρχαίων ἐκ βρούνζου ἀντικειμένων», *Ἀρχαιολογικὴ Ἐφημερίς*, 90-97; Ζέγγελης 1926: 49.

[46] Ζέγγελης 1924b, 101.

scientific field was in fact born by initiatives taken by officials of the Hellenic Archaeological Service and it evolved within National Institutions. Moreover, it derives that between 1834 and 1939 (the period studied for the purposes of this paper), archaeometry follows a slow and unorganized, yet systematic and ever improving course, in an era of great archaeological revelations, plotted by people who dared to face the challenges and take the responsibility to care for the unique archaeological treasures brought to light unannounced.

8bibliography

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Η αρχαιομετρία στην Ελλάδα: 100 και πλέον χρόνια πριν

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Abstract: Archaeometry originates in Europe and more precisely from revolutionary France in the last decade of the 18th century and is due to the combination of stoichiometric chemical analysis and the "cabinets de curiosité" which included antiquities. Chemical analysis of antiquities is also related to the first archaeological excavations.

As far as Greece is concerned, up to now it was believed that interest for archaeometry began in the 1960s together with the renaissance of the Greek Archaeological Service. But recent studies show that although the term archaeometry was not in existence, physicochemical investigation of antiquities started in Greece before the middle of the 19th century and is related to the foundation of the modern Greek state and its care for antiquities.

The significance of research in the history of archaeometry is as important as the history of archaeology and the history of science in general. Bibliography for the Greek facts is scarce. Information is dispersed in archaeological papers. Aim of this research is to present a chronological tree on which new data can be uploaded.

The scientists that were involved in archaeometry were the following chemists: in the 19th century Xavier Landerer (1809-1885), Anastasios Christomanos (1841-1906) and Constantinos Mitzopoulos (1844-1911). At the end of the 19th century beginning of the 20th Othon Rhousopoulos (1856-1922), George Krinos (1850- 1935) and Anastasios Damvergis (1857-1920), while in the first quarter of the 20th c. Ioannis Vamvakas (1870-1960) and Constantinos Zengelis (1870-1957). All of them were chemists and almost all university professors.

From the results so far, it is assumed that although archaeometry was considered important for the archaeologists, and scientists participated in state comittees, the latter were asked for their services as a favor or through *ad hoc* commissions. Archaeometry was not institutionalized in Greece until the 1980s when the "Archaeometry Lab" was founded at the National Center for Scientific Research "Demokritos". Moreover a "Chemistry Laboratory" functioned since 1980 informally at the National Archaeological Museum of the Greek Archaeological Service until it was institutionalized in 2003 as a Department of Physical-Chemical Research while in 2014 it merged with the Conservation Department and was given the name Department of Conservation, Physical-Chemical Research and Archaeometry.

KEYWORDS: ARCHAEOMETRY, XAVIER LANDERER, ANASTASIOS CHRISTOMANOS, CONSTANTINOS MITZOPOULOS, GEORGE KRINOS, ANASTASIOS DAMVERGIS, OTHON RHOUSOPOULOS, IOANNIS VAMVAKAS, CONSTANTINOS ZENGELIS.

ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ: ΑΡΧΑΙΟΜΕΤΡΙΑ, ΞΑΒΕΡΙΟΣ ΛΑΝΔΕΡΕΡ, ΑΝΑΣΤΑΣΙΟΣ ΧΡΗΣΤΟΜΑΝΟΣ, ΚΩΝΣΤΑΝΤΙΝΟΣ ΜΗΤΣΟΠΟΥΛΟΣ, ΓΕΩΡΓΙΟΣ ΚΡΙΝΟΣ, ΑΝΑΣΤΑΣΙΟΣ ΔΑΜΒΕΡΓΗΣ, ΟΘΩΝ ΡΟΥΣΟΠΟΥΛΟΣ, ΙΩΑΝΝΗΣ ΒΑΜΒΑΚΑΣ, ΚΩΝΣΤΑΝΤΙΝΟΣ ΖΕΓΓΕΛΗΣ.

Εισαγωγή

Αρχαιομετρία είναι η εφαρμογή των θετικών επιστημών στην αρχαιολογία και τη συντήρηση των αρχαιοτήτων με σκοπό να απαντηθούν ερωτήματα όπως η χρονολόγηση, η προέλευση, ο εντοπισμός, το αρχαιοπεριβάλλον, ο χαρακτηρισμός των υλικών και η τεχνολογία κατασκευής των τέχνεργων, η αυθεντικότητα, η διάβρωση και η συντήρηση τους.

Ο όρος Αρχαιομετρία είναι ένας νεωτερικός όρος που καθιερώθηκε τη δεκαετία του 1950 από τον Christopher Hawkes στην Οξφόρδη (Pollard *et al.* 2007). Συνώνυμα του όρου αρχαιομετρία είναι οι όροι *archaeological chemistry* (αρχαιολογική χημεία) και *archaeological science* (αρχαιολογική επιστήμη) όροι που όμως δεν έχουν επικρατήσει στα Ελληνικά. Σήμερα η αρχαιομετρία έχει εισαχθεί ως μάθημα σε προπτυχιακές σπουδές αρχαιολογίας και ως πρόγραμμα σε μεταπτυχιακές σπουδές πολλών πανεπιστημίων διεθνώς, δεν έχει όμως αναγνωριστεί ως αυτόνομος κλάδος της επιστήμης.

Η απαρχή της εφαρμογής των θετικών επιστημών στην αρχαιολογία χρονολογείται στην επαναστατική Γαλλία την τελευταία δεκαετία του 18ου αιώνα και οφείλεται στον συνδυασμό της τελειοποίησης της σταθμικής χημικής ανάλυσης και στο περιεχόμενο των "cabinets de curiosité" των αιθουσών των θαυμάτων της εποχής, ένα είδος προδρομικών μουσείων που περιλάμβαναν αρχαιολογικά αντικείμενα (Pollard 2013). Θα μπορούσαμε να πούμε ότι το αναλυτικό ενδιαφέρον για τις αρχαιότητες γεννήθηκε στην Ευρώπη ταυτόχρονα με τη γέννηση της επιστήμης της χημείας (Bourgeois 2013).

Όσον αφορά στην Ελλάδα, μέχρι σήμερα ήταν κοινά αποδεκτό ότι το ενδιαφέρον για την αρχαιομετρική έρευνα ξεκίνησε τη δεκαετία του 1960 μαζί με την αναγέννηση της Αρχαιολογικής Υπηρεσίας. Νεότερα όμως δεδομένα (Μωραΐτου, υπό δημοσίευση; Μωραΐτου 2020) δείχνουν ότι, αν και δεν υπήρχε σαν όρος η αρχαιομετρία, η χημική διερεύνηση των αρχαιοτήτων ξεκίνησε στην Ελλάδα πριν τα μέσα του 19ου αιώνα και συνδέεται άμεσα με την ίδρυση του νέου Ελληνικού κράτους και τη μέριμνα για τις αρχαιότητες.

Η σημασία της έρευνας σχετικά με τις παλαιότερες αρχαιομετρικές μελέτες είναι τόσο σημαντική, όσο σημαντική είναι και η ιστορία της αρχαιολογίας και γενικότερα των επιστημών. Η βιβλιογραφία για τα ελληνικά δεδομένα είναι ελάχιστη. Κι αυτό γιατί οι πληροφορίες είναι διάσπαρτες μέσα σε αρχαιολογικές δημοσιεύσεις. Στόχος της παρούσας έρευνας είναι να παρουσιαστεί ένα χρονολογικό δέντρο πάνω στο οποίο θα αναρτώνται όλα τα νεότερα στοιχεία κάθε φορά που αυτά αποκαλύπτονται.

Οι πρωτοπόροι στην Ελλάδα

Τα παλαιότερα αποτελέσματα που έχουν προκύψει είναι τα ακόλουθα: για τον 19ο αιώνα αφορούν στον χημικό Ξαβέριο Λάνδερερ (1809-1885) και στη συνέχεια στον Αναστάσιο Χρηστομάνο (1841-1906) και τον Κωνσταντίνο Μητσόπουλο (1844-1911). Στα τέλη του 19ου και αρχές του 20ου αιώνα υπάρχουν περισσότεροι επιστήμονες που ασχολούνται με την αρχαιομετρία με προεξάρχοντα τον χημικό Όθωνα Ρουσόπουλο (1856-1922), αλλά και τον καθηγητή του Πανεπιστημίου Γεώργιο Κρίνο (1850-1935) και τον Αναστάσιο Δαμβέργη (1857-1920). Προπολεμικά δραστηριοποιείται στα Χανιά ο Ιωάννης Βαμβακάς, ενώ στην Αθήνα πρωταγωνιστεί ο καθηγητής του Πανεπιστημίου Κωνσταντίνος Ζέγγελης (1870-1957). Όλοι οι θετικοί επιστήμονες που ασχολήθηκαν με την αρχαιομετρία ήταν χημικοί, καθηγητές, υφηγητές ή διδάκτορες του πανεπιστημίου, ενώ όλοι εκτός από τον Βαμβακά παρείχαν υπηρεσίες και στην συντήρηση των αρχαιοτήτων.

Ξαβέριος Λάνδερερ (1809-1885) (εικ.1)

Με την ίδρυση του νέου Ελληνικού κράτους προσφέρει τις υπηρεσίες του στην αρχαιολογία και τη συντήρηση ο Βαυαρός φαρμακοποιός του βασιλέα Όθωνα και καθηγητής της χημείας στο Πανεπιστήμιο και το Σχολείο των Τεχνών (Πολυτεχνείο) Ξαβέριος Λάνδερερ (1809-1885). Ο Λάνδερερ γεννήθηκε στο Μόναχο, όπου σπούδασε φυσικές επιστήμες και ιατρική και πέθανε στην Αθήνα.

Ο Λάνδερερ μαζί με τον Έφορο Κυριακό Πιττάκη γράφουν οι δύο τους την Εφημερίδα Αρχαιολογική από

Εικόνα 1. Ξαβέριος Λάνδερερ (1809-1868) (πηγή: ελαιογραφία του Σπυρίδωνος Προσαλέντη, συλλογή ΕΚΠΑ).

το 1838 έως το 1860[1]. Ο Λάνδερερ δημοσίευσε 21 μελέτες. Μάλιστα στο τεύχος 29 δημοσιεύει μόνος του. Αν ανατρέξει κανείς στην Εφημερίδα αυτής της περιόδου θα δει ότι επί είκοσι δύο χρόνια ο Λάνδερερ έγραφε για διάφορα θέματα που ενδιαφέρουν την αρχαιολογία όπως «περί ζωγραφικής», «περί της υέλου των αρχαίων Ελλήνων», «περί του χρωματισμού των εκ μαρμάρου αρχαίων οικοδομημάτων», «χημική ανάλυσις τινός εντρίμματος», «περί τινός νέου κυανού χρώματος», «περί του μέλανος χρωματισμού της Ποικίλης Στοάς», «περί χρωματισμού εικόνων και αναγλύπτων», «περί τινός μίγματος χρησίμου προς υποκαπνισμόν», «περί πιθανής εγχαράξεως γραμμάτων και επί μαρμάρου σημειών δια επιθέσεως διαβρωτικού τινός μίγματος», «περί χημικής αναλύσεως κυανού χρώματος», «περί του φαιού χρωματισμού των κιόνων των αρχαίων ναών», κ.ά πολλά που δείχνουν την πρωτοπόρο συμβολή του στην αρχαιομετρική έρευνα στην Ελλάδα. Σε έγγραφο τού 1838 αναφέρεται η ανάθεση στον Λάνδερερ δοκιμών κατασκευής εκμαγείων από λεπτότερο γύψο (Πετράκος 2009: 484).

Ο Λάνδερερ γράφει όμως και για την συντήρηση (Λάνδερερ 1839: 271): «Περί της καθαρίσεως των αρχαίων

[1] Ο Β. Πετράκος (2013, ΙΙ, σ.15) αποσιωπεί τον Λάνδερερ και αναφέρει ότι ο Πιττάκης ήταν «σχεδόν μοναδικός συντάκτης».

σκευών και νομισμάτων», «τα καθαρισθησόμενα αργιλώδη σκεύη τίθενται εις καθαρόν ύδωρ συγκερασθέν πρότερον μετά του δικατημορίου του υδροχλωρικού οξέως ακράτου. Παρά του ρηθέντος οξέως διαλύονται ολίγον κατ΄ολίγον τα τιτανώδη μόρια και η διάλυσις δύναται να επιταχυνθεί έτι περισσότερον δια αποξύσεως των μορίων με ξύλινην μάχαιραν ή δια σαρώθρου» και παρακάτω: «τα νομίσματα εξ αργύρου... δυνάμεθα να αποκαταστήσωμεν την επιφάνειαν λαμπροτάτη και μεταλλικήν εάν θέσωμεν το νόμισμα εις αρκετόν ποσόν ύδατος κεκραμμένου με κιτρικόν ή κάλλιον θειϊκόν οξύ», ενώ «τα χάλκινα νομίσματα εις υδροχλωρικόν οξύ».

Ο Λάνδερερ στην εισαγωγή του βιβλίου του «Χημεία εφαρμοσμένη εις τας τέχνας» του 1846 (Λάνδερερ 1846), χαρακτηρίζει τη χημεία «επωφελή επιστήμη ιδίως προς εφαρμογήν αυτής εις τε τας επιστήμας και τέχνας». Στον νόμο για τις επιστημονικές και τεχνολογικές συλλογές του 1834 ισότιμη συλλογή με αυτή του Κεντρικού Μουσείου των αρχαιοτήτων είναι και το «Εργαστήριον Χημικόν με την απαιτούμενην αποσκευήν» (δύο από τις 13 συλλογές που ιδρύθηκαν τότε). Βλέπουμε λοιπόν πόσο χρήσιμη ήταν ήδη η χημεία στην αρχαιολογία, όπως και στη βιομηχανία (μεταλλουργίαν, λιθουργίαν, υαλουργίαν, αλατουργίαν, πυροτεχνίαν, χρωματουργίαν και ζυμοτεχνίαν). Άλλωστε ο Λάνδερερ το 1871 έγραφε και τα «Ανάλεκτα κοινοφελών διατριβών δι' επιστήμονας, βιομηχάνους, τεχνίτας, γεωπόνους και άλλους» (Δελή, 2017; Δελή, 2019; Λάνδερερ 1871) όπου παραθέτει και συνταγές για τη συντήρηση των αρχαιοτήτων.

Ο Ερρίκος Σλήμαν απευθύνθηκε στον Ξ. Λάνδερερ, αλλά και ό Ερρίκος Σλήμαν σε ξένους θετικούς επιστήμονες (Shliemann 1989: 76, 78, 108, 110, 111, 143, 153, 157, 165, 203, 1210, 257, 293, 330). Το 1877 εμπιστεύτηκε τις αναλύσεις των ευρημάτων του των Μυκηνών στον John Percy (1817-1889) μεταλλουργό στη Βασιλική Σχολή Ορυχείων του Λονδίνου (Schliemann 1964, 416-430; Science Museum, n.d.).

Αναστάσιος Κ. Χρηστομάνος (1841-1906) (εικ.2)

Θεωρείται ο θεμελιωτής της επιστήμης της χημείας στην Ελλάδα και είναι ο πρώτος Έλληνας που ασχολήθηκε με την αρχαιομετρία. Από το 1863 δίδαξε χημεία στο Πανεπιστήμιο Αθηνών έως το 1906, ενώ διετέλεσε και πρύτανης του Πανεπιστημίου. Το 1887 ιδρύθηκε το Χημείο στην οδό Σόλωνος, του οποίου επέβλεψε την κατασκευή.

Όπως αναφέρει η Φανή Μαλούχου Tufano (Μαλλούχου-Tufano 1998: 63-64), ο Χρηστομάνος μαζί με τον Γεώργιο Ζαβιτσάνο, καθ. Της Φαρμακευτικής Χημείας και διάδοχο του Λανδερερ στο Πανεπιστήμιο και τον Αριστείδη Βουσάκη της Σχολής των Τεχνών, ως μέλη επιτροπής ορίστηκαν να κάνουν δοκιμές στην υδρύαλο (και συγκεκριμένα το πυριτικό κάλιο) που σύστησε ο Γάλλος χημικός Frédéric Kuhlmann το 1873 για τη στερέωση των μαρμάρων της Ακρόπολης των Αθηνών.

Εικόνα 2. Αναστάσιος Χρηστομάνος (1841-1906) (πηγή: ελαιογραφία του Α. Παπαντωνίου 1907, συλλογή ΕΚΠΑ).

Στην Αρχαιολογική Εφημερίδα του 1898 στη δημοσίευσή του Κυκλαδικά, ο Χρήστος Τσούντας παραθέτει τις χημικές αναλύσεις που έκανε για αυτόν ο Χρηστομάνος σε δύο αργυρά αντικείμενα από τις Κυκλάδες ένα διάδημα και ένα φιαλίδιο(Τσούντας 1898: 187).

Ένα σημαντικό έγγραφο του 1898 του Τσούντα, που εντόπισε ο Χάρης Τσέλιος (2018; 2021) στο Αρχείο της Αρχαιολογικής Υπηρεσίας, είναι μια αίτηση για τεχνολογική εξέταση αρχαίων ευρημάτων από την ανασκαφή στην Χαλανδριανή της Σύρου. Ο Τσούντας διατυπώνει ξεκάθαρα γιατί πρέπει να μελετάμε την αρχαία τεχνολογία πιστεύοντας ότι «η εξακρίβωση της φύσης των υλών μπορεί να ρίξει φως στις σχέσεις των νησιωτών με άλλους πολιτισμούς».

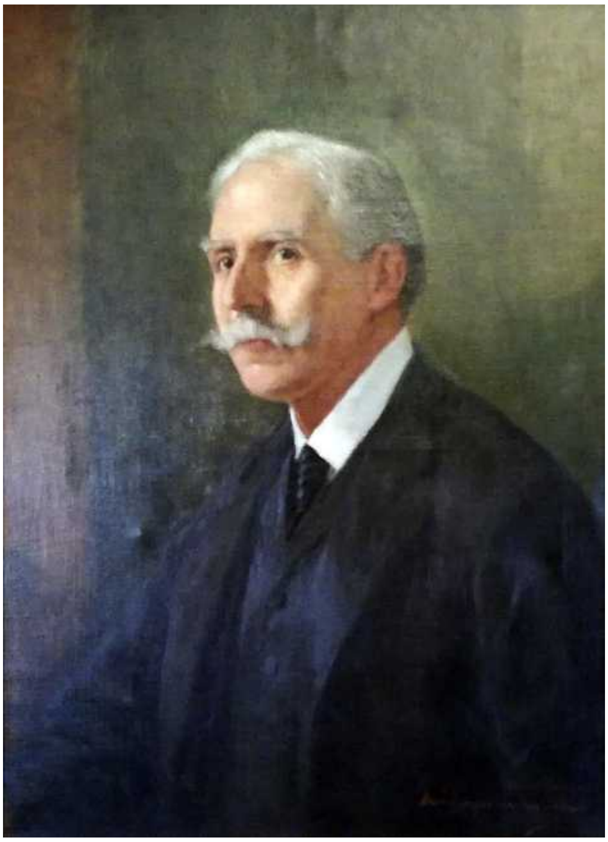
Τέλος γνωρίζουμε ότι το 1901 συμμετείχε με τον Α. Δαμβέργη και τον Κ. Μητσόπουλο σε επιτροπή για την εξέταση των θραυσμάτων των Αντικυθήρων (Τσέλιος 2018; 2021).

Κωνσταντίνος Μ. Μητσόπουλος (1844-1911) (εικ.3)

Ήταν ο πρώτος που αποφοίτησε με διδακτορικό δίπλωμα φυσικών επιστημών από το Εθνικό Πανεπιστήμιο το 1868. Σπούδασε φυσική, χημεία, πυροχυμική, γεωλογία, γεωδαισία, μεταλλουργία, μεταλλευτική, μεταλλευτικό δίκαιο και μηχανουργική για έξι χρόνια στο Πανεπιστήμιο του Φράιμπουργκ με υποτροφία της Κυβέρνησης. Διορίστηκε έκτακτος καθηγητής στο Πανεπιστήμιο και το Πολυτεχνείο το 1875 και τακτικός το 1888. Το ακαδημαϊκό έτος 1900-1901 εξελέγη πρύτανης του Πανεπιστημίου. Το 1910 διορίστηκε διευθυντής του Πολυτεχνείου. Ήταν ο πρώτος ειδικός γεωλόγος και ορυκτολόγος της Ελλάδας, εισηγητής της Πειραματικής Ορυκτολογίας και από τους κυριότερους συντελεστές της προαγωγής των φυσικών επιστημών στην Ελλάδα. Εξέδιδε το περιοδικό «Προμηθεύς» (ΔΕΑΜ Φ 1901, κιβ. 438 και το Άστυ, αρ φύλ. 3671, 28.01.1901: 1.).

Το 1878 δημοσίευσε στα γερμανικά μελέτη της μυκηναϊκής μεταλλουργίας και περιέγραψε τη διάβρωση των χάλκινων και αργυρών ευρημάτων των Μυκηνών (Mitzopulos 1878).

Εικόνα 3. Κωνσταντίνος Μητσόπουλος (1844-1911) (πηγή: ελαιογραφία, συλλογή ΕΚΠΑ https://www.greekencyclopedia.com/mitsopoylos-kwnstantinos-patra-1846-athina-1911-p3939.html).



Εικόνα 4. Γεώργιος Κρίνος (1850- 1935) (πηγή: ελαιογραφία του Ευάγγελου Ιωαννίδη, συλλογή ΕΚΠΑ).

Επίσης συμμετείχε το 1901 με τον Α. Δαμβέργη και τον Α. Χρηστομάνο σε επιτροπή για την εξέταση των θραυσμάτων των Αντικυθήρων.

Γεώργιος Κρίνος (1850- 1935) (εικ.4)

Απόφοιτος του Εθνικού Πανεπιστημίου (1872) και διδάκτωρ της φιλοσοφίας επί Χημεία του Πανεπιστημίου Χαϊδελβέργης. Καθηγητής του Πανεπιστημίου Αθηνών της Φαρμακευτικής Χημείας και Συνταγολογίας[2].

Το 1888 μαζί με τον Όθωνα Ρουσόπουλο διενήργησαν πειράματα σε διάφορα έγχρωμα τεμάχια μαρμάρου και πωρόλιθου της Ακρόπολης καθώς και σε κατιωμένα χάλκινα αντικείμενα. Για τα χάλκινα προτείνουν μεθόδους καθαρισμού και προστατευτικού επιχρίσματος που αναφέρονταν στον οδηγό της Πρωσσίας που κυκλοφορούσε την εποχή εκείνη. Για τα χρώματα αφού έκαναν χημικές αναλύσεις σύστησαν την στερέωσή τους με υδρύαλο και συγκεκριμένα το πυριτικό νάτριο (Κρίνος, Ρουσόπουλος 1888).

2 http://jupiter.chem.uoa.gr/pchem/lab/krinos.html

Εικόνα 5. Αναστάσιος Δαμβέργης (1857-1920) (πηγή: ελαιογραφία της Άννας Φαραντάτου, συλλογή ΕΚΠΑ, Καραμαλούδη 2019: 71).

Αναστάσιος Κ. Δαμβέργης (1857-1920) (εικ.5)

Κρητικής καταγωγής. Σπούδασε στο Φυσικομαθηματικό Τμήμα της Φιλοσοφικής Σχολής με δάσκαλο τον Χρηστομάνο και πήρε το διδακτορικό του από το Πανεπιστήμιο της Χαϊδελβέργης, όπου συνέχισε τις σπουδές του με υποτροφία. Ξεκίνησε τη σταδιοδρομία του στις Στρατιωτικές Σχολές. Παράλληλα δίδασκε στο Βαρβάκειο Λύκειο. Διετέλεσε Τμηματάρχης στο Υπουργείο Οικονομικών. Από το 1893 μέχρι τον θάνατό του υπήρξε τακτικός καθηγητής της Φαρμακευτικής Χημείας στο Πανεπιστήμιο της Αθήνας.

Το 1888 συμμετέχει σε επιτροπή με τους Χρηστομάνο, Κρίνο, Dorpfeld και Ρουσόπουλο για την αξιολόγηση της κατάστασης διατήρησης των μαρμάρινων, πώρινων και χάλκινων ευρημάτων της Ακρόπολης και την εύρεση λύσεων για τη βελτίωσή της.

Από το 1900 του ανατίθενται χημικές αναλύσεις τεμαχίων χαλκού από το ναυάγιο των Αντικυθήρων, ενώ το 1901 συμμετέχει σε επιτροπές με τους Μητσόπουλο και Χρηστομάνο και τους Καββαδία και Χελδράϊχ για την εξέταση ευρημάτων των Αντικυθήρων. Τα αποτελέσματά του δημοσιεύονται στον Τύπο της εποχής και στο περιοδικό Αρμονία (Δαμβέργης 1901).

Το 1907 ο Στάης του αναθέτει την ανάλυση φαιομέλανων κηλίδων από χρυσούς μυκηναϊκούς ρόδακες (Στάης 1907a) και εκείνος αποφαίνεται ότι βρήκε ίχνη χαλκού και αργύρου, οπότε συμπεραίνει ότι πρόκειται για κόλληση μετάλλου σε μέταλλο.

Το 1911 συμμετείχε σε επιτροπή μαζί με τον Ρουσόπουλο και τον Σωτηριάδη για την εξέταση και γνωμάτευση για την συντήρηση των γλυπτών έργων του Παρθενώνος (ΑΕ, 1912: 119-121). Ο Δαμβέργης υποβάλλει έκθεση «περί της χημικής εξετάσεως των μαρμάρων», η οποία περιλαμβάνει: ανίχνευση μαγειρικού άλατος, ποσοτική ανάλυση δειγμάτων μαρμάρου και ποσοτική ανάλυση του εν υδροχλωρικώ οξύ αδιάλυτου συστατικού του μαρμάρου.

Σε έγγραφα από το Αρχείο του πανεπιστημίου τα οποία παραθέτει η Φωτεινή Καραμαλούδη (2019) αναφέρεται ότι κατόπιν παράκλησης του διευθυντή της Γαλλικής Αρχαιολογικής Σχολής, ανέλυσε σκόνη που βρέθηκε εντός δοχείου σε τάφο των Δελφών και πιστοποίησε ότι πρόκειται για ψιμύθι, καλλυντικό της εποχής. Επίσης έκανε ανάλυση σε παλαιά σκωρία από αρχαίο χωνευτήριο του Λαυρίου.

Τέλος το 1912 συμμετείχε σε επιτροπές για τη συντήρηση της ζωγραφικής στις μαρμάρινες στήλες της Δημητριάδος και συνέταξε έκθεση με τίτλο «Παγασαίων ζωγραφιών συντήρησις» όπου προτείνει στερέωση με νιτρική κυτταρίνη και προστασία με καστανόχρους υαλοπίνακες (Δαμβέργης 1912).

Όθων Α. Ρουσόπουλος (1856-1922) (εικ.6)

Ο Όθων Ρουσόπουλος, γιός του αρχαιολόγου Αθανάσιου, ήταν υφηγητής του Πανεπιστημίου με σπουδές στη Γερμανία και ιδρυτής της ιδιωτικής «Βιομηχανικής και Εμπορικής Ακαδημίας». Όπως οι προγενέστεροι και σύγχρονοί του χημικοί Ξ. Λάνδερερ (Μωραΐτου, υπό δημοσίευση; Δελή, 2019), Κ. Μητσόπουλος, Α. Χρηστομάνος και Α. Δαμβέργης, προέβη σε αναλύσεις αρχαίων υλικών που του εμπιστεύονταν διάφοροι αρχαιολόγοι, είτε αυτοτελώς είτε στο πλαίσιο μιας μελέτης συντήρησης, μόνος του ή με τα μέλη μιας επιτροπής. Από το 1900 έκανε αναλύσεις στην ιδιωτική «Βιομηχανική και Εμπορική Ακαδημία» του.

Έτσι, το 1888 από την Ακρόπολη ανέλυσε, μαζί με τον Κρίνο, χρωστικές από τα τεμάχια που έλαβαν ως δείγματα και αναγνώρισε οξείδιο του σιδήρου και κιννάβαρι για το κόκκινο, βασικό ανθρακικό χαλκό για το αιγυπτιακό μπλε και ανακάλυψε ότι το πράσινο περιέχει υδροξείδιο του χαλκού με ίχνη οξειδίου του σιδήρου. Αξίζει να αναφερθεί η παρατήρησή του ότι «το κιννάβαρι αμαυρούται διά του χρόνου τη επιδράσει του φωτός» (Ρουσόπουλος και Κρίνος 1888).

Στο κιβ. 438 της Διεύθυνσης Εθνικού Αρχείου Μνημείων με χρονολογία 1901 και 1902 βρέθηκαν τα αποτελέσματα οκτώ αναλύσεων δειγμάτων από τα ευρήματα του Ναυαγίου των Αντικυθήρων. Τα αποτελέσματα είναι

Εικόνα 6. Όθων Ρουσόπουλος (1856-1922) (πηγή: Εγκυκλοπαίδεια Πυρσός 1933).

χειρόγραφα πάνω σε τυποποιημένο Δελτίο, όπου αναγράφεται τυπογραφικά «Χημείον της Εν Αθήναις Βιομηχανικής και Εμπορικής Ακαδημίας»:

- Ποιοτική «Ανάλυσις τεμαχίου αρχαίου αγάλματος» αρ. 36 (28/XII/1900).
- Ποιοτική «Ανάλυσις ακαθαρίστου τεμαχίου αγάλματος αρχαίου εκ των ευρεθέντων εν Αντικυθήροις» αρ. 36 (25/XII/1900).
- Ποσοτική «Ανάλυσις αρχαίου αγάλματος (πτυχής)» αρ. 55α (28/III/1902).
- «Ανάλυσις ποσοτική μεταλλικού πυρήνος μελαίνης χειρός» αρ. 55β (29/III/1902).
- «Ανάλυσις εξωτερικού (κόνεως) μελαίνης χειρός» αρ. 61 (7/IV/1902).
- Ποιοτική «Ανάλυσις μίγματος ερυθρού ευρεθέντος εντός ορειχαλκίνης χειρός των Αντικυθήρων» αρ. 63 (9/IV/1902).
- Ποιοτική «Ανάλυσις τεμαχίου εκ του διαφράγματος ενός των αγαλμάτων των Αντικυθήρων» αρ. 64 (10/IV/1902) .
- Ποιοτική «Ανάλυσις του αγγείου του θεωρηθέντος μήλον της έριδος» αρ. 65 (10/IV/1902).

Το 1902 συμμετέχει σε επιτροπή με τους Πέτρο Ζαλοκώστα και Άγγελο Σκιτζόπουλο για γνωμάτευση επι του καθαρισμού και της συντηρήσεως των εν τω Εθνικώ μουσείω χαλκών αρχαίων (ΦΕΚ Β/157/5.9.1902: 685-687).

Ο Bosanquet (1904) αναφέρει ότι ο Ρουσόπουλος, ο «χημικός σύμβουλος» του Εθνικού Αρχαιολογικού Μουσείου, ανέλυσε το ερυθρό περιεχόμενο ενός πίθου από τη Φυλακωπή της Μήλου όμοιο με το ερυθρό στο φόντο της τοιχογραφίας των κρίνων.

Όπως αναφέρουν οι Burrows και Ure (1907-1908: 297, fn. 11), ο Ρουσόπουλος «είχε την καλοσύνη» να αναλύσει το ερυθρό χρώμα μιας βοιωτικής κύλικας και ενός αγαλματιδίου μάγειρα (cook) και τα αναφέρει και τα δύο ως οξείδια του σιδήρου.

Ο ίδιος ο Ρουσόπουλος, ευχαριστώντας τους αρχαιολόγους Π. Καββαδία, Χ. Τσούντα, Β. Στάη, Κ. Κουρουνιώτη, Π. Καστριώτη, Γ.Π. Βυζαντηνό, R. Dawkins, A. Mosso παραθέτει στις δημοσιεύσεις του (Rhousopoulos 1903; 1908; 1909a; 1909b) τα αντικείμενα, τις ανασκαφές από όπου προέρχονται, τα χρώματα και τα αποτελέσματα των αναλύσεών του. Έτσι γνωρίζουμε ότι ανέλυσε χρωστικές από το Σέσκλο, το Διμήνι, τις Μυκήνες, τη Νάξο, τη Σύρο, τη Σαλαμίνα, τη Σπάρτη, τη Θήβα και τη Χαλκίδα. Ανέλυσε, επίσης, τις χρωστικές των λευκών ληκύθων, την πήλινη Κλαζομενιακή σαρκοφάγο του Εθνικού Αρχαιολογικού Μουσείου (Ρωμαίος 1907: 202) και φαιομέλανες κηλίδες πάνω σε χρυσούς μυκηναϊκούς ρόδακες που είχε προηγουμένως αναλύσει και ο Δαμβέργης (Στάης 1907a: 48; 1907b) .

Το 1911 συμμετέχει σε επιτροπή μαζί με τον Δαμβέργη και τον Σωτηριάδη για να εξετάσει και γνωματεύσει «περί της συντηρήσεως των γλυπτών έργων του Παρθενώνος». Στην έκθεσή του προτείνει τη στερέωση του μαρμάρου με διαπότιση με αραιό διάλυμα υδροξειδίου του βαρίου και θειικού οξέος (Ρουσόπουλος 1912).

Από το 1909 έως το 1912 ασχολείται με τις στήλες της Δημητριάδος. Η χημική ανάλυση των χρωστικών της ζωγραφικής στις στήλες της Δημητριάδος έδειξαν ανόργανες ενώσεις χαλκού, σιδήρου, υδραργύρου κ.τ.λ., καθώς και ίχνη οργανικής ουσίας που αποδίδονται πιθανώς στην αρχαία φαίδρυνση (Ρουσόπουλος 1912: 261-262. Η δρ Χαρίκλεια Μπρεκουλάκη έχει αναλύσει τις χρωστικές και τα συνδετικά μέσα των στηλών, αλλά δεν έχει δημοσιεύσει τα αποτελέσματα). Στην έκθεσή του διαφαίνεται και ένας ανταγωνισμός με τον Δαμβέργη λέγοντας ότι η γνώμη που εκφράζει ο Δαμβέργης, εν αγνοία του, συμφωνεί τελείως με τη δική του που είχε εκφράσει τρία χρόνια νωρίτερα.

Το 1913 στην Έκθεση Γ ‘ «Περί της συντηρήσεως των εν Δήλω και Μυκώνω αρχαιολογικών ευρημάτων» (Μωραΐτου 2020) παραθέτει τα αποτελέσματα επτά αναλύσεων:

- «Ανάλυσις της εν τη χαλκίνη κεφαλή λευκής ύλης».
- «Ανάλυσις χανδρών πιθανώς εξ υάλου».
- «Ανάλυσις χάνδρας πιθανώς εξ ηλέκτρου».
- «Ανάλυσις της λεγομένης αιγυπτιακής πορσελάνης».
- «Ανάλυσις λευκής ύλης ευρεθείσης υπο τον βόθρον της καθάρσεως».
- «Εξέτασις υφάσματος ευρεθέντος εντός της κάλπης Ηλιοδώρου».
- «Ανάλυσις των επί των κονιαμάτων χρωμάτων».

Ιωάννης Ν. Βαμβακάς (1870- 1960) (εικ.7)

Διδάκτωρ Χημείας του Πανεπιστημίου της Αθήνας, συνέβαλλε το 1895 στην ίδρυση του πρώτου αγορανομικού και ερευνητικού χημείου στα Χανιά της Κρήτης, ενώ υπήρχε ακόμα Τουρκική Διοίκηση

Εικόνα 8. Κωνσταντίνος Ζέγγελης (1870-1957) (πηγή: http://jupiter.chem.uoa.gr/pchem/lab/ Αλούπη .html)

Εικόνα 7. Ιωάννης Βαμβακάς (1870-1960) (πηγή: Βαμβακάς 1991).

(Κανδήλης 1954). Το 1900 ορίζεται διευθυντής του εν Χανίοις Χημείου της νεοσύστατης Κρητικής Πολιτείας. Το 1913 αναλύει για λογαριασμό του αρχαιολόγου Ιωσήφ Χατζηδάκη επτά δείγματα από λάμες και ξίφη που βρέθηκαν στο Αρκαλοχώρι της Κρήτης (Hadzidakis 1912-1913). Αποφαίνεται ότι η πρώτη ύλη πρέπει να ήταν από την Κρήτη γιατί στον μινωικό χαλκό βρήκε πυριτικό οξύ όπως και στα μεταλλεύματα που ανέλυσε από την Γαύδο, την Κυδωνία, την Σέλινο και από αλλού. Αναλύσεις από τα χαλκούχα μεταλλεύματα της Κρήτης δημοσίευσε στο «Εργασίαι του εν Χανίοις Δημοσίου Χημείου» το 1913 (Βαμβακάς 1913: 232). Το 1928 εκπόνησε μελέτη για μια κυανού χρώματος χρωστική που βρέθηκε σε μινωϊκή τάφή (Βαμβακάς 1928) και το 1933 ανέλυσε έναν μετεωρίτη που είχε βρεθεί στην Κρήτη (Βαμβακάς 1933). Το 1915 το Χημείο συγχωνεύεται με το Χημείο του Υπουργείου Οικονομικών και το 1929 μετονομάζεται σε Παράρτημα Χανίων του Γενικού Χημείου του Κράτους.

Κωνσταντίνος Δ. Ζέγγελης (1870-1957) (εικ.8)

Σπούδασε στη Φυσικομαθηματική Σχολή του Πανεπιστημίου της Αθήνας και το 1891, σε ηλικία μόλις 21 ετών, αναγορεύτηκε διδάκτωρ. Το θέμα της διατριβής του ήταν: «Η επιστήμη της φύσεως παρ' Ομήρω» (Ζέγγελης 1891). Το 1896 υποβάλλει διατριβή επί υφηγεσία με τίτλο: «Περί Χημικής συγγενείας». Ο νεαρός Ζέγγελης τελειοποιεί τις σπουδές του στα Πανεπιστήμια της Χαϊδελβέργης, της Λειψίας, της Γενεύης και των Παρισίων. Το 1897 και για μια οκταετία διδάσκει χημεία και μεταλλουργία στο Πολυτεχνείο. Το 1906 αναγορεύεται καθηγητής της Ανόργανης και Φυσικής Χημείας του Πανεπιστημίου Αθηνών. Το διάστημα 1924-1925 διετέλεσε πρύτανης του πανεπιστημίου και το 1927 εξελέγη πρόεδρος της Ακαδημίας Αθηνών, ενώ το 1929 γερουσιαστής.

Το 1905 συμμετείχε στο Α' Διεθνές Αρχαιολογικό Συνέδριο που έλαβε χώρα στην Αθήνα. Τίτλος της ανακοίνωσής του: «Περί του χαλκού της προϊστορικής εποχής» (Zengelis 1905). Εκεί δημοσιεύει τα αποτελέσματα 13 αναλύσεων σε χάλκινα προϊστορικά ευρήματα από το Σέσκλο και τις Κυκλάδες.

Όπως αναφέρει η Λυκιαρδοπούλου-Πέτρου (Λυκιαρδοπούλου-Πέτρου 2012), υπάρχει χειρόγραφο σημείωμά του στο Νομισματικό Μουσείο με τα αποτελέσματα αναλύσεων σε αρχαία νομίσματα που είναι ενδεικτικό για την έμπρακτη συμβολή του στην αρχαιολογία το 1907. Επιπρόσθετα η Φανή Μαλλούχου-Tufano (1998: 258) έχει εντοπίσει τη συμβολή του στα έργα συντήρησης των μνημείων της Ακρόπολης[3].

Ο Ζέγγελης είχε πρωταγωνιστικό ρόλο τη δεκαετία του 1920 με τη συμβολή του στην ανάλυση και συντήρηση δύο χάλκινων αγαλμάτων του Εθνικού Αρχαιολογικού Μουσείου: του εφήβου του Μαραθώνα και του Ποσειδώνα του Αρτεμισίου (Μωραΐτου 2014; Μωραΐτου 2018). Το 1935 κλήθηκε από την αρχαιολόγο Άννα Αποστολάκι να προσδιορίσει «το είδος του χρώματος, όπερ εχρησιμοποιήθη δια την βαφήν κοπτικών υφασμάτων» της συλλογής του τότε Μουσείου Κοσμητικών Τεχνών, μετέπειτα Ελληνικής Λαϊκής Τέχνης και τώρα Νεώτερου Ελληνικού Πολιτισμού (Μαργαρίτη, Χανιαλάκη 2017).

Συζήτηση-Συμπεράσματα

Ένα πρώτο συμπέρασμα που προκύπτει είναι ότι εξ αρχής η αρχαιομετρία ήταν συνυφασμένη, όχι μόνο με την αρχαιολογία, αλλά και με την συντήρηση των αρχαιοτήτων. Αυτό αποδεικνύεται από το γεγονός ότι οι περισσότερες αναλύσεις γίνονταν στο πλαίσιο διαγνωστικών μελετών συντήρησης. Φαίνεται λοιπόν ότι τα θεμέλια για τον όρο conservation science και επιστήμη συντήρησης, που έχουν επικρατήσει διεθνώς, είχαν ήδη τεθεί από τότε. Φαίνεται επίσης ότι ο κυριότερος λόγος που η αρχαιομετρία δεν έχει αναγνωριστεί ως αυτόνομος κλάδος της επιστήμης, και κατά συνέπεια ως επάγγελμα, είναι γιατί αντιπροσωπεύει ένα μεθοδολογικό στάδιο στις επιστήμες της αρχαιολογίας και της συντήρησης που απαιτεί τη διεπιστημονική συνεργασία με θετικούς επιστήμονες[4].

Ένα δεύτερο συμπέρασμα είναι ότι η αρχαιομετρία, όπως και η συντήρηση των αρχαιοτήτων, αναπτύχθηκαν στην Ελλάδα ταυτόχρονα με την αρχαιολογία. Το επίσημο κράτος όριζε διεπιστημονικές επιτροπές για τη συντήρηση μείζονος σημασίας μνημείων (τα μάρμαρα των μνημείων της Ακρόπολης, τα πώρινα και μαρμάρινα γλυπτά της, τα ευρήματα των Αντικυθήρων και τις ζωγραφισμένες στήλες της Δημητριάδος) στις οποίες συμμετείχαν οι θετικοί επιστήμονες. Από ιδρύσεως Ελληνικού κράτους οι αρχαιολόγοι αποζητούσαν την αρχαιομετρική μελέτη των ευρημάτων τους, και αυτό γινόταν εκτός υπηρεσίας από τους θετικούς επιστήμονες σε επίπεδο κρατικής υποστήριξης, προσωπικής εξυπηρέτησης ή με παροχή υπηρεσιών.

Παρά την αποδεδειγμένη ανάγκη της, η αρχαιομετρία δεν θεσμοθετήθηκε στην Ελλάδα παρά 150 περίπου χρόνια αργότερα, τη δεκαετία του 1980, στο ΕΚΕΦΕ «Δημόκριτος» με τη δημιουργία του «Εργαστηρίου Αρχαιομετρίας» (Μανιάτης 1993). Την ίδια δεκαετία του 1980, εξοπλίστηκε και λειτούργησε, επι Γενικού Εφόρου Αρχαιοτήτων Ν. Γιαλούρη, άτυπα το «Χημείο» του Εθνικού Αρχαιολογικού Μουσείου (Μωραΐτου 2009; 2016). Το εν λόγω Χημείο θεσμοθετήθηκε το 2003 ως «Τμήμα Χημικών και Φυσικών Ερευνών» (ΠΔ 191/2003, ΦΕΚ/Ά /146 άρθρο 51), ενώ το 2014 συγχωνεύτηκε με το Τμήμα Συντήρησης και πήρε την ονομασία: «Τμήμα Συντήρησης, Χημικών - Φυσικών Ερευνών & Αρχαιομετρίας». Καθοριστικό ρόλο στη διάδοση της αρχαιομετρίας στην Ελλάδα έπαιξε και η ίδρυση της Ελληνικής Αρχαιομετρικής Εταιρείας το 1982.

Αξιοσημείωτο είναι τέλος ότι οι επιστήμονες της εποχής που ασχολήθηκαν με την αρχαιομετρία στην Ελλάδα ήταν μεν θετικοί επιστήμονες, καθηγητές πανεπιστημίου, χημικοί κυρίως, ωστόσο με βαθιά γνώση της αρχαίας ελληνικής γραμματείας, πράγμα που οφειλόταν βέβαια και στο γεγονός ότι οι θετικές επιστήμες (φυσική, μαθηματικά, χημεία) υπάγονταν στη Φιλοσοφική Σχολή μέχρι το 1904.

[3] Ο καθηγητής υπήρξε στενός συνεργάτης του Ν. Μπαλάνου και διενήργησε εργαστηριακές αναλύσεις της ερυθρωπής απόχρωσης του μαρμάρου, που σήμερα ονομάζουμε πορτοκαλοκάστανη πατίνα. Η Μαλλούχου-Tufano (2008, 258-9) παραπέμπει επίσης σε δημοσίευμα της Καθημερινής (17.4.1929) όπου ο Ζέγγελης αναφέρεται στη συντήρηση της δυτικής Ζωφόρου (Μαλλούχου-Tufano 2008: 258-259).

[4] Η Ελένη Αλούπη (2007) εύστοχα είχε αντιστοιχίσει την αρχαιομετρία με την οικονομετρία, η οποία τελικά ενσωματώθηκε στην οικονομική επιστήμη.

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Applications of *In-Situ* Non-Destructive Techniques for Documentation, Identification of Pigments, and Authentication of Sigillia, and Promotion of our Cultural Heritage, in the Library of Halki Theological School

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Abstract: In this work non-destructive analyses were performed on important Byzantine documents, "sigillia" kept in the Theological School of Halki, Istanbul, Turkey, employing portable ATR-FTIR spectroscopy. Analyses were carried out on tassel samples by using both transmittance and reflectance techniques and the type of silk was identified. Also, FTIR analysis was performed on the written part of the document, which was identified as parchment.

KEYWORDS: SIGILLIA, FTIR SPECTROSCOPY, SILK, PARCHMENT, HISTORIC TEXTILE

Introduction

One of the most important sources of political and ecclesiastical history during the Byzantine centuries are sigillia. These are imperial or ecclesiastical documents whose content varies. The most popular of all are the imperial sigillia or chrysobulla, because of their content and because of the gold seal, the stamp of the Byzantine emperor (Tsougarakis 1999). However, the importance of any sigillia that have been saved, such as the patriarchal sigillia, which were released by the Ecumenical Patriarch, should not be underestimated (Paizi–Apostolopoulou 2001). Today a significant number of sigillia are preserved, both patriarchal and imperial, the oldest of which date back to the 11th century. These documents allow us to form a rough picture not only of their content but also of their material form. The large size of paper, parchment or sigillia made of papyrus; the golden, lead or wax seal with the silk mantle (such as in the patriarchal letter of Pope and Patriarch of Alexandria Samuel, from the Holy Monastery of St. Stephanus of Meteora (Mantzana and Tsodoulos 2011)), in order to ensure the authenticity of the document; the majestic signature of the emperor, written in gold letters, in the case of an imperial sigillium, or of the archbishop and the synodic metropolitans, in the case of the patriarchal, are indicative of the formality and importance of this type of archival material (Karagiannopoulos 1972). Sigillia and their contents are prominent mainly after the fall of Constantinople, as they previously accompanied other official documents (Karagiannopoulos 1972). From the mid-15th century onwards they are autonomous official documents issued by the Ecumenical Patriarch, which endorse or remove privileges from churches and monastic institutions under their jurisdiction. Thus, while formerly the patriarchal sigillium accompanied the imperial chrysobull, it became the main document for conferring and granting privileges to temples and monasteries of the empire (Paizi–Apostolopoulou 2001). Most sigillia, with few exceptions, follow the same structure. In the upper central part of the sigillium is the name of the Ecumenical Patriarch and his title with variations "*......Archbishop of Constantinople, New Rome and Ecumenical Patriarch*" (Mantzana and Tsodoulos 2011). Then comes the main body of text and finally the signature of the synodal metropolitans. Their consent may have been a regulator, amid disputes between monastic institutions. An example is the claim to a monastery tower in Lechonia of Volos, on the one hand, by the Monastery of St. Vissarion of Doussiko of Trikala and by the Monastery of St. Lavrentios of Pelion on the other (Tsodoulos 2012). Many times, sigillia assign large estates and *metochia* to monastic administration, such as the assignment of Porta Panagia, the so-called Monastery of Megalon Pylon (Tsodoulos 2015). Others affirm or validate grants such as properties, privileges, etc. For example the sigillium of the Maria Angelina Komnini Doukaina Palaiologina, Doukissa of Epirus, to her brother Joasaf, one of the patrons of the Holy

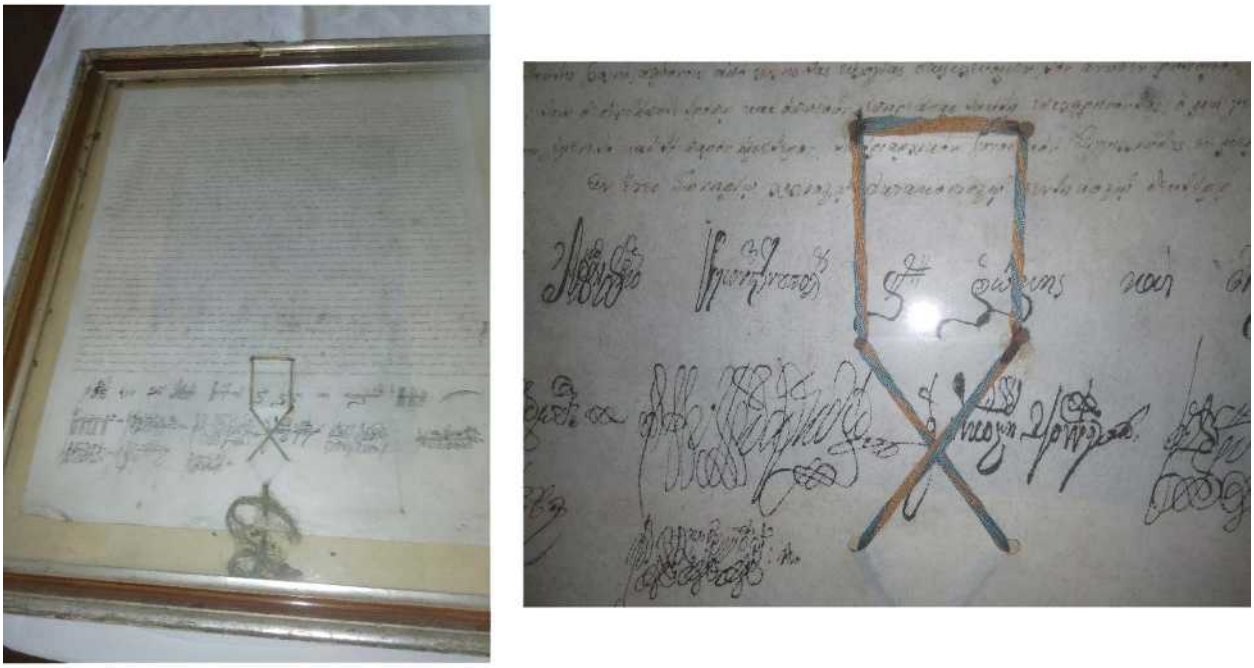

Figure 1. Sigilium signed by Ecumenical Patriarch Germanos IV, AD 1852.

Figure 2. Sigilium with lead seal, signed by Ecumenical Patriarch Meletios III, AD 1845.

Monastery of Great Meteoron (Mantzana and Tsodoulos 2015). Others such as the sigillium of the Ecumenical Patriarch Anthony to the Monastery of Megalon Pylon contain aphorisms and similar. (Demetracopoulos 1999).

Material and techniques

All measurements were conducted *in situ* at the Library of Halki Theological School. Two different sigillia are presented here, both of the Patriarchal type. The first sigillium (Figure 1) is signed by the Ecumenical Patriarch Germanos IV with the signature inscription "*εν έτει σωτηριω χιλιοστω οκτακοσιοστω πνετηκοστω δευτερω*" to inform us of the date, AD 1852. The second sigilium (Figure 2) has a lead seal with silk mantle. The signature inscription "*ΜΕΛΕΤΙΟΣ ΕΛΕΩ ΘΕΟΥ ΑΡΧΙΕΠΙΣΚΟΠΟΣ ΚΩΝΣΤΑΝΤΙΝΟΥΠΟΛΕΩΣ ΝΕΑΣ ΡΩΜΗΣ ΚΑΙ ΟΙΚΟΜΕΝΙΚΟΣ ΠΑΤΡΙΑΡΧΗΣ 1845*" informs us that this sigillium was signed by Ecumenical Patriarch Meletios III in the year AD 1845.

FTIR analysis

The infrared analysis of historic tassels was carried out by using both transmittance and reflectance techniques. The FTIR transmittance spectra were recorded on a Bruker Tensor FTIR spectrometer, by preparing KBr discs. About 1 mg of the ground textile powder was mixed with 100 mg of KBr and pressed into a pellet. 100 spectra were accumulated (1 cm^{-1} resolution).

The FTIR-attenuated total reflection (ATR) spectra of the samples were recorded on a Bruker Tensor FTIR spectrometer with a diamond ATR unit. 100 spectra were accumulated (2 cm^{-1} resolution). Standard correction for ATR spectrum was applied.

Spectral manipulations such as baseline adjustment, smoothing, obtaining the second derivative and band fitting procedures were performed using the GRAMS/AI 7.02 (Thermo Electron Corporation) software package. Band fitting was done using a Gaussian function and fitting was undertaken until reproducible and converged results were obtained with squared correlations better than r^2 ~0.9999.

Results and discussion

In Figure 3 the absorbance spectrum of ATR-FTIR spectra of the tassel is presented (raw and in KBr preparation) along with a reference spectrum of a 120 year old *Bombyx mori* silk textile.

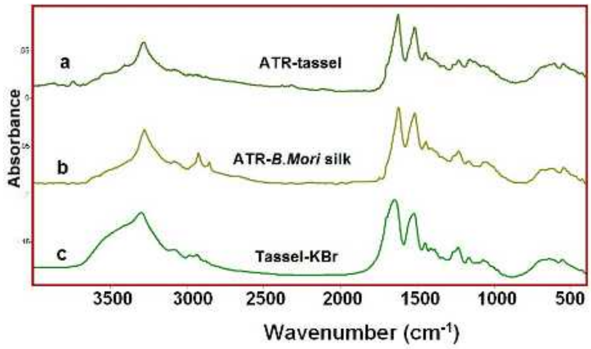

Figure 3. FTIR-ATR spectra of tassel fibres (a) a 120 year old silk textile (b) the FTIR absorption spectrum of Tassel fiber prepared as KBr disc (c).

Raw silk is a proteinaceous fibre consisting of two major proteins: The main fibrous component fibroin, and the amorphous protein sericin (Li *et.al.* 2013; Garside and Wyeth 2007). In commercial use, sericin is normally removed by degumming. However, some historic silks were composed of raw or partially degummed silk, thus for those samples, some or perhaps all of the sericin remained. For this reason, fibroin and sericin bands were analyzed in detail (Figure 4). The 997 cm^{-1} and 974 cm^{-1} bands are characteristic fibroin bands. The strong 1620 cm^{-1} band together with 1680 cm^{-1} component are amide 1 bands of β-sheet structure. The presence of alpha-helix structure (1652 cm^{-1}) can be estimated from the second derivative profile.

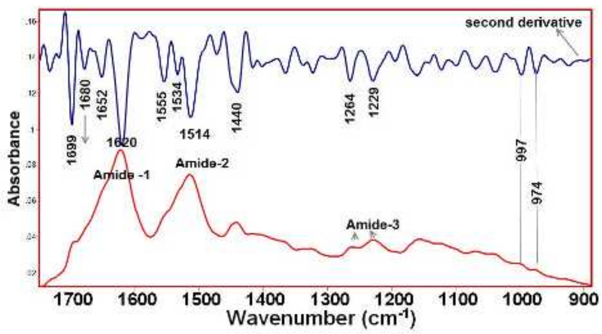

Figure 4. The 1700-900 cm^{-1} region of ATR-FTIR spectrum of studded tassel.

The FTIR spectra of the paper part of the documents were obtained by DRIFT-FTIR using a Bruker alpha spectrometer as mention above, and 50 spectra were accumulated in 4 cm^{-1} resolution (Figures 5 and 6).

As observed, the three bands at 1387 cm^{-1}, 1342 cm^{-1} and 1315 cm^{-1} are due to COH and HCC bending vibrations of cellulose. The bands at 1387 cm^{-1} and 1342 cm^{-1} are typical of crystalline cellulose (Kavkler *et al.* 2011). Parchment paper is made from cellulose fibres prepared from trees or plants such as cotton or flax. Paper can be made which mimics the thickness and smooth surface of parchment.

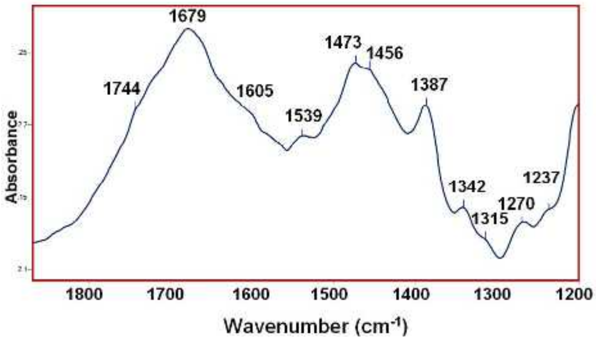

Figure 5. DRIFT-FTIR spectrum of cellulose bands of the paper part.

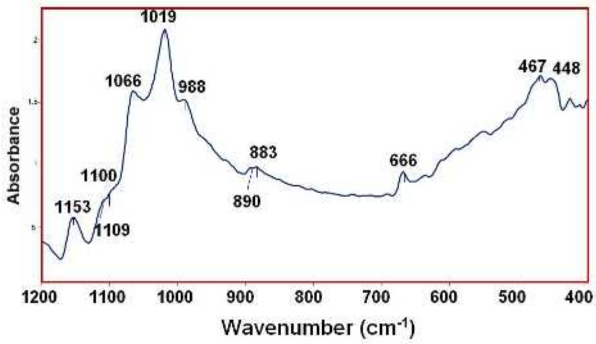

Figure 6. The 1200-400 cm^{-1} vibration region of DRIFT-FTIR spectrum of the paper part.

Conclusions

In conclusion, manuscripts such as sigillia, apart from any paleographic, historical, literary and artistic value, constitute valuable religious relics as sacred objects and monuments of ecclesiastical art, and in no case should they be treated as cold and lifeless museum objects. In this work, we were given the opportunity to work on two remarkable sigillia of the patriarchal type kept at the Library of the Halki Theological School. It was discovered that both sigillia are made of parchment, with the silk mantle made from *Bombyx mori* silk textiles.

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Archaeometric Investigations on Sarcophagus no. 1993/74 in the Diachronic Museum of Larissa, Thessaly, Central Greece, II: Study of Colour Traces

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ABSTRACT: Non-destructive analysis by means of portable X-ray fluorescence (pXRF) and Raman spectroscopy of colour traces on sarcophagus no. 1993/74 in the Diachronic Museum of Larissa (Thessaly, Central Greece), are presented. This sarcophagus is of the so-called "architectural type" and dates to the Late Classical Period. The main question to be answered concerns the pigments that were used and therefore the reconstruction of the artist(s)'s colour palette.

KEYWORDS: XRF, RAMAN SPECTROSCOPY, PIGMENT ANALYSIS, SARCOPHAGUS, PARIAN MARBLE, DIACHRONIC MUSEUM OF LARISSA.

Introduction

The existence of colours on the surface of sculptures and architectural elements is well known from ancient sources (Brecoulaki 2008). Information about pigments used for decoration can be derived from written sources (Theophrastus, Vitruvius, Plinius), where we can find information not only about the presence of colour in antiquity, but also about the origin of those colours, the process of preparation and application (Brecoulaki 2008; Katsaros 2009). In the present day, the study of coloured parts of archaeological material using analytical non-destructive techniques in order to identify their composition and chemical formula, is a well-established field of research (Katsaros 2009; Ganetsos *et al.* 2019).

Most of the archaeological materials (paintings, sculptures, architectural elements etc.) are unique in their nature and not able to be moved, therefore it is of great importance to choose the most suitable analytical method. According to Lahanier (1991) the "right" method has to be non-destructive, quick, applicable to different materials, sensitive, multi-elemental and portable.

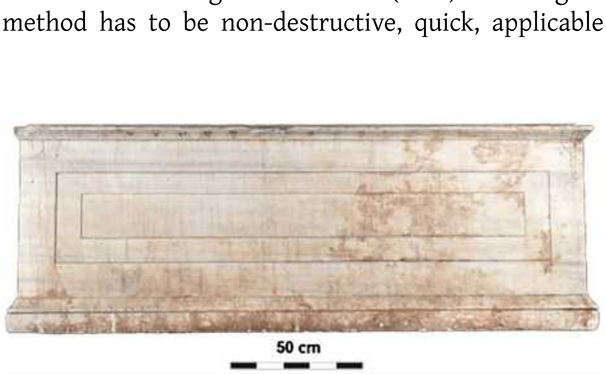

Figure 1. Sarcophagus no. 1993/74 in the Diachronic Museum of Larissa

In the present work, a case study is presented to identify chemical formula of colour traces on the sarcophagus no. 1993/74 in the Diachronic Museum of Larissa (Figure 1). For this purpose, portable XRF and Raman spectroscopies were used for a full non-destructive approach of pigment identification and thereafter for the reveal of exact colour decoration.

Material and techniques

The site of the analyses was the Diachronic Museum of Larissa. The sarcophagus under examination here was discovered by chance in 1993 during the course of municipal works in N. Douka St., in the south-eastern part of modern Larissa.

It is constructed of Parian marble and belongs to the so-called "architectural type" (imitating the shape of an ancient Greek temple or house). The case is preserved intact and measures: 2.29–2.33m long x 0.86–0.89m wide x 0.83m high, externally. Its pedimental lid is preserved in a fragmentary state, consisting as it does of a variety of large and small fragments. The sarcophagus dates from the Late Classical Period (early 4th century BC).

Along its upper and lower edges the case bears plain mouldings with painted decoration, and currently there are colour traces of its patterning: a Lesbian cymatium on the lower moulding with erect ivy leaves in blue on a red background, and an Ionic cymatium on the upper moulding with alternating blue and red leaves on a yellow background (Figure 2, left). A band of painted decoration also runs around the vertical face of the

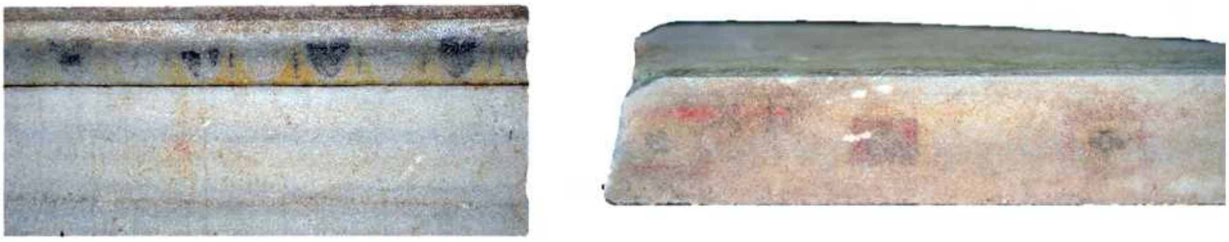

Figure 2. Details of the sarcophagus case (left) and lid (right), with colour traces

lid, consisting of a meander and abacus ornaments in red and black on a yellow background (Figure 2, right). Finally, the tympana of both pediments of the lid are adorned with the erect figure of an animal (propably a lion) painted in yellow (Katakouta and Palioungas 2020).

XRF spectroscopy

For the qualitative determination of the chemical elements of the examined colour traces two different portable handheld XRF spectrometers were used. Firstly, a Thermo Scientific Niton XL5 handheld XRF analyzer, which provides an ultra low light element detection (Mg-U), with a 6–50 kV x-Ray Tube of Ag anode and a standard 8mm spot size collimation. A second set of measurements were carried out using the thermo Scientific Niton XLp XRF analyzer with an Am-241 source and a solid-state detector. For the data acquisition from both XRF instruments built-in software was used and measurements were saved as Unicode ASCII files, the format being compatible for further analysis with specialized software. Due to the nature of the investigation (only qualitative analysis) a further calibration for the specific set of samples used for quantitative results (eg soil, metal etc.) wasn't needed except the built-in shutter calibration that was applied.

Raman spectroscopy

Supplementary to XRF analyses, Raman spectroscopy was applied. Measurements were performed with the Rock Hound Delta Nu Raman Spectrometer, which has a near infrared 785nm laser source in order to minimize fluorescence caused by the organic traces and an 8cm^{-1} resolution. Raman spectra in this work were received in the wavenumber range of 200cm^{-1} to 2000cm^{-1}. Prior to measurements, calibration tests were conducted on ideal pigment samples made for this purpose (Katsaros 2009; Caggiani, Cosentino and Mangone 2016) to ensure the correct Raman shift measurement and operation.

For further analysis, processing and evaluation of measurements for both XRF and Raman techniques the scientific software SpectraGryph was used (F. Menges, *SpectraGryph-Optical Spectroscopy Software*, Version 1.2.6, 2017).

Table 1. XRF results along with the estimated pigment

Measuring Point	Visible Colour	Chemical Elements	Estimated Pigment
All the spots with red traces from case and lid	Red	Hg, Fe, Ca	Vermilion/cinnabar (HgS) Maybe in a mixture with hematite because of the presence of Fe (Figure 3)
All the spots with yellow traces from case and lid	Yellow	Fe, Ca	Iron oxide/yellow ochre ($FeO(OH){\cdot}nH_2O$)
Greyish spots from the lower moulding of the case	Blue-Grey	Cu, Ca	A copper based pigment such as azurite or Egyptian blue ($CaCuSi_4O_{10}$)

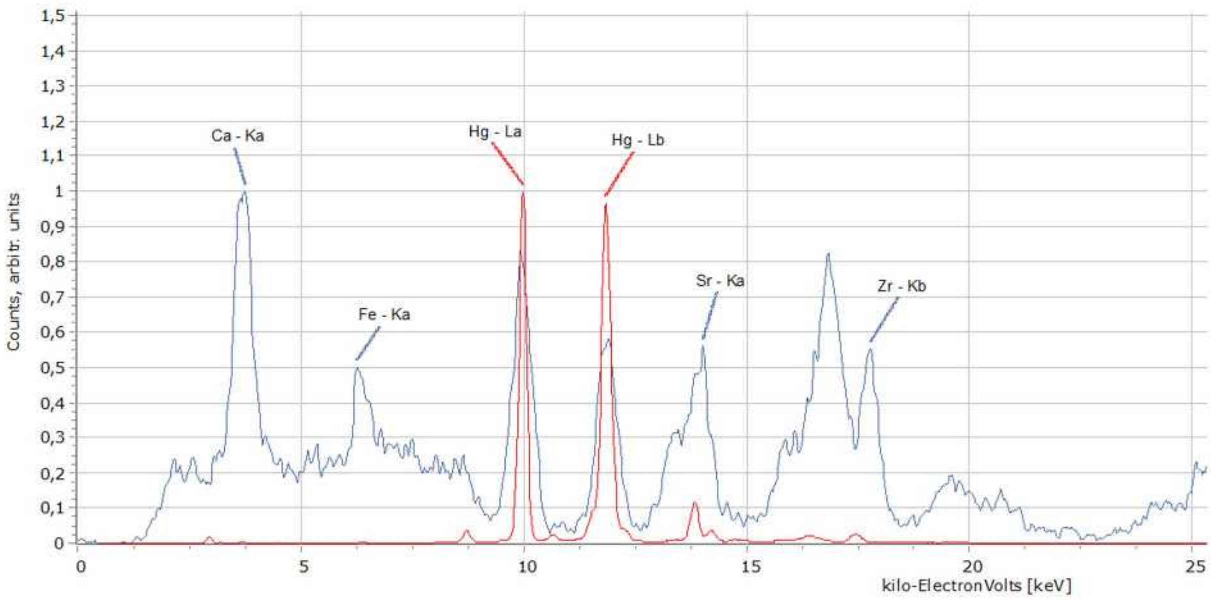

Figure 3. XRF spectra. Blue line: lower moulding of the case. Red line: reference spectrum of cinnabar showing Hg lines (Larsen, Coluzzi and Cosentino 2016)

Table 2. Raman spectroscopy results along with the identified pigment

Measuring Point	Colour	Raman Shift (cm^{-1})	Pigment
All the red traces from case and lid	Red	254vs, 280w(sh), 344m	Vermilion/cinnabar (Figure 4)
All the yellow traces from case and lid	Yellow	224s, 287m, 434vs, 557m, 624m, 1005vs, 1100s, 1150m, 1264w, 1405w	Jarosite (Figure 5)
Lower moulding of the case	Blue	360m, 376m,429vs, 480m(sh), 570w, 1035w,1091s	Egyptian blue (Figure 6)

Results and discussion

The chemical elements identified from the XRF analysis were mercury (Hg), iron (Fe) and calcium (Ca) for red traces, iron (Fe) and calcium (Ca) for yellow traces, copper (Cu) and calcium (Ca) for blue traces. The presence of calcium (Ca) in every measurement, likely refers to the marble surface and not to the pigment.

Table 1 presents analytically the results from the qualitative chemical analysis with aforementioned XRF apparatuses along with the estimated pigments. Measurements have been taken from all the visible colour traces on the sarcophagus, both on the case and the lid.

Figure 3 represents an XRF spectrum of red colour along with the reference spectrum of cinnabar from the Pigments Checker database (Larsen, Coluzzi and Cosentino 2016).

All Raman measurements were, as expected, quite noisy either due to environmental contamination from the burial environment or due to the presence of organic mixtures of the binding material. The analysis of the Raman spectra reveals vibrations of mercury sulfide

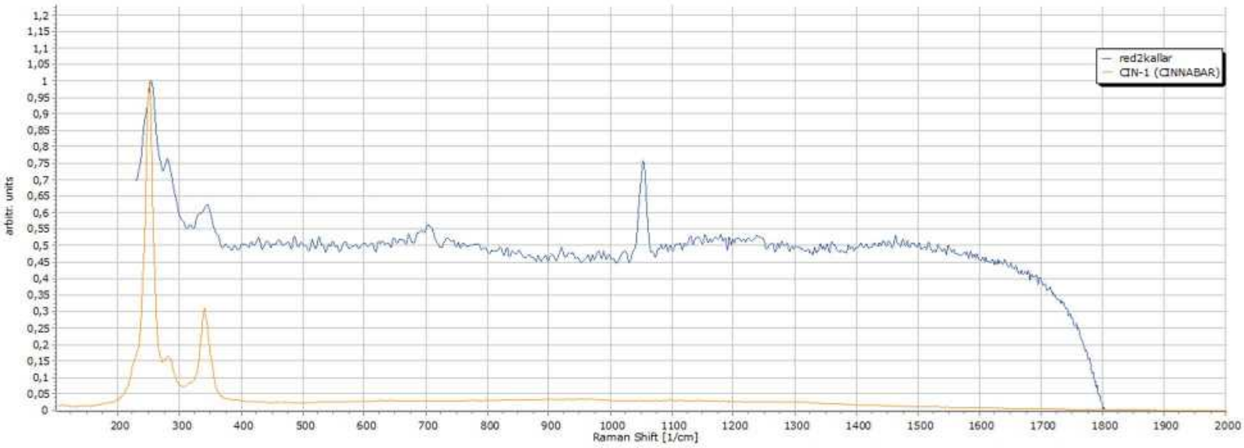

Figure 4. Blue line: Raman spectra of the red colour. Orange line: cinnabar reference spectrum

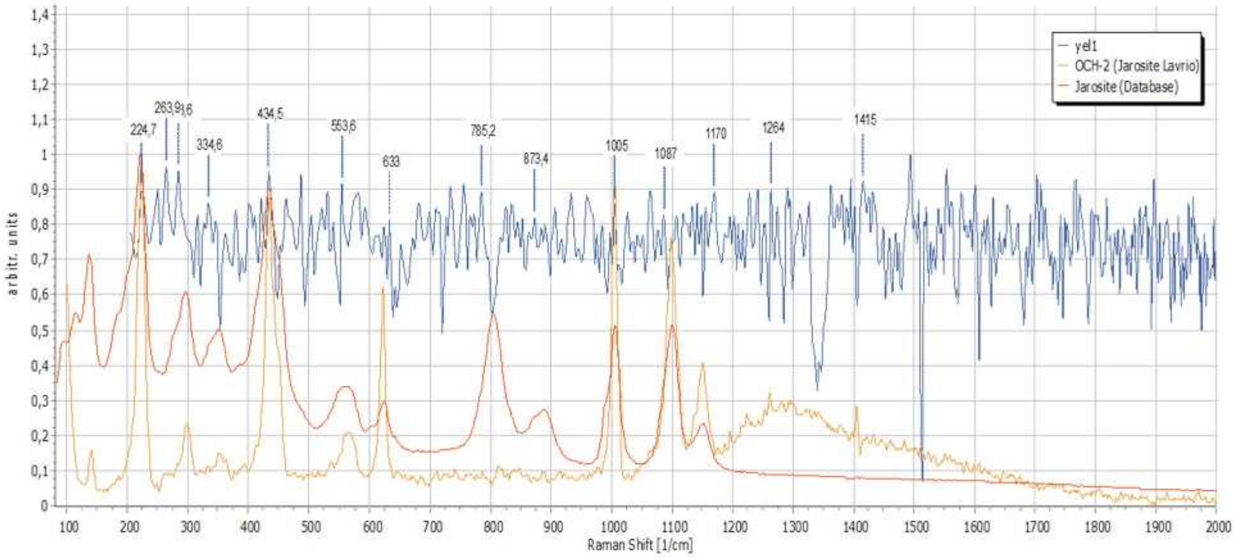

Figure 5. Blue line: Raman spectrum of the yellow traces. Orange line: reference spectrum of jarosite from Lavrio. Red line: Reference spectrum of jarosite from the international RRUFF base

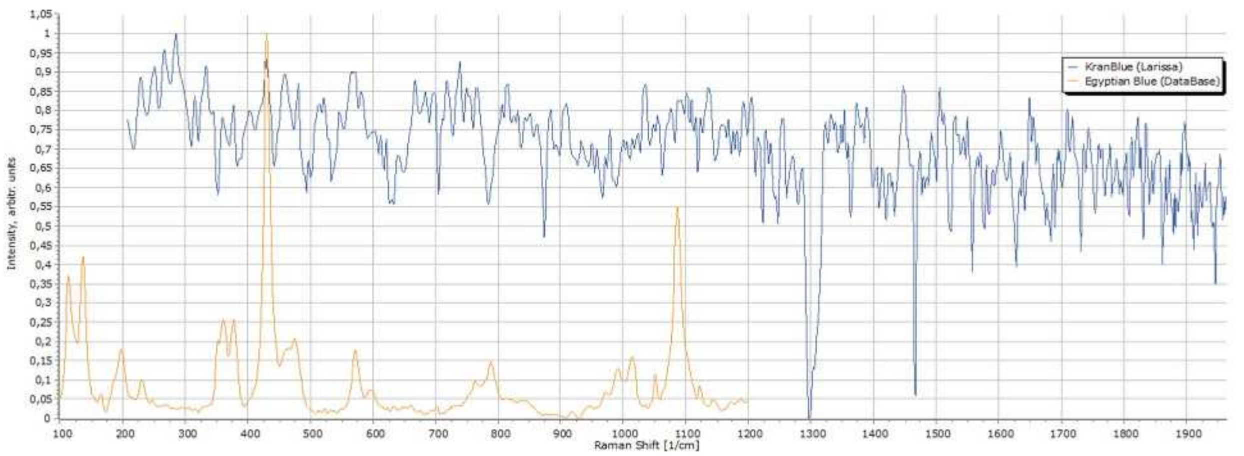

Figure 6. Blue line: Raman spectrum of the blue traces. Orange line: reference spectrum of the Egyptian blue pigment from the Pigments Checker database

(HgS), yellow iron oxide ($FeO(OH)\cdot nH_2O$) and calcium copper silicate ($CaCuSi_4O_{10}$).

Table 2 presents analytically the results of the chemical compound determination of the pigments using Raman spectroscopy. Measurements are averaged from different coloured spots of the sarcophagus, specifically the most well preserved.

Figures 4–6 show a Raman spectrum for each colour along with its reference spectrum from the Pigments Checker database.

Conclusions

Through the present study, we were given the opportunity to work on a remarkable archaeological artefact, that of the Late Classical Period's sarcophagus no. 1993/74 in the Diachronic Museum of Larissa.

Summarizing the results from the XRF and Raman analytical techniques employed in this work it may be concluded that the presence of calcium (Ca) in every XRF reading is due to the marble background.

Red colour traces were identified as cinnabar based on the presence of mercury (Hg). From XRF analyses on clear marble spots and the absence of iron (Fe) as a trace element in marble, the coexistence of iron in XRF measurements of cinnabar may be explained either as a product of contamination from the burial environment, or from the nearby yellow pigment which is based on iron (Fe), or even as a trace element from the cinnabar source (Katsaros (2009) mentions that cinnabar from Caucasian mines contains iron traces). Also, at the same Raman spectrum of cinnabar a peak at 1053cm^{-1} was identified as organic.

For the yellow colour traces, XRF analysis reveal the use of iron oxide (Fe_xO_x). Additionally, the Raman analyses revealed that the ore used for the production of this yellow pigment was jarosite. More analytically, i) in Raman spectra of the present work there is a vibration peak at 287cm^{-1} which is matched to the characteristic vibration peak of jarosite at 294cm^{-1} and, ii) the obtained spectrum (as a spectral line) is exactly identical to that of jarosite from the mines of Lavrio, Greece (refence spectra line taken from Katsaros 2009).

Blue colour traces based on the presence of copper (Cu) and the matching of Raman spectra with the reference material, were identified as Egyptian blue (Katsaros, Liritzis and Laskaris 2010).

All the above-mentioned results are in accordance with the literature for similar research and the colour palette in use during the Classical period (Flourentzos 2011).

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