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Of Goblins and Gods

3,500 years of Cobalt and its Pigments

Andrew J. Shortland, Victoria Kemp,
Lasse Hermansen Bjørnland, Patrick Degryse (eds)

Leuven University Press

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Preface

Professors of archaeological science, perhaps especially those associated with work in Egypt, are used to getting odd emails and cold calls from unfamiliar but very, very enthusiastic individuals. It is a "courageous" academic who dips their toe into the world of amateurs speculating on pyramids, temples or mysterious objects. However, amongst the eccentrics and the misguided, there is the occasional glint of gold or, in this case (to stretch a simile beyond the breaking point), cobalt. An email out of the blue, sent in January 2019 by Lasse Hermansen Bjørnland, curator at the Blaafarveværket (Blue Colour Works; BCW), a mining and industrial heritage museum located at Åmot, in Modum, Norway, is the reason this book came into being.

It quickly became clear that the BCW was a very important source of cobalt pigments in the 19th century, with long-standing links with the other major European cobalt source, which is in Germany. Lasse wondered whether there might be interest in carrying out some analytical research on the mines and collections of the BCW.

The joint work which started with this email was, sadly, interrupted by the COVID-19 pandemic, which curtailed travel between the UK and Norway. However, in 2022, it was finally possible for Andrew Shortland and Dennis Braekmans to go out to Norway, visit the mines and meet the BCW team in person. The BCW has a captivatingly beautiful setting and the mines have a fascination and state of preservation rarely seen. Rightly, it is one of the most visited tourist sites in Norway, even though due to the climate it is only able to open for the (relatively short) summer season. On their visit, Andrew and Dennis were privileged to meet Tone Sinding Steinsvik, curator of the sites and creator and sustainer (with her late husband) of the foundation that is now the museum. Her enthusiasm for all things connected with the BCW was infectious and led to the bringing together of colleagues and friends from around the world to the site for an academic workshop. This workshop was made possible by the generosity of Tone and the hard work, kindness and hospitality of Lasse, Sverre Følstad, Camilla Løchen and all the BCW staff. The workshop was held from 6-8 September 2023, and 15 papers were presented, with speakers from academic institutions in 9 different countries attending, some crossing continents to be there—from as far away as the USA and Hong Kong.

The book that lies before you is a reflection of this workshop. It is not meant to be an exhaustive presentation or review of research performed on ancient cobalt ore extraction and cobalt pigments, as not all materials studied could be

included (e.g. Spanish and Italian majolica, a major use of cobalt as a pigment for pottery and tiles, is not discussed) and some fields of research are still very much developing (e.g. the origin and nature of smalt used in textile or paper bleaching). Nevertheless, this volume gives an oversight of methods and approaches used in this type of research and aims to provide snapshots of the extraction and use of cobalt from many regions in the world, from its application in Bronze age pyrotechnologies; through pre-industrial high-value painting and porcelain making; to its use in mass-produced materials, such as paper. This volume is organised into three parts, with the first part presenting the nature of cobalt use through the ages, the second part discussing sources and signatures used in cobalt characterisation, and the third part discussing applications of cobalt as a pigment. The publication is kindly sponsored by the BCW, which allows this volume to be freely available online and gives it the widest circulation possible.

In the first chapter, cobalt compounds used throughout history are discussed. Cobalt metal is a relatively modern innovation, and it is now vital in the production of high-specification batteries and various steel alloys. As such, cobalt is a "critical metal", meaning that its production is vital to many industries and the restriction in the exploitation of major ore deposits for the metal to a small number of (often conflict-ridden) countries is a cause for major concern. Cobalt compounds have been used for more than 3,500 years and were for most of that time employed exclusively in pigments. Cobalt ores are relatively rare in exploitable resources, and their exploitation has always been a dangerous pursuit. The presence of arsenic in many of the ores has led to severe health consequences for workers, which has in the past been blamed on supernatural spirits and goblins—*kobolds*, from which the word cobalt is ultimately derived. However, cobalt's use to create beautiful, deep-blue pigments has led to it featuring in some of the most important works of art and religious objects, the colour blue being associated with heaven, eternity and the divine. Cobalt therefore has a name that is derived from goblins, but a use that connects it clearly with the gods.

In the second chapter, a series of objects that now may be regarded as works of art but that previously had several very different uses are examined. All have the use of the element cobalt derived from its various compounds as an important or dominant feature of their decoration. Similarities and contrasts in the use of cobalt and how it relates to very high-status objects is discussed. The symbolic importance of cobalt blue, and its relationship to deities and religious figures, is also illustrated.

In the third chapter, the history of the BCW is discussed. Through most of the 18th and 19th centuries and into the 20th century, the cobalt industry has been predominantly linked to the German state of Sachsen (Saxony) and to Germany in

general. It was there that modern cobalt pigment production started, with Saxony historically being the largest producer. There is an exception, however: in the early 19th century, at the end of the zenith of the cobalt pigment trade, a Norwegian producer, the BCW, became one of the most notable blue colour works in the cobalt market. Little has been published on the BCW outside Norway. However, much archival material is preserved, and a large and well-documented collection of cobalt products is kept by Stiftelsen Modums Blaafarveværk—Bygdemuseet I Modum (Modum Blue Colour Works Foundation—Modum Local History Museum). An international research collaboration combines archive research with science-based archaeological methods to analyse the preserved cobalt products, with the goal of tracing Norwegian cobalt to historical objects.

The fourth chapter discusses how cobalt ores are not very common and almost always exist in the presence of multiple other elements. Mineral resources for cobalt extraction originate from varying geological contexts in terms of host rock type and mineralisation age. Therefore, cobalt ores tend to have a characteristic fingerprint of elemental and isotopic compositions, and there is substantial potential to distinguish sources and to link cobalt pigments to an associated ore or factory. This chapter explores the potential of combined elemental and lead isotopic analysis to not only provenance cobalt sources, applied to German and Norwegian mines, but also study their often complex processing and preparation into pigments, such as smalt.

In the fifth chapter, an overview of the great variety of chemical signatures of cobalt colourants observed in European glassware between the end of the 17th and the beginning of the 20th centuries is given, and the possibility of assigning some of them to known cobalt deposits is discussed. Excluded from this discussion are cobalt sources distributed only outside the continent of western Europe and/or originating from other geographical areas of the world. Prior to this period, between the end of the 12th century and the 18th century, three main types of cobalt ore (sometimes processed as zaffre and/or smalt) were used successively in Europe by glassmakers and ceramicists. They are all thought to have come from the Erzgebirge (on the German–Czech border, also known as the Ore Mountains or Krušné Hory). From the 18th century and especially after the third quarter of the 18th century, the chemical signatures of cobalt colourants tend to show more variability, and new groups seem to appear simultaneously.

The sixth chapter discusses cobalt ore from Kashan, Iran, renowned for its critical role as a trade commodity across the Islamic world and with China, particularly during the Mongol period. The blue colour derived from the Kashan pigment seen in Islamic ceramic glazes and the earliest blue-and-white porcelain of China established aesthetic standards that influenced ceramic production for

centuries, including the blue-and-white porcelain of Europe. This chapter reviews the history of the cobalt mine in Kashan by analysing historical accounts and presenting the results of chemical analyses of the ore and the cobalt pigments used in ceramic glazes.

The seventh chapter presents Alderley Edge in Cheshire, England, a well-known site of Bronze Age, Roman and post-medieval copper and lead mining. For a short spell in its history, however, Alderley Edge also became a site of considerable interest, when cobalt ores were identified during the Napoleonic period—a time when communication with mainland Europe was severed. The location of cobalt mining at Alderley Edge has been known since the 1980s, but in 2021, a chance subsidence outside the known area of cobalt mining led to the discovery of a section of mine sealed since its closure around the second decade of the 19th century. The chapter sets out the background to this discovery and the finds that were made, and it provides a general outlook on cobalt mining at Alderley Edge.

The eighth chapter introduces the key aspects of ancient cobalt utilisation in Late Bronze Age glassmaking and elucidates how trace-elemental analysis of cobalt-coloured glasses has played a pivotal role, providing crucial insights into the Late Bronze Age glass system. The earliest documented use of cobalt as a colourant dates to the reign of King Tuthmosis III (1479-1424 BCE), in the Egyptian 18th Dynasty. The discovery of cobalt as a colourant enabled ancient glassmakers to simulate the rich blue hue of lapis lazuli, a stone highly prized by ancient Egyptians for its symbolic and religious significance. Vessels and jewellery made of glass were rapidly integrated into Egyptian New Kingdom society and became an indicator of high status. Therefore, glasses are often found connected with archaeologically significant sites, such as elite burials, palaces and temples. Cobalt-coloured glasses are a compositional subgroup within Late Bronze Age glasses and possess significant informational value owing to the use of discrete cobalt sources during the 18th Dynasty, the Ramesside Period and the Late Period glassmaking eras, thereby allowing researchers to potentially determine the epoch of glass production. As a human-made substance, glass required a resourced infrastructure providing refined raw materials, expert artisanship and the knowledge of high-temperature working. Therefore cobalt glasses are well placed in archaeology to provide in-depth information about production, ancient trade networks, cultural exchange and the wider infrastructure supporting the Late Bronze Age glass industry.

The study of cobalt in the early Islamic period, the topic of chapter nine, has focused on the use of cobalt in the famed blue-and-white ceramic wares of the Abbasid period, often in direct comparison with Chinese earthenware as well as

porcelain. The cobalt source chemical signature was thus extrapolated from a fairly small number of ceramic samples to vitreous materials more generally. More analytical data have since become available on early Islamic cobalt-blue glass, allowing a reassessment of the nature and composition of the cobalt-blue pigments used in the first few centuries of Muslim rule. This chapter attempts to redefine the cobalt signatures of early Islamic glass in direct conjunction with regional base glass characteristics and discusses the possible processing of cobalt minerals and their provenance. The compositional evidence shows that at least four different cobalt pigments were used in early Islamic glass production, in combination with different base glasses, with a clear preference for Mesopotamian raw glass. This suggests a globalised trading system for both the cobalt pigment and finished cobalt-blue glass artefacts. It is not yet possible to determine the origins of the cobalt ores, partly due to a likely elemental differentiation and differential solubility of the pigment within the glass melt. However, it can be assumed that the cobalt sources were primarily located in the Caucasus; Central Asia; or, perhaps, the Arabian Peninsula, as cobalt-blue glass mostly corresponds to base glass from Mesopotamia or farther east (Iran, Central Asia). Ultimately, a comparative and large-scale approach will be needed to narrow down these possibilities.

Chapter 10 presents the use of smalt and other blues in painting from South Asia and Iran. Technical examination and analysis of works on paper created at centres within South Asia and Iran from the 15th to 19th centuries found that from the late 15th century, a glassy blue pigment coloured with cobalt was occasionally used in place of or in conjunction with traditional blue artists' pigments, such as ultramarine and indigo. This glassy cobalt-based pigment is similar to smalt, a blue pigment used by European artists from the early 15th century onwards. Compositional analysis shows that the pigment used in Iranian and Indian art works from the second half of the 17th to the late 18th century matches European smalt and that it is likely smalt imported from Europe was used. However, samples from earlier art works have more variable compositions and cannot be definitively shown to be European smalt. The glassy blue pigments used on earlier works on paper may instead have been derived from crushed glass or glaze of local origin.

The eleventh chapter reviews the production and use of blue Sancai and blue-and-white porcelains from the Tang (618-907 CE) to the Qing (1368-1912 CE) dynasties. In the Tang dynasty, blue Sancai was produced by the Gongyi kiln throughout the entire dynasty and by the Liquanfang kiln between 730 and 760 CE. Most blue Sancai was used for funerary ceramics in tombs. Later, around the 9th century CE, Tang blue-and-white porcelain was made by the Gongyi potters. It was the earliest Chinese blue-and-white porcelain. In total, 39 fragments and wares have been found at the kiln, in a tomb, in port cities and in a shipwreck. These

findings identify Tang blue-and-white as export wares related to the Maritime Silk Road. The production and use of blue-and-white porcelain declined dramatically in the Song dynasty (960-1279 CE). Only four sherds have been discovered, in two Buddhist temples. From the Yuan dynasty onwards, archetypal blue-and-white porcelains produced in Jingdezhen dominated the Chinese and international markets. Countless blue-and-white wares were used by royal families and ordinary people as daily wares, burial ceramics, sacrificial offerings, export porcelains, etc. The technology of cobalt materials is also reviewed in this paper. During the Tang dynasty, the source of cobalt material was probably the Middle East. Song dynasty potters perhaps employed the local ore from Zhejiang to produce porcelains. However, the imported cobalt pigment occupied the main market again in the Yuan and early Ming dynasties. Mid-Ming potters used local cobalt pigment and late Ming potters mixed imported and local ores together to produce those porcelains. In the Qing dynasty, craftspeople mastered the manufacture of top-quality cobalt pigment, and Jingdezhen potters applied a wider range than before of other coloured pigments to blue-and-white porcelains. Besides the use and production of blue-and-white porcelains from the Tang to the Qing dynasty, the technology of cobalt pigment in Jingdezhen is also reviewed. The traditional processing method of cobalt pigment included five steps—washing, filling bowls, firing, selection and grinding.

In the twelfth chapter, the applications of cobalt in Fürstenberg porcelain is presented. The blue enamel formulations there seem to run parallel with developments at the Meissen production, though small differences can be noted: all of the early Fürstenberg blue porcelain contains Ni, while only some is enriched in Ba and no Zn can be identified in the underglaze "F" marks and other decorative aspects.

Further work on the BCW will be possible through grant C16/24/004 of the Special Research Fund of KU Leuven, including scholarships for PhD students alongside analysis and fieldwork. Interest in the BCW, as well as our collaboration, therefore, remains truly international, with further workshops planned for the years to come. We would like to acknowledge that none of this would have been possible without the support, enthusiasm and knowledge of Tone Sinding Steinsvik. She is the inspiration and driving force for both the continuing development and conservation of the BCW sites and for the increasing international academic and scientific interest in its work. This volume is dedicated to her, with grateful thanks.

Part 1

Cobalt through the ages

Chapter 1

Cobalt: Of goblins and gods

Andrew J. Shortland[1]

Introduction

This short paper introduces cobalt and gives a background to the history of that element, from the first use of cobalt compounds in the Late Bronze Age to their modern use in advanced batteries and steels. The history of the use of cobalt compounds is much longer than that of the metal, which was only separated in the 18th century CE (Stwertka 2012). Throughout the history of cobalt, the extraction of the material, especially from arsenic-bearing ores, has presented severe problems and significant health impacts for the miners—something that is still happening today. Historically, these problems and impacts have been so severe that supernatural explanations involving spirits and mischievous goblins have been employed to explain health symptoms and early deaths. In contrast, the pigments derived have often been used in the most prestigious works of art, frequently linked to kings or gods. This tension is briefly examined here.

The element

Cobalt is a hard, silvery, magnetic, metallic element with a high melting point that sits on the top row of the transition metals in the Periodic Table. With atomic number 27, it is between iron (26) and nickel (28), with both of which it shares a number of similarities. Indeed, its chemical properties are similar to those of manganese, iron, nickel, copper and zinc (Thomas and Gillingham 2020). This means that these elements can substitute for each other in cobalt and related ore minerals and have a tendency to follow similar reaction pathways if those ores are refined. This has important consequences for archaeologists and historians tracing cobalt sources, as discussed at length in papers in this volume.

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Cobalt is a hard metal, with a Mohs hardness scale value of 5.5, which is greater than that of most other comparable metals—for example iron (4.0) and copper (3.0)—and closer to metals specifically known for their hardness, such as titanium (6.0). Its magnetic properties make it especially valuable, and it is used in alloys and magnetic sensors and recording materials. The high melting temperature of 1495°C means that it can also be used in high-temperature environments, such as turbine blades in aircraft (Thomas and Gillingham 2020).

Cobalt has valence electrons [Ar] $4s^2 3d^7$ and commonly occurs in the 2+ oxidation state (Co^{2+} = [Ar] $3d^7$ $4s^0$), although it can also adopt the 3+ form (Co^{3+} = [Ar] $3d^6$ $4s^0$) (RSC, no date). Once again, along with other transition metals, its compounds tend to be coloured, sometimes strongly coloured. In the case of cobalt, the 2+ oxidation state usually forms a deep-blue colour ("cobalt blue"), whereas the 3+ has a less deep hue of pale pink or purple. The presence of other elements can radically change these colours, and cobalt-containing compounds have been used for millennia as a pigment (Hatch 2021). Cobalt is a particularly strong colouring element and is the strongest of the top row of the transition metals. This means that relatively small amounts of cobalt can impart a distinctive colour to a material, such as glass. Indeed, it is so strong, that about 0.05 weight per cent CoO in a glass will usually impart a definite blue colour, whereas perhaps 5 or 10 times as much copper would be required to do the same.

Figure 1.1: Cobalt ore from the Blaafarveværket mines, Modum, Norway.

Cobalt metal was first separated and identified as a new element by George Brandt, working as director of the Bergskollegium (Chemical Laboratories of the Swedish School of Mines), in 1735 (RSC, no date). However, it took some years for his identification of a new element to be ratified and agreed to by the scientific community as a whole. Cobalt was the first of many new metals to be discovered that was unknown as a metal in ancient times. Part of the reason for this was the fact that it is relatively rare, making up only 0.0025% of the Earth's crust—which is less than nickel (about 4 times as abundant) and copper (about 3 times as abundant), for example—and similar to perhaps much less popularly known elements, such as scandium and yttrium (Schulte, no date).

Cobalt sources and mining

Ores of cobalt come in a range of forms, often as sulphides or arsenides (e.g. Fig. 1.1). The most important include cobaltite, smaltite and euythrite (Mindat.org, no date). Cobaltite (CoAsS) is a hydrothermal mineral that occurs in veins with other sulphides, such a chalcopyrite, pyrite and arsenopyrite. This means that the cobalt is often found with iron and copper. The mineral is not very easy to identify in hand specimens, with its metallic, silver-grey lustre being common to many sulphides with similar habits. Similarly, smaltite ($CoAs_2$) is also often found in hydrothermal veins and can form alongside cobaltite. Its habits and colour are again similar to those of cobaltite and many other ore minerals, making them difficult to identify. However, both of these minerals can be associated with secondary minerals, such as eurythrite ($Co_3(As)_4)_2.8H_2O$), which is a hydrated weathering product of cobalt arsenate and typically found in oxidised cobalt deposits. It has a distinctive pink colour caused by the cobalt 3+ ion, which means that it, and the unweathered sulphides/arsenides associated with it, can be distinguished from other minerals of related elements.

Formation processes of cobalt minerals include a variety of different geological routes linked to the production of ore minerals and their weathering. Briefly, the basic process is one linked with magmatism. Cobalt can be concentrated by magmatic processes into specific igneous rocks. As mentioned above, cobalt tends to follow similar chemical paths to the transition elements close to it in the periodic table; therefore rocks rich in iron, for example, tend to have increased contents of cobalt. This means that cobalt tends to be concentrated into mafic and ultramafic rocks, and within those rocks to specific, especially iron-rich, minerals. The action of water within and on these igneous rocks leads to the second process that can concentrate cobalt—hydrothermal activity. The movement of very hot, mineral-rich fluids through magmatic bodies can result in the concentration of elements

in these fluids, leached from the rocks through which they are percolating. When the fluids potentially leave the magmatic body and enter the host rocks, they can form veins, and, where they encounter very different temperature, pressure or pH regimes, they can precipitate ore minerals, including cobalt-rich minerals. Often these cobalt-rich minerals will be in intimate association with minerals of many other, similar elements, as discussed above.

The weathering of both igneous rocks and hydrothermal veins can result in the next type of cobalt concentration, which is linked to sedimentary processes. As the primary rocks are broken down and the minerals they contain are fragmented and potentially altered, sedimentary processes can sort and concentrate particular mineral types into specific beds, very significantly increasing their bulk concentration in certain elements (for example cobalt) and making them viable for mining operations. Weathering processes, especially in extreme tropical environments, can result in further concentration of iron and its associated elements into lateritic soils, resulting in the concentration once more of cobalt into exploitable deposits. All of these types of cobalt deposits have been, and are, exploited for the production of cobalt compounds and metal.

The precise original source of the cobalt in many of these deposits is unclear, and the concentration processes are often little understood. This is often because the process of formation of the deposits are usually very complex and often multi-stage. While ore bodies that are exploited (or have the potential to be) are usually well studied in terms of the lateral distribution and concentration of ore, the reasons why the ore might be there in the first place is frequently less well studied. As the demand for cobalt becomes greater and the known existing sources diminish or become more difficult (for a whole range of reasons) to exploit, the quantity and quality of research on the genesis of cobalt mineralisation is very likely to increase.

Cobalt production and uses

Global production of cobalt has increased greatly over the past 15 years, from around 60,000 tonnes in each of 2004, 2005 and 2006 to 170,000 tonnes in 2020 (Cobalt Institute 2022; USGS 2022). This change has largely been driven by hugely enhanced production in the country that supplies the majority of the world's cobalt production, the Democratic Republic of Congo (DRC). In 2021, the DRC was home to nearly 70% of the world's cobalt production. Other significant suppliers include Russia, Australia, the Philippines and Cuba, but none of these countries remotely approaches the production capacity of the DRC. Refining of the cobalt ore, to make material that can be used, is concentrated in China.

DRC production of cobalt has been the subject of widespread concern (Frankel 2016) on several levels. Cobalt is one of 40 or so metals and minerals that are classified as "critical". "Critical" metals and minerals are defined as those crucial materials without which the world's economic systems would be severely affected and the supply of which is considered "at risk" for some reason. In 2022, cobalt topped the Critical Materials Index List due to its extraction mostly as a by-product of the production of other metals and the restriction of cobalt ore exploitation largely to the DRC, which is generally not regarded as one of the most stable states. In 2022, the DRC was ranked in the top 15 most corrupt states in the world (out of 180; Transparency.org 2023). The working conditions of those employed in the DRC mines and the environmental damage the mining is causing add to the concerns about its production.

Figure 1.2: Drift in the Blaafarveværket mines in Modum, Norway.

Cobalt extraction and refining

Extracting cobalt ores has followed the pattern of many other minerals through history. Early extraction tended to focus on following mineral-rich veins deep into the ground using shafts and drifts to maintain close contact with the vein as it changes in orientation or size (Fig. 1.2). This can be an expensive and slow way to extract ores, and in modern times open-pit mining is more often used. As mentioned above, cobalt ores are rare and tend to be intimately mixed in with the sulphides, arsenides and other compounds of other metals. This means that they have always needed to be sorted and beneficiated by crushing and then processed to concentrate the part of the ore with the most cobalt in it. Hand sorting was an early way of doing this, but floatation and magnetic separation allow for more automation and are now widely preferred. Once the ore is as concentrated as it can be, smelting and refining can begin. This process of changing the ore into a metal may not necessarily take place adjacent to the ore source; indeed, some cobalt refining can be thousands of kilometres away from the initial source of the ore. Smelting involves heating the ore, usually in a furnace, to separate the metal from the sulphur and the arsenic. Further refining can improve the purity of the cobalt metal and make it a usable material. In addition to smelting in a furnace, electrolysis techniques can be used to separate out the metal either from a solution or from a melt.

The pure cobalt metal can be used in this form or can go on to be alloyed with other metals, especially tungsten, nickel or chromium, to produce a speciality alloy with precisely the properties needed for the application.

It should be noted that the extraction of cobalt ore and its refining to produce a metal can have significant environmental and social effects. Large-scale open-cast mining can seriously damage the environment, and the processing of ores can result in a waste material that is hazardous in many ways. Similarly, the smelting and refining processes use very large amounts of power and, again, result in potentially poisonous waste products. Perhaps chief amongst the hazards of the mining and production of cobalt and its compounds is the frequent association of cobalt with arsenic. Arsenic is a very poisonous element, and long-term exposure to an atmosphere, water or food that is rich in arsenic can have serious long-term effects. This is considered further later in this paper.

Cobalt uses

Metal

In modern times, the most important use of cobalt is as a metal (Cobalt Institute 2022), and 57% of cobalt metal is used in batteries, specifically in electrodes for lithium-ion and nickel-cadmium cells. It is therefore an important component of many of the devices that we use routinely, such as mobile phones. The significant recent increase in the demand for and supply of cobalt can be attributed in the main to a huge rise in the demand for high-power batteries. With the introduction and normalisation across the world of electric vehicles, especially cars, this demand is bound to rise further.

Some 13% of cobalt metal is used in nickel-based alloys. Their excellent high-temperature properties and corrosion resistance make them a natural alloy to use in aerospace applications, particularly aero and rocket engines and other types of turbine blades. A further 8% of cobalt produced goes into tool materials, where it acts with other metals as a hardener in steels and is used especially in cutting devices, magnets and high-speed steels.

In addition to these three common uses as a metal, cobalt has other, less common applications in medical and dental implants, hard disc drives, other electronics, and even ammunition.

Compounds and pigments

The other major use of cobalt is for pigments. While the extraction for refining to metal for the uses defined above dominates the modern uses of cobalt, before the 18th century, cobalt compounds (not yet identified as such) were exclusively used for pigment making.

Despite the bold assertion in *Encyclopaedia Britannica* that "Cobalt has been detected in Egyptian statuettes and Persian necklace beads of the 3rd millennium BCE", the first identified regular use of cobalt as a pigment is in Egypt in the 16th century BCE (Kaczmarczyk 1986). Here cobalt was used to colour glass and glazed vessels, amulets and jewellery a deep-blue colour. Slightly later, and for only a limited period of time, cobalt was also used as a pigment to decorate particular Egyptian ceramic wares, specifically "Palace ware", more prosaically also known as "blue-painted ware" (Shortland 2012). Cobalt compounds continued to be used, with some time gaps and uncertainties, from this period on and in many areas of the world, as local cobalt ores and the technology to develop them into useful colouring compounds were found and exploited. However, it is often unclear in what form the cobalt compounds were transported from the ore source

to the production site for the ceramic, glass or other material. As far as can be ascertained, it seems that the ore itself may have been transported. Thus, it appears there was no processed cobalt pigment as such, only cobalt ores being directly used in the subsequent production of blue objects. As far as is known, the first texts that refer to cobalt pigments deliberately created to be traded as a pigment can be refer to it as *zaffre* (alternatively *zaffer, saflor or safflor*), "smalt" and other terms (Hermanson, this volume; Delamare 2013). Smalt is probably the most interesting and important and was probably first produced in the 16th century in Europe. Smalt is a cobalt-coloured, potassium-rich glass that was a deliberately created pigment that could be easily sold, transported and used. It was often made in facilities close to the mines where the cobalt ore was extracted. Broadly speaking, after the ore was sorted to select the most cobalt-rich fraction, this was melted with wood ash and silica, and the resulting end product is referred to as smalt. Different facilities had different processes to ensure that the smalt was as pure as possible and free from elements or compounds that might affect its colour. The final smalt was sorted, powdered and graded for use in different industries.

Smalt and its related materials were the most important pigment made with cobalt compounds for many centuries (Delamare 2013). However, at the very end of the 18th century and throughout the 19th, improvements in the understanding of chemistry and its practical application led to a range of new pigments (Hatch 2021). These new pigments have been given a modern reference number, all of which follow the same format. The first letter is a "P" for "pigment"; the second letter relates to the colour: "B" for blue, "G" for green, etc.; and the sequential number that follows relates broadly to when the pigment was first used (the lower the number, the earlier it was discovered).

The first of these new pigments was "cobalt blue", PB28, which is a cobalt aluminium oxide and often called "Thénard's blue" after its inventor (Hatch 2021). This was first developed in 1802. Two further blues, known as Cerulean Blue, were developed in the 1860s, specifically PB35, a cobalt tin oxide, and PB36, cobalt chromium aluminium oxide. The production of these new pigments had a very serious effect on the often very well-developed factories that had for decades or even centuries been producing smalt. Parallel developments led to cobalt being used to make other colours, including, from the 1780s onwards, Cobalt Green (PG19, PG26 and PG50, using zinc and chromium in combination with cobalt); in 1848, Cobalt Yellow (PY40, a potassium cobalt nitrate, also known as "Aureolin"); and in 1859, Cobalt Violet (PV14, cobalt phosphate).

Gods and goblins

The title of this volume reflects two contradictory aspects to the way cobalt has been used and viewed.

Cobalt and kobold

The word cobalt was given to the element by its discoverer in 18th century. He drew the name from the German word *Kobold*, which may have links to such English words as goblin and hobgoblin. The origin of this words seems to lie in the Greek *kobalos*, which means "an impudent rogue, a mischievous rascal" (Brown 1878, 230) or a "babbler, evil-doer, profligate" (Brown 1878, 230, quoting Hesychios). From this word comes a group known as

> Kobaloi, who in legend were impudent, thieving, droll, idle, mischievous gnome dwarfs, who robbed Herakles when asleep, and were captured by him. Amused at their antics, he spared their lives and, according to one account, made a present of them to the Lydian Queen Omphale. [Brown 1878, 230]

From this classic band of diminutive thieves and rogues came similar mythologies across Europe, especially in Germany, where they could have local names, for example the "*Heinzelmännchen*" of northern Germany or the "Galgenmännlein" of southern Germany. The brothers Grimm, in *Deutsche Sagen*, wrote about "Hinzelmann", and the city of Köln has an especially strong link to these gnomes or elves. In legend, the Heinzelmännchen of Köln were "kleine nackende Männchen" (little naked men) who did all the household tasks for the people of the city overnight, so that the latter could be lazy during the day. However, a tailor's wife wanted to see them, so she spread peas on the stairs so they would trip and fall and then still be there in the morning. The Heinzelmännchen were so annoyed that they left and never returned, and "Doch sollen mit den Heinzelmännchen auch die guten Zeiten Cölns verschwunden seyn" (and with the Heinzelmännchen, the good times of Köln also disappeared) (Weiden 1826, 200-202). This is the first sort of kobold: generally helpful household sprites or fairies, who could be mischievous when slighted or annoyed.

However, in myth, there was a second place where kobolds could be found, and that was in mines. Here, their influence was thought to be much less helpful and much more malign. As some of the papers in this volume will emphasise, mining for cobalt has always been, and continues to be, a dangerous and unpredictable occupation. The collapse of drifts or shafts was always possible and, even if

this did not happen, falls from gantries and stairs were a daily risk. The slightest failure in rock, equipment, structures, or even other miners could have terminal consequences. As often in such situations, those sensitive to superstition started to see accidents and rock falls as caused by evil spirits, by kobolds. A typical account of this sort of superstition can be found in *Histoire Generale du Monde et de la Nature*, by Pedro de Valderrama, published sometime between 1617 and 1619 (quoted in Lea 1939).

> The subterranean spirits are those who dwell in caverns and other recesses of the earth, where they kill or suffocate or render insane miners in search of precious metals. The Germans call them Kobolds. They are gnomes, dwarfs not over an ell in height, and they help in cutting stones, getting out metals, packing them in baskets and hauling to the surface. They laugh and whistle and perform a thousand tricks, but their services often rebound to the injury and death of those whom they serve. They cut the ropes, break the ladders, cause the fall of rocks, send poisonous vapor; and you will see rich mines abandoned for the fear of them . . . It is they who cause earthquakes . . . They are not only the guardians of the mines, but of hidden treasures, which they allow no one to take…".

This passage also highlights another hazardous aspect of mining that was blamed on kobolds—poisonous vapours. As discussed above and covered in more detail in Chapter 3, cobalt occurs as a compound of other metals, metalloids and non-metals. A very common associated element is arsenic. Arsenic is highly acutely toxic when ingested or inhaled (World Health Organization 2024). Safe levels of arsenic in drinking water, the major concern for arsenic poisoning in modern times, are set at a provisional guideline value of 10 parts per billion. In certain areas of the world, for example parts of Bangladesh, thousands of people a year die from causes attributed to chronic arsenic exposure.

The symptoms of acute arsenic poisoning include "vomiting, abdominal pain and diarrhoea. These are followed by numbness and tingling of the extremities, muscle cramping and, in extreme cases, death" (World Health Organization 2024). With longer-term, chronic exposure, the first symptoms are often pigmentation changes in the skin, followed by lesions and hard patches, especially on the hands and soles of the feet. Arsenic is also carcinogenic, especially causing cancers of the skin, bladder and lungs. Beyond that, "other effects of long-term exposure to high levels of inorganic arsenic include peripheral neuropathy, gastrointestinal symptoms, conjunctivitis, diabetes, enlarged liver, high blood pressure and cardiovascular disease" (World Health Organization 2024). Some

of these symptoms are clearly identifiable in the ill affects thought to be caused by kobolds.

Blues of the gods

In complete contrast to the negative associations that were common in the extraction of cobalt ores, the product that they were being used to produce had hugely positive connotations. The first blue pigment was created in Egypt and the Near East in the 3rd millennium BCE. So-called Egyptian Blue was the first artificial pigment ever produced, earlier pigments being extracted from natural compounds, such as ochres and charcoal. Egyptian Blue was related to vitreous materials production, specifically blue glazes on ceramics known as faience. By the 2nd millennium BCE, it was extensively used, tons of it being employed in the decoration of ancient Egyptian temples. It continued to be used up to the Roman period. However, the use of blue decoration in the form of a naturally blue stone is older than Egyptian Blue. By far the most important blue stone to be used is lapis lazuli, which was first used in the Indus Valley in the 8th millennium BCE. Lapis is a rare mineral, and for millennia the only source known in the Old World was in northeastern Afghanistan, although other sources, in Russia and Chile, are now important.

Lapis lazuli has a bright blue colour, often with golden flecks of the iron sulphide pyrite. The combination of deep blue and gold can be very striking and probably leads to the name given to the stone. *Lapis* is Latin for "stone", and *lazuli* comes from Arabic and in turn from the Persian for "sky" or "heaven". Lapis lazuli therefore translates as "stone from heaven", and the lazuli part feeds into many European languages. For example, *azul* is Spanish and Portuguese for "blue", and *azure* is an old-English heraldic term, again for "blue". Hence lapis lazuli was always associated with heaven, strongly linked to the colour blue's obvious associations in a more general sense with the sky and, by implication, heaven. The deep blue of the sky, so commonly seen in the countries of the Fertile Crescent and North Africa, and its closeness to the colour of lapis lazuli, linked the two symbolically and tied in the colour blue to these positive and heavenly ideas. Many cultures have strong positive and negative magic associated with colours, and a very good example of this is ancient Egypt. Blue was associated with both the heavens and the primeval flood, signifying both life and rebirth. The association with the River Nile meant that blue was associated with crops and fertility (Wilkinson 1994, 107-108).

Figure 1.3: Modern drawing of the Egyptian God Amun-Re, portrayed in blue. Drawing © Eternal Space https://commons.wikimedia.org/wiki/File:Amun_(God).png

The links of the colour to positive outcomes is also reflected in the use of the colour blue to depict gods (e.g. Fig. 1.3). Some of the earliest examples of this are, once again, in Egypt, where evidence is plentiful because the preservation of coloured depictions on temples and tombs is so good. Perhaps the most interesting Egyptian god to be routinely depicted in blue is Amun-Re. Amun-Re (alternatively Amen or Imen) was one of the most important gods in Egypt and the key god of the famous Temple of Karnak at Thebes, now known as Luxor (Wilkinson 2000, 155). Indeed, Amun-Re was sometimes depicted as being made of lapis lazuli, showing his link to the sky and eternity.

This association of blue with gods existed not only in Egypt; it was widespread even across cultures that were not related. Other Eurasian examples include quite a number of Hindu deities, perhaps most importantly Shiva and Vishnu. Here, the symbolism is slightly different. The deities, while depicted as blue, do not have blue skin; rather, they have a blue aura. This aura radiates a blue colour because blue is the colour of the infinite (the sky and the ocean) and the all-inclusive, which is an important characteristic of the gods—hence the depiction of so many

of the Hindu gods as blue. In the Central America, several Aztec and Mayan gods were also blue and seem to have acquired their colours independently from the developments of Eurasia. In the Mayan world, blue was also one of the most beneficial colours, linked with sky, water and the sky gods, along with green. There is, therefore, if not universal, at least a widespread association of blue as a beneficial colour associated with key gods.

This association continues into the Christian period, where again key individuals are stylistically portrayed in certain ways. One of the most important of these portrayals is of the Virgin Mary, and from very early in the depictions, she is most often shown dressed in blue. There are several reasons for this association. The colour blue stretches back through biblical history as important and is specifically mentioned in the Bible's Book of Numbers, verse 4:6, as the colour of the cloth spread over the Ark of the Covenant—Mary is sometimes described as the new Ark of the Covenant. However, the very old tradition of blue being associated with the sky, heaven, purity and divinity is also very important.

One of the most important pigments for the depictions of Mary and other biblical characters was ultramarine, which was itself a pigment derived from ground-up lapis lazuli. This pigment was used very sparingly at first, as it was extremely expensive. It was used in some of the first oil paintings in the 15th and 16th centuries, and again was often restricted to being used in key areas of the painting associated with gods or religious images. The use of cobalt-based pigments carried on alongside the use of ultramarine, and as a substitute for it where ultramarine was too costly or not available.

The colour blue, including cobalt blues, therefore has a long association with the depictions of gods and deities, despite the negative connotations associated with the mining of the ores and processing of the materials.

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Chapter 2

Cobalt through the ages, illustrated through a selection of objects demonstrating its use

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Introduction

Cobalt has been used as a pigment for the past 3,500 years, and the way in which it has been used has changed through this time. This short paper looks at six objects from that history and draws from them both the variations and commonality of cobalt use. The earliest use of cobalt occurs in Egypt, in the middle of the 2nd millennium BCE, where it is used predominantly in glass and in a glazed ceramic called faience. One of the most spectacular uses of this early Egyptian glass is in the golden death mask of Tutankhamun, which immediately established cobalt blue with a clear link to kingship and the gods. This is the first object considered. The second object is also of glass, this time Roman. It was, and perhaps still is, one of the most famous objects in the British Museum—the cameo glass Portland vase. It shows a continuity with the death mask with deep-blue glasses still being used in extremely high-status objects, although the glass compositional type is new. The recycling of Roman glass in the medieval period leads on to the next discussion, the stained-glass windows of Canterbury Cathedral. Some of the blue glass here, amongst the earliest glass in the windows, is derived from Roman cobalt-coloured glass tesserae. The reuse of this Roman glass in cathedral windows seems to cease as a new cobalt source situated in Saxony becomes available, and it is this source that is linked to the next object. The development in Saxony of the technology of smalt allows the pigment to be widely transported and then incorporated into artist pigments, especially in this case the relatively new oil-based paints. Early oil paints are used to produce a whole series of religious and classically inspired paintings—here Titian's *Diana and Acteon* is discussed. The next object type also seems to have used this Saxon cobalt, along with pigments from more local sources. This is the Chinese porcelain known as Famille Rose, and it shows how the use of cobalt-

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blue decoration on ceramics following the Chinese tradition becomes increasingly important. Finally, the development of true chemistry and a new understanding of the natural world leads to the development of synthetic pigments in large numbers. The Impressionist painters were early adopters of these pigments, and here Monet and the *Water Lilies* series illustrates the genre. Intriguingly, the use of the paints in these last artistic works has links back to the very beginning of the use of cobalt in Egypt, where the same colouring compounds are used.

The death mask of Tutankhamun

Tutankhamun's death mask is an iconic artefact and perhaps the most famous and recognisable archaeological object ever (Tiradritti 1998). It is a masterpiece of funerary art, created at the height of Egypt's New Kingdom (1550-1070 BCE), when craftspeople were employed in their thousands to decorate and equip the tombs of the Egyptian King and his court (Romer 1984). The tomb of Tutankhamun, now known as KV62, was discovered in 1922 by archaeologist Howard Carter in the Valley of the Kings on the West Bank of the Nile, near the ancient capital of Thebes, modern-day Luxor (Carter and Mace 1977). It was a very rare example of a tomb found in an almost complete state, relatively unrobbed, and it gives an idea of the funerary goods that would have accompanied an Egyptian king into the afterlife. Tutankhamun reigned for a comparatively short period of time, probably only 9 years, and died in his twenties. Perhaps, therefore, the tomb would have contained only a small fraction of the goods that might have been placed in the much bigger tombs of more long-reigned and famous kings. However, his brief reign was significant, as it saw the end of the "Aten heresy" of his father Akhenaten and the restoration of traditional religious practices after that tumultuous period (Aldred 1988). Tutankhamun's death, in around 1323 BCE, and the subsequent burial rituals reflect the religious beliefs and cultural practices of ancient Egypt in the New Kingdom, where the preservation of the body and provision of burial goods were crucial for the afterlife journey of the deceased (Spencer 1982).

The death mask of Tutankhamun is a marvel of ancient Egyptian artistry, crafted from solid gold and decorated with intricate details and a wide range of inlays. Standing at approximately 54 cm tall and weighing around 11 kg, the mask probably shows the king's features. The face is particularly well depicted, although there has been debate, too long to go into here, that the mask may have been made for someone else, perhaps even a woman (Eckmann et al. 2023; Reeves 2015). The mask contains multiple layers of symbolism and ritual meaning. In ancient Egyptian religion, death masks played a crucial role in funerary rituals, serving as a protective amulet for the deceased and ensuring safe passage into the afterlife

(Spencer 1982). Tutankhamun's death mask has a rich religious symbolism, reflecting the king's divine status and his role as a mediator between the mortal realm and the gods. The king is depicted wearing the *nemes* headdress, in life a cloth that covered the forehead, was tucked behind the ears and fell to shoulder length. It is distinctively banded with horizontal stripes and is one of the most common headdresses that kings are depicted wearing. The inclusion of the uraeus serpent and vulture atop the headdress, symbolising protection and kingship, underscores Tutankhamun's divine authority and connection to the deities. Moreover, inscriptions invoking protective spells and deities, such as Anubis and Osiris, reinforce the mask's function as a talisman for the king's journey through the underworld and his eventual resurrection in the afterlife. Excellent original images of the mask can be found on the Griffiths Institute website by searching through the Burton photographs of the excavation for "Carter Number 256a", the excavation number of the mask.

The *nemes* headdress, especially the uraeus and the ceremonial beard, are inlaid with faience, a quartz-cored, glazed ceramic that was very popular and widespread in Egypt in the New Kingdom. However, the stripes of the headdress are somewhat different. The gold of the death mask has indentations beaten into it to accept the blue inlays to make the striped pattern. It is often thought by those who casually glance at these inlays that they are of lapis lazuli; indeed, that may well be the effect that the artist wished to convey. Even some catalogues mistakenly identify the inlays as lapis (for example, Tiradritti 1998). However, they are in fact of cobalt-coloured blue glass, and the use of glass inlay (especially dark blue) is extensive in the burial goods found in Tutankhamun's tomb (Carter and Mace 1977). This glass dates to the last half of the 14th century BCE and is one of three technologies, more or less related, that use cobalt colourants—the other two being faience, already mentioned, and an unusual cobalt pigment used on contemporary so-called blue-painted pottery (also known as Palace ware, due to palaces being the most common find site of the ceramic). The use of cobalt in glass and faience technologies stretch back only 100 years or so earlier than Tutankhamun and represents the first known use of cobalt as a pigment (Lilyquist et al. 1993; Shortland 2012). The source of the pigment is thought to be the alums of the Western Desert of Egypt and is discussed further in Chapter 8. The use of this pigment seems short lived, perhaps only a few hundred years, and the source seems to change subtly over that period. The deep blue that the pigment produces, with a subtle purple tinge, is very well demonstrated in the death mask and in other items from this same tomb.

Overall, the death mask and other similar high-status objects establish dark blue and, by implication, cobalt as an important symbolic colour in the depiction of royalty and gods.

The Portland vase

The Portland vase is an ancient Roman object of unparalleled beauty that has captivated the imaginations of scholars, artists and admirers for centuries (British Museum Online Catalogue, no date). The most likely date for the production of the vase is the 1st century CE, during the reign of Emperor Augustus or his successors, and it was probably made in Rome. However, its precise origins remain subject to speculation. Even its purpose is uncertain, with the possibility that it served either as a funerary urn, a luxury vessel for perfumes or oils, or a ceremonial object for religious rites. An excellent scholarly study of the vase was carried out by numerous authors and published in *Journal of Glass Studies* (vol. 32, 1990).

The vase has a long history connected with it (British Museum Online Catalogue, no date, Painter and Whitehouse 1990a, b and c; excellent images of the vase can be found in these latter sources). The earliest known mention of it is by a French person, Nicolas-Claude Fabri de Peiresc, who saw it in Rome during the winter of 1600-1601, when it was in the collection of Cardinal del Monte. It passed into the possession of the Barberini family, one of the most powerful in Rome, where remained for more than 150 years, until it was sold to repay gambling debts. It passed briefly into the hands of a dealer, James Byres, and then to Sir William Hamilton, in the early 1780s. Hamilton was Envoy Extraordinary to the Kingdom of Naples and a keen antiquarian and collector. He is perhaps better known as the husband of Emma Hamilton, who became the mistress of British Vice Admiral Horatio Nelson, 1st Viscount Nelson, who was killed in 1805 leading the British fleet to victory at the Battle of Trafalgar (Haworth and Haworth 1988). Hamilton brought the vase back to England in 1783 and sold it to the Duchess of Portland very soon after. It is this ownership that gives the vase its modern name. The fame of the vase spread; in its period its level of fame was perhaps similar to the death mask of Tutankhamun now. In 1810, the Duke of Portland lent the vase for safekeeping to the British Museum, and it was put on display. Unfortunately, as the British Museum Online Catalogue (no date) recounts, "at 3.45 p.m. on 7 February 1845, a young man named William Lloyd, suffering from acute paranoia brought on a by a week-long bout of drinking, picked up a sculpted stone in the room where the vase was displayed and smashed both it and the showcase into fragments". The vase was restored soon after and has had several periods of subsequent restoration as the old conservation work was consolidated or improved, sometimes involving

completely dismantling the vase and reconstructing again. In 1945, a hundred years after the unfortunate accident, the vase was bought for the British Museum, where it has remained ever since.

The Portland vase is 24.5 cm high and made of a dark blue and opaque-white cameo glass, which has been blown with the white glass on the outside and the blue on the inner. The opaque-white glass has then been very carefully cut away to reveal the dark blue glass beneath, creating the intricate scenes on it, a technique known as cameo. Two amphora-like handles reach from the shoulder of the vessel to the neck. The decoration consists of two scenes, one of two women and a man and one of two men and a woman plus Eros, with his bow hovering above. Rather curiously, the vase seems to have been truncated at some time in the past and a new base was added, now separated and displayed alongside (British Museum 1945,0927.2). The disc-shaped base was cut out of a larger scene and is a different style and colour to the main vase. They therefore do not belong together but have been associated since at least the 17th century and perhaps from antiquity (Tait 1991).

Over the centuries, scholars, artists and collectors have offered various interpretations of the Portland Vase, ranging from aesthetic appreciation to allegorical analysis (Painter and Whitehouse 1990d and e). Some have interpreted the vase's imagery as symbolic of the triumph of love over adversity, while others have seen it as a reflection of the duality of human nature and the eternal struggle between order and chaos. The scenes shown are from Greco-Roman mythology, perhaps the story of Peleus and Thetis (British Museum Online Catalogue, no date). The vase's association with the Emperor Augustus and his patronage of the arts highlights its political and social context within the Roman Empire, where cultural patronage served as a means of asserting imperial authority and prestige.

The glass of the vase has been analysed several times by different scientists, and all the analyses show the same results (Bimson and Freestone 1983; Freestone 1990; Turner 1959). The white overlay glass is high in lead, with significant antimony. The white colour of the opaque glass is generated by the presence of small particles of calcium antimonate in the glass (Rooksby 1959), which scatter the light and make the glass opaque. The blue glass is "almost black in transmitted light", and it has been speculated that this is an attempt to "reproduce the visual effect of natural onyx cameos as closely as possible" (Bimson and Freestone 1983, 59). Onyx is a naturally banded stone that has been repeatedly used over the millennia to produce cameos, especially small objects, such as the bezels of finger rings and brooches. The blue glass is coloured by cobalt (0.12% CoO) with significant iron and manganese. Both glasses are typical Roman natron-fluxed glasses with high sodium and low levels of potassium and magnesium.

The vase's enduring legacy can be seen in the numerous replicas, copies and homages produced over the centuries, as well as its influence on subsequent generations of artists and craftspeople (Briel 2024). It was particularly influential in the ceramics production of Josiah Wedgewood, an innovator and entrepreneur working in northern England in the 18th century. The most famous product of the Wedgewood factories was jasperware, with its matt, "biscuit" finish and designs closely modelled on the Roman and later cameos (Wedgewood 2023). Wedgewood worked for years to perfect the recipe and ensure that failure rates in the kilns were at an acceptable level. Such was the fame of the Portland Vase (then known as the Barberini Vase, after its earlier owners), that Wedgewood was determined to copy it (Wedgewood 2023). It took him 3 years and countless attempts before, in September 1789, he produced a version that he was satisfied with. He sent the first version of the vase to a great friend of his, Erasmus Darwin. The Wedgewood and Darwin families were very close, and Wedgewood's daughter, Susannah, married Erasmus's son, Robert. Their fifth child was Charles Darwin, the naturalist. The copy of the vase was unveiled to an invited group at the home of Sir Joseph Banks, where so many people wanted to see it that 1,900 tickets had to be printed. After that, it was shown at the Wedgewood showroom in Greek Street, Soho, London, where it was also extremely popular. It sold in large numbers, despite a high price, and went a long way to cementing the reputation of Wedgewood and his factory in the mind of the contemporary public. Wedgewood said that he regarded his copy of the Portland Vase as his "great work" (Wedgewood 2023).

The windows of Canterbury Cathedral

Founded in the 6th century CE, Canterbury Cathedral holds a venerable place in the annals of Christian history as the seat of the Archbishop of Canterbury, the leader of the Church of England. Throughout its long history, the cathedral has undergone numerous renovations, expansions and reconstructions, each leaving its mark on its architectural landscape. Its stained-glass windows, installed over the centuries, reflect the evolving tastes, religious beliefs and artistic styles of their respective periods, bearing witness to the enduring legacy of faith and creativity in the cathedral's sacred spaces. These spectacular artworks, adorning the sacred spaces of the cathedral, serve as windows to the divine, illuminating the stories of saints, martyrs, and biblical narratives for worshippers and visitors alike. Dating from the medieval period to the present day, these windows encompass a wide range of styles and techniques, from the brilliance of the 12th-century "miracle windows" to the intricate detail of the 20th-century "War memorial windows" (Bell 2002). The windows serve as visual sermons, conveying the central tenets

of Christian faith and doctrine through narrative imagery and symbolic motifs. Biblical scenes, such as the Nativity, Crucifixion and Resurrection, are depicted, inviting worshippers to contemplate the mysteries of salvation and redemption. Saints and martyrs, including Thomas Becket, Augustine of Canterbury and Ethelbert of Kent, are also commemorated in glass. Moreover, its vibrant hues, ranging from deep blues and rich reds to radiant golds and greens, evoke the heavens and precious stones and would have been truly stunning to the population of the period.

Master craftspeople carefully assembled the windows, using lead canes to hold together individual pieces of coloured glass and applying painted details to enhance the imagery. The earliest stained glass yet known was recovered from the excavation of St Paul's Church, Jarrow, in northern England. It dates to the second half of the 7th century CE, when St Paul's was a monastery. Several colours are present, including blue, red, aqua and green. However, the windows in such churches were usually small, and it is only with the new architectural styles and technologies of the 12th century CE, when the use of thinner walls, higher arches, flying buttresses and larger windows meant that the quantity and importance of glass was hugely increased in the designs. This new, "Gothic" architecture is best seen in spectacular cathedrals, such as Salisbury, Notre Dame (Paris), Chartres, Köln, and, of course, Canterbury. Massive, near-simultaneous building projects across western Europe led to a huge demand for window glass, which exploited a new glass technology developed first in the 8th century CE in Germany (Wedepohl and Simon 2010). Western Europe did not have the evaporitic lakes that could provide its glass industries with the natron that had been used by the Romans (in the Portland Vase, for example; see earlier in this chapter). However, it did have vast, ancient forests. The ash of the trees, perhaps especially of beech, was found to be a good substitute. It resulted in a wood-ash glass that was rich in potassium and low in sodium and therefore compositionally very distinct from the Roman glass. This type of glass was produced in very large quantities, especially in the forests of France, the Low Countries and Germany (Jackson and Smedley 2004).

The new windows required bright colours, which were developed to complement the window schemes. Particularly dominant in the windows is the colour blue—a deep, vibrant cobalt blue that stands out against the reds and golds of the windows. However, the earliest production of this blue glass has a very different chemical composition to the later productions (Bidegaray and Pollard 2018). From the 13th century CE and after, the great majority of the glass in the windows, of all colours, is made of the wood-ash flux, the northern European type mentioned above. However, in the 12th century CE, while the majority of the colours are of this type, blue glass is distinctive. The blue glass has the same composition as

the earlier Roman glass, with a flux derived from soda from evaporitic lakes in Egypt and elsewhere—the same type of glass that is used in the Portland Vase. The proposed explanation for this is that the early blue window glasses are made from the recycling of glass tesserae, the small stones and artificial stones used to make mosaics (Freestone 1992). These were excavated from Roman sites by medieval artisans and remelted to make glass. This is attested by archaeological finds and by the writings of Theophilus, who described the melting of blue and green tesserae and the combining of the melted tesserae with colourless glass by the French in the 12th century CE (Bidegaray and Pollard 2018; Freestone 1992). It is possible that tesserae were used because there was no known cobalt source at the time—the Saxon cobalt sources (discussed next) only being discovered in the 13th century CE. Thus, the reuse of Roman materials enabled this early production of blue glass for these spectacular windows.

Diana and Actaeon, by Titian

Diana and Actaeon is a masterpiece created by the renowned Italian Renaissance painter Titian, sometime between 1556 and 1559 CE. It is a large painting, measuring approximately 185 cm by 202 cm, and is housed in the National Gallery in London. It is part of a thematic group, or cycle, of large paintings commissioned in 1550 CE after Titian met Prince Philip of Spain, the future King Philip II. Titian regarded the paintings as the visual equivalent of poetry and used the term *poesie* for them (from the French for "poem"), a name by which they are collectively still known (National Gallery, no date). Good images can be found on the National Gallery website, by searching the catalogue for NG 6611 and NGS 2839.

The poesie depicts scenes from Ovid's *Metamorphoses*, a masterpiece of mythological storytelling that weaves together numerous tales of transformation. Comprising 15 books, it spans creation to the deification of Julius Caesar, exploring themes of love, power and the unpredictable nature of existence. Central to *Metamorphoses* is the motif of metamorphosis itself, where gods and mortals undergo profound changes, often as punishment or reward. The stories range from the tale of Daphne and Apollo to the epic journey of Orpheus into the underworld; however, in this painting, Titian captures a pivotal moment from Ovid's mythological narrative. The story of Actaeon is told in *Metamorphoses* Book III. Actaeon, a hunter and a mortal man, accidentally stumbles upon the goddess Diana and her nymphs bathing in a secluded forest pool. Startled by Actaeon's intrusion, Diana is depicted at the right of the composition, her face partly obscured by her left arm and glowering at Acteon. Actaeon raises his arms in shock and surprise, recoiling from the scene, realising the gravity of his intrusion. Behind him, his

hunting dogs can be seen. They are oblivious to the unfolding drama, but omens of his fate are expressed in the collapsed building and particularly in the stag's skull that hangs on the archway above Diana's legs. Diana, in retribution for him violating the privacy of her bath, will turn Acteon into a stag, and he will be torn apart by his own hounds, a story told in the *Death of Acteon*, the next part of the poesie.

The composition is carefully orchestrated to draw the viewer's eye towards the central figures, Diana and Actaeon. Diana's commanding presence dominates the scene, her elongated figure and graceful pose picked out by the light. Surrounding her are the startled nymphs, their gestures and expressions conveying a sense of alarm and modesty. Titian masterfully captures the dramatic tension of the scene through his use of light, colour and composition. The play of light and shadow creates a sense of depth and atmosphere, enveloping the figures in an ethereal glow. The rich, vibrant colours add to the dynamism of the painting, with hues of blue, green and flesh tones contrasting against the dark background of the forest.

Titian was a very technical artist and was interested in artistic innovation in terms of composition and technique. One of the most interesting of these innovations was his use of the pigment smalt. Smalt is discussed elsewhere in this volume at length. It was one of the first pigments to be developed utilising cobalt compounds and employed in paintings and consists of a finely ground dark blue glass. Titian was not the first to use smalt, but he started to use it as it became common with his contemporaries, presumably as it also became easy to buy from his pigment suppliers, the *vendicolori* (colour sellers) of Venice. Smalt became very common in the second half of the 16th century (Dunkerton et al. 2016, 34) and gave an attractive blue colour similar to the very expensive ultramarine, which was derived from lapis lazuli. However, smalt has a serious disadvantage: it tends to lose its colour with time, turning dull grey or even translucent brown, especially when it is not mixed with lead white, which tends to preserve it somewhat. Dunkerton et al. (2016, 34) argue that the impact of this deteriorating pigment on Titian's work has been underestimated and that, because he used smalt extensively, its deterioration can have a major effect of the look of his paintings. Titian's later paintings have for a long time been considered "more subdued in tone", to the point of looking almost monochrome. This is linked to the way that Titan used colour later in his life, but it is confused by the way in which the blues of the smalt have faded. The colours we see now may, therefore, not be how the colours originally appeared.

In *Diana and Actaeon*, Titian uses both high-quality ultramarine and smalt (Dunkerton et al. 2016, 73). In the sky through the arches, for example, the vivid blues are smalt and lead white, with a layer of ultramarine on top. The smalt has lost its colour, fading to a grey colour, and this accounts for the rather patchy

colouration of the sky—it was not intended to look like this originally. The depiction of foliage in the top right is also badly affected by the deterioration, looking browner than they did originally and more washed out (Dunkerton et al. 2016, 75). Therefore, by Titian's use of the "latest technology" of the cobalt glass smalt, his later works have been affected by discoloration of the glass and the loss of its colouring, while earlier cobalt glass objects discussed in the chapter retain their brilliant colours although they are many times this painting's age. Research is ongoing into why smalt fades, but a strong link has been found to the loss of alkalis from the glass through leaching, which changes the oxidation states (see Robinet et al. 2011 and references therein).

Famille Rose porcelain

Porcelain, a delicate, high-fired, glassy glazed ware that can be translucent when thin enough, is one of the most celebrated and costly ceramics known. Its various types are divided by experts into different categories, wares and "families". One of these is the "Famille Rose" style, which represents a pinnacle of artistic achievement and technical mastery in the realm of ceramic art. Originating in the Qing dynasty, during the 18th century CE, Famille Rose porcelain is renowned for its vibrant palette, intricate designs and delicate beauty. The term Famille Rose, meaning "pink family" in French, was coined by European collectors in the 19th century CE to describe a distinct style of Chinese porcelain characterised by its use of pink overglaze enamel. Famille Rose is a development of earlier styles, such as Famille Verte and, possibly, Famille noire, which relied on a combination of underglaze cobalt blue and overglaze coloured enamels. This allowed for a wider range of colours and decorative possibilities than earlier underglaze blue-and-white wares. Chinese artisans created elaborate scenes of figures, landscapes, flora and fauna. However, it is the development of an often-dominant pink enamel, typically derived from colloidal gold, that served as the hallmark of Famille Rose ware, lending it a distinctive appearance (Wood 1999).

Famille Rose porcelain emerged during the reign of the Qing Emperor Yongzheng (1723-1735 CE) and reached its zenith in his reign and that of his successor, Qianlong (1736-1795 CE). In this period, Famille Rose wares were produced primarily for the imperial court and elite patrons, serving as diplomatic gifts, tribute items and symbols of dynastic prestige. The imagery depicted often conveyed auspicious motifs and traditional Chinese symbols, such as the peony (a symbol of wealth and honour), the lotus (representing purity and enlightenment), and the dragon (symbolising imperial power and good fortune). Moreover, the popularity of Famille Rose porcelain in western markets during the 18th and

19th centuries CE reflects the broader cultural exchange between China and the West, as well as the enduring appeal of Chinese decorative arts on the global stage (Li 2007).

The development of the technique itself may have been influenced by Jesuit missionaries and European tastes for coloured enamels. Indeed, the Chinese name for the ware was *falangcai*, meaning "foreign colours". Recent work on the pigments of the Famille Rose palette has revealed some interesting patterns as regards the blue pigments used. Blue is used in two different ways on the Famille Rose decoration—in both underglaze and overglaze roles. Underglaze blues are decoration that is added onto a "biscuit-fired" body before the glaze is applied over the top. This is the way that the vast majority of the famous Chinese blue-and-white wares are decorated and the way reign marks were added on the underside of pieces. However, the other colours and another blue are applied on top of the glaze after it has been fired. These are "overglaze colours", which are then fired again at a slightly lower temperature than the first glaze firing to fix them in place. Analysis of the underglaze and overglaze blues has shown an interesting pattern (Giannini et al. 2017). In the Qing dynasty, the underglaze cobalt blue in the Famille Rose and the blue-and-white wares was characterised by a cobalt that was relatively high in manganese, with lesser levels of zinc and nickel. This has long been established as characteristic of the local, Chinese cobalt source. However, the overglaze enamels of the Famille Rose had low levels of manganese and significant levels of nickel, zinc, arsenic and bismuth. This pattern closely matches the pattern seen in smalt and in enamels made from European cobalt sources. This, therefore, gave the first indication that Chinese *falangcai* wares were not just made from recipes for "foreign colours" or followed ideas passed on by the Jesuits for how colours could be produced. At least in the case of the blues, the actual pigment was making the long journey from Europe to China in this period. Substantial work in the Blue Colour Works archive, reported on briefly in this volume, shows that there is clear archival evidence to support this export. Ongoing analytical work suggests that there may be two sources of European cobalt used, an earlier one in the 18th century CE, presumably sourced from the German mines, and a later, 19th century CE one that may be Norwegian. This is the subject of current investigation and is discussed further elsewhere in this volume.

Water Lilies, by Claude Monet

Claude Monet was an iconic French painter and the leader of the Impressionist movement, renowned for his ground-breaking techniques and captivating interpretations of light and nature. He was born in Paris in 1840, and his early

years were marked by struggles, but his passion for art was evident from a young age. Defying traditional methods, he opted for a more experimental approach to painting, including *en plein air* painting—venturing outdoors to capture the interplay of light and shadow directly onto the canvas. He was particularly drawn to landscapes, seascapes and gardens, often returning to the same subjects at different times of the day to explore the nuances of light and atmosphere. He produced a number of painting "series", for which he returned again and again to paint the same scene in different light and conditions. Monet's brushwork was revolutionary, characterised by loose, expressive strokes that conveyed movement and emotion and avoided strict delineation, to capture the essence of his subjects Heinrich (2000).

One of these famous series is the *Water Lilies*, which numbers nearly 300 individual works (Musee de l'Orangerie, no date; see the many images on this website). It took Monet nearly three decades and was inspired by the gardens of his estate in Giverny, northwest of Paris. Many were painted late in his life, when he decided to "undertake something on a grand scale", a "great project", after a period of depression following the death of his son, in 1914. He continued the work until his death, in 1926, at the age of 86. Following the end of World War I in 1918, 22 of these paintings were donated to the French state and installed in the Musee de l'Orangerie in two specially designed rooms. The remaining large-scale *Water Lilies* canvasses remained at Giverny until after World War II (National Gallery, no date a). The painting discussed here is one of the latter, and it is truly monumental in scale, 200 cm high and 426.7 cm long. From the scale of the piece, it is thought it must have been painted in or after 1916, when Monet had an especially large studio built to accommodate work on the largest of the canvasses. The painting was bought by the National Gallery in 1963. As noted by the National Gallery, it made an immediate effect, with one commentator noting, "It is a great area of drifting, nebulous colour with which it is very difficult to establish any consistent relationship. The only proper reaction would be to dive into it and drown" (National Gallery, no date b). It is currently on loan to the Tate Modern in London and hangs alongside later works by Pollack, Rothko and Mitchell (Roy 2007).

The National Gallery has carried out several studies of the palette used by Monet, and the descriptions here are derived from Roy (2007). Roy states that there are very few accounts of Monet's specific choices of painting materials. A list provided by his colour supplier Moisse suggested that it included lead white, cobalt violet (light), synthetic ultramarine, cadmium yellow and zinc yellow. Other lists include viridian, deep madder lake and "bleu de cobalt", or cobalt blue. In total the National Gallery lists 20 pigments that were used by the Impressionists

(Caves 2024). Specifically for this *Water Lilies* painting, Roy (2007) describes the full palette as: lead white, cobalt violet (light), viridian, cobalt blue, French ultramarine, vermilion, cadmium yellow and zinc/barium yellow. This is an interesting list of pigments and reflects the time in which Monet was working. While some of the pigments, for example lead white, had been used for hundreds of years, the great majority were more recent inventions. For example, cadmium was only first recognised as a possibility for producing yellow pigments in the first half of the 19th century, but its use was severely restricted as cadmium itself was rather rare. The problem of its rarity was resolved by the second half of the century, when it became a popular colour. Its discovery and exploitation for use are linked the rapidly expanding and codifying academic subject of chemistry. While there were rare professors of chemistry at some universities stretching back to 1700 CE, other universities were later to recognise the subject. The University of Oxford first recognised chemistry as a separate discipline in 1860, with the building of the first purpose-built chemistry laboratory in the university. It was attached to the newly built Museum of Natural History and modelled, somewhat eccentrically, on the abbot's kitchen at Glastonbury Abbey (University of Oxford Department of Chemistry, no date). Certainly, the 19th century was the time when new chemical elements were being discovered and exploited. It is interesting to note that many of the elements used and many of the compounds produced were very poisonous, containing highly toxic elements, such as cadmium, mercury and arsenic.

Two pigments on the list of those in the *Water Lilies* contain cobalt: cobalt violet light and cobalt blue. As discussed in the previous chapter, cobalt violet light is now given the reference code PV14 and is chemically identified as cobalt arsenate. It is chemically the same as the mineral erythrite, also discussed earlier, a weathering product of primary cobalt arsenic ores. It was first synthetically produced in 1880, but, being highly toxic, has now largely been replaced with cobalt violet deep, a cobalt phosphate, which first appeared as an artist's pigment in 1890 (CAMEO 2020). The pigment cobalt blue was available earlier, the procedure for making the pigment having been first published by L. J. Thénard in 1803/1804—hence the common name "Thénard's blue" for the pigment. The first work on this type of pigment was carried out by Leithner, in Vienna, in 1775, but it was Thénard, in 1803, who found that combining aluminium hydrate with cobalt phosphate of cobalt arsenate most easily produced a pigment—a cobalt aluminate (Eastaugh et al. 2008, 119).

Cobalt aluminate is still a common compound in use today. However, there is an interesting twist to this story that refers back to the Egyptian New Kingdom and the period of Tutankhamun. As mentioned before, cobalt was used in three

products in this early period: glass, faience and ceramics—namely Palace ware. The Palace ware pigment has been analysed, and was found to be cobalt aluminate, the same as the modern pigment (Noll 1981; Noll and Hangst 1975; Shortland et al. 2006). However, on ceramics, this pigment was used for a only very short period of time, probably a few decades, after which it disappeared from the record until its rediscovery more than 3,000 years later. It is an interesting circle in the use of cobalt pigments—the first cobalt compound used as a paint, the technology for which was lost for millennia, is now commonly used again today.

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Part 2

Sources and signatures

Chapter 3

Norwegian cobalt production and uses

Lasse Hermansen Bjørnland[1]

Introduction

The Blaafarveværket (Blue Colour Works; BCW), in Modum, Norway, was one of the most significant European producers of cobalt in the 19th century. It supplied the earthenware, paper, and textile industries with smalt, zaffre and cobalt oxide, and it had a large customer base in the United Kingdom, the Netherlands, Belgium, France, Germany and Denmark. There were also well-documented exports to China.

This paper describes the on-site cobalt production at the BCW and how those products were applied in European and Chinese industries. The focus of this paper is on the production of smalt and zaffre; the production of so-called "chemically clean" cobalt oxides is mentioned only briefly.

The archival material is collected from the BCW's private archive, Modums Blaafarveværk RA/PA-0157, which is held at the Norwegian Riksarkivet ("national archives"). The BCW archive is extensive, consisting of about 500,000 pages spread over 543 boxes. It gives detailed information on sales and production and includes some social aspects of the BCW's history. Part of the archive is also digitalised: https://media.digitalarkivet.no/db/browse?page=2&archives%5B0%5D=no-a1450-01000000006338

There is also much historical material online at www.googlebooks.com, and the archive of the Danish Asian Company, held at the Danish Rigsarkivet ("national archives"). Also, the Rentekammerets archive ("treasury archive") in the Riksarkivet holds much important information regarding the first period of the BCW's history. At the Riksarkivet, information regarding the BCW's largest customer, Smith, Goodhall & Reeves (RA/PA-0586), is also preserved. This archive contains detailed records on the company's cobalt trading between 1829

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and 1848. Parts of this archive are also digitalised: https://media.digitalarkivet.no/db/browse?archives%5B%5D=no-a1450-01000000007378&start_year=&end_year=&text=

The Stiftelsen Modums Blaafarveværk (Modum Blue Colour Works Foundation) manages the remains of the cobalt production as a museum. The museum encompasses over 10 km, including the remains of the processing site at Haugfoss; the blue colour works with adjoining workers' villages and the colour works director's house; and Skuterud, where the cobalt mines and mineworkers' village can be found (and which is the discovery site of the mineral skutterudite, $CoAs_3$). Part of the building mass has been reconstructed and part of it is preserved. Among the original buildings are the melting hut (late 18th century); the arsenic refinery (1840s); and the workers' village at Skuterud (constructed between the 1780s and the 1820s) (Fig. 3.1). In addition, a large part of the original cobalt mines is accessible to the public both over- and underground.

At the site of the colour works, a collection of 82 cobalt samples is kept and displayed. There is also an informal collection of cobalt concentrate, unlabelled pigments and similar items kept in the store of the Foundation. These samples are well documented, many with dates of production and classification.

The Norwegian blue colour works in Modum

Det Kongelige Modumske Blaafarveværket (The Royal Modum Blue Colour Works) was founded by a royal decree on 1 April 1776. The works were founded based on the mining of cobalt minerals, discovered in 1772 on Skuterud Farm in Modum, about 50 km west of Christiania (the early name for the Norwegian capital, Oslo). With it being a royal enterprise, the Danish-Norwegian crown gave itself a monopoly on all known and unknown cobalt sources in Modum. It also imposed severe restrictions on the possibility of future cobalt production by non-state entities within the Kingdom of Denmark-Norway (Lindeman 1993).

In the works' founding document, it was made clear that operations were not limited to just mining the cobalt ore, but would extend to producing a saleable pigment; therefore, a "blue colour works" was to be constructed and operated locally, on site in Modum (Lindeman 1993). The technology and the specialists were to be imported from the German states of Hessen and Saxony, where, in the case of the latter, a large-scale cobalt production had been in operation since the 16th century (Bruchmüller 1897).

Social history

The planned blue colour works in Modum required a large workforce, so the social infrastructure necessary to support this was formed simultaneously with the construction of the production site (RA/EA-3115 1782). Two identical villages were built, one close to the cobalt mines and one close to the colour works. The villages consisted of identical buildings constructed along a street, with each building having two family apartments and two "widow's chambers". Outhouses for livestock and a small plot of land for farming were also available.

The workers who lived on the BCW property had access to some basic social benefits, consisting of primary school education, healthcare, sickness and injury pay, a poor-relief fund and a pension. This early form of a welfare system was partly financed by taxation imposed on the workers, partly by workers' fines and partly by the contribution from the owners of the BCW.

In order to gain from these benefits, the workers had to abide by the owners' rather paternalistic rules. These included that the workers had to apply for the director's permission to marry, were not permitted to house "strangers", and had to promptly pack up and leave if they were fired. During its state ownership, the BCW also had its own judicial system.

All Norwegian mining firms with more than 30 employees were required by the school law of 1827 to provide basic education for their workers' children (Mikkelsen 2018, 170). The BCW provided its workforce with schools for their children's basic education. Two schools were founded in 1783 (RA/EA-3115 1783), and an additional, evening school operated from the 1820s (Böbert 1978).

The BCW was also required to employ a doctor or surgeon to provide its workers with treatment and medicine (Böbert 1978). By law, the company was only required to provide the workers themselves with medicine, but from 1812, it also granted free medical care to family members, paid for from the BCW's own accounts (RA/EA-3115 1811-1812). In addition, the BCW appointed its own pharmacy, from the 1840s (Böbert 1978).

The BCW was also required to give its workers full pay for up to 2 months if they were injured during the course of their duties, and half pay for the same timespan if they became too sick to work owing to injuries incurred outside the mines (Böbert 1978). This benefit was also dictated by Danish-Norwegian law and was standard at all Norwegian mines (Mikkelsen 2018, 197). In addition to sickness and injury pay, the workers were granted a pension if they became disabled or too old to work. The pension was usually between one-third or one-half of full pay for workers and 10% of the late husband's pay for widows. Even fatherless children were paid a small compensation until they were confirmed (a

Protestant Christian religious rite that occurred at around 14 years old), when they were recognised as adults (Böbert 1978).

The mining year was divided into 13 months, to make bookkeeping easier. Each of the first 12 months had 4 weeks, and the last month of the year had 5 weeks (Böbert 1978). Payments were usually made in cash, and the law of 1842 made it illegal for mining companies to force workers to take foodstuffs or other goods as payment in times of low cashflow. This was a motivator for working at the BCW, since work in agriculture and on large estates could mean being paid in food, clothes and the like. However, we find occasional examples of payments in goods at the BCW as well (SAKO/A-123 1841-1847, 261).

It is important to note that not all workers had a right to the same benefits. In 1847, the works employed around 800 workers, but only 316 of these were granted free accommodation in the workers' villages (Moen 1984, 84), which meant not only that they paid no rent, but also that they had access to a plot of land for farming. There were, nevertheless, perfectly legal ways that the BCW could avoid its obligations to provide pensions for the disabled and the elderly, usually by dismissing them before any requests were stated (Moen 1984, 85). Yet there are examples of the BCW showing more care for individual workers than they were required to by law. In 1806, responding to a worker who had lost his arm in a water wheel accident, the BCW took the man's large family and his young age into account and granted a pension on full pay (RA/EA-3115 1805-1806).

The workers in the colour works and the BCW's craftspeople, such as carpenters and barrel makers, often passed down their occupation through the family. Usually, the father taught his sons the trade and the families stayed on for generations (Moen 1984, 100). At the mines, the workforce mainly consisted of farmers' sons from nearby communities. Usually, most came from farming families that leased their properties, or from families of *husmenn* (tenant farmers) and those working areas of poorer topsoil (Moen 1984, 133, 141-142). Many started working at a young age; Moen researched the age of all first-time hired workers between 1822-48 and claims that 35.3% were hired at the age of 12-16 years (Moen 1984, 135).

Moen shows that the populations of skilled workers and craftspeople at the BCW, along with the families of miners who lived on the BCW property, were quite stable and that people worked for the BCW for significant periods of their life. In contrast, the unskilled farmers' sons who worked in the mines usually worked for less than 2 years before quitting (Moen 1984, 185). Many sought mining work in times of bad harvest, drought and bad economic conditions. For some, it seems that the goal of their mining career was to save money to purchase their own land (Moen 1984, 186).

The golden years

In 1813, during the Napoleonic Wars, the Danish-Norwegian state mortgaged the BCW, and in 1814 the union between Denmark and Norway was dissolved. In the years that followed, it was unclear who had rightful ownership. This led in 1822 to the works coming under private German control, but despite the non-local management, production and profitability grew in the years that followed (Lindeman 1993). Skilful marketing and leadership combined with implementation of new German technology gave the works access to new markets and increased its production to meet rising demand. By the year 1835-1836, the profit of the BCW was 47,051 Norwegian *spesidaler* (Hagen 2022, 321), which today would be approximately 17.8 million Norwegian Krone.

The production mainly consisted of the cobalt products smalt and zaffre. Smalt is a pulverised cobalt-coloured glass, and zaffre is a stamped, washed and calcinated cobalt ore mixed with stamped quartz or sand. Both products were used as a colourant.

The production reached a peak in the 1830s and 1840s. In 1825-1826, the total production of cobalt products was 1,249 centner and 89 pounds (about 62,000 kg). At its height, in the year 1837-1838, the total cobalt production had risen to 4,408 centner and 92 pounds (220,000 kg) (Böbert 1978). Here it is important to note that the two historic records that indicate yearly productions do not fully match (Lindeman 1993, 81). As an example, we can see that the head of the BCW's mining production, Karl Friedrich Böbert, claimed 4,408 centner in 1837-1838, while his successor, Amund Lammers, claimed 4,178¾ centner (208,000 kg) for the same period (Hagen 2022, 321). It is therefore important to view the production numbers with caution.

By 1840, the total staff of the BCW consisted of 1,343 individuals. Between 1836 and 1840, this led to an average yearly production of the equivalent of about 125,000 kg of smalt and nearly 60,000 kg of zaffre (Kgl. Finants-, Handels- og Told Departement 1843).

Markets

The United Kingdom was one of the most important markets for smalt and zaffre in this period. To indicate the Norwegian position on said market, the total import of smalt and zaffre to the UK between 1827 and 1834 is reproduced in Tables 3.1 and 3.2.

Table 3.1: Quantities of smalt imported to the UK (converted to kg from lbs (454 g) by the author by multiplying the number of lbs by 0,45359265). Based on *Tables of the Revenue, Population, Commerce & c. of the United Kingdom and Its Dependencies. Part IV. 1834, 1835, 155.*

	1827	1828	1829	1830	1831	1832	1833	1834
Sweden				4				
Norway	70,847	70,528	65,448	115,196	93,821	140,423	31,982	34,840
Prussia			3					
Germany	128,333	127,564	86,610	71,241	72,895	44,755	22,468	11,585
The Netherlands & Belgium	37,220	26,962	18,796	15,148	10,867	5,112	4,656	8,196
France					9		52	177.8
Spain						3,197		
United States								2,791
Total	236,400	225,054	170,857	201,589	177,592	193,487	59,158	57,589.8

Table 3.2: Quantities of zaffre imported to the UK (converted to kg from lbs by the author by multiplying the amount of lbs (454 g) by 0,45359265). Based on *Tables of the Revenue, Population, Commerce & c. of the United Kingdom and Its Dependencies. Part IV. 1834, 1835, 183.*

	1827	1828	1829	1830	1831	1832	1833	1834
Sweden			91.6	12.7	4.5			
Norway		17,491	16,578		348.3	3,734	56,688	49,719
Germany		183,719	55,009	86,572.6	102,563	114,967	99,396	93,415
The Netherlands & Belgium		151		127	281.6	2,379		
Spain				27.6				
Denmark		1,592						
Total		202,953	71,678.6	86,739.9	103,197.4	121.080	156,084	143,134

The overall imports of smalt were declining in the last years covered by the table, with a dramatic drop in 1833, while at the same time, the import of zaffre was relatively stable. The drop in smalt imports in 1833 was due to the import duty that was implemented in 1832 (Letter of the Secretary of State, transmitting a report on the Commercial Relations of the United States with Foreign Nations for the year ended September 30, 1864, 398). Most likely the duty was implemented to support national British smalt production. The more stable import of zaffre indicates the same, seeing that the British smalt industries were dependent on foreign zaffre as their raw material. There is much documentation of Norwegian zaffre being used by Mawdsley & Smith, the British smalt manufacturers. In June 1838, Smith, Goodhall & Reeves bought 80 quintals (4,064 kg) of "Danish" zaffre. "Danish"

is a misunderstanding of the country's nationality, as the zaffre came from the BCW in Norway (RA/PA-0586 1835-1838, 432). The Netherlands itself was not a producer of cobalt, but merely a consumer and an exporter. All zaffre and smalt exported from the Netherlands was first imported from other countries, mainly Saxony and other German states, and, from the 1780s, Norway. The Dutch operated many colour mills in the Netherlands, where the German colours could be refined.

Two Norwegian producers in Modum

It is thought that the state's monopoly on the cobalt mineralisations in Modum ended after the fall of the Danish-Norwegian union. New minable ore sources were discovered north of the Blaafarveværk-owned territory, which led to the formation of a new local cobalt producer, Snarum Koboltverk (Snarum Cobalt Works) (Lindeman 1993, 67). This led to yet more lengthy court cases, this time between the BCW and its new local rival. However, the archive for the Snarum Cobalt works does not describe any production of smalt at Snarum, only of zaffre and cobalt oxides (Müller 1843). The Snarum Cobalt Works went bankrupt and ceased production in 1848.

Figure 3.1: Photograph of the Blaafarveværket, Modum, Norway. In the centre of the picture are the calcination huts and arsenic refinery. To the left are the half-timbered colour mill, the stamping mill, the oxide hut and parts of the melting hut. From the centre, stretching across to the right, is a horizontal pipe called a poison catcher (photograph © Stiftelsen Modums Blaafarveværk; undated, but probably from the 1860s-1880s).

Due to the development of the synthetic blue pigment synthetic ultramarine, in the 1820s, the demand for smalt dropped notably, starting in the middle of the 1840s (Lindeman 1993, 6). This, coinciding with British smalt production and import duty, as discussed earlier, lead to a depression in the cobalt trade. In 1848, the BCW had a smalt storage in London worth 7,000 pounds sterling that suddenly saw a drastically decreasing demand (Lindeman 1993, 82).

In January 1849, the BCW in Modum was handed over to the probate court (Lindeman 1993, 89). Its production continued first under British and then, from 1855 to 1898, Saxon ownership. The production was downscaled and focused more on production of cobalt oxides, *schlich* (concentrated ore), white arsenic and concentrate of nickel. However, this diversification was not enough to save the works, and the BCW ceased its mining activities for good on 30 November 1898.

Norwegian production of smalt and zaffre

The cobalt ore minerals were extracted from the mines and separated ("dressed") into different qualities (Fig. 3.2). The quality was determined by the proportion of cobalt the ore contained and how contaminated it was by minerals consisting of other significant elements, mainly copper and iron. Great stress was put on correct separation, as the future treatment of the ore was determined by it.

The dressing, or separation, of the ore was mainly performed by boys ages 11 to 18. They were under the supervision of experienced leaders and paid by the weight of ore they separated. Mostly the dressing was done by visual inspection, with the worthless parts of the mineral being knocked off with a hammer and the quantities of cobalt minerals subsequently determined. The finest qualities were "rich ore" or "yellow ore". These qualities had a high content of cobaltite (CoAsS). Then there was "ordinary ore", which could have a high content of cobalt but also contained small quantities of harmful iron. "Copper-containing ore" was an ore finely impregnated with cobalt but contaminated with copper, arsenic and sulphur. There was also *Grubenklein*, cobalt-containing gravel that was collected after blasting, which usually had a low cobalt content and had to be washed before separation (Müller 1843).

Dressed cobalt ore was sent to stamping mills for crushing. Due to the generally low cobalt content, it was essential to pulverise the ore to be able to rid it from contamination and worthless "dead rock". The stamped ore was "washed" on washing tables. The water carried away the lighter particles, leaving behind a mass richer in cobalt.

Figure 3.2: Photograph of four miners drilling by hand in the Blaafarveværket cobalt mines in Modum, Norway, in 1864. The men are dressed in woollen clothes and white shirts and are equipped with iron drills and sledgehammers. Their oil lamps hang on the mine wall next to them (photograph by Karl Gercke, 1864; © Stiftelsen Modums Blaafarveværk).

Rich ore or yellow ore had only to be washed once. The concentrate was called schlich nr. 1. The waste from the first washing was washed a second, third and fourth time to extract the lesser qualities. Mostly the schlich was separated in nr. 1, 2, 3 and 4 (Böbert 1978). Of the poorest qualities the schlich was "reduced to an impalpable powder" (Anon. 1850). According to calculations done in 1840, every 100 kg of dressed cobalt ore gave on average only 2 kg schlich after stamping and washing (Böbert 1978).

The schlich that was left on the table was dried in an iron pan and taken to the colour works. There it was calcinated, or roasted, in a "calcination hut" to remove the sulphur and arsenic. The calcination oven was connected to a horizontal pipe construction (see Fig. 3.1) called giftfang (poison catcher), to trap the arsenical fumes. The fumes travelled through the poison catcher, and the arsenic settled as a soot as it cooled. About 20-42% of the concentrate was lost during calcination (Böbert 1978).

One notable feature about the production in Modum was the method of "concentration melting". Due to the low cobalt content in much of the extracted ore, the poorest schlich had to undergo further refining before being used. Cobalt metal was extracted by melting the poorest schlich with coal and bottle glass. This made it possible to separate out harmful iron and copper oxides (Müller 1843).

The cobalt metal that was extracted was stamped and calcinated. By applying this method, it was possible to produce high-quality smalt from poor-quality cobalt ore (Böbert 1978).

After calcination, the schlich was mixed with stamped and cleaned quartz, as well as potash. To varying degrees swamp eschel (a pale, finely pulverised smalt) was also added (Lindeman 1993, 40). The mixture was placed in crucibles and fused together in a furnace. When the mixture was properly fused, metallic lumps of waste material were tapped off and the liquid blue glass was ladled into containers of cold water to make it rapidly cool and shatter into brittle lumps of blue glass (Fig. 3.3).

The blue glass was stamped, milled, washed and left to settle in pools of water. This had the effect of separating the material into different grain sizes. Great stress was put on correct separation because different uses (and prices) were appropriate for the different grain sizes of what was now smalt.

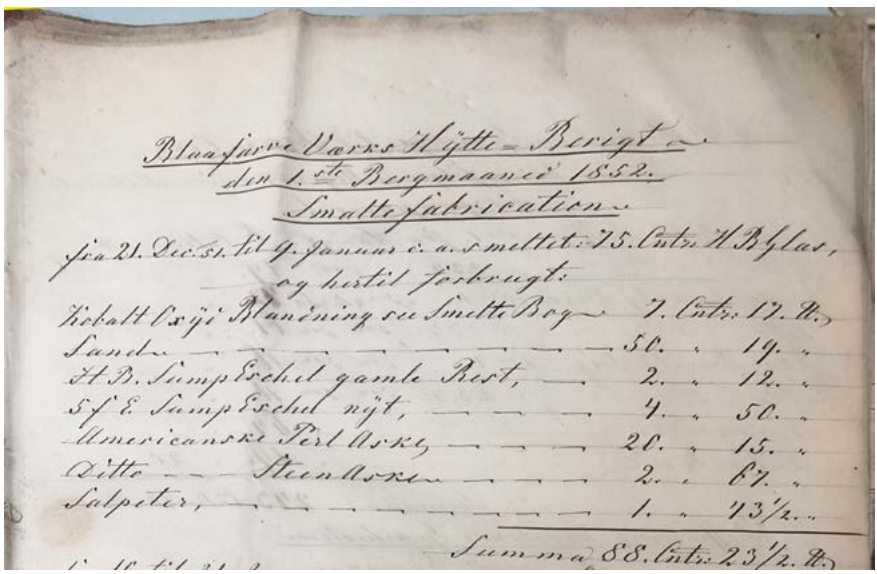

Figure 3.3: A Blaafarveværket report on the production at the hut in 1852. It states that between 21of December 1851 and the 4 January 1852, 75 centners (3.7 tons) of HB glass was produced by using 7 centners (348.6 kg) and 17 pounds (8.4 kg) of cobalt oxides, 50c. (2.4 tons) 19p. (9.4 kg) sand, 2c. (99.6 kg) 12p. (5.9 kg) of HB swamp eschel (old), 4c. (199.2 kg) 50p. (24.9 kg) of 5FE swamp eschel (new), 20c. (996 kg) 15p. (7.47 kg) of American pearl ash, 2c. (99.6 kg) 67p. (33.36 kg) of American stone ash, and 1c. (49.8 kg) 43 ½ p. (21.66 kg) of saltpetre. 1 Norwegian pound = 498 grams; 1 Centner = 49.8 kg (RA/PA-0157/H/He/L0442).

The wet smalt was dried and then sieved to remove lumps. All the smalt was classified according to the international standard, the Saxon or "standard" pattern, where the shade of blue and the grain size was indicated by letter grades.

The different shades of blue were divided in O (ordinary), M (middle) and F (fine). If the smalt was determined to be of an F quality, it would be further subdivided by means of the addition of additional Fs. The finest quality was 5F, or FFFFF (Lindeman 1993, 44-45). After the shade of blue had been classified, the smalt was given an additional letter or term based on its grain size. The term Skrivesand (writer's sand) was given to the coarsest size; a C to the middle size; and, finally, an E for the most finely pulverised smalt (Fig. 3.4).

Figure 3.4: Photograph of four glass containers in the collection of the Stifelsen Modums Blaafarveværk, Modum, Norway, containing different qualities of smalt.

Zaffre was a less-processed product that mainly consisted of calcinated schlich and stamped quartz. This meant that the purchaser of this product had to refine the material further in order to produce a usable colour product. Due to zaffre being more of an intermediate material than a finished product, it was subject to less taxation than smalt. Zaffre was also classified using the Saxon "standard" pattern, based on the quality of the finished blue that the zaffre would produce. But the zaffre could only gain a maximum of 3Fs (Lindeman 1993, 46). To mark the product as zaffre, it was given an S at the end (likely because the German and Norwegian word is *Safflor)*.

Customers

The customers of cobalt products were producers of paper, textile and starch; colour refiners; smalt makers; artists; and the producers of ceramics and glass. However, it mostly remains unclear where the Norwegian cobalt products ended up. The exported smalts, zaffres and oxides usually changed hands through dealers and speculators multiple times before arriving at the genuine end user. This had to do with the nature of the cobalt colours. A little goes a long way; therefore, it was often the case that the cobalt producers traded their products to large trading houses, who could make the smaller sales to different producers. Indeed, when the BCW was starting out, their leaders were advised to trade with "tradesmen who take large quantities" (Henckel 1783, 179; translated by Lasse Hermansen Bjørnland). They were also told:

> One infinitely larger advantage must it be for a colour works itself to be able to sell its colours to them, that otherwise had to take them from second or third, yes even, fourth parties than to trade them to these middlemen. [Henckel 1783, 179; translated by Lasse Hermansen Bjørnland]

Selling to the end users, alas, very seldomly occurred. In the late 18th and early 19th century much of the Norwegian produce was traded on the stock exchange in Copenhagen or exported to large trading houses in the Netherlands (Lindeman 1993, 51, 53). Later in the 19th century, it was often still the case that large trading houses bought sizeable quantities, which they then traded to third parties, who they themselves might sell the products on. Therefore, the products could change hands many times and over a significant period of time before being applied (for example, see RA/PA-0586 1835-1838).

There was a wider, global demand for smalt, which was served though the main markets and dealers in Europe, especially in Amsterdam and London (Kgl. Finants-, Handels- og Told Departement 1843). The largest competitors were the blue colour works in Saxony and the British producers (Tables of the Revenue, Population, Commerce & c. of the United Kingdom and Its Dependencies. Part IV. 1834, 1835, 155). Outside of Europe, China was the most important consumer country, but also the USA and Japan were seen as potential markets (Stortingsforhandlinger 1845, 64). There were sporadic attempts to export Norwegian smalt to both Japan and USA in the early 1840s, but due to low prices in Japan (RA/PA-0157 1845-1846, 202-203), British competition and high taxes in USA, respectively (Stortingsforhandlinger 1845, 64), large-scale trade never materialised.

Export of Norwegian smalt to China happened sporadically from the late 18th to the mid-19th century and, as always, most of this export happened through third parties. The first documented export was in 1792, when Det Asiatiske Kompagni (The Danish Asian Company) exported Norwegian smalt to Canton (Asiatiske Kompagni 1792). Later, in the 1830s, the export to China often went through large British trading firms, such as Smith, Goodhall & Reeves (RA/PA 0586 1835-1838); however, the BCW was not an active contributor in this re-export.

There had been some substantial shipments of smalt undertaken through the British trader Isaac Solly Lister in the early 1820s (RA/PA-0157 1822-1823, 4). In this, the BCW was somewhat more involved, but it was mainly Lister who organised the export. In April 1823, Lister claimed that he had sold 65 barrels of smalt in Canton, one of the largest sales of Norwegian smalt in China that is documented in the BCW archive.

Later, in 1843, the BCW funded two expeditions to China in the aftermath of the First Opium War. The potential for more open trade with China was seen with interest, "as we now have 4 ports there to choose between" (RA/PA-0157 1842-1843, 178; translated by Lasse Hermansen Bjørnland). The expeditions in the 1840s were special in that the BCW took a more active part in the export. The most important of these expeditions was organised by George Fredrik Egidius, the Norwegian consul in the Netherlands. Smalt was shipped to Amsterdam, then via Jakarta to Canton. The other expedition was a short-lived event where the BCW collaborated with the German firm Behn Meyer & Co. There the trade route went via Singapore to Canton (RA/PA-0157 1839-1844, 381).

The trade through Egidius reached its zenith in 1846, when 42 barrels of Norwegian smalt were sold in Canton (RA/PA-0157 1841-1846, 865). In the last years of the 1840s, the trade in China dwindled. By 1848, it was claimed that the price of the finest smalts on the Chinese market had fallen from between 75-80 dollars per Picul (1 picul = ca. 60 kg) to 50 dollars (Liljevalch 1848, 132-133). As a matter of fact, the truth was graver than that. On 15 August 1846, Egidius admitted that, due to a large incoming shipment of British smalt, Norwegian 3FC grade smalt was sold for only 40 dollars per Picul (RA/PA-0157 1846-1847, 228). There is, however, little information on exactly who the Chinese customers were other than they were in the porcelain trade.

In the end, it became apparent that large-scale trade with China was harder than had first been assumed. Large shipments of British and American smalts saturated the market (RA/PA-0157 1845-1846, 206), and the lowered prices were not sustainable, given the cost of shipments and Indonesian duty (RA/PA-0157 1846-1847, 224). The relationship between Egidius and the BCW became strained after the Chinese expedition met a dead end in early 1847. Finally, Egidius relayed

a message from China that advised small shipments, just 20 barrels twice a year, for the immediate future, to not saturate the market and wait out the competitors (RA/PA-0157 1846-1847, 222). The BCW's trade with China ended soon after.

Qualities and their uses

The quality of smalt was significant in determining what the application would be. Overall, the grain size seems to have had a greater influence than the shade on how the colour functioned in production. The shade of blue in highest demand overall was 3F, regardless of whether the smalt was to be used in staining paper or in enamelling. On the other hand, the demand per grain size varied.

On the European markets, the 3FE pigment was most requested (Smith et al. 1835-1838). The fine texture of the FE pigment meant that it was somewhat lighter in its blue shade than coarser equivalents. A lighter colour was often regarded as negative, but the small grain sizes are believed to have been easier to mix into paper pulps, textiles and starch. One thing that supports this reasoning is that producers of paper, textiles and starch bought almost exclusively the FE qualities (Hagen 2022, 297).

On the Chinese markets, the 3FC was the most important. This was apparent in the prices. The 3FE and 2FE was priced at 22 dollars for 60.4 kg, which was unusual, as in Europe 3FE was priced higher than 2FE. 3FC, on the other hand, was priced at 51 dollars (RA/PA-0157 1845-1846, 202). The C quality "appears of a deeper colour" than the E, "although obtained from the same glass" (Vivian 1818, 70). It seems that the deeper shade of blue was the reason for the Chinese preference for the C. This was expressed by the BCW's trade partner Egidius in 1846:

> It is to be recognised as an absolute that the E-types are unfit for the Chinese market, where blue colour is not used to treat textiles and paper, but exclusively to colour porcelain. [RA/PA-0157 1845-1846, 203; translated by Lasse Hermansen Bjørnland]

The Chinese seemed to purchase European smalt, rather than zaffre, and this may be connected with the use to which it was put. Recent work on the pigments used in Chinese Qing dynasty Famille Rose porcelain has confirmed previous work that suggested the underglaze blues used were derived from a local, Chinese cobalt source. However, overglaze enamels were made with a distinctively different cobalt pigment, which has the compositional characteristics of European smalt (Giannini et al. 2017). Some Norwegian zaffre was exported to China, but it does not appear that it gained much interest. The lack of interest was mirrored by the

European counterparts. Egidius expressed "God knows if the Chinese understand how to extract an oxide product from the zaffre" (RA/PA-0157 1846-1847, 233; translated by Lasse Hermansen Bjørnland).

In contrast, in Europe, zaffre was the preferred cobalt colourant used in the earthenware, ceramics and porcelain decoration. This preference was due to its use in underglaze transfer printing. Smalt was also used as an enamel colour in Britain, but, as noted below, by the 19th century there was limited demand for smalt in this industry.

> The fine-coloured Smalt received from you would not answer any profitable end for the Potteries in this country. It would answer for very light colour in enamel painting, but the quantity used for that I suppose is so very trifling indeed, that it would not be worth the trouble. [RA/PA-0157 1828-1829, 276; translated by Lasse Hermansen Bjørnland]

It seems that zaffre was used exclusively in the British potteries, at least in the 1820s-1840s. Zaffre was also in high demand among British smalt producers, as noted before (RA/PA 0856 1835-1838).

From the late 1840s, the Norwegian BCW also produced so-called chemically clean cobalt oxides. These were produced by diluting schlich in sulphuric acids. The collection of the Foundation preserves samples of PKO (cobalt phosphate), RKO (black cobalt oxide), and FKO (grey cobalt oxides) produced in Modum in the 1840s and 1850s. These products were mainly used in the glass and ceramics industries in the last half of the 19th century.

From 1868 to 1898, the BCW's main product was schlich that was sent for future refinement to the headquarters of the firm that then owned the Norwegian site, which was in Saxony. In addition, secondary elements that were associated with the cobalt was also exploited, leading to the production of concentrates of nickel and white arsenic. The nickel was also exported to Saxony and used in alloys, while the arsenic was mainly exported to Great Britan or Sweden or remained in Norway to be used for production of green pigments, medicine, glass production or pesticides.

Conclusion

The BCW in Modum was one of the most significant producers of cobalt products in the 19th century. It was one of the main global suppliers of smalt, zaffre and cobalt oxides throughout large parts of the 19th century. This paper has identified the different products of the works and discussed their classification as smalt,

schlich and zaffre. It has also detailed their various uses and the different qualities of the product, especially in that the different textures, shades of blue, and degree of processing were of great importance to the customer. Although there is much that remains unknown about the end users of the Norwegian cobalt products; however, it is hoped that further research can shed new light on this subject in the future.

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Chapter 4

Provenancing smalt: The potential of geological analysis

Patrick Degryse[1] and Andrew J. Shortland[2]

Introduction

A prime purpose of the scientific analysis of archaeological artefacts has always been the study of their provenance and of the trade and exchange of finished objects and raw materials. In the art world, such detailed "forensic" analysis is also increasingly being used to verify the attribution of fine art, as well as of decorative and applied arts (e.g. Shortland and Degryse 2022). One of the key techniques employed there involves identifying pigments in the object in question and comparing their characteristics to those in a database of objects or pigments that have good provenance and a well-determined date. The scientific examination of archaeological and historical artefacts relies on the assumption that there is a scientifically measurable property that will link an artefact to a particular source or production site. The inter-source differences must exceed intra-source variation for source discrimination to be possible (the provenance postulate; Weigand et al. 1977). Depending on the type of the material analysed (e.g. clay versus ceramic or ore versus metal), elements or their isotope ratios are chosen for their occurrence as major or trace element and for the nature of the geological-mineralogical information they provide. Nearly every element of the periodic table has been used at some time to compare the typical composition of source materials to that of artefacts, or to assign compositional groupings to objects (Degryse 2023). It is recognised, though, that no one single method of analysis alone is sufficient for provenance studies, as overlaps are common when potential sources are compared (Kempe and Harvey 1983). Many techniques from the geosciences have been explored for provenancing purposes, but trace element profiles and isotope ratio analysis have proven indispensable (Degryse and Bentley 2018).

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Studying blue pigments is especially important in ancient materials research, as the colour blue has been essential in art since its very inception as the pigment "Egyptian blue", in the early 3rd millennium BCE (Hatton et al. 2008). As such, it was the first artificially generated pigment, following on from natural compounds used for white, black, yellow and red. Egyptian blue was used alongside rare naturally blue minerals, such as azurite or lazurite, and copper compounds used to colour glazes on quartz-based ceramics known as faience. The 16th century BCE saw two important developments. The first was the discovery of how to make glass. The second was a new blue colourant that was used in both this new glass and in the longstanding production of blue faience: compounds that contained cobalt (Shortland 2012). The use of cobalt is certainly the more interesting, as cobalt ore sources have since been used to generate deep-blue colourants and pigments of different dates for local use or more distant trade, in the production of a range of materials, such as ceramics, glass, paper or textiles, and even in laundry, as a whitening agent (Delamare and Rouchaleau 2013).

Cobalt is a critical metal today and has been one of the critical minerals throughout history. Usable cobalt sources are relatively rare, and because they almost always contain multiple other elements, creating a pure colourant from them was difficult, requiring particular extraction processes and refinement techniques for its ancient use (Gratuze et al. 1996). However, as the unwanted secondary elements in different cobalt sources vary and almost always persist (to a limited extent) into the pigment made from them, cobalt colourants tend to exhibit a characteristic "fingerprint" of elemental compositions that can be linked to the ore body and associated factory. Objects made with such cobalt colourants retain this fingerprint, and scientific analysis can thus inform us of the origin of the primary cobalt ore used for production of the artefact (Gratuze et al. 1996).

The earliest cobalt source exploited was the cobaltiferous alum deposit of the oases in the Western Desert of Egypt (Shortland et al. 2006). This type of cobalt was used in Late Bronze Age (LBA) to Early Iron Age vitreous materials and is primarily recognised by the association of the cobalt with elevated levels of aluminium, nickel, zinc and manganese, along with a few other elements at trace levels. This source was long thought to have been the only cobalt used during the LBA, but other cobalt signatures have since been identified in connection with Mesopotamian glasses (Walton et al. 2012) as well as glass and faience artefacts from Ramesside Egypt (Abe et al. 2012), which can be distinguished by their nickel, zinc and manganese contents. Using mostly correlations between cobalt, nickel and zinc, Gratuze et al. (2018) were able to demonstrate two major changes in the chemical make-up of cobalt colourants in glass making during the late antique and early medieval periods. Roman cobalt-blue glasses show a relatively

constant composition characterised by a high Co/Ni ratio. Sometime between the late 4th and the beginning of the 6th century, this ratio drops significantly, although continuous recycling of ancient glass resulted in the persistence of earlier cobalt signatures throughout the 1st millennium CE. In the course of the second half of the 8th century CE, a new type of cobalt appeared in the eastern Mediterranean. This cobalt compound has elevated levels of zinc and low nickel contents and is characteristic of Islamic glass production and the first Islamic blue-and-white Abbasid ceramics, between the 9th and 11th centuries CE. From the end of the 12th century onwards, mines in central Europe began to be exploited (Bidegaray and Pollard 2018; Gratuze et al. 1996) with a cobalt source that was similar in composition, but with significant indium as trace element. There is not enough evidence to establish whether the late antique nickel-rich cobalt colourant is related to the discovery of a new cobalt deposit or simply to the exploitation of deeper mineral veins of the same deposit. Varying phases within the same deposit can potentially generate different compositional signatures, such as oxidised minerals at the exposed surface compared with sulphide veins further below. In contrast, there can be no doubt that the fundamental change in the composition of the cobalt colourant during the eight centuries of Islamic glassmaking reflect the exploitation of new cobalt deposits. The geographical location of this Islamic cobalt source remains to be found (Matin and Pollard 2015, 2017).

In Europe from 1400 CE, smalt, a dark blue, crushed, cobalt-coloured glass, was the main way in which cobalt pigment was traded (Delamare et al. 2013). Other relatively impure cobalt compounds, such as slig (crushed, washed, and calcined cobalt ores) or zaffre (produced by heating slig mixed with crushed quartz), were, similarly, traded and used in the colouring of many materials. The main European cobalt source exploited was in Saxony, at Schneeburg and neighbouring towns, and although this source waxed and waned due to political and economic crises, it remained the most important source until the 19th century (Delamare et al. 2013). Other very limited attempts at cobalt extraction were made in England, France and Spain, but their production volumes were very small (Delamare et al. 2013). One of the most important later sources exploited was the Blaafarveværket (Blue Colour Works; BCW) in Norway, active for nearly a century and "from 1823 to 1849 … the largest producer in the world. It employed 2,000 people and supplied three-quarters of the world market for cobalt blues" (Delamare et al. 2013). Despite this, it is comparatively little known and studied. Worldwide smalt production lasted until the late 19th century CE, when it was superseded by novel methods for producing blue colours, including modern synthetic pigments.

Provenancing smalt

For all time periods in the entire pre-industrial World, 10 to 12 cobalt source fingerprints have now been identified, of which some are known only from the finished product, meaning their ore source is still debated (Gratuze et al. 2018). Interestingly, from the middle of the 18th century CE onwards, the chemical signatures of Co colourants tend to show more variability and become more complicated (Gratuze, this volume). This may be due to changes in production technology, changes in the mixing of sources, or Co being such a powerful colourant that little is needed and the resulting trace signatures may be diffuse and hard to recognise. To the archaeologist and (art) historian, cobalt colourants are a valuable tool, since they allow a pigment to be traced from its production site right through to a finished object, which may itself have been traded. Compositional variations in cobalt-coloured materials indicate the use of different raw materials and/or production processes, and this use, in turn, has implications for the underlying exchange networks. Long-distance trade in pigments and objects can therefore be reconstructed where the particular characteristics of a cobalt ore body are accurately known (including possible varying compositional signatures within the same deposit).

In addition to trace element contents, lead isotopic signatures may enable distinguishing between sources, because many Co sources originate from geologies varying in genesis type and age. A proof-of-principle of this approach, investigating smalt from Norway and Saxony, was published by Hermansen Bjørnland et al. (2024). Lead isotope ratio analysis (LIA) (ratios $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$) has been used since the 1960s to investigate ancient materials, in particular to trace the provenance of lead, silver and bronze (mainly from the Mediterranean Bronze Age) and has subsequently been applied to study a range of inorganic archaeological materials (Degryse 2012; Degryse and Shortland 2009). LI signatures of different ore deposits may vary because of a different geological formation age and/or initial chemical composition of the deposit. Criticism on the early use of LIA in archaeology has been addressed, making use of kernel density estimates (KDE) as a non-parametric way to compare ore sources and artefacts. Current LI data are, moreover, used to characterise ore sources according to the laws of radioactive decay and geochemistry, thus providing geological information (e.g. De Ceuster et al. 2023).

The BCW (Fig. 4.1) was a producer of cobalt products (especially smalt and zaffre) during the 18th and 19th centuries CE. Based near Modum in Norway, it exploited local cobalt ores and a range of other raw materials, both locally sourced and brought in from more distant areas. Geologically, the Skuterud Cobalt Mines

are situated in the Modum Complex, which is part of the Kongsberg sector of the pre-Cambrian supracrustal rocks of southeastern Norway (Bjerkgård et al. 2020). The Modum Complex consist mainly of steeply dipping, folded metasediments containing elongate outcrops of metagabbro-amphibolite bodies of varying size. Within the metasedimentary rocks are sulphide-rich lenses known as *fahlbands*, and the Skuterud Mines exploit the most westerly fahlband, where the mineralised zone was richest in cobalt. The cobalt mineralisation consists of cobaltite (CoAsS), skutterudite ($CoAs_3$) and cobalt-bearing minerals of arsenic. The Norwegian Geological Survey also lists glaucodot ((Co,Fe)AsS) and safflorite ($(Co,Fe)As_2$) (Bjerkgård et al. 2020). However, the genesis of the cobalt mineralisation at Skuterud is not well understood, and more research is needed on the subject.

Figure 4.1: Photograph of (**left**) the Blaafarveværket open-cast mine in Modum, Norway; (**upper**) Co ore minerals; (**lower**) underground galleries.

The BCW is now a museum, and study of its archive has detailed the type and quantity of production at the site, showing that it was perhaps the most important producer of cobalt products in the early 19th century and the largest mining operation in Norway. The archive gives details of some of the production processes for specific products and shows that these processes changed with time. It details the type and source of the raw materials used in production, specifically, quartz and potash. The quartz was local, coming from a quartz mine owned by the BCW. Some of the potash was produced by the BCW, but most of the potash came from Norwegian, German and American producers (Lindeman 1993); e.g. in 1783, the BCW director complained that the Norwegian potash produced "too much gal [waste] in the glass melt" and was therefore not suitable for smalt production. Thus, the source of potash changed through time. The production at the BCW at Modum lasted for just over a hundred years, eventually ending in the 1890s. At least two production methods are described in the archive for the manufacture of smalt, the first involving roasting of the sulphide ores to oxides and the second, a conversion to sulphate and then hydroxide using sulphuric acid and sodium carbonate. Another methodology was used to create cobalt oxides, especially later in the production period. In view of the raw materials listed here to make smalt, it can be assumed that the lead isotopic composition of the end product will be largely inherited from the cobalt ore used. Neither the silica sources nor the potash flux are likely to have any significant lead contents associated with them.

Held in the archive at the BCW are two collections of raw materials and products (Fig. 4.2). The first is a collection of a total of 82 samples in glass vials, including smalt and cobalt oxides donated to the BCW museum by the Norwegian University of Science and Technology (known by its Norwegian acronym, NTNU). These samples were collected in the 1920s or 1930s by the university at the BCW. Most of the 82 samples are smalts, some dated, some not, the earliest dating to 1782 and the latest to 1854. There are also two samples of cobalt oxides that date to 1849. In addition, there are in this collection examples of smalt labelled "Schwartzfels" and "Cöln", indicating that they are German. They are probably linked to German cobalt mines and blue colour works that were contemporary with the BCW and interacted with them, along with other producers (Delamare et al. 2013). In contrast to the Modum ore deposit, the Erzgebirge (Erzgebirge, in Saxony, Germany, and Krušné hory, in Bohemia, Czech Republic) is one of the most studied geological areas in Europe. It is part of the metamorphic basement of the internal Mid-European Variscides on the northwestern border of the crystalline Bohemian Massif core complex (Seifert and Sandmann 2006), composed of medium- to high-grade metamorphic mica schist and gneiss next to postkinematic granites, hosting polymetallic sulphide base metal deposits (Ag-Bi-Co-Ni-U-

bearing veins) mined for, amongst others, cobaltite and skutterudite (e.g. Seifert et al. 2001). With the fundamental differences in geology between the Norwegian and the German cobalt sources should come a different isotopic signature of the cobalt ore extracted, and thus a different LI signature of the smalt produced from these ores. In effect, the cobalt ore is expected to be the main contributor to the lead content, and thus the lead isotopic composition of the smalt, like that of all other raw materials, will have virtually no lead (e.g. silica or wood ash).

Figure 4.2: Photograph of (**left**) examples from the collection of raw materials and products (smalt, slig, oxide, etc.) of the Blaafarveværket mine in Modum, Norway; (**right**) crucibles for smalt making with glass attached, held at the Blaafarveværket museum.

The potential of lead isotope ratio analysis

Initial geochemical analysis on a small selection of BCW smalt showed that the output was a product with on average 65% silica and 13% potash (Hermansen Bjørnland et al. 2024). Elemental analysis (including of trace elements) combined with lead isotope analysis shows that different sources of silica were likely used, as signatures are variable—e.g. in rare earth elements (REE) patterns, which are sensitive to variations in igneous systems and their weathering to sedimentary rocks (Degryse and Shortland 2009). This supports suggestions based on archival research that external sources of silica and plant ash were employed on occasion. The Norwegian cobalt ores consistently produce smalt that is very low in manganese and zinc, with some nickel, and significant iron and arsenic. The smalts also seem to have relatively raised bismuth and uranium contents (Hermansen Bjørnland et al. 2024). These elements thus act as a potential signature to provenance Norwegian smalts found or used elsewhere. It should be noted that the Saxon ores

were exploited for bismuth and later uranium, so it is likely that smalt made from those deposits will also contain significant amounts of these elements (Veselovsky et al. 1997). Smalt produced between the 12th and 18th centuries CE from German Erzgebirge ore deposits is already well characterised in terms of elemental composition, and can be divided into three main compositional groups (Gratuze 2023): materials made with Co ore from the Freiberg area can be dated between the 12th and the end of the 14th century CE and are characterised by an association of Co with Zn-In-Pb; materials made with Co ore from the Schneeberg area dated between the early 15th century CE and 1525 are characterised by an association of Co with Ni-Mo; and materials made with Co ore from the same Schneeberg area but dated between 1525 and the end of the 19th century CE are characterised by an association of Co with As-Bi-U-Ni(-W). Conversely, some of the BCW samples have quite extreme values in lead isotopic composition, which may be expected from material made with a pre-Cambrian ore source such as the Modum Complex cobalt deposit, with lead isotope ratios for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ up to 28.9, 16.5 and 41.1, respectively. The lead isotope ratios for the German smalt samples are much more homogenous, with lead isotope ratios for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ between 18.48 and 18.60, 15.64 and 15.65, and 38.4 and 38.6, respectively. The Norwegian BCW and German Schwartzenfels and Köln samples are thus very distinct, indicating the potential for fingerprinting various geological sources, although more isotopic analyses are certainly required.

Global terrestrial cobalt resources are mostly associated with stratiform sediment-hosted copper deposits, magmatic nickel-copper sulfide deposits and cobalt-nickel laterites of different geological ages (Horn et al. 2021). Historically mined deposits next to the Modum and Erzgebrige areas comprise an array of mineralisations, such as Mesoproterozoic (1.3 to 1.1 Ga old) magmatic cobalt ores in Norway (Sandstad et al. 2012); the Mesozoic Kupferschiefer stratiform sediment-hosted deposits of central Europe (Borg et al. 2012); the Triassic sandstone-hosted deposits of the Cheshire Basin in the UK (Warrington 2012); and the polymetallic cobalt-rich vein deposits of late Palaeozoic age in Scotland, northern England and Wales (e.g. Horn et al. 2021 and references therein), of Variscan deformation age in France (Cugerone et al. 2018), and of Variscan to Alpine age in Spain (Fanlo et al. 2004). All these deposits have a widely varying geological age and a similarly heterogenic formation type, and thus chemical composition, and can thus be expected to have a different lead isotopic composition (although, of course, overlap may exist).

Since the analysis involved may be performed on valuable ancient materials or objects of art, it is important that the chemical fingerprinting for trace elements and lead isotope ratios can be done through laser ablation-inductively coupled

plasma-mass spectrometry (LA-ICP-MS). This technique combines a low degree of invasiveness (termed quasi-non-destructive) with allowing high-quality measurements of concentrations of major to trace elements and/or their isotopic compositions in artefacts (Degryse and Vanhaecke 2016). As a technique, LA-ICP-MS was only introduced to archaeometry about two decades ago, but its impact and development has been such that there are many important applications still to be discovered (Degryse and Rademakers 2023).

Conclusion

Elemental and LIA analyses showed that the BCW production is more complex than a simple use of local materials. It seems probably that some plant ash or quartz is being imported to the facility to use with or instead of local equivalents, a notion backed up by references in the archive. This makes the final compositions of the smalt quite variable. Nevertheless, exceptional lead isotope ratios are seen in the BCW smalt, as is to be expected from the use of the pre-Cambrian Modum cobalt ores. This is in contrast to at least the lead isotope compositions of smalt made with German ores, which are much more homogenous and seem to reflect a Variscan geology (although more analyses are certainly required). As a consequence, there is potential for the BCW and German smalt to be traced when they are exported from the factory and used in other industries in Europe and farther afield. Moreover, in view of their varying geological origin in terms of age and composition, it is possible that many of the historically exploited cobalt deposits can be distinguished in this way.

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Chapter 5

Variations in the chemical signatures of cobalt colourants used in glass from the 17th to the early 20th centuries

Bernard Gratuze[1]

Introduction

Along with manganese, cobalt is one of the few colouring agents used by glass and ceramic artisans that did not have other craft applications (metallurgical or otherwise) in ancient societies. These two mono-isotopic metals, furthermore, share the characteristic of having been isolated as an element only in the 18th century, whereas their use as a glass colouring agent dates back to the 2nd millennium BCE. Although they are often found together in mineralogical deposits, they differ greatly in terms of their abundance in Earth's crust, with cobalt being almost 40 times less abundant than manganese.

Both elements are found together in deposits, such as asbolane, a hydroxide deposit formed by alteration, with the cobalt content going as high as 35%. Likewise, certain evaporitic deposits, such as Egyptian alum, contain high cobalt, as do laterites, where it is associated with high iron and nickel contents. However, unlike manganese, which is mainly present in the form of oxide and hydroxide mineralisation, the primary mineralisation exploited for cobalt is sulphide or arsenide and their oxidised derivatives, although cobalt is probably more abundant on Earth associated with manganese in the form of asbolane. Cobalt has also been recovered as a by-product of silver and copper metallurgy. Cobalt and manganese also differ in the trace elements associated with them, which can be used to trace their origin. While the trace elements associated with manganese are also commonly found in the constituents of glass (such as barium and strontium), those associated with cobalt appear to be much more diverse (Ni, As, Bi, Cu, Zn, In, Pb etc.) and are generally less abundant in the silica and flux used by glassmakers. It is probably to these parameters that we owe, since the 1980s, the number and the success of studies on the origin of cobalt used by glass makers over time, compared

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with the number and success of studies concerning manganese (Curatola 1979; Dayton et al. 1980; Delamare 2009; Gratuze and Picon 2005; Gratuze et al. 1992, 2018; Kaczmarczyk 1986; Matin and Pollard 2017; Seccaroni and Haldi 2016; Shortland et al. 2006; Smirniou and Rehren 2013; Walton et al. 2012).

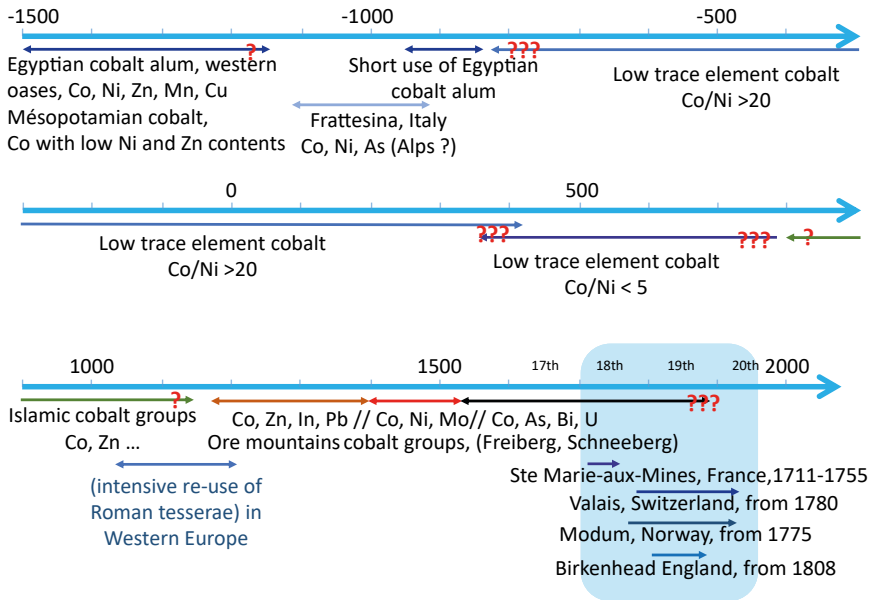


Figure 5.1: Timeline of cobalt ore sources used by Mediterranean and European glassworkers between the mid-2nd millennium BCE and the early 20th century CE.

Studies on the origin of the cobalt ores used by the European glass and ceramic industries have highlighted the successive use of three main chemical characteristic groups of cobalt colourants between the end of the 12th century and the 18th century (Gratuze et al. 1992, 1996; Pappalardo et al. 2004; Zucchiatti et al. 2002, 2006) (Fig. 5.1):

- 1st group: chemical association Co-Zn-In-Pb probably originating from the Freiberg, Germany, area and observed from the end of the 12th century to the end of the 14th century (≈ 1400);
- 2nd group: chemical association Co-Ni-(Mo) probably originating from the Schneeberg, Germany, area and observed from the beginning of the 15th century until the first quarter of the 16th century (c. 1525); and

- 3rd group: chemical association Co-As-Bi-U-Ni-(W), probably also originating from the Schneeberg area and observed from 1525 to the 19th century. Smalt production probably ceased in this region at the end of the 19th century (Porter 1997).

During the 18th century, cobalt chemical signatures start to show more variability, and new compositional groups seem to emerge simultaneously (Figs. 5.2 and 5.3). Some elements, such as barium, show high contents in some smalt productions (up to several per cent) (Freestone 1993; Gratuze et al. 1996; Zlámalová Cílová et al. 2020), while arsenic, which can also be added separately as a clarifying or fining agent, can no longer be considered as a systematic tracer of cobalt. From the beginning of the 18th century, new cobalt mines were exploited in western Europe:

- Sainte Marie-aux-Mines, France, where cobalt was exploited at Rauenthal (Christian vein) and a colour mill (*Farbemühle*) was in operation between 1711 and 1755 (Goergler 1991; Lougnon 1985, 243; P. Clerc, personal communication);
- Valais, Anniviers—Tourtemagne, Switzerland, and several mines were exploited in the area (Grand-Praz, Kaltenberg/Prafleuri, Gollyre, Plantorin) between 1780 and 1898 (Meisser 2003). The cobalt ores were sold to various blue colour works (*Blaufarbenwerke*) in Germany (e.g. Schwarzenfels/Mottgers in Hesse, in 1820, or Oberschlema, in Saxony, between 1891 and 1898). Some of these ores, which contained more nickel than cobalt, were roasted locally and sold to an English refinery;
- The Seacombe Smalt Works in Birkenhead (UK, https://archaeology.co.uk/articles/news/out-of-the-blue-the-seacombe-smalt-works.htm), which operated between 1808 and 1860, may have processed some English cobalt ores originating from Cornwall, Cumberland and Cheshire, which have been exploited in the mid-19th century (Virtue 1851, iii, xvi); and
- Modums Blaafarveværket (Blue Colour Works; BCW), located at Åmot, in Modum (Buskerud, Norway), which operated between 1776 and 1898.

Moreover, cobalt seems to have been mined in Sweden as early as 1855. To this list, according to Henry Atherton (1855), we can add Spain (specifically Asturias), Hungary, England (specifically Cornwall) and various parts of the Americas, where cobalt ores were mined to be exported in the mid-19th century.

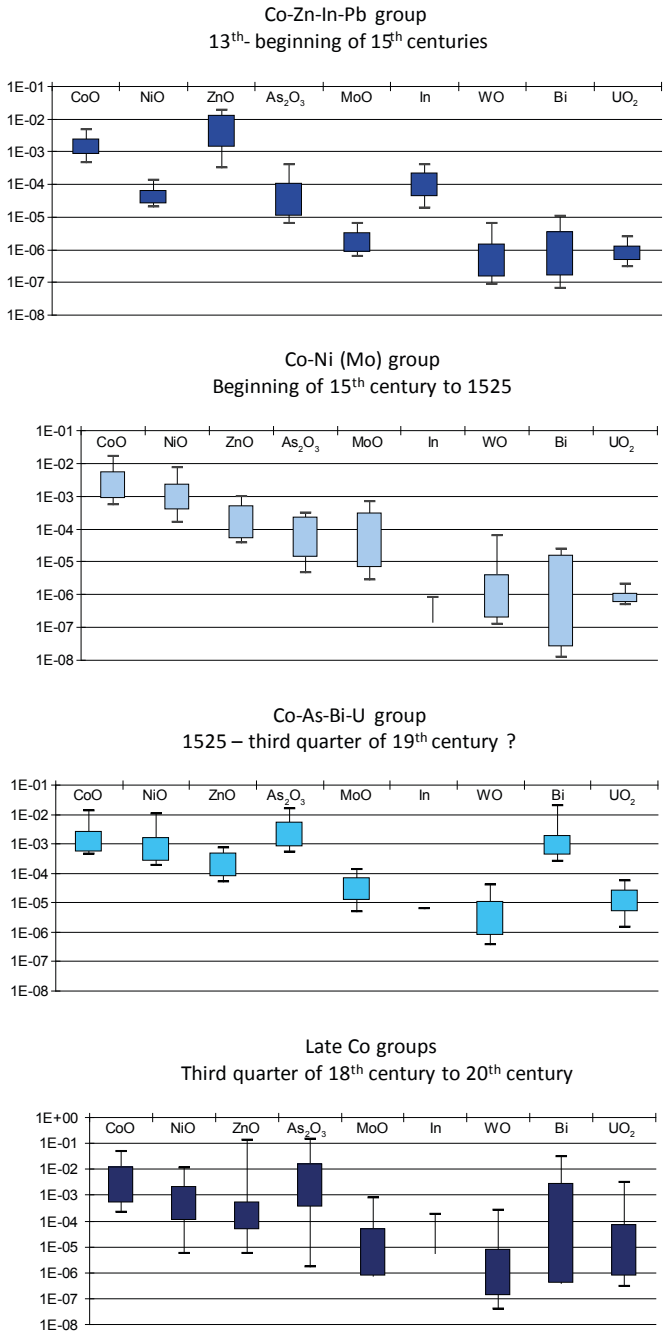


Figure 5.2: Variations in concentration for the main characterising trace elements in European cobalt-coloured glasses between the 13th and 20th centuries.

The aim of this article is to investigate whether it is possible to identify, among the diverse chemical fingerprints observed for smalt from the 18th century onwards, some of these new cobalt mines (Fig. 5.2).

Materials and methods

The data used to study the changes in cobalt supply come from various research programmes dealing with the circulation and composition of glass objects during the modern period. They concern:

- Glass beads from France; Germany; Quebec, Canada; parts of Africa; Réunion Island, Yakut burials, and East Asian and Pacific shipwrecks, dating from the 17th to the 19th-20th centuries. Programmes on French beads are developed with Laure Dussubieux and Adelphine Bonneau. Programmes on Canadian beads are developed with Adelphine Bonneau;
- Glass beads and objects from the *Gagliana Grossa* shipwreck (1583, Gnalić Island, Pašman Island, Croatia) and objects from the Amsterdam glass bead workshop (17th century), used as a compositional reference for the Schneeberg Co-As-Bi-U group. Programmes on the Gagliana Grossa and Amsterdam bead workshops are developed with Adelphine Bonneau;
- Cobalt-blue glass, enamels and glazes originating from France and dated to the 17th to 19th century, and from other European countries and dated to the 18th and 19th centuries;
- Smalt particles used to whiten Dutch paper dating from the mid-18th century to the early 19th century (1755 to 1815); and
- Smalt particles from the BCW in Modum, Norway (dating from 1827, 1832, 1834 and 1839).

In order to determine the chemical fingerprints of the cobalt colourants as reliably as possible, only samples containing more than 500 ppm cobalt were considered for the reference groups. The chemical elements considered are mainly Co, Ni, As, Bi, U, but also Cu, Zn, Mo, Ba, W and REEs.

The analyses of the different objects used for this study were carried out at the Centre Ernest-Babelon of the Institut de recherche sur les archéomatériaux (IRAMAT) in Orléans, France, using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The instrumentation used consists of a Resonetic Resolution M50 laser probe operating at 193 nm coupled to a Thermo Fisher Scientific ELEMENT XR mass spectrometer (Gratuze 2016).

Cobalt chemical fingerprints since the 18th century

Until the last quarter of the 18th century, variations in the compositions of cobalt-blue glasses corresponded to those defined for the Co-As-Bi-U group. From the 18th century onwards, we observe the emergence of cobalt-blue glasses containing less and less bismuth and uranium and, to a lesser extent, nickel and arsenic (Fig. 5.3). For example, most of the smalt particles analysed from Dutch papers dated after 1780 contain less bismuth and uranium, no longer corresponding to the Co-As-Bi-U group but reflecting the appearance of new cobalt colourants or, perhaps, more refined ores.

To a lesser extent, there also exist glasses that contain more nickel, arsenic, uranium and bismuth—smalt particles originating from two Dutch papers dated from 1794/95 and 1815 (5% As_2O_3 for 0.3% CoO) and the smalt produced by the BCW in 1827 and 1834 (up to 11% A_s2O_3 for 1% CoO) (Fig. 5.4) contain more arsenic.

Some smalt particles originating from the same Dutch papers of 1794/95 and 1815 have also been found to have unusually high uranium contents (500 to 3000 ppm). Although some smalts from the BCW also have some high uranium contents (up to 700 ppm), their U_2O/CoO ratios are lower than those found in the Dutch papers (Fig. 5.4).

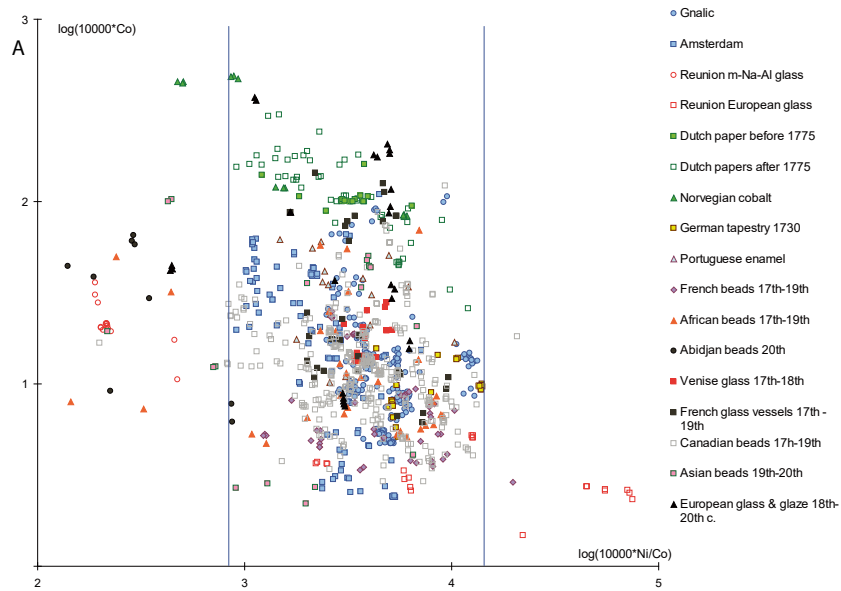
A small group of forest-plant-ash glass beads, probably made in Bohemia and dated to the end of the 18th century, found on the island of La Réunion and in the *La Boussole* shipwreck (1788, Vanikoro, Solomon Islands), contain up to 7 times more nickel than cobalt oxides (NiO 1336 ppm / CoO 267 ppm at Vanikoro and NiO 1806 ppm / CoO 248 ppm at Réunion) (Fig. 5.3).

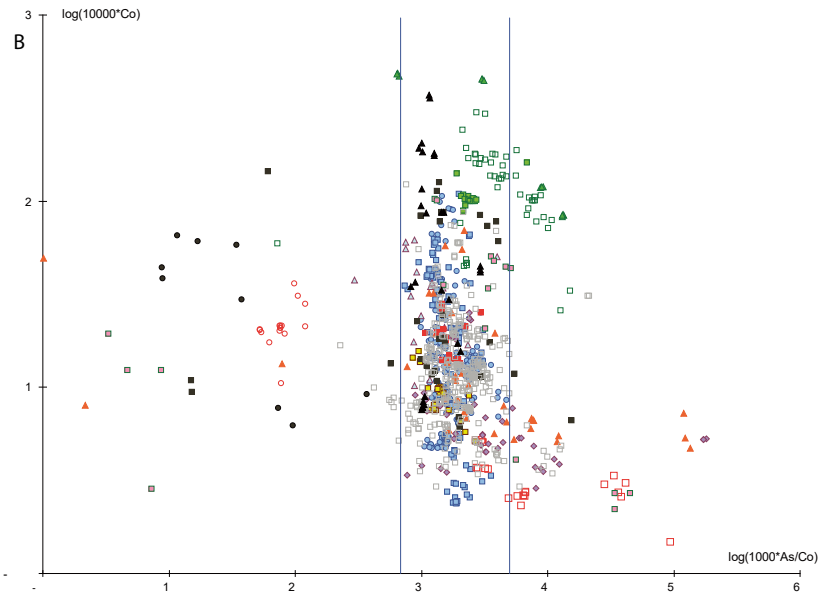
High levels of bismuth (up to a few per cent) are occasionally found in cobalt-blue glass, but these levels do not appear to be specific to any particular period or area of production.

It should be noted that from the 18th century onwards, arsenic was used as an opacifying, colouring or fining agent, and therefore is no longer necessarily associated with cobalt. Although the use of arsenic increased from the 18th century onwards, the first references to its use in glass colouring recipes date back to the 16th and 17th centuries (Moretti 2002; Moretti and Toninato 2001; Moretti et al. 2004). Accidental contamination by uranium salts, used as colouring agents, seems less likely before the second half of the 19th century, when these salts began to be used.

Another characteristic of some cobalt-blue glasses and smalt particles produced in the 18th century is the high barium content found in some of them. For example, some smalt particles used by Dutch paper manufacturers between 1755 and 1795 contain several per cent by weight of barium oxide (up to 7.6%). Similarly high barium contents (between 0.4 and 3.5%) have been found by Zlámalová Cílová and colleagues (2020) in smalt produced in Soví huť, Bohemia, 16th-17th centuries; by Xia and colleagues (2019) in smalt particles from Chinese works of art dated between the 14th/18th and 19th centuries (between 1.6 and 8.9%); by Freestone (1993) for some ceramic production of the Limehouse Porcelain Manufactory, London, UK (10% BaO); in some smalt particles from Sainte-Marie-aux-Mines, France (between 6 and 10% BaO; Gratuze et al. 1996); and in cobalt-blue enamel present on 18th century glass objects found in Orléans and Poitiers, France, and containing up to 1.2% BaO (Buisson et al. 2023). In some other 18th century unpublished objects from Poitiers, higher contents of BaO have also been encountered in the cobalt-blue enamel layer (0.4% <CoO< 0.9%; 0.65% <BaO < 4.9%).

The presence of high barium grades at both Soví huť and Sainte-Marie-aux-Mines suggests that these are not characteristic of a production zone, but, rather, reflect the occasional presence of barium-rich minerals in the gangue of cobalt ore veins.


A
log(10000*Co)
log(10000*Ni/Co)
Gnalic
Amsterdam
Reunion m-Na-Al glass
Reunion European glass
Dutch paper before 1775
Dutch papers after 1775
Norvegian cobalt
German tapestry 1730
Portuguese enamel
French beads 17th-19th
African beads 17th-19th
Abidjan beads 20th
Venise glass 17th-18th
French glass vessels 17th - 19th
Canadian beads 17th-19th
Asian beads 19th-20th
European glass & glaze 18th-20th c.


B
log(10000*Co)
log(1000*As/Co)

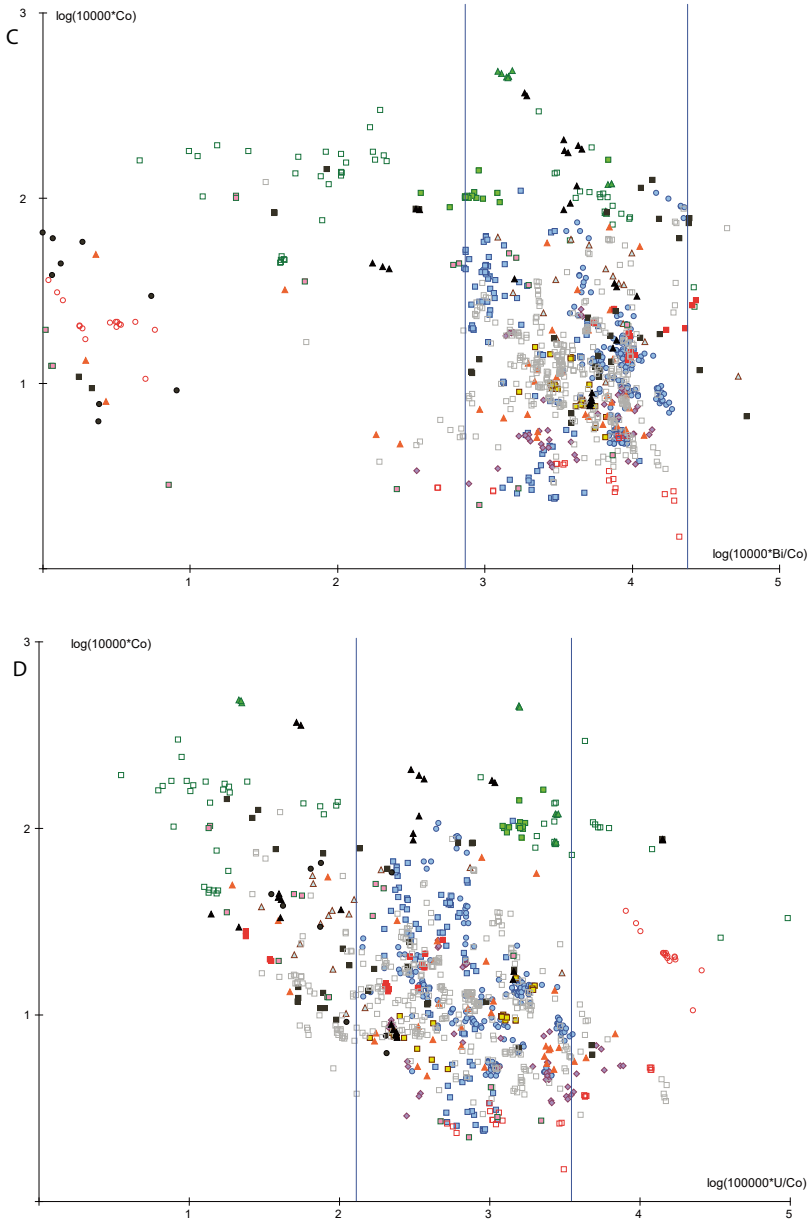


Figure 5.3: A to D. Variations observed in the ratios of nickel (A), arsenic (B), bismuth (C) and uranium (D) to cobalt for the European cobalt coloured glasses between the 17th and the 20th centuries. The vertical lines, mark the variations observed for the Co-As-Bi-U group associated with the Schneeberg area.

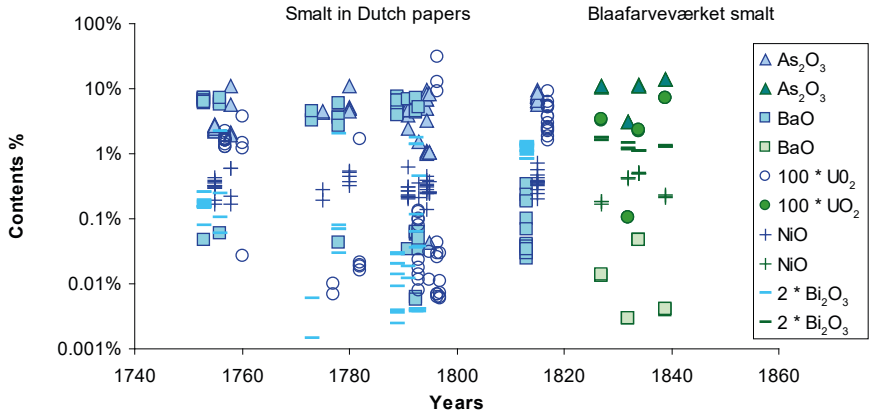


Figure 5.4: Variations in the content of arsenic, barium, uranium, nickel and bismuth oxides in smalt particles found in Dutch papers or produced by the Blaafarveværket factory in Modum, Norway, between 1755 and 1839.

High levels of nickel, uranium or bismuth may appear to be more characteristic of certain production areas or certain types of mineralisation. In his description of the Valais mines, Meisser (2003, 62) gives the following information for the Kaltenberg veins: "Brown radiohalos of 100 to 300 microns, in the chlorite accompanying the Kaltenberg mineralisation, were described by Hirschi in 1939 without identifying the radioactive mineral responsible for this phenomenon. Recent analyses by Schafer have identified uraninite (UO_2), in tiny grains sometimes embedded in gersdorffite (NiAsS)". However, mining of the Kaltenberg veins did not begin until 1854, some 20 to 50 years after the production of the Dutch paper in which high levels of uranium were measured.

The presence of nickel-rich mineralisation is also highlighted by Meisser for the Grand-Praz vein:

> The year in which the deposit was discovered is unknown. The first mining period lasted from 1780 to 1789, when 50 tonnes of rich ore were extracted. It was carried out by 30 to 40 miners from the Harz region of Germany, probably because they were much more familiar with this type of vein ore with its peculiar mineralogy than the locals. In 1820, the discovery of significant mineralisation enabled a further 50 tonnes of ore to be extracted and sold to the "Blaufarbenwerk" at Schwarzenfels/Mottgers in Hesse, Germany. From 1849 to the end of 1852, the reopened mine produced 127.75 tonnes of ore in three and a half years, with grades ranging from

> 18% to 36% nickel and cobalt, averaging 14% nickel and 8% cobalt. Between 1853 to 1858, 51.2 tonnes of ore with a grade of 20% nickel and cobalt were mined… Grand-Praz was the first mine in the Val d'Anniviers to be exploited intensively. In brief, between 1780 and 1858, almost 280 tonnes of ore with an average grade of 14% nickel and 8% cobalt were extracted. [Meissner 2003, 60-61]

These high nickel contents, combined with the fact that the mine was exploited in the 1780s, make this mineral a potential candidate to explain the high nickel contents found in the glass of beads from La Réunion and the *La Boussole* shipwreck at Vanikoro.

The Val d'Anniviers also hosts several veins rich in bismuth, which were mined in the Saint Luc district in the mid-19th century (Meisser 2003). It is important to note that the Ni-Co-As-Bi-Ag-U co-occurrence is common for the mineral deposits exploited for cobalt in Europe and that these are not specific to any particular geographical area.

In addition to the mineralogical data of the cobalt deposits exploited, other authors have compared different ways of production of smalt and zaffre (saffron) and described their main characteristics. For example, in 1855, Atherton (1855) mentions that zaffre/ore from Saxony contains cobalt, iron, arsenic, nickel and bismuth, while zaffre/ore from Norway contains cobalt, iron, arsenic and copper. He also states that zaffre from Saxony contains much less iron than Norwegian zaffre.

Analyses of the smalt particles present in Dutch papers produced before 1780, in which the smalt can be assumed to be of Saxon origin, and those produced between 1827 and 1839 by the BCW in Norway, highlight the considerable variability in the composition of these productions, and also show that the differences highlighted by Atherton probably relate to well-dated production batches and cannot be generalised to all productions over time (SP and NP are used below for Saxon and Norwegian productions, respectively). For example, we do not observe any real difference between the two productions in the contents of iron (Fe_2O_3 1.8 ± 0.4 for SP vs 1.8 ± 1.0 for NP); nickel (NiO 0.32 ± 0.12 for SP vs 0.34 ± 0.14 for NP); or copper (CuO 0.07 ± 0.02 for SP vs 0.05 ± 0.004 for NP). The measured values for arsenic and bismuth are higher in the Norwegian productions (As_2O_3 9.8 ± 4.0, Bi_2O_3 0.66 ± 0.12%) than in the Saxon ones (As_2O_3 3.2 ± 2.1, Bi_2O_3 0.13 ± 0.24%).

The chemical elements present in cobalt mineralisation and traditionally used to differentiate cobalt sources until the 18th century (Ni, Zn, As, Mo, In, Pb, Bi, U) therefore seem to be less relevant for distinguishing the different smalt productions from the end of the 18th century onwards. It therefore could be appropriate to turn to other geochemical markers that can help differentiate the cobalt ores used, such as REEs.

Assuming that smalt is produced from quartz, potash and cobalt ores, it can be assumed that any REEs present in smalt will be derived mainly from the cobalt ores or, rather, the residual rock present in the cobalt gangue, rather than from the other constituents. The REE content of quartz and potash can be considered negligible.

Looking at the distribution profiles of the REEs normalised to Earth's continental crust (ECC; Wedepohl 1995) in the smalt particles present in the Dutch papers and those produced by the BCW (Fig. 5.5), we can see that the smalt particles have very different profiles. While some particles contain virtually no REEs and have relatively flat profiles, others contain higher concentrations and have very pronounced profiles, with a strong positive anomaly for medium-heavy and heavy REE (Fig. 5.5). Regardless of the origin of the smalt particles, the minimum and maximum content ranges from 1.3 to 47.9 ppm for lanthanum; 2.6 to 105.2 ppm for cerium; 0.4 to 50.7 ppm for dysprosium; and 0.2 to 23.3 ppm for erbium. This type of profile, with enrichment in yttrium, medium-heavy and heavy REE appears to be characteristic of some cobalt mineralisations (Decree et al. 2015; Slack 2012), but not of Saxon or Norwegian smalt. The same type of profile (Fig. 5.5) was already shown in the cobalt-blue Egyptian glass ingots from the Bronze Age shipwreck off the coast at Uluburun, Türkiye (Lankton et al. 2022). The REE concentrations appear to be directly related to the alumina content of the smalt particle, and therefore probably to the residual amount of gangue mineral in the cobalt ore concentrate.

Two main REE profiles are observed for the smalt particles present in the Dutch papers analysed. The first concerns two papers from 1755 and 1758. It is characterised by a strong samarium-positive anomaly followed by a europium-negative anomaly. The second, present in two other papers from 1794/95 and 1815, does not show this negative europium anomaly and has a different shape of distribution between gadolinium and lutetium. The REE profiles of the smalt produced by the BCW in 1827, 1834 and 1839 are remarkably similar to those of the Dutch paper from 1794/95 and 1815.

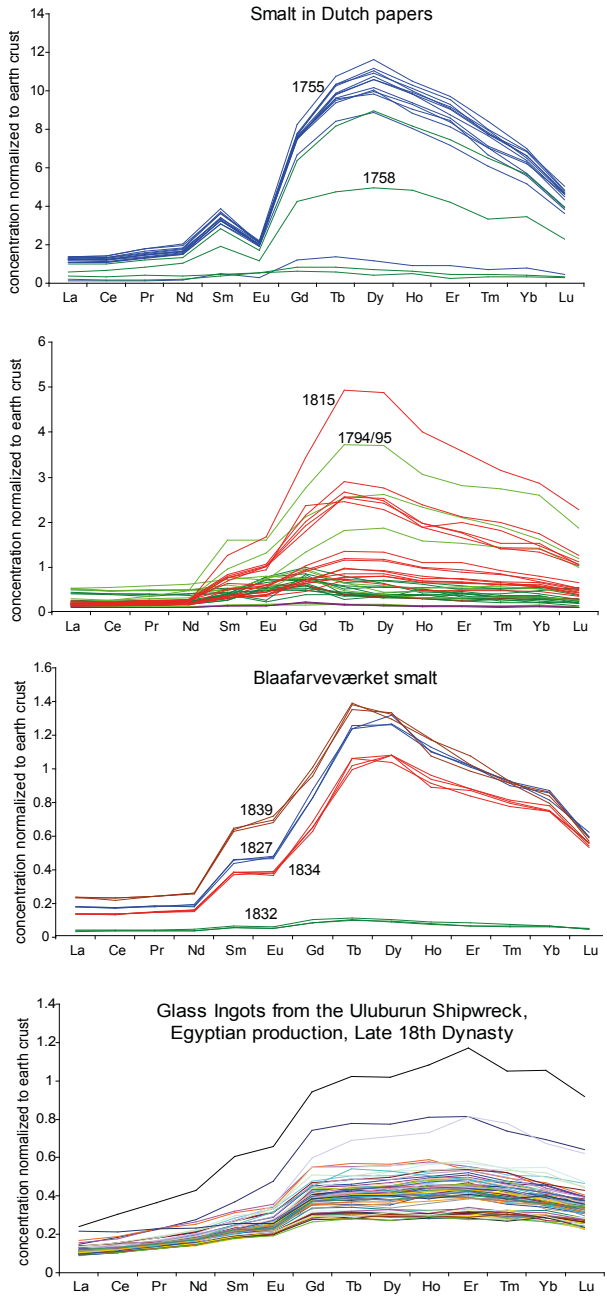


Figure 5.5: Rare earth element profiles (normalised to Earth's continental crust, ECC; Wedepohl 1995) for smalt particles found in Dutch papers or produced by the Blaafarveværket factory in Modum, Norway, between 1755 and 1839, compared with those of the cobalt-blue glass ingots from the Uluburun shipwreck, Türkiye.

We must remain cautious when interpreting the REE profiles and must bear in mind that the import of ores other than those from the Schneeberg region by the Saxon smalt works could lead to the existence of several REE profiles within the Saxon productions. However, if we consider that the first export of smalt from the BCW took place in the mid-1780s, we cannot help but make a connection between the REE profile of the Dutch papers of 1794/95 and 1815 and the smalt particles produced by the BCW.

There are two main difficulties in extrapolating the results obtained on smalt particles to cobalt-blue glass. First, the dilution factor of smalt in glass varies greatly, and can range from 5 to 100 for a glass containing 500 ppm cobalt oxide, according to the minimum and maximum cobalt oxide contents measured for the smalt particles analysed (CoO from 0.26 to 4.9%). Second, it is necessary to consider the superposition of the REE profiles of glass and smalt, as the REE profile of the smalt may be partially or completely masked by that of the glass if it contains high levels of REE or if the smalt used did not have a very distinctive profile.

The cobalt-blue glass beads from La Réunion and the *La Boussolle* shipwreck at Vanikoro (Fig. 5.6, top) are likely to have attenuated REE profiles. As noted above, the cobalt colourant used in this glass has a high nickel/cobalt ratio, which may be associated with certain Swiss cobalt veins. However, due to the low concentration of cobalt oxide (230 to 273 ppm) in the glasses, the REE profiles are not distinct in the beads discovered at Vanikoro. Moreover, some REE contents are close to the detection limit for the beads found at La Réunion.

In some cases, the cobalt-blue glass has REE profiles enriched in medium-heavy and heavy REE. This enrichment is probably due to the cobalt colouring agent. This type of REE profile (Fig. 5.6, bottom) is present in four out of five glass vessels analysed from Poitiers and Orléans (Buisson forthcoming; Buisson et al. 2023) that were decorated using the splashing technique (also known as pick-up decoration; Pulido Valente et al. 2021). The high cobalt content (CoO 0.39 to 0.89%) of the cobalt-blue glass layer present on the vessels suggests that the glass worker may have directly picked up pure or slightly diluted smalt to decorate these objects. The cobalt-blue glass is also characterised by high levels of barium (BaO 0.65 to 4.9%), similar to those found in the smalt particles in the Dutch papers of 1755 and 1758. Furthermore, the REE profiles of vessels Cars V38 and Cor V59 from Poitiers, and Orl 11 25 and Orl 25 5 6 from Orléans are comparable to those of the smalt particles in the same Dutch paper. It can be concluded that the smalt found in the four vessels and the two Dutch papers came from the same smalt factory. For the time being, we assume that this factory was probably located in the Schneeberg area.

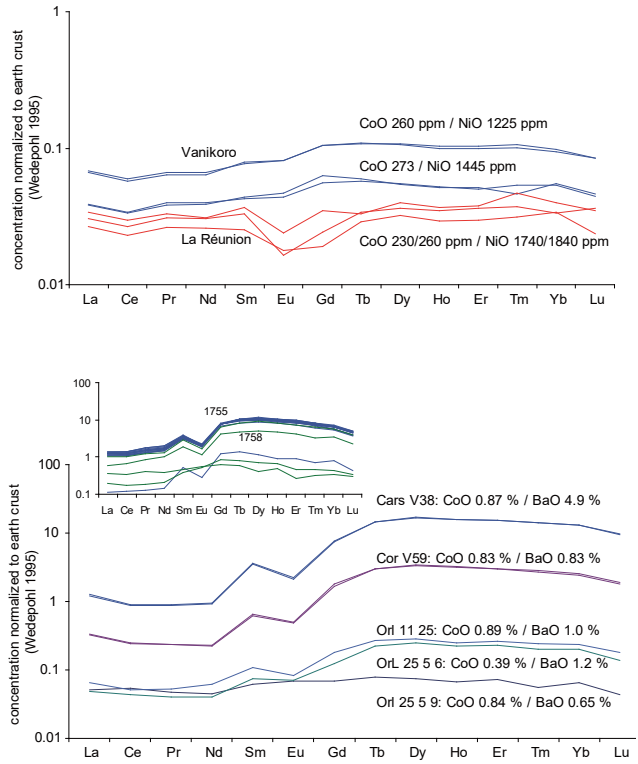


Figure 5.6: Rare earth element profiles (normalised to Earth's continental crust, ECC; Wedepohl 1995) for the 18th-century cobalt-blue glass bead from La Réunion (France) and Vanikoro (Solomon Islands) (**top**) and for some 18th-century cobalt-blue enamels used for splash decoration on glass from Poitiers and Orléans (France) (**bottom**), compared with that of smalt from Dutch papers of 1755 and 1758 (inset top of bottom).

Conclusion

Before the middle of the 18th century, it is relatively easy to trace the production of cobalt colourants such as zaffre and smalt. However, the situation began to change in the third quarter of the 18th century with the development of new production centres for smalt and the geographical diversification of cobalt mines exploited.

With the exception of one or two specific cases, the Ni/Co and As/Co ratios of cobalt-coloured vitreous materials do not show any significant variation after the third quarter of the 18th century. In addition, arsenic was added by glass makers as a fining, colouring and opacifying agent, making the element no longer useful for cobalt provenance studies.

The ratios of uranium, bismuth and barium to cobalt show greater variability. However, it is possible that glass objects used to define the Saxon Co-As-Bi-U compositional reference groups do not reflect the full diversity of Schneeberg cobalt ores over time, as they are based primarily on objects from the late 16th and mid-17th centuries.

An examination of REE profiles in smalt particles used to bleach Dutch papers reveals a difference between paper produced before and after the last quarter of the 18th century. Furthermore, the REE profiles of the smalt particles in papers dated from 1794/95 and 1815 are similar to the REE profiles of the smalt particles produced by the BCW.

Nevertheless, REE profiles of Co sources in glass objects can be diluted or obscured by the REE within the raw materials of the glass itself. Singular REE profiles can sometimes be observed in cobalt glass, and our data highlight that Schneeberg cobalt was still prevalent in Europe up to the mid-19th century. Late 19th and early 20th century glass appears to be characterised by the use of pure cobalt colourants, probably added directly to the glass as cobalt oxide.

Acknowledgements

Thanks to Vincent Serneels, Patrick Clerc and Lasse Hermansen Bjørnland for providing information on cobalt mining in Val d'Anniviers, Sainte-Marie-aux Mines and Modum, respectively. We are also grateful to Laure Dussubieux and Adelphine Bonneau for allowing us to use our joint data on French and Canadian cobalt glass beads for this paper.

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Chapter 6

The cobalt mine at Kashan, Iran: A brief overview of its history, from the pre-Mongol period to the early 20th century

Moujan Matin[1]

Introduction

In the history of West Asia, few mines are as well known as the cobalt mine in Kashan, central Iran. The extensive knowledge we possess about this mine, along with the numerous references to it in Persian and Chinese historical manuscripts, reflect its profound impact on the development of Islamic ceramics and the production of blue-and-white porcelain during the Yuan (1279-1368) and Ming (1368-1644) dynasties in China. Located in the village of Qamsar, southwest of Kashan, the mine was strategically close to workshops producing fine luxury ceramics in Kashan. The earliest application of the ore in ceramic decoration appears to date to the 12th century CE, when it was used on various Islamic underglaze-painted wares, lustrewares, and *mina'i* wares of Kashan. The expansion of Mongol rule into Iran in the 1220s temporarily disrupted production for a few decades. It soon resumed, with cobalt blue becoming even more prevalent, for instance as the dominant secondary colour on lustrewares and as the primary base glaze colour on *lajvardina* ceramics. As different parts of the Mongol Empire were governed by various descendants of Genghis Khan, the Ilkhanids in Iran and the Yuan dynasty in China, extensive trade and technological exchange facilitated the transportation of cobalt from Kashan to China. This exchange played a pivotal role in the emergence of one of the most influential ceramics globally: blue-and-white porcelain.

Archaeometric analysis has significantly enhanced our understanding of the use of cobalt from Kashan as blue pigment in ceramics. In the mid-20th century, as the field of scientific analysis of archaeological ceramics developed, primarily through the use of the X-ray fluorescence (XRF) facility pioneered by Edward Hall at the Archaeological Research Laboratory, University of Oxford, a set of 63 Chinese blue-and-white porcelain pieces, including some from Hall's personal

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collection, underwent analysis. Young (1956) published the results, highlighting the manganese-to-cobalt ratios to indicate various cobalt sources. Garner (1956, 48) subsequently proposed the use of an imported cobalt source, suggesting that "as far as fourteenth century wares are concerned, the Chinese had to rely entirely on imported cobalt, and it was not until later, possibly in the early fifteenth century, that native ore was discovered". Garner also mentioned cobalt ores in Persia as likely sources used in the earliest Chinese blue-and-white wares.

Allan (1973) published a seminal English translation of the final chapter of the Persian treatise entitled *Arayes-al jawaher va nafayes-al atayeb* (*The Virtues of Jewels and the Delicacies of Perfumes*), dated 1301, by Abu'l-Qasim Kashani. As a member of the Abu Tahir family, with generations of pottery workers in Kashan, he transitioned to become a historian in the Mongol court. In his treatise, he meticulously described various precious stones, metals, perfumes and other substances of the time, including the raw materials used by potters in Kashan, such as the cobalt minerals sourced from the mine in Qamsar. The English translation of this treatise therefore provided a new understanding for Western scholarship of the potential source of cobalt used in West and East Asia.

Archaeometric analyses of cobalt blue used in medieval Islamic ceramics were not conducted until much later, and even then, they were sporadic (Table 6.1). The most comprehensive analyses were carried out by Wen (2012), who employed portable XRF to conduct non-invasive analyses of a wide range of both Islamic and Chinese ceramics. These data, along with the various types of cobalt pigments suggested, have aided in establishing the extensive use of cobalt from Kashan. Wen (2012, 249-251) identified seven different categories of cobalt pigment compositions based on varying ratios of Co, Fe, Zn, As and Ni. Among these, the possible source of the cobalt-blue pigment applied to ceramics of Type D, characterised by the presence of iron (Fe); arsenic (As); and, occasionally, copper (Cu) was suggested to be Kashan.

Furthermore, various analyses of Chinese blue-and-white porcelain, published in both English and Chinese (see, e.g., Feng and BaoRu 2008; Wen and Pollard 2009; Wen et al. 2007), showed that the blue pigment used during the Yuan period and prior to the Xuande reign of Ming Dynasty (1426-1435) was characterised by high levels of iron and arsenic and low levels of manganese, while lacking zinc. This suggests that, like the Type D Islamic pigment, it likely originated from Kashan itself (Table 6.1). Kashan blue as used in Chinese blue-and-white porcelain usually imparts a distinctive hue, featuring a deep blue shade with a subtle black tint due to its iron content, which is discernible in porcelain from this period. The fate of Kashan cobalt in China beyond this period remains unclear. Cobalt compositions after 1426 CE appear to contain high manganese and low iron, and

it is uncertain whether at this time Kashan cobalt was combined with other sources or entirely replaced by Chinese local sources (see Matin and Title 2025, 63, 77).

Table 6.1: Cobalt source attributions in publications on ceramics with cobalt pigment belonging to the Fe-Co-As-(Cu) compositional type found in cobalt from the Kashan mine.

	Seljuq Iran	**Ilkhanid Iran**	**Timurid Iran**	**Safavid Iran**	**Qajar Iran**	**Fatimid Egypt**	**Ayyubid and Mamluk Syria and Egypt**
Gratuze et al. 1996			Samarqand (UGBP)				
Degli Agosti and Schweizer 2002				Unknown provenance (UGBP)			
Koss et al. 2009	Kashan (mina'i)						
Osete-Cortina et al. 2010		Takht-i Sulaiman (lajvardina tiles)					
Wen 2012	Kashan (lustre)		Unknown provenance (UGP and UGBP)				Unknown provenance (UGP and UGBP)
	Kashan (mina'i)						
Wen and Pollard 2014	Kashan (mina'i)						
Matin et al. 2020					Tehran (polychrome tiles)		
Matin 2022	Moshkin Tepe (monochrome stone paste)						
Holakooei et al. 2023		Takht-i Sulaiman; Rayy, Sultaniya, Yazd, Kashan (lajvardina tiles)					
Matin and Ownby 2023						FFS	

UGP: underglaze-painted; UGBP: underglaze-blue-painted; FFS: Fustat Fatimid sgraffito

Some of the earliest surveys of the Kashan cobalt mine were carried out by Schindler (1896, 114-116) and Ladame (1945, 196). Recent reports published by Stöllner (2004) and Matin (2013) provide detailed insights into the geological aspects of the mine, including its cobalt minerals and their compositions. Comparing the chemical compositions of the ore with those of cobalt pigments in Chinese and Islamic ceramics has helped confirm the source of the cobalt used.

Kashan cobalt in manuscripts

In medieval and late Persian manuscripts, cobalt is referred to as *lajvard*, the precursor to and equivalent of the Latin term *lazuli*. The Persian term *lajvard* originates from the village of *Laj* in Badakhshan, Afghanistan, renowned as a historical source of lapis lazuli (Zavush 1996, 207). Its association to cobalt arises from the lazuli hue that it imparts in ceramic glazes and glass. Determining whether *lajvard* refers to cobalt or lapis lazuli often depends on the context of the text. The distinction between the two is elaborated in folios 22b to 26b of the Persian manuscript MS.Ouseley.15 at the Bodleian Library, University of Oxford, which has not thus far been the subject of detailed study. The author explains that authentic *Badakhshi lajvard* comes from Badakhshan, and that *Kashi lajvard* (i.e. attributed to Kashan) or "working lâjvard" (*lajvard-i amal*) looks black like kohl (presumably indicating cobaltite within the magnetite-rich ore) and only reveals its true *lajvard* hue when fired in a kiln. Matin and Pollard (2015) provide a review of known Persian accounts from the early 14th to the 20th century, as well as 19th and 20th-century European accounts on Iran, often referring to cobalt as *lajvard*.

In Chinese accounts, Kashan cobalt is usually referred to as either *Hui hui Qing* or *Hui Qing*, translated as "Mohammedan blue", or *Su Lai Man Qing*, presumably a Chinese transliteration of "Suleimani blue". Other variations, such as *Su Ma Li* or *Su Ma Ni*, occur in the records from the early Qing dynasty (1644-1911) and may be another transliteration of Suleimani or possibly a reference to Sumatra, Indonesia, a possible stop on the maritime road through which Kashan cobalt may have been imported to Jingdezhen, where Chinese blue-and-white porcelain was produced (see Feng and BaoRu 2008; Wang 1982; Watt 1979, 69-80; Wen 2012, 70-130).

Geology and mineralogy

The Kashan cobalt mine, located at approximately 33°48'N, 51°24'E, about 35 km southwest of Kashan and 7 km northwest of Qamsar, is associated with an intrusive microdioritic body penetrating Qom formation limestone (Fig. 6.1).

This intrusion has led to the formation of skarn zones, as well as vein-type ores. Mineralisation mainly occurs at the contact zone between the microdioritic body and the Qom formation. The cobalt mineralised vein is about 210 m long and has an average width of 2.5-3.0 m, striking approximately north–south along a main fault in the region, with a westward dip of 82° (Borna 1989, 18) (Fig. 6.2).

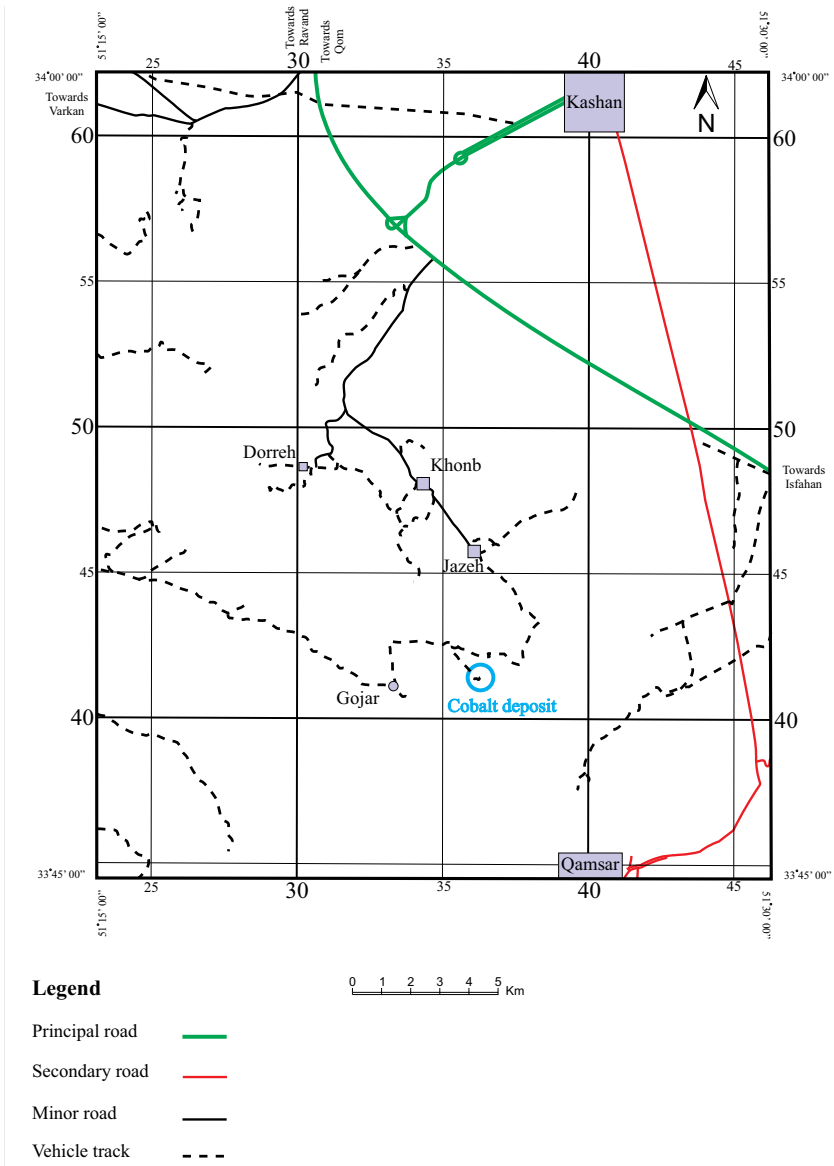

Figure 6.1: Sketch map showing routes through the cobalt mine of Qamsar, Kashan.

Figure 6.2: Photograph of an outcrop of the main mineralised vein of the cobalt mine of Qamsar, Kashan.

The primary constituent of the ore is magnetite (Fe_3O_4), adding a significant impurity to the final cobalt pigment. The main cobalt mineral in the vein is cobaltite (CoAsS), characterised by fine-grained, silver-coloured crystals dispersed within magnetite veinlets (Fig. 6.3a). In the upper oxidised zones of the ore body, cobaltite is replaced by erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), a secondary mineral formed through cobaltite oxidation (Fig. 6.3b). Erythrite appears as extensive pink coatings, known as cobalt bloom, often filling fractures. Pyrite and chalcopyrite are also present in the ore, occasionally introducing copper into the final pigment composition.

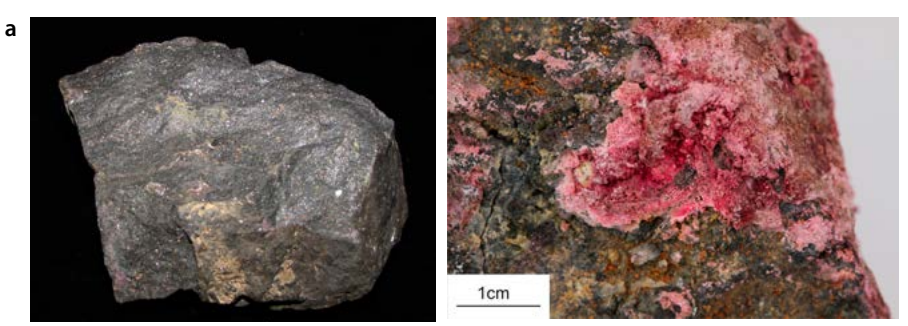

Figure 6.3: Photograph of the main cobalt minerals: (**a**) cobaltite; and (**b**) erythrite.

Ore treatment process

Various accounts describe the processing and preparation of the ore. According to these sources, ore processing involved two main stages: crushing and grinding, followed by a washing process. Zarrabi provided a detailed account of the process:

> They first take the stones out of mine, crush and grind them [on a piece of rock], and then pour them in big jars of water. The gangue, which is the heavy sediment, precipitates quickly, and then the water suspension is poured in another jar. After a couple of hours, the *lajvard* [cobalt-bearing mineral] sinks to the bottom and the water becomes clear. The cobalt compounds are then collected, and when losing some of their water, they are rounded up and left to dry. They are then transported to Kashan and some other cities and are sold to monument painters and others at the price of one to five thousand *tomans*, or less, per one *mann* [roughly 3 kg]. It does not have a certain price; each year they sell it at a different price. [Zarrabi 1878, 226]

Schindler (1896, 114-116) also mentioned this process as the "top water and bottom water" method (referred to as *sar-i ab va bun-i ab* in Persian). Matin and Pollard (2017) conducted preliminary experiments to replicate these processes based on Zarrabi's description. As shown in Figure 6.4, after crushing and grinding of the ore, the resulting powder was poured into a tall container and given an optimal

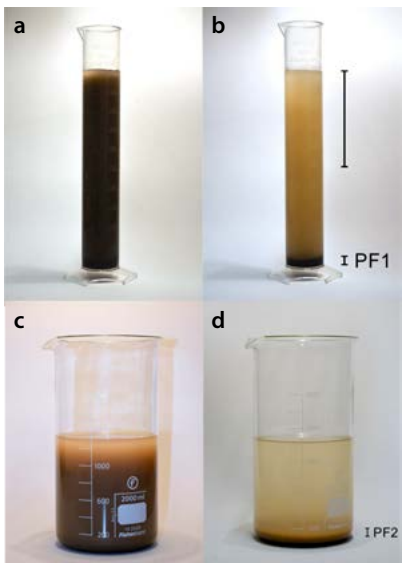

Figure 6.4: Photographs showing the stages of the ore washing process: (**a**) ground ore powder is added to water; (**b**) heavy minerals precipitate (PF1); the top suspension is collected and poured in another container (**c**); the collected suspension is given ample time to precipitate (**d**), after which the final precipitation (PF2) is gathered and left to dry.

amount of time that allowed quick separation of heavy magnetite minerals (PF1) and floatation of lighter erythrite minerals (top suspension in Fig. 6.4b). Although the aim was to remove magnetite, the mineral cobaltite, being denser, precipitated along with the magnetite, resulting in its removal rather than enrichment.

Subsequently, the top water suspension enriched in the lighter mineral erythrite was separated and transferred to another container, where it was allowed ample time to completely precipitate (PF2). The final precipitate was collected and left to dry. The efficacy of this washing process was determined by factors such as ground ore powder grain size, container shape and volume, and the optimal precipitation time. Matin and Pollard's (2017, 73) experiments showed that the final precipitation was enriched in cobalt by 4 times compared with the ore (4.9 wt% CoO in final precipitation compared with 1.2 wt% CoO in the ore) (Fig. 6.5).

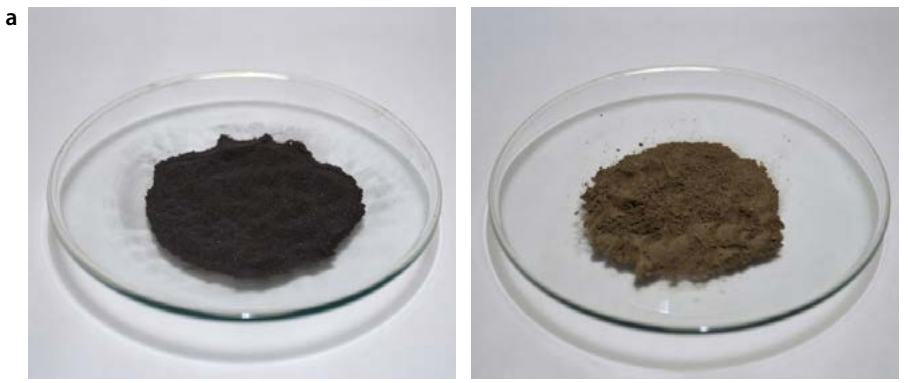

Figure 6.5: Photographs of (a) ground ore powder; and (b) the final result of the washing process (PF2).

During a survey of the mining site, various sherds of glazed coarse pottery were found that may have been used as containers for the washing process (Fig. 6.6). Historical accounts (Matin and Pollard 2015) suggest that the final powder may have been mixed with grape treacle and shaped into balls of approximately 1 *charak* weight (1.5 pounds, 680 g), as specified by Wulff (1966, 163), before being transferred to pottery production sites.

Figure 6.6: Photograph of pottery sherds from large jars that were presumably used for the washing process, scattered across the mining site at Qamsar, Kashan.

Chinese sources describe a slightly different process, involving density separation along with magnetic separation to eliminate impurities. The English translation of *Tao shuo* (*Discussion on Ceramics)* (preface dated 1764) documents this process:

> The *Mohammedan Blue*, which when broken with a hammer exhibited cinnabar-red points, was called "First-class Blue" [presumably erythrite], that which had silver stars being called "Medium Blue" [presumably cobaltite]. Every catty [16 ounces] of the raw material yielded three ounces of blue. After the blue had been crushed and the larger pieces picked out, the remnants and fine powder were treated with water, holding in suspension magnetic iron ore, to draw out the impurities which sank with it to the bottom. From each sixteen ounces by means of this process, another five- or six-tenths of an ounce of true blue could be extracted. [Bushell 1910, 69]

At the pottery sites, further processing of the enriched cobalt powder took place, as mentioned in 19th and 20th-century accounts by the master potter Ali Mohammad Isfahani (1888, 7) and European observers, such as Rochechouart (1867) and Schindler (1896, 115-116). Ali Mohammad described a process of mixing the enriched cobalt powder with borax, placing it in an earthenware vessel in a kiln, and breaking the vessel once cooled to obtain a silver-like substance. This

substance was then mixed with the original enriched cobalt powder and silica in equal proportions to prepare the blue pigment (Matin and Pollard 2015, 2017, 737-740). Rochechouart (1867, 320) described a process of mixing the enriched cobalt powder with borax and grape treacle, while Schindler (1896, 114-116) suggested a combination of borax, potash and grape treacle. Pilot experiments conducted by Matin and Pollard (2017) demonstrated phase separation, with dispersed, silver-like cobalt compounds evident within the borosilicate glass matrix formed after firing. Within this glass phase, the iron content dissolved as a flux. However, these experiments did not yield a consistent cobalt phase visible to the naked eye in the sample.

Ownership and decline of the Kashan cobalt mine

Information regarding the ownership and organisation of labour at the Kashan cobalt mine is scarce. Kashani's manuscript from the Ilkhanid period suggests that people assumed the mine was the property of the Prophet Suleiman, and little information was available until the 20th century. In November 1923, three members of the Lajvardi family of Kashan penned a letter to the Iranian parliament, asserting their ownership of the *lajvard* mine and expressing dissatisfaction with governmental intervention in mine affairs (Library of the Iranian Parliament, Acc. No. 464161). The English translation of the section of the letter relevant to the cobalt mine of Kashan is given below:

> The *lajvard* mine of Qamsar, Kashan, was given to our ancestors during the Safavid period. It has been under our ownership ever since, and various commercial transactions have been carried out. The mine is now divided into 482 shares among the Lajvardi family. The mine was so tied to our ancestors' interests that we became known because of the name of the *lajvard* mine and are now well known by the name Lajvardi throughout the country, especially in Tehran. Formerly, the products of the mine, which were only two colours of light and dark blue used for painting and pottery decoration, had purchasers and the family made a living from selling these products. This was until recently when pigments started to be imported from Europe. The pleasing, original colour was no longer used, due to its higher price, and similar western pigments were instead used by painters and potters. The government's restrictions on the importation of these new pigments were not successful, hence the mine remained under the earth. Now it has been a while that the representative of the Ministry of Public Benefits intends to seize the mine, and now and again he whispers

> something about plans to rent out the mine. However, no one would rent it that easily since it is not in an operational state. Indeed, the members of the Lajvardi family have not been able to use the mine for almost thirty years. [Anon. 1923]

The exact cessation date of the mining operations remains uncertain. Wulff (1966) mentioned the exploitation of the mine by a local family based on his 1936-1941 observations. A conflicting account by Bazl (1965, 1704) relating to 1939 suggests that the cobalt mines near Kashan had ceased operation around 40 years prior to their observations. Andrews (1962) noted the absence of cobalt ore production in Persia over the past century, despite significant ore reports in 1930, particularly between Isfahan and Yazd in the central region. Poor communication infrastructure has been cited as a contributing factor to the lack of ore development.

Another cobalt mine in Isfahan, as referenced by Andrews (1962), is situated in the Anarak area of central Iran, known for the occurrence of "five elements group" mineral deposits. These deposits exhibit enrichments in cobalt, nickel, arsenic, silver and uranium. Key cobalt and nickel deposits within Anarak include Mes-kani, Talmessi, Gowd-i Morad, Shebarz, Chahshur, Cheshmeh Ab-i Shoorab and Cheshmeh Karim, as documented by such sources as Ghorbani (2013) and Mazaheri Kuhanestani et al. (2013). Among these, Mes-kani and Talmessi are particularly well known as significant sources of cobalt and nickel, as highlighted by Ladame (1945), Andrews (1962), and Khoei et al. (2009). The Co/Ni ratios in ores from Mes-kani and Talmessi exhibit considerable variation, ranging from 1:0.3 to 11:35.4, as reported by Khoei et al. (2009).

The Anarak mines' history still remains largely unexplored, and there is limited information available. However, it is plausible to consider it as a potential source for Ni-Co blue pigments used in the Islamic world, similar to those found on Abbasid blue-on-white painted Samarra-type pottery from the early Islamic period (see Kleinmann 1991; Wood et al. 2007).

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Chapter 7

Cobalt mining at Alderley Edge, Cheshire, UK

Nigel Dibben[1]

Introduction

In 2021, a shaft previously unknown to the local community opened in a field at Alderley Edge, Cheshire, England. The shaft had been spotted by a ranger working for the National Trust, the landowner. The National Trust is a registered charity in England with the purpose of protecting properties and countryside. The National Trust leases the mines on its property at Alderley Edge to the Derbyshire Caving Club (DCC), an amateur organisation dedicated to exploring and recording disused mines and natural caves. The National Trust asked the DCC to secure and explore the shaft, which was subsequently identified as an extension to a known cobalt mine. The find created considerable interest locally and nationally as it gave access to a section of the mine undisturbed since it had been abandoned in the early 19th century. This paper provides the geological and historical background to mining at Alderley Edge. It then provides the history of cobalt mining at Alderley Edge, so far as this can be elucidated from contemporary publications and observation on (under) the ground, in greater detail. Following this history, it describes and illustrates the known cobalt workings, as rediscovered by the DCC from 1980 to the present.

Geological background

Alderley Edge is the name given to a town and a hill feature in the northeast of Cheshire, about 10 miles south of Manchester and 3 miles west of Macclesfield. The Cheshire-Shropshire basin is a Triassic subsidence feature approximately 100 km north–south by 55 km west–east, stretching from south of Manchester to north of Shrewsbury (Plant et al. 1999, 12). The centre of the basin is at approximately 100 m above mean sea level (ASL) and is formed from a post-glacial lake

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surrounded by hills to approximately 200 m ASL developed along a range of faults surrounding the basin.

At Alderley Edge, there are faults running roughly north–south to the west and east of the high ground. The western fault downthrows on the west side, whereas the eastern fault downthrows on the east side, leaving the Alderley Edge "hill" as a horst block of sandstone, conglomerate and clay. The uplifting of this block has meant that the mines excavated within it are above the surrounding land and therefore substantially well drained.

Within the block, the strata dip down to the west towards the centre of the "basin" at an angle of approximately 12 degrees from the horizontal. The mines have been developed in the top 30 m or so of the landform, and, as a result, each of the major mines is developed in a different stratum. The mined strata are within the Helsby Sandstone Formation and Wilmslow Sandstone Formation in the Sherwood Sandstone. Table 7.1 shows the hierarchy of rock units as per the British Geological Survey, together with their designated acronyms (DCC 2023; British Geological Survey 2023; Plant et al. 1999, 13).

The principal ores found at Alderley Edge are those of copper, with those of lead a close second. These ores are derived from sulphides formed in the northwest–southeast faults found across the fault. They were mined as sulphides up to the mid-19th century and then as carbonates found adjacent but away and usually down-dip from the faults. The cobalt-bearing ores are principally found along a range of north–south faults on the eastern side of the horst block, although traces can be seen in mines farther west. A wide range of minerals have been identified at Alderley Edge over time, and there is a summary list in Carlon and Dibben (2012), part of which is reproduced in Table 7.2.

Table 7.1: Geological classifications. Rocks present at Alderley Edge are shown in italics (after British Geological Survey 2023).

Super-Group	Group	Formation	Member	Description	Presence at Alderley	Age
New Red Sandstone (NRS)	Mercia Mudstone (MMG)	Sidmouth Mudstone (?)	Northwich Halite (NWH)	Halite with partings of mudstone	Not present	Anisian
		Bollin Mudstone (?)	Bollin Mudstone	Siltstones, mudstones and sandstones	Not present on Edge but abutting to east	Anisian
		Tarporley Siltstone Formation (TSF)	Tarporley Siltstone	Siltstones, mudstones and sandstones	Not present on Edge but abutting to east	Anisian
	Sherwood Sandstone Group (SSG)	Helsby Sandstone (HSF)	Nether Alderley Sandstone (NASM)	Fluvial sandstone		Anisian
			West Mine Sandstone (WMSM)	*Aeolian >> fluvial*	West Mine (aeolian)	Anisian
			Wood Mine Conglomerate (WMCM)	*Sandstone with sporadic conglomerates, particular towards the base, and siltstones*	Wood Mine (fluvial)	Anisian
			Beacon Lodge Sandstone (?)	*Sandstone with sporadic conglomerates, particular towards the base, and siltstones*		Anisian
			Engine Vein Conglomerate (EVCM)	*Sandstone with sporadic conglomerates, particular towards the base, and siltstones*	Engine Vein	Anisian
		Wilmslow Sandstone (WSF)		Sandstone with sporadic siltstones	Lower part of Engine Vein	Olenekian
		Chester Pebblebeds (CPBF)		Conglomerates	Not present	Induan

Table 7.2: Mineral species containing cobalt recorded and reported from Alderley Edge [* occurs at this locality; ? likely to occur but not yet proven] [Abundances: C = Common; UC = Uncommon; R = Rare; VR = Very rare]. Data compiled from Ixer and Vaughan (1982) and Braithwaite (1994).

	West Mine	Wood Mine	Engine Vein	Opencast	Stormy Point Mines	Elsewhere in the area	Abundance
Primary Minerals							
Cobaltite (Co,Ni)AsS			*		*	*	UC
Pararammelsbergite (Ni,Co)As_2			*		*		R
Bravoite (Ni,Fe,Co)S_2	?	*	*	?	*		C
Secondary Oxides							
Erythrite $Co_3As_2O_8.8H_2O$		*	*		*		VR
Wad and asbolite (asbolane) mainly Mn,Co,Ni complex oxides	*	*	*	*	*	*	C

History of the Alderley Edge mines

The earliest traces of mining at Alderley Edge date to the Early Bronze Age, evidenced by hammer-stones and a wooden shovel (Table 7.3). The hammer-stones were found during excavation in an abandoned mining area in 1872 (Boyd-Dawkins 1875, 1876). At about the same time, a wooden shovel was found in an old working (Sainter 1878). Although the finders had no means of dating these items, their antiquity was recognised at the time, and a more detailed examination of the mine was carried out in the early 20th century (Roeder 1901; Roeder and Graves 1905), bringing to light a large number of hammer-stones. At the time, one theory was that these were evidence of Roman mining (Roeder and Graves 1905). In 1992, the wooden shovel recorded in 1878 was donated to Manchester Museum (Garner et al. 1993; Timberlake and Prag 2005). It was subsequently carbon dated to 1888-1677 BCE (Timberlake and Prag 2005, 36), providing the first clear indication of Bronze Age mining. This and the finding of Roman activity led to a research project and archaeological investigation, which found further evidence of Bronze Age mining in smelting pits with carbon residues dated to 2280-1890 BCE (Timberlake and Prag 2005, 41). The mining appears to have been concentrated on copper carbonate ores (malachite and azurite) for extraction of copper metal, although mining for the same ores for pigments remains a possibility.

Table 7.3: Timeline of Alderley Edge mining and relevant legislation.

c. 1900 BCE	Date obtained from charcoal found in smelting pit at Engine Vein
1750±50 BCE	Date obtained from wooden shovel found at Brynlow
c. 75 BCE	Date obtained from timber in Roman workings
300-320 CE	Age of coins found at Engine Vein in Roman hoard
1598	Reference to "myne holes" in parish boundary walk
1688	*Mines Royal Act* 1688 enacted
1693	*Royal Mines Act* 1693 enacted; Mr Legh of Ridge
1696	Mr Crosse and others; dispute with Mr Legh
1700-1710 or 1730s	Area may have been mined by a Mr Abbadine
1758-1768	Charles Roe and Macclesfield Copper Company
1764	JW marked initials in Brynlow
1770s?	Mr Whitfield and Mr Heaton prospecting
1780s	Mr Patten from Warrington; Wizard Restaurant built, known at the time as "Miners Arms"
1791	Mines were working for copper and lead
1804	Exploration by James Ashton
1 January 1805	Lease to Ashton and others for 14 years (Alderley Mine Company)
1806	Cobalt recognised at Alderley
1807	Steam-powered crusher installed in Windmill Wood
1800s	Surgery may have been built as mine office
1808	Agreement to sell cobalt to a Yorkshire pottery
1809	Experiments with cobalt ore in Wallasey
1810-1811	Alderley Mining Company dissolved
1857	Area investigated by James Michell
1858	Lease taken out (12 April 1858); opencast mining at West Mine
1859	Alderley Edge Mining Company Limited incorporated (13 August 1859)
1861	Visit by British Association
1862	Michell killed by fall in mine (November 1862)
1863	West Mine crossing "Great Slide'
1864	Possible opening of Wood Mine
1865	Change of proprietors; visit by Japanese and Stanley family
1866	"GL" marked initials in Brynlow
1869	Richer ore being worked
1870	Substantial drop in output
1872	*Metalliferous Mines Regulation Act* 1872 enacted
1873	Drop in quality of ore
1874	Working in Field area; Boyd-Dawkins visit; wooden shovel found
1877	Boiler explosion and mine closed
1878	Sale of effects and company wound up (24 May 1878)
1911-1912	Alderley Mining Company Limited operating
1914-1915	Allan Gibb (300 tons of ore, 35 tons of precipitate)
1916-1917	Only one caretaker at mines
1918-1919	Alderley Copper Company Ltd operating
1926	Sale of effects; end of mining

In 1995, excavation work by the DCC led to the discovery of a pot of Roman coins from the 4th century CE. As soon as these coins were recognised, the excavation ceased until there was an archaeological excavation of the shaft in 1997 (Timberlake and Prag 2005), from which timbers were recovered and carbon-dated to 360-280 BCE or 250 BCE-15 CE. Charcoal in the shaft was dated to c. 50 CE and this is believed to reflect the working period more accurately (Timberlake and Prag 2005, 89). The Roman shaft and level appear to have been mined to undercut and drain the Bronze Age workings, which were likely to have been inundated with water at the time.

After the Roman era, there is no clear evidence of mining until 1693, a significant date in English mining as, at this point, the monopoly on Mines Royal—copper and other mines potentially yielding silver and gold; defined in Pettus (1670)—was lifted and mining restarted in many locations (HMG 1693).

From this time on, mining took place at intervals throughout the 18th century. In the early 19th century, in 1805, mining resumed and then ended around 1814. In 1857, the site was explored by a Cornish miner and smelter, James Michell, who, with the help of chemist William Henderson, applied the wet method (using hydrochloric acid) to the extraction of copper from malachite-impregnated sandstone to the ores at Alderley Edge (Henderson 1860). This operation lasted from 1857 to 1877 and was profitable throughout (Warrington 1981). The last (brief) period of working was from around 1911 to 1919, and although a new processing plant was built, the extent of underground working appears to have been very limited and work was sporadic during this period (Russell 1919).

Cobalt mining at Alderley Edge

In 1804, James Ashton, a Derbyshire miner, searched the Edge, and in consequence of his representations, a company was formed to work the mines. The parties were "James Ashton himself, Mr. Bury and Mr. Dodge, of Stockport, Messrs. Horne and Stackhouse, Dr. Jarrold &c. A lease of the mines was taken for fourteen years from January 1, 1805" (Stanley 1843, 36). The names Stackhouse and Horne do not appear in the later, 1808 lease, but they were still associated with the cobalt industry when their bankruptcy was announced in 1820 (Anon. 1820).

Cobalt ores were first discovered in the neighbourhood around 1806, by a miner who had worked on the Continent and seen the cobalt ores of Saxony (Bakewell 1811). They may have been observed first at Mottram St Andrew, a village close to Alderley Edge with mines in the same formation (Bakewell 1811, 9; Holland 1808, 17). The finding of cobalt was reported by Henry Holland in his survey of Cheshire (Holland 1808, 16) and by Sowerby (1811, 69). As a result, the Stockport

Company, which had leased the Alderley Edge mines from Sir John Thomas Stanley in 1805, searched for cobalt on their property. In 1806, samples were sent to pottery works owner Josiah Wedgwood II, but the result of this interaction appears to have been rejection (Prag 2016, 383). Nevertheless, in October 1807, Lady Stanley wrote that "1.000*l* per annum (the symbol *l (lower case L) was used to represent the pound currency £ at this time*), plus a tonnage payment for all in excess of a certain amount," had been offered for the Alderley ore and that "this year the concern will begin to be profitable, though I do not expect my diamond necklace quite yet; when the Man has made 5,000*l* by the mine, I am to have a very handsome one" (Stanley 1899, 297-298). It emerged that in 1808, Sir John Thomas Stanley had let the "cobalt mines" lease for £1,000 to Mr Plowes of Ferrybridge, 3 miles from Pontefract, in West Yorkshire (Stanley 1843, 36). Mr Plowes was part of a pottery firm at Ferrybridge, Yorkshire, known then as Tomlinson, Plowes & Co. but also referred to as Seaton and Plowes [Plough] (Meteyard 1871) and later as John Plowes & Co. (Anon. 1813).

In 1811, John Seaton, John Fox Seaton and Robert Seaton of Seaton, Plowes and Co were declared bankrupt, and in the notice of the meeting of creditors (Anon. 1811), reference is made to the "Smalt or blue concern" formerly carried on by the pottery at Ferrybridge. Newspaper advertisements in 1813 (Anon. 1813) offer for sale the equipment and stock-in-trade of "John Plowes & Company, Ferrybridge", including 35 tons of British-made smalts.

When this outlet became unavailable to the Alderley Edge Mines, the lease was returned to the Stockport Company, who, still finding sufficient cobalt, established a smalt works at Wallasey Pool, on the Mersey, where a considerable quantity was bought and sold. There is evidence in the Stanley letters that cobalt ore had already been sent to Liverpool before the failure of John Plowes and Company; in October 1809, Sir John Stanley was in Liverpool to be present at an experiment upon the cobalt ore (Stanley 1899, 322). This is also a reference to the "Seacombe [sic] Company" (Stanley 1899, 337). The smalt works were eventually closed due to competition from overseas cobalt supplies and to the surcharge placed on the smalts manufacturing works by His Majesty's Excise for glass duties at the end of the Napoleonic Wars (Hunt 1884, 259). The Secombe works are believed to have continued processing cobalt ores after being taken over by Mawdsley and Smith in 1820 (Anon. 2020).

Identifying the cobalt mines at Alderley Edge

In the 1970s, a descent was made of a well behind the Wizard Inn at Alderley Edge, but apart from the observation of a side passage, no further discoveries were made. In 1984, with a fresh set of explorers active in the DCC, another visit was made to the well, and this time the side passage was found to connect with some previously unknown mine workings. These were explored, access to them was improved, and a survey was made (Johnson 1984, 17). The mine was initially named the Wizard's Well Mine and was recognised as being developed on a north–south alignment. It was also recognised at the time that the mine may have been the cobalt mine referred to in the literature. Work on the exploration of the accessible parts of the mine continued over the years until it was found to extend for approximately 140 m (north–south) on various levels. The total surveyed length at this stage was 170 m, with a maximum depth of 18 m below surface (Dibben 2006). The mineralisation in the mine was examined by sample (Carlon, personal communication) and by portable XRF in situ (Timberlake and Mills 2003). The former gave results of around 150 ppm cobalt and 1500 ppm manganese, amongst other species, while the latter, which sampled a number of locations, gave results ranging from 300 ppm to 3000 ppm cobalt. The XRF results suggested that a yield of up to 0.3% could be possible.

The findings in 2021

In 2021, a new hole appeared in a field approx. 100 m south of The Wizard and was noticed by the National Trust ranger, who notified the DCC. The DCC has more than 50 years' experience in securing, reopening and exploring the disused mines at Alderley Edge and works closely with the National Trust to keep the mines safe and to enable public access. The newly revealed shaft was capped with a locked lid by the DCC, and then infill was removed to a depth of 11 m. At its base, the shaft was found to connect with approx. 184 m of mine workings on one horizon (dipping gently down towards the south) (Fig. 7.1). These had not, apparently, been entered since the mine closed, as artefacts were found in relatively good condition in an atmosphere depleted of oxygen. There was a limited area of roof collapse, and two filled shafts were met and bypassed easily. The artefacts included leather shoes (Fig. 7.2a); a pottery bowl, internally brown glazed (approx. 170 mm in diameter and 110 mm deep) (Fig. 7.2b); clay (tobacco) pipes (Fig. 7.2c); and a windlass roller complete with winding handle, rope and hook (Fig. 7.3).

In addition to the artefacts, there was some graffiti, the most interesting of which was the wording "WS 20th Aug 1810", written with candle smoke on the

roof close to one of the shafts to the north of the section (Fig. 7.2d). There is little doubt that this is original (the day was a Monday), although no names have been associated with the initials. Another date, 1811, was found written near the shaft towards the south end. There are also initials, such as "RB" (twice) and "JP co", which may represent the start or end of "JP's" work. Access to the discovery was restricted from the start to protect the environment and the artefacts; access will in due course be closed completely. The find created considerable interest in historical mining circles (NAMHO 2023, 6-8), the archaeological press (Hilts 2022), and the national press (e.g. Anon. 2022). The extension to the mine was surveyed by members of the DCC, and the main survey of the mine was updated (Fig. 7.7) (Dibben 2012).

The National Trust (owners of the site) organised a survey of the mines using laser scanning, leading to the creation of both a "fly-through" video and a 3D image of the extension. With the support of the National Trust, part of an episode of a British archaeological reporting programme, "Digging for Britain", was filmed at the Lockdown Shaft and in the mine (Fig. 7.4) and subsequently broadcast on 8 January 2023.

Figure 7.1: Photograph of a typical section of the newly opened part of the Cobalt Mine at Alderley Edge, with props, deadwalling and smoke from candles; the ore is visible in thin layers below the ceiling (photograph by Ed Coghlan).

Figure 7.2: Photograph of artefacts from Alderley Edge: (**a**) shoe; (**b**) bowl; (**c**) clay pipe; and (**d**) graffiti (photographs by Nigel Dibben).

Figure 7.3: Photograph of the windlass in the Cobalt Mine (Lockdown Shaft section) at Alderley Edge with rope and hook attached. The handle may be T-shaped or may have had a handle at the end of one branch of the T (photograph by Nigel Dibben, 9 November 2021).

Figure 7.4: Photograph of programme presenter Alice Roberts (left) talking to Derbyshire Caving Club member Ed Coghlan (centre) during filming at Alderley Edge by the camera operator (right), who is using an iPhone for the filming (photograph by Nigel Dibben, 29 August 2022).

Processing the ore

The cobalt ore was not fully processed on-site. It appears from observation in the mine to have been a soft material easily separated from the country rock (sandstone). The cobalt mineral, a black oxide of cobalt, was separated from the other minerals as far as possible and packed into barrels (Bakewell 1811, 9). The barrels were sent to the processor (for example, Plowes at Ferrybridge), where the blue cobalt oxide was produced and manufactured into "zaffre" and smalt.

Zaffre was a fused mixture of cobalt oxide and flint used to impart a blue colour to pottery. Smalt was pulverised glass made of cobalt oxide, silica and potash, used to give paper a blue tint.

The mines from south to north

In time, the DCC realised that the mineralised region could be traced northwards from Finlow Hill wood, about 350 m south of The Wizard, across the western end of Engine Vein (200 m north of The Wizard), and up to Saddlebole in the north of Glaze Hill (800 m north of The Wizard). All along this length, cobalt minerals have been found. Actual and probable cobalt workings are marked on Figure 7.5. All names here are modern names assigned by the DCC in the absence of any known historical names.

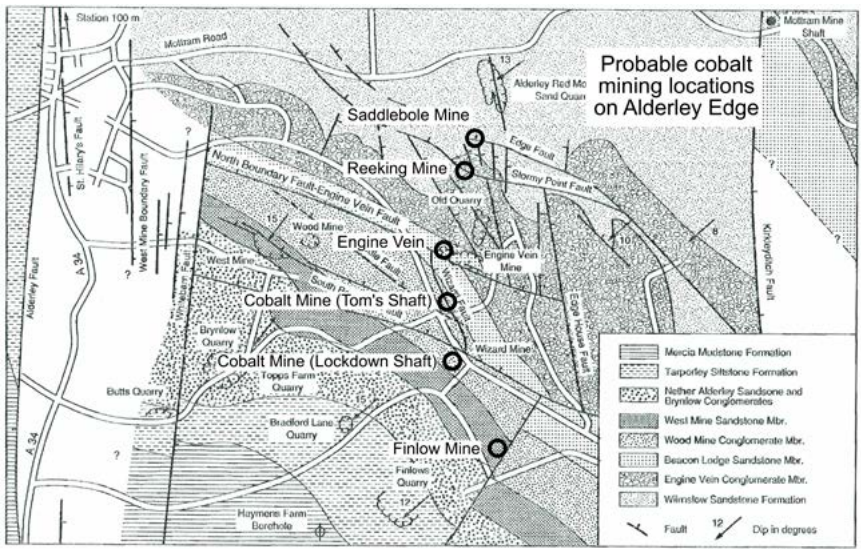

Figure 7.5: Geological map of Alderley Edge (modified from Rowe and Burley 1997 with the addition of suspected or actual cobalt workings, marked by open circles).

Finlow Mine

The mine in Finlow wood was reopened in two phases by the DCC. As far as can be seen, the whole of the mine has now been made accessible. It consists of two roughly parallel veins with shafts to the surface and cross-cuts between them. In common with all other "cobalt" workings, the mine was worked in a series of short passages with constant changes in level, showing that the deposits were quite irregular. Passages are generally about 0.8 m wide and 1.2 m high, with a flat-arched roof. Water was encountered at depth, but it is likely that it was removed by lifting up shafts. Ore was removed by scraping it out with curved metal scrapers so as to minimise the amount of gangue (sand) extracted. The waste heaps on the surface are small, even allowing for their age of nearly 200 years.

Bradford Lane

Clear evidence of a mine under Bradford Lane has not been found, but a blind shaft was excavated to the bottom on the north side of the road, just south of the junction with Macclesfield Road. There are reports of the finding of an arched mine passage on the east side of the Macclesfield Road when an electricity cable was laid in the 20th century.

Lockdown Shaft

North of Bradford Lane and west of the Macclesfield Road lies the extension to the mine found in the 1980s, known as Lockdown Shaft and described above. Between this section and Bradford Lane, there are two distinct circular features formed by the waste heaps around shafts. One of these is thought to connect with the flooded section in the known Cobalt Mine, but this connection cannot be proved until the flooded section can be surveyed accurately.

The Cobalt Mine

The southernmost accessible section of the Cobalt Mine is reached from Lockdown Shaft, described above. The next shaft open to the surface is known as Holly Shaft and is centred in a large heap of mine spoil. North again there is a shaft known as Trackside Shaft and then, inside the small mining museum, is Tom's Shaft. This is currently used as the main point of access. Tom's Shaft lies more or less on the outcrop of the fault, and 25 m to the northeast is the Well Shaft, sunk in the hanging wall and intersecting the fault at depth. Well Shaft was used as a water supply to the Wizard Inn but was most probably excavated to enable drainage of the entire mine. Farther north from Tom's Shaft is another shaft on the fault, and then the workings break surface about 25 m beyond. There are signs of workings or trials continuing up to the Engine Vein, where the cobalt fault is represented by a cross-fault that has interrupted the deposition of copper minerals in the Engine Vein mine. Figure 7.6 shows a typical section of passage in the Cobalt Mine close to Tom's Shaft. A map of the accessible parts of the Cobalt Mine is presented in Figure 7.7.

Figure 7.6: Photograph of a chamber on the fault in the Cobalt Mine at Alderley Edge with a round shaft in the floor. The black coating is cobaltian wad (photograph by Paul Deakin).

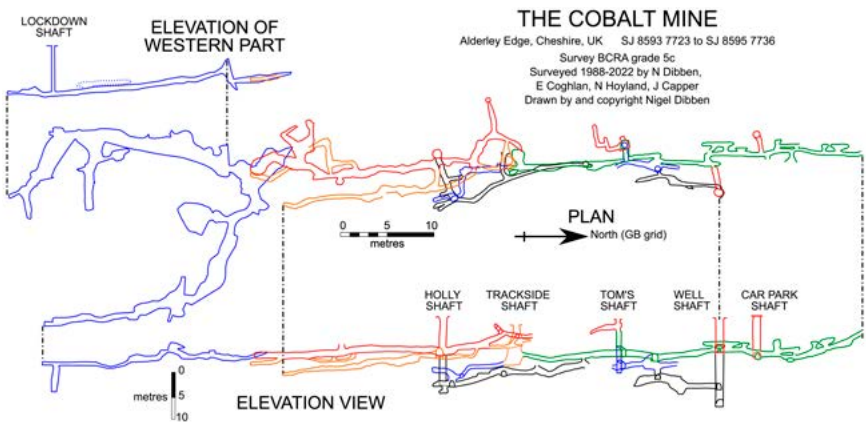

Figure 7.7: Plan and elevation map of the Cobalt Mine at Alderley Edge, surveyed by Nigel Dibben, Ed Coghlan and others (drawing by Nigel Dibben, 2022).

Engine Vein (cobalt workings)

There is a possibility that the area where the cross-fault from the Cobalt Mine direction crosses the vein in Engine Vein was worked in the early 19th century. Some of the passages in that area are similar to those in the Cobalt Mine. This section of the mine may even be the starting point for the cobalt mining phase. The fault that terminates the Engine Vein on the southwest side is mineralised, but although the chamber adjacent to it has been worked for copper, there is no sign of the vein or fault itself having been worked. It is possible that the fault was too wet at the start of the 19th century for the miners to exploit it at that time.

Canyon Opencast area

Work by the DCC in 2001 included excavating and recording a shaft near the Canyon Opencast and Old or Great Quarry. The passages off this shaft resemble those in the other cobalt mines, and it is now felt that the north–south fault on which the cobalt mine was developed extends, or has parallels, farther to the north. One mine excavated in the Canyon Opencast area (known as Pine Shaft) is about 8 m deep and has two branch passages at 4 m and 5 m below surface.

Saddlebole Mine

The northernmost suspected site of cobalt mining is at Saddlebole. For many years, this was believed to be an early copper mine, but archaeological excavation in 1999 did not provide evidence of early mining, and it is now believed that Saddlebole was mined in the early 19th century for cobalt. Saddlebole has at least

eight mine-related features, including a shaft; two linked, small level sections near the top of the hill; and what appears to be a lower level on the east side of the hill.

Conclusion

The surface evidence strongly suggests that cobalt workings lie in the region between the so-called Cobalt Mine and the Engine Vein. We are aware of flooded workings south of the Cobalt Mine, and work is currently in hand excavating infill from a mine in the north of the site. Work will continue on a small scale by the DCC volunteers, which, we hope, will over time present a fuller picture of the extent of cobalt mining at Alderley Edge.

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Part 3

Applications

Chapter 8

Cobalt in Late Bronze Age glassmaking: Insights from archaeometric analyses and case studies

Victoria Kemp[1] and Andrew J. Shortland[2]

The first uses of cobalt in the Late Bronze Age

The introduction of cobalt in ancient Egypt marks a milestone in the history of Egyptian material culture and technological innovation. The first known use of cobalt dates to the 18th Dynasty (1550-1295 BCE), during the reign of King Tuthmosis III (1479-1424 BCE), when it was employed in the manufacture of glass. Probably slightly later it is also found in faience, and later still as a pigment on "Palace ware", a distinctive, and short-lived, blue-painted ceramic (Arnold et al. 1993). It was previously believed that the technology for glass production was imported to Egypt from Syria, following the successful military campaigns of Tuthmosis III; however, establishing who were the originators of glassmaking remains contentious, due to the contemporaneous chronological development of the technology in both regions (Beck 1934; Shortland 2001, 214). Egypt was already renowned for its extensive use of natural and manufactured blue stones and materials used for pigments, protective amulets and jewellery. The colour blue was especially significant for the Ancient Egyptians and held many important associations: it was the colour of the Nile, and it represented creation and fertility and symbolised the realm of the gods and divine truth and justice (Birren 1950, 37). Before the introduction of cobalt, copper was used to impart a turquoise hue to vitreous materials; however, it was the discovery and integration of cobalt that enabled craftspeople to create the deep and vibrant blue reminiscent of lapis lazuli, which was apparently favoured.

In life, glass, faience and stone jewellery were both amuletic and decorative; they were also part of the important protocol of gift giving from the king to his courtiers and from elite members of society to their family and servants. In turn,

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gifts from courtiers were presented to the king and made as offerings to the gods (Feucht 1999, 386; Kemp 2006, 387). Jewellery held significant purpose and played an important role in Egyptian mortuary cults. In death, amulets were an integral part of the interment and were worn by the deceased for protection as they traversed the underworld (Aldred 1971, 34; Wilkinson 1971, 7). Notably, the colour of the amulet was a vital part of the symbolism of the amulet itself, bestowing protection or powers on its owner (Aldred 1971, 34; Aston et al. 2000, 62). Some amulets, therefore, were created in vast numbers, and it is likely that they were accessible and affordable (Hodgkinson 2015). Some of the semi-precious stones used by ancient Egyptian craftspeople to produce amulets, jewellery and fine goods originated from domestic sources; however, lapis lazuli was not local and ultimately came from the Badakhshan Province in Afghanistan. The correspondence between the king of Egypt and the rulers of Babylonia and Mitanni in cuneiform tablet ABL 1240 reveals that the high demand for lapis lazuli by Egypt created an acrimonious political tension, arising due to the escalating costs and challenges associated with mining the stone (Oppenheim 1970, 12). Considering these factors, the establishment of an industry capable of producing an alternative source of (artificial) lapis may have been one of the motivations for founding the first glassmaking workshops in Egypt.

Sources of Late Bronze Age cobalt

Farnsworth and Ritchie (1938) were the first to identify cobalt as the primary colourant in dark blue LBA glasses. Subsequent compositional research on Late Bronze Age (LBA) Egyptian cobalt-blue glasses, explored further by Kaczmarczyk, established that these glasses contain levels of aluminium, manganese, nickel and zinc that are elevated compared with those of contemporaneous copper-coloured glasses (Kaczmarczyk 1986). Relatively high concentrations of these elements are also present in cobalt-coloured faience and in the Palace ware blue pigment. Additionally, most of these elements exhibit strong correlations with each other, providing a characteristic elemental signature for the likely source of the cobalt colourant (Kaczmarczyk 1986). Kaczmarczyk (1986) identified the source as cobaltiferous alums from the Western Desert of Egypt, with analyses by Shortland and colleagues confirming compositional matches to materials from the Kharga and Dakhla Oases (Kaczmarczyk 1986; Shortland 2006; Shortland et al. 2006). This particular composition makes up much of the early cobalt glass and faience, as well as that from important 14th century BCE sites, such as Amarna and Malkata, and is now known as Type A. However, analysis of later cobalt-coloured glass from the Ramesside Period (19th-20th Dynasties, 1295-1069 BCE)

shows subtly different patterns. This cobalt source, known as Type R, has slightly lower concentrations of zinc compared with other typical earlier cobalt glasses, suggesting a source distinct from the manganese-rich cobaltiferous alum derived from the Western Oasis. It has been suggested by Abe and colleagues that the introduction of the Type R cobalt source coincides with the military campaigns of Rameses II (1279-1213 BCE), and that these campaigns may have had an influence regarding the introduction of a new source (Abe et al. 2012). However, this link seems tenuous at best. In addition, analytical evidence from the Abe et al. study shows the concurrent use of both the Type A and the Type R sources during the Ramesside Period, suggesting that the transition was not due to a complete depletion of the Western Desert source. Two later cobalt sources have also been identified in ancient glass research, commonly referred to as Type N1 and Type N2. These can be seen in glass and faience from the Egyptian Late Period through the Ptolemaic to Roman times (post-1069 BCE). Glasses manufactured using cobalt from both of these Type N sources have only trace amounts of nickel and lower zinc than those manufactured using Type A (which have amounts roughly equal to those using Type R). They can be split by manganese context into lower-manganese Type N1 and higher-manganese Type N2 (Abe et al. 2012). The source or sources of these Type N cobalt colourants are uncertain.

Processing ancient cobalt

Evidence suggests that the routine production of cobalt-blue glass in Egypt commenced as early as the reign of Tuthmosis III, requiring the institution of cobalt ore extraction and refinement processes (Kemp et al. 2021; Lilyquist et al. 1993, 41). Unfortunately, no extant textual sources provide descriptions of these ancient processes, meaning that the sole evidence available derives from the material itself, particularly the discernible compositional distinctions between colourless and cobalt-coloured glasses (Gratuze et al. 2018).

Practical experimentation by Shortland et al. (2006) successfully demonstrated what this process may have been: The Egyptian cobalt-rich alum is mined in the form of small masses of rock and subsequently ground to a coarse powder, which is mixed with water. The alum dissolves and can thus be extracted as a sulphate-rich liquid, with the other, insoluble gangue minerals being left behind. This liquid could then have been reacted with natron, a naturally occurring sodium carbonate used in a plethora of ancient Egyptian processes, especially washing and embalming. The chemical equation for the reaction is thus:
$XSO_4\,(aq) + Na_2CO_3\,(aq) + H_2O\,(l)$ converts to $X(OH)_2\,(s) + Na_2SO_4\,(aq) + CO_2\,(g)$ (where X is Al, Mg, Fe, Co, Mn, Ni or Zn) (Shortland et al. 2006).

Figure 8.1: Photographs of (**left**) cobalt alum in veins in host rock; (**right**) dark blue glass made from the granular artificially produced pigment (right side of Petri dish).

The mixture initiates a vigorous reaction, leading to the formation of a precipitate. This can be dried and then heated to temperatures of 800°C to 1000°C. The resulting product can be used as a blue pigment and was then added to the raw glass mixture, which consisted of silica, lime and soda, although the precise moment when the colourant should be added (whether prior to or after the fluxing of the raw materials) is still debated.

Characteristics of standard Late Bronze Age cobalt-blue glass

Cobalt emerges as the most potent of transition metal colourants. According to Bamford (1977, 42), the linear absorption coefficient of glass attributed to cobalt surpasses that of other transition metal ions by a factor of at least 5. Consequently, relatively small amounts, as little as 0.04% CoO, can impart a profound deep-blue hue in the glass (Lankton et al. 2022a; Shortland and Eremin 2006). Type A cobalt-blue glasses manufactured during the Egyptian New Kingdom period exhibit a distinct compositional subgroup in addition to their transition element characteristics: low potash and high alumina contents. The relatively low potash content is around 1.1% K_2O, contrasting with the typical potash content of plant-ash glasses, which ranges between approximately 2% to 4% (Lilyquist et al. 1993, 56; Shortland and Eremin 2006). Recent research analysing the composition of 25 cobalt-coloured glasses of Egyptian origin produced between 1400-1300 BCE reveals that while the potash content in some glasses may occasionally surpass this threshold, such instances are infrequent (Lankton et al. 2022a). The concentration

of alumina, at roughly 2.6% Al2O3, is markedly higher compared with the 1% found in other LBA glasses (Kaczmarczyk 1986; Shortland and Eremin 2006; Shortland et al. 2007).

Table 8.1: Compositional characteristics of cobalt-blue glass where content of Co ranges between 0.05% and 0.3% (Freestone 1991, 40; Shortland and Eremin 2006).

Source of Glass	Source of Cobalt/ Type	Period Used	Al	Ni	Zn	Mn	Fe
Egypt	Dakhla and Kharga Oases/ Western Desert Type A	1550-1295 BCE 18th Dynasty					
Egypt	Unknown Type R	1295-1069 BCE Ramesside Period					
Egypt	Unknown Type N1	664-300 BCE Late Period/Ptolemaic Period					
Egypt	Likely an Iranian asbolane source; Type N2	664-300 BCE Late Period/ Ptolemaic Period					

The distinctive low-alkaline potash composition observed in LBA cobalt glasses has prompted multiple theories regarding composition of the alum source and the flux, and regarding the production process (Abe et al. 2012; Rehren 2001). However, the most likely theory is that cobalt was extracted from the alum through precipitation with natron, resulting in a cobalt pigment with a high sodium (but very low potash) content; as a consequence, less plant ash was needed in the glass production process (Tite and Shortland 2003).

To achieve the desired blue hue, glassmakers frequently combined both copper and cobalt colourants; the study of 200 ingots from the Uluburun shipwreck, Türkiye (ca. 1300 BCE), revealed copper and antimony traces in cobalt-blue glass, indicating the deliberate incorporation of cullet to achieve the intended colour, consistent with Egyptian texts (Lankton et al. 2022b). In analytical studies, Co+Cu glasses are often reported as an individual subgroup and hold their own compositional definition. Co+Cu glasses are defined as glasses which contain more than 0.05% CoO and more than 0.1% CuO (Shortland and Eremin 2006) or glasses which possess a minimum of 300 ppm Co and 850 ppm Cu (Smirniou and Rehren 2013). These glasses exhibit an elevated average concentration of 1.69% Al2O3 and increased levels of Ni, Zn, and Mn compared with standard

LBA glasses, thereby maintaining the characteristic elemental profile signifying the usage of the same Type A cobaltiferous alum colourant source widely used in the New Kingdom of Egypt.

Late Bronze Age cobalt glassmaking and -working centres

Three primary Egyptian sites are linked to cobalt glass production and/or working, with the earliest known site located at the palace complex of Malkata, the residence of Amenhotep III (1390-1352 BCE) (Keller 1983). Notable discoveries at Malkata, including glass slag, crucibles, glass rods and vessel fragments, suggest the presence of glassworking activities at the site. However, critical evidence confirming Malkata as a true glassmaking site has been lost, leaving its status in this regard unconfirmed (Mass et al. 2002).

The founding of the city of Amarna by Akhenaten (1352-1336 BCE), son of Amenhotep III, marks a pivotal era in Egyptian history and holds considerable significance, particularly in the context of LBA glass studies. Amarna evolved into a remarkable metropolis, characterised by the construction of expansive edifices, including palaces, government offices, temples and designated areas for craftspeople (Boyce 1995). The quantity of glass finds excavated from Amarna demonstrates the existence of a large glassworking industry that operated within the city. This industry was an integral component of a broader network of craftspeople specialising in the production of vitreous materials (Jackson and Nicholson 2007; Shortland 2000). In addition to a glassworking site, Amarna was confirmed as a true glassmaking site based on the substantial archaeological evidence of glass finds, frit and semi-finished glass (Rehren and Pusch 2005; Schoer and Rehren 2007; Smirniou and Rehren 2011). The Egyptian 18th Dynasty represents a "golden age" in glass production and artisanship, both of which appear to decline following the death of Akhenaten and the ascension of his son, Tutankhamun (1336-1327 BCE), with the city of Amarna consequently abandoned (Snape 2014, 163; Van Dijk 2000, 281).

The next known major glass sites appear in the archaeological record 40-50 years later, in the Ramesside Period. The site of Qantir, alternatively referred to as Qantir-Piramesses, is situated approximately 100 km northeast of contemporary Cairo, in the eastern Nile delta. It was initially established by Seti I (1294-1279 BCE) and subsequently ascended to the status of capital city during the reign of Ramesses II (1279-1213 BCE) (Shaw and Nicholson 1995, 237). The glassmaking complex at Qantir was instituted during the reign of Rameses II, and finds from the site show that the workshops were largely engaged in the production of industrial quantities of red glass, although some cobalt-blue and purple glasses were also

discovered at the site (Pusch and Rehren 2007, 129; Rehren and Pusch 2005; Shaw and Nicholson 1995, 237).

Lisht is the last proposed Egyptian LBA glass workshop, active between 1295 and 1070 BCE (Keller 1983; Mass et al. 2002). Excavations at the site have yielded significant glass finds indicative of glassmaking activities, including glass waste and slag, fragments of glass vessels, blue glass canes and rods, strings of glass and faience beads, and remnants of ceramic crucibles with adhered glass (Keller 1983; Kozloff and Bryan 1992). These finds indicate that cobalt-blue glass was not produced at this site, although several other colours, including black, brown, copper-blue, green, purple, white and yellow, are attributed to the site (Brill 1999; Keller 1983; Mass et al. 2002). This temporal overlap shows contemporaneous Ramesside glass production at Lisht and Qantir.

Glass and cobalt outside Egypt

Cobalt glass is notable for its seemingly exclusive use and production in Egypt, with finds of cobalt glass in Mesopotamia being exceedingly rare. The exceptions are a unique group of ceremonial glass axes from Nippur, in present-day Iraq, inscribed with the names of three kings and dated by these inscriptions to the 14th-13th centuries BCE. The analysis of these glasses reveals another distinct cobalt source, as the Nippur glasses lack the correlations between cobalt and aluminium, manganese, nickel and zinc that are characteristic of contemporary Egyptian Co-glasses. Furthermore, the average quantity of cobalt in the Nippur glasses is twice that of the Egyptian ones (Walton et al. 2012). Another instance of cobalt glass manufactured outside Egypt is the Eridu fragment, considered to be one of the oldest examples of glass, dating back to 2050 BCE. The fragment was excavated by Harry Reginald Holland Hall in 1919, from Abu Shahrain in modern day Iraq; it is described as translucent blue in colour and "bubbly" in texture and is believed to be part of a larger lump. The fragment was analysed in 1956 using spectrographic analysis, which gave the major elemental composition of the glass, indicating that the glass was coloured with both cobalt and copper. Notably, the potassium oxide value is 4.5%, which is significantly higher than the characteristically low potash levels of Egyptian cobalt glass. Moreover, the elevated alumina level of 2.5% may indicate a cobaltiferous alum source (Garner 1956). The dating of both the Nippur axes and the Eridu fragment does not seem to match the compositions of glass seen, and both remain unexplained compositional outliers.

The Uluburun shipwreck

Discovered in 1982, 6 miles southeast of Kaş, in southwestern Türkiye, the Uluburun shipwreck is one of the most important archaeological examples of LBA international trade. Notably, it represents the archaeological site with the largest assemblage of LBA glass finds, with approximately 350-400 kg of glass ingots (Pusch and Rehren 2007, 136), and is believed to have sunk in approximately 1300 BCE (Bass et al. 1989; Manning et al. 2009). The ship sank with a full cargo comprising more than 20 tons of goods from Cyprus, the Levant, Nubia, Mesopotamia and Egypt, largely consisting of raw materials and metals, including raw copper in the form of slab ingots; ingots of tin; and luxury goods comprising ivory, gold and carnelian (Bass 1987; Pulak 2008). Based on the similarity of the ship's inventory to the register of gifts exchanged between the rulers of Egypt and Mesopotamia detailed in a near-contemporary diplomatic archive known as the Amarna letters, it is possible that the Uluburun vessel was carrying diplomatic gifts to a foreign royal court (Moran 1992; Pulak 2001).

Most significantly, approximately 200 ingots of turquoise and dark blue glass were recovered from the wreck. They are in two shapes: The dark blue ones are relatively broad and flat, whereas the light blue ones are narrower and deeper. Initially, both Egyptian and Mesopotamian origins were speculated on, and some initial elemental analysis confirmed that the major composition of some of the ingots resembles that of core-formed vessels from Egypt (Bass et al. 1989; Pulak 1998). Jackson and Nicholson (2007) showed that the dark blue ingots have very similar dimensions to ingot "crucibles" or "moulds" excavated from Amarna. It was their work on the trace element analysis of three Uluburun ingots in 2010 that showed that all three sampled ingots exhibit compositions that are consistent with Ti, Cr, La and Zr contents of Egyptian-manufactured glass (Jackson and Nicholson 2010). However, it was not until the extensive research conducted by Lankton et al. (2022a) that the analysis conclusively confirmed the Egyptian origin of all 192 ingots in the study. That study also provided other insights, notably that 92 of the Uluburun ingots were coloured primarily by cobalt and 46 ingots are classified as Co+Cu coloured glass. Compositional analysis of the ingots also revealed that LBA glassworkers were capable of producing approximately 40 kg of coloured glass per batch, and that the ingots came from multiple Egyptian workshops, suggesting a broader production network in the late 18th Dynasty (Lankton et al. 2022b). Therefore, the Uluburun ingots demonstrate that cobalt-coloured glass was being manufactured on a significant scale by the end of the 18th Dynasty (1550-1295 BCE).

Dating Late Bronze Age glasses using cobalt

Historically, dating glass has relied on two main methods. The first method involves examining the cartouche inscribed or applied to the object, such as the Munich Chalice, a light blue, core-formed vessel which bears the cartouche of Tuthmosis III in dark blue. The second method involves dating objects using the associated context or find site, such as the discovery of a small vase of translucent white glass in the tomb of Tutankhamun. In theory, glass objects can be stylistically dated, particularly if certain vessel shapes are known to have been produced during specific time periods (Nolte 1968). However, this has proved difficult for LBA vessels and impossible for other LBA glass items, the prime example being beads, which were eminently transportable and tradable over long distances and time periods (Kemp et al. 2019; Varberg et al. 2015, 2016). Therefore, as discussed previously, elemental analysis has proved crucial for gaining insights about the provenance of LBA glasses, the raw materials used, and the identification of colourants. However, since different cobalt colourant sources are used at different times, the era in which a glass was manufactured can be indicated by the distinctive composition of the cobalt colourant used.

The dating of glasses coloured with cobalt has been demonstrated using trace element analysis on a series of fragments of undetermined age excavated at the archaeological site of Serabit, in the Sinai Peninsula (Kemp et al. 2023). Serabit is the site of a turquoise mine and of a temple which was built in the 12th Dynasty and dedicated to Hathor, the patron goddess of turquoise miners. Serabit was abandoned at the conclusion of the 12th Dynasty, but mining activities were reinstated during the 18th Dynasty, with subsequent rulers enhancing and expanding the temple structure. During this time, the temple received numerous votive offerings, including a substantial quantity of glass objects (Petrie 1906; Simpson 1990). Final building activities, offerings and inscriptions are recorded at the temple in the mid-20th Dynasty, between the reigns of Rameses IV (1153-1147 BCE) and Rameses VI (1143-1136 BCE), after which the site was abandoned once again (Mumford 2006). Petrie recovered approximately 970 glass fragments from the temple site, and stated that a larger quantity of glass items were likely placed at the temple but that they were destroyed following the departure of the Egyptian mining organisation (Petrie 1906, 122, 139). Therefore, from the perspective of glass research, this site emerges as a major consumer site of glass vessels and objects, spanning a period of approximately 300 years.

Figure 8.2: Photographs of fragments of cobalt-coloured and Co+Cu coloured glass fragments from Serabit (overarching accession number AN1896-1908.E.4486; from left to right: OX193, OX414, OX183 and OX127; photograph © Ashmolean Museum, University of Oxford).

The study by Kemp et al. (2023) analysed 42 fragments, all of which were confirmed to be of Egyptian provenance using trace element analysis. Six fragments were coloured primarily using cobalt, and 8 fragments were identified as Co+Cu glasses, all exhibiting elevated levels of Al_2O_3, Mn, Ni, and Zn, thus conforming to the characteristic composition of cobalt-blue glasses manufactured in the 18th Dynasty. A purple glass fragment from Serabit (OX444) contained not only an elevated concentration of 0.21% of the expected purple colourant manganese (MnO), with 0.80% Fe_2O_3, but also a relatively high concentration of cobalt, at 0.09% CoO.

The deliberate addition of cobalt likely contributed to the observed darker purple hue. OX444 exhibits notably reduced alumina content compared with the early New Kingdom Type A glasses containing cobalt, along with diminished Zn and heightened Ni levels, aligning it with the Type R source utilised during the 19th-20th Dynasties (Abe et al. 2012). This dating corresponds with the composition of the yellow glass discovered within the same fragment, affirming the date of production within the Ramesside Period (Kemp et al. 2023).

Fragment OX641, a white glass fragment with a blue pattern applied, represents one of the most significant finds from the study. The analysis showed that the white glass is consistent with LBA plant ash compositions, whereas the Co+Cu blue glass applied as decoration on the same fragment has 0.49% MgO and 0.91% K_2O, characteristic of natron glasses produced in the Iron Age (Lilyquist et al. 1993, 56). The blue glass contains 1.0% Al_2O_3 and low levels of nickel,

zinc and manganese, thereby conforming to the compositional signature of Type N1 cobalt used in blue natron glasses during the Late Period (Abe et al. 2012; Kemp et al. 2023). Therefore, three distinct phases of Egyptian core-formed vessel glassmaking are represented at Serabit: plant-ash glass with Type A cobalt from the 18th Dynasty, plant-ash glass with Type R cobalt from the Ramesside Period, and natron glass from the Ramesside or later periods. These correspond with the known epochs of Egyptian activity at the site.

A second study by Kemp et al. (2021) analysed a polychrome glass fragment, EA64163, which was stylistically attributed to the tomb of Amenhotep II (KV35), and therefore thought to be a piece of glass from the early 18th Dynasty. Elemental analysis determined that the major element composition of all three colours of glass on the fragment (red, white and blue) contained an average of 1.2% MgO and 1.4% K_2O. The blue glass was coloured by Co+Cu with higher levels of manganese, iron, and lead and low levels of nickel and zinc, therefore compositionally inconsistent with the Type A cobalt that was the only source in the early 18th Dynasty, but consistent with later glasses (Abe et al. 2012; Mass et al. 2002). Therefore, both the major elemental composition and the distinct composition of the associated elements of the cobalt ore suggest that this fragment was not part of the funerary equipment of Amenhotep II and is much more likely to be an intrusive piece of later, Iron Age natron glass.

Conclusion

The utilisation of cobalt as a colourant in ancient Egypt, particularly during the LBA, marked a significant advancement in material culture and technological innovation. Cobalt was first introduced during the reign of King Tuthmosis III and was widely used in the production of vitreous materials, such as faience, and in glassmaking. Its integration was a step change in Egyptian artistry and craftsmanship, notably in the production of vibrant blue glass, distinct from previous turquoise hues, which had been achieved through the use of copper-based colourants. Analytical research has established the unique compositional characteristics of different cobalt glasses by the identification of the characteristic concentrations of associated elements, in the 18th Dynasty and the Ramesside and Late Periods. Combined with trace element analysis, the study of ancient cobalt-blue glasses has become one of the most significant indicators of raw materials, production, development and distribution of LBA glasses, as highlighted by the study of glass fragments from Serabit, which revealed variations in cobalt usage, reflecting advancements in glassmaking techniques and material availability over time. The discovery and analysis of cobalt glass ingots recovered from the

Uluburun shipwreck not only exemplifies the extent of international commerce and diplomatic relations during the LBA, but also confirms Egypt's ability to produce cobalt-blue glass at significant scale. The identification of distinct cobalt sources in ancient glasses has proved instrumental in determining not only the provenance of the colourant itself, but also the potential epoch of glass production. Therefore, through interdisciplinary research, the study of cobalt glass unveils not only ancient technological networks of raw material exchange and product distribution, but also broader socio-economic dynamics of the ancient world.

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Chapter 9

Early Islamic cobalt-blue glass: Colourant and matrix

Nadine Schibille[1]

Introduction

The use of cobalt to colour vitreous materials has been the subject of intensive archaeometric research in recent years (e.g. Colomban et al. 2021; Cunningham 2019; Giovanni and Riccardi 2021; Gratuze et al. 2018; Hunault 2014; Jiang et al. 2020; Ma et al. 2022; Matin and Pollard 2017; Molera et al. 2021; Spataro et al. 2019; Wen and Pollard 2016). Cobalt is relatively rare in Earth's crust, and since not many mineral sources of cobalt were accessible in ancient times, the compositional fingerprint of cobalt can provide additional information about the origins of the pigment and about supply networks in the medieval glass and glazing industry more generally. This inference is based on the assumption that the compositional characteristics of the starting material (cobalt minerals) are proportionally dissolved and transferred to the glass matrix and can thus be identified and traced by analysing the glass (Spataro et al. 2019; Wood et al. 2007). However, it is unlikely that this is always the case, as roasting procedures are often involved in cobalt extraction and elemental fractionation may well ensue in the silica matrix (Jiang et al. 2020). Taking these potential chemical processes into account, it is, nevertheless, possible to distinguish cobalt-blue glass and the underlying cobalt pigment on the basis of its compositional properties, even if the enduring question of the most probable mine of origin of the cobalt mineral cannot yet be answered conclusively.

Cobalt occurs in association with nickel, copper and iron, as an impurity of asbolane ores ($(Ni,Co)_{2-x}Mn^{4+}(O,OH)_4 \cdot nH_2O$). It can be enriched in sedimentary deposits, such as cobaltiferous alums, and is also found in independent minerals and ores, the most important of which are skutterudite ($CoAs_{2-3}$), cobaltite (CoAsS) and linnaeite (Co_3S_4). Different accompanying elements can therefore be expected in

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cobalt-blue glass, depending on the type of mineral source used for the production of the cobalt-blue pigment. Geographical and chronological differences in the use of cobalt minerals in glassmaking over time have been identified. For example, the earliest cobalt used for the production of dark blue vitreous materials in LBA Egypt is associated with the exploitation of cobalt-rich alums from the Western Oasis and typically has elevated levels of aluminium, manganese, nickel and zinc (Kaczmarczyk 1986; Shortland et al. 2006). The cobalt underlying LBA glass from Nippur, in southern Iraq, has been found to be more or less enriched with iron, aluminium, and, occasionally, arsenic, while manganese, nickel and zinc are not as high as in Egyptian counterparts (Walton et al. 2012). Cobalt-containing glass from Ramesside-period Egypt differs from earlier glass in having lower concentrations of zinc (Abe et al. 2012), whereas Roman cobalt-blue glass up to the 4th century CE generally lacks clear compositional characteristics (Abe et al. 2012; Gratuze et al. 1992, 1996, 2018, 1992). Sometime in the 4th century CE, a cobalt with a more pronounced nickel content was introduced into Mediterranean glassmaking (Freestone et al. 2023; Gratuze et al. 2018; Schibille et al. 2020b). Further changes in the cobalt signature can be recognised in the early Islamic period. The presence of zinc in the absence of arsenic has long been considered a typical feature of cobalt-blue glass and ceramic glazes from the Abbasid period (Gratuze et al. 2018; Matin and Pollard 2017; Wood et al. 2007). This observation, however, is based on a small amount of archaeological materials and a fairly limited amount of analytical data. It is therefore not clear whether high zinc values are a characteristic feature of early Islamic cobalt-blue glass in general.

In order to establish the novelty of cobalt-blue pigments in the early Islamic period, it is crucial to compare a sufficient number of blue glasses from across the Islamic world, stretching from Spain in the west to Afghanistan in the east. The aim of this article is thus to classify early Islamic cobalt-blue glass both in terms of its base glass and in terms of the minor and trace elements associated with the cobalt colourant. The main purpose is to investigate whether there was, indeed, a clear break with earlier traditions and recipes; whether a chronological and/or geographical evolution of cobalt-blue glass can be traced; and to what extent it is possible to identify different areas of production and sources of the cobalt-containing compounds. To this end, the published compositional data of 208 samples of cobalt-blue glass from various early Islamic sites (8th-11th centuries) were re-evaluated and classified according to their base glass and cobalt signatures. This comparative assessment highlights various combinations of elements associated with the cobalt used and demonstrates that different cobalt minerals were exploited more or less simultaneously, although there also appears to be a chronological shift in the predominant cobalt type.

The base glass

The Arab conquest of the early 7th century CE fundamentally transformed the geopolitical landscape of the Mediterranean region. By 640 CE, the whole of Syria and Palestine were under Muslim rule, followed by Egypt in 642 CE (Milwright 2010; Robinson 2010; Walmsley 2007). Under the Umayyads, the territory grew rapidly, incorporating the Caucasus, Transoxiana and the Maghreb, and by 711 CE, it encompassed most of the Iberian Peninsula. At its greatest extent, toward the end of the Umayyad Caliphate, it was the largest empire the world had yet seen (Fig. 9.1). In 750 CE, the Umayyad dynasty was overthrown by the Abbasid dynasty, who moved the capital of the caliphate from Damascus to Baghdad, thus shifting the geopolitical and socio-economic centre of gravity farther east (Kennedy 2007; Walmsley 2000). The glass finds discussed here come from areas that in one way or other belonged to this vast Islamic Empire (Fig. 9.1). The chronological range covers the first few centuries of Muslim rule, that is, the 8th to the 10th-11th centuries CE.

Figure 9.1: Map showing the largest extent of the Umayyad Caliphate, c. 750 CE (green shading) and sites mentioned in the text (created using ArcGIS World Map, hosted by Esri, USGS; https://worldmap.maps.arcgis.com/apps/mapviewer/index.html).

This is a period of profound technological change in glassmaking. Not immediately after the Arab conquest, but from the turn of the 9th century, glassmakers turned to new recipes based on soda-rich plant ash instead of mineral natron as fluxing agent (Phelps 2018; Phelps et al. 2016; Schibille 2022b). This change seems to have taken place first in Greater Syria, while mineral natron continued to be

used in Egyptian glass production at least until the second half of the 9th century CE (Schibille 2022a and b; Schibille et al. 2019). Hence, plant-ash glass co-existed alongside natron glass and only gradually replaced it (Henderson et al. 2004; Phelps 2018). In the course of this process, primary glass production was decentralised and essentially democratised as the number of primary workshops multiplied, resorting to the use of local raw materials and recipes (Schibille et al. 2022a, 2024). The analytical data of glass from different geographical regions, such as the Iberian Peninsula (De Juan Ares and Schibille 2017; Schibille et al. 2020a), Mesopotamia (Henderson et al. 2004; Schibille et al. 2018) and Central Asia (Chinni et al. 2023; Fiorentino et al. 2019; Meek et al. 2025; Schibille et al. 2024), show unique compositional characteristics that confirm the existence of local productions by the 9th or 10th centuries CE. As a result, glass, at least in the form of raw glass, was no longer traded to the same extent and over the same long distances as during the Roman and late antique periods (Meek et al. 2025). Of course, glass still travelled, but probably more in the form of finished objects and/or special products, such as high-quality colourless glass from the region around Samarra (Abe et al. 2018; Brill 1999; Henderson et al. 2016; Phelps 2018; Schibille et al. 2022a, 2024), and, as will be discussed in the following, cobalt-blue glass.

Relevant glass groups from the early Islamic period include so-called Levantine 2, which was defined on the basis of the remains from the primary glassmaking furnaces at Bet Eli'ezer, in Israel (Brems et al. 2018; Freestone et al. 2000); Egypt I; and Egypt II (Gratuze and Barrandon 1990; Schibille et al. 2019), all of which adhere to the old mineral natron recipes, and various plant-ash glass groups that differ according to their production zones (Lü et al. 2023; Meek et al. 2025; Schibille 2022b, 2024). A cursory examination of the available analytical data revealed that no cobalt-blue glass with significant cobalt concentrations was found in combination with a Levantine 2 or Egypt I base glass. In this context, it is striking that among the nearly 1,000 tesserae from the Great Umayyad Mosque in Damascus we analysed, there is not a single cobalt-blue sample that matches the base glass of Egypt I, although 65% of the samples belong to this primary production group. All the cobalt-blue tesserae from Damascus are either of an Apollonia-type Levantine 1 or an Egyptian Foy 2 composition, two late antique glass groups dating to the 5th to 6th or 7th century CE (Schibille et al. 2022b).

Of the 208 samples included in the present study, only 13 are natron-type glasses, all of which correspond to the so-called Egypt II compositional group (Fig. 9.2a, b). Eight of these natron glasses are Egyptian glass weights (Schibille et al. 2019); two are vessel fragments with incised decorations recovered from Nishapur, in eastern Iran (Schibille et al. 2022a); another vessel fragment and a

miniature bottle were collected in el-Ashmunein by Jean André Périchon, at the end of the 19th century (Nenna 2023). Egypt II is an Abbasid glass group dating to the 8th-9th centuries CE and is characterised by low aluminium concentrations relative to titanium concentrations, as well as fairly high lime contents coupled with low strontium levels (Bimson and Freestone 1987; Schibille et al. 2019). On account of the relatively low soda concentrations and the slightly elevated aluminium values, the cobalt glasses appear to belong to the later subgroup of Egypt II, dated to after 815 CE (Schibille et al. 2019). This, and the fact that no cobalt was found in earlier Islamic glass, may well point to an interruption in the production and use of cobalt-blue glass in the first two centuries after the Islamic conquest of the eastern Mediterranean.

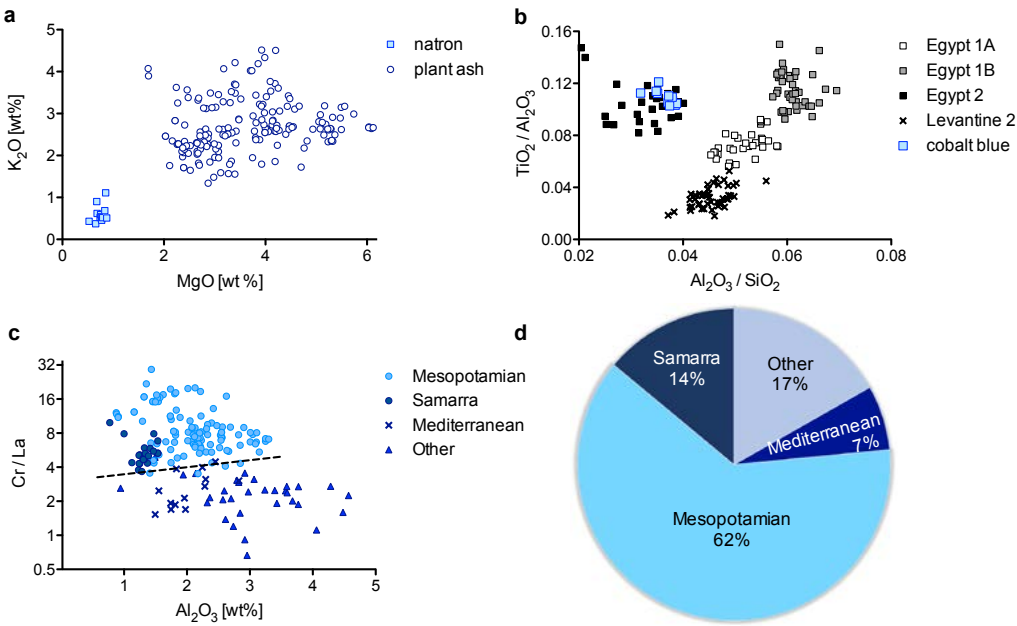

Figure 9.2: Base glass characteristics of the 208 cobalt-blue glass samples included in this study: (**a**) potassium and magnesium oxides separate a small group of natron glass; (**b**) TiO_2/Al_2O_3 versus Al_2O_3/SiO_2 ratios identify the natron glass as Egypt II (for Egyptian reference groups, see Schibille et al. 2019); (**c**) comparison of Cr/La and Al_2O_3 showcases different plant-ash glass groups, with the dotted line separating Mesopotamian glass from all other glasses; (d) the pie chart shows the proportions of the different soda-rich plant-ash glasses within cobalt-blue samples.

All other glass fragments containing more than 100 ppm cobalt are soda-rich plant-ash glasses (Fig. 9.2a). These cobalt-blue plant-ash glasses are seen in all kinds of different objects, such as glass beads from Ribe (Sode et al. 2022) and glass bangles from Siraf (Swan et al. 2017), mosaic tiles from Samarra (Schibille et al. 2018), glass-working waste from Gorgan (Schibille et al. 2022a), elongated flasks from various sites (e.g. Samarra, el-Ashmunein), as well as scratch-engraved bowls and beakers. The places where these cobalt-blue glasses were found include Madinat al-Zahra in al-Andalus (unpublished data by the authors); Israel (Phelps 2018), Samarra in Iraq (Schibille et al. 2018); several Iranian assemblages, from Gorgan, Nishapur (Schibille et al. 2022a) and Siraf (Swan et al. 2017); the glass from Bukhara, in Uzbekistan (Schibille et al. 2024); Ctesiphon, Iraq (unpublished data by the authors); and Merv, Turkmenistan (Meek et al. 2025). The distinctive compositional features exhibited by the plant-ash glass from some of these regions make it possible to classify the glass into supra-regional production zones (Lü et al. 2023; Schibille 2022b). For example, as previously shown in relation to LBA glass, elevated ratios of chromium to lanthanum are diagnostic of glass produced in Mesopotamia from local raw materials (Shortland et al. 2007). This particular compositional discriminant also applies to early Islamic plant-ash glass produced in Mesopotamia in the narrow sense, i.e. in the catchment areas of the Tigris and Euphrates rivers (Schibille 2022b). If we apply this criterion (Fig. 9.2c), it turns out that about 75% of the early Islamic cobalt-blue glass included in this study has a Mesopotamian (including Samarra) raw glass signature (Fig. 9.2d) and that 12 samples exhibit either Levantine or Egyptian base glass characteristics (grouped together under the heading Mediterranean). Only glass weights from Egypt are made from a Mediterranean base glass. The group "other" refers to all samples that cannot be attributed to any of these well-established compositional groups and covers glass from Iran (Schibille et al. 2022a; Swan et al. 2017), as well as Central Asian glass finds from Merv (Meek et al. 2025) and some isolated samples.

In short, analysis suggests that the vast majority of early Islamic cobalt-blue plant-ash glass is made from base glass that can be attributed to regional production zones east of the Euphrates, in Mesopotamia, Iran and Central Asia. Most importantly, this is independent of the place of discovery, i.e. the archaeological site where the samples were retrieved. For example, the cobalt-blue glass from Madinat al-Zahra, near Cordoba in al-Andalus, has distinctive high Cr/La ratios, which strongly suggests a Mesopotamian origin. At the same time, the other elements, such as aluminium, calcium, titanium, zirconium and rare earths, are highly variable, forming different compositional clusters. This implies that objects from various Mesopotamian production centres came to al-Andalus in batches, which is confirmed by stylistic considerations (Zamorano, in preparation). Similarly,

the cobalt-blue fragments from Bukhara, in Uzbekistan, are invariably of a Mesopotamian composition (Schibille et al. 2024), and the remains of an elongated blue flask recovered from el-Ashmunein, in Middle Egypt, are compositionally similar to the corresponding bottles found in Samarra (Schibille et al. 2018). Although Mesopotamian glassmaking does not have a complete monopoly on cobalt-blue glass during the early Islamic period, this strong geographical bias could be important in identifying possible sources of cobalt in the long term.

The cobalt pigment

As mentioned above, two cobalt types were predominant in Mediterranean glassmaking in the period immediately before the Arab conquest in the 7th century: a largely non-descript Roman cobalt pigment that has no clear elemental associations, and a late antique cobalt mineral with higher nickel concentrations and thus much lower CoO/NiO ratios (< 4; Gratuze et al. 2018). Both cobalt pigments were used in combination with Levantine as well as Egyptian natron-type glass. The late antique, nickel-rich cobalt gradually replaced the earlier Roman cobalt from the 4th century onwards, but Roman cobalt can still be found among 6th-century glass assemblages. In addition, glass recycling must always be reckoned with, and the latest occurrence of the Roman cobalt pigment cannot be determined with any accuracy. The complexity of the matter is illustrated, for instance, by some cobalt-blue vessels and window glass fragments from the 10th and 11th centuries that appear to have been coloured with a Roman cobalt pigment low in nickel (Pactat 2022). Islamic cobalt pigments from the Abbasid period have, instead, long been associated with substantial amounts of zinc oxide and typically no arsenic. This zinc-rich cobalt was identified in blue-and-white glazes (Seccaroni and Haldi 2016; Wood et al. 2007) and contemporary glass (Brill 1999; Gratuze et al. 2018).

The legacy data on cobalt-blue glass synthesised here paint a more complex picture. In fact, the glass can be split into four different pigment groups independent of the base glass type. The cobalt in early Islamic glass, with Co > 100 ppm, exhibits differential correlations with either Ni, Cu, Zn or As (Fig. 9.3). The classification at low cobalt concentrations is not clear-cut, and the higher the cobalt contents, the clearer the elemental associations. Perhaps the most obvious is a small group (n = 12) with high arsenic contents that is positively correlated with cobalt (Fig. 9.3c). None of the other elements are elevated in this subset of samples, suggesting that arsenic is solely associated with the cobalt mineral. The presence of arsenic is considered an elemental marker of Iranian cobalt ores (Matin and Pollard 2017), which coincides with the find spots of these samples in Iran. The high-arsenic

cobalt was identified in bangles from Siraf, some fragments from Gorgan, and a single sample each from Rayy and Nishapur (Schibille et al. 2022a). The largest cobalt group (n = 80) has low Co/Ni ratios (< 10) and a strong correlation between the two elements (Fig. 9.3a). About one-quarter of the samples (n = 57) have a cobalt pigment rich in zinc (Co/Zn < 1; Fig. 9.3b), while another quarter (n = 56) show a correlation between cobalt and copper (0.2 < Co/Cu < 0.9; Fig. 9.3d). The four different cobalt pigments can be found in combination with the various base glasses, although there are certain regional patterns. The natron-type Egypt II glass contains mainly the copper-rich variant, and the cobalt-blue glass from Samarra belongs largely to this pigment group, too, although some samples from Samarra are coloured with a cobalt rich in zinc (Schibille et al. 2018). The zinc-rich cobalt group includes Mesopotamian glass recovered from Viking period Ribe (Denmark) and Central Asian glass from Merv (Turkmenistan), but also some other Mesopotamian as well as Levantine and Egyptian soda-rich plant-ash glasses. The nickel-containing cobalt was used in conjunction with all the different base glasses. Hence, with the exception of the cobalt rich in arsenic, no clear geographical distribution can be recognised.

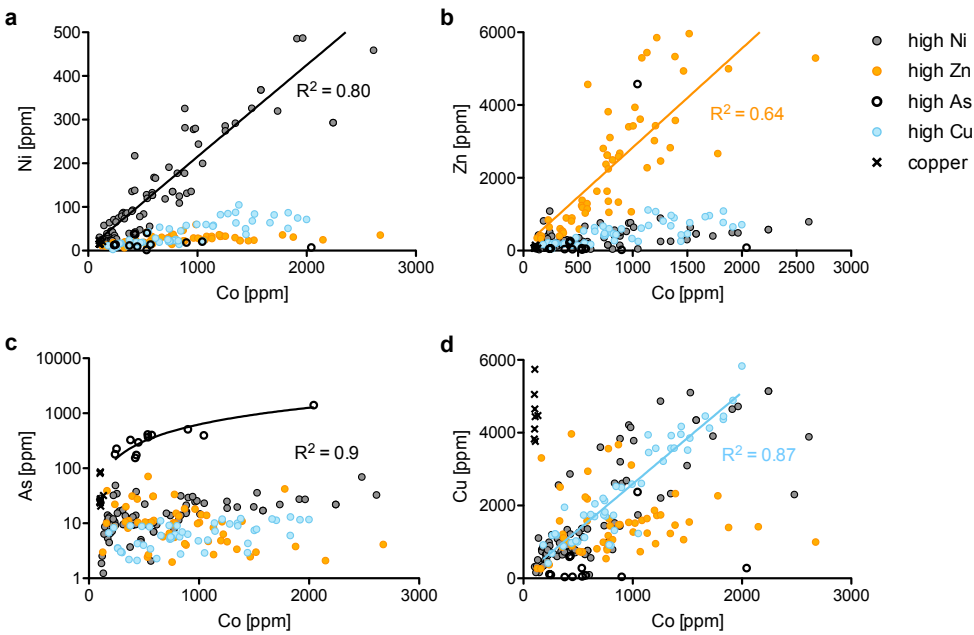

Figure 9.3: Graph showing the chemical signature of the cobalt pigments. (**a**) Ni and Co are strongly correlated in a subgroup of cobalt-blue glasses; (**b**) Zn versus Co identifies a high-zinc cobalt group; (**c**) As is elevated in a handful of samples; (**d**) a substantial number of samples are coloured by a copper-rich cobalt compound.

The glass assemblages dated to a single century from Viking Ribe, Abbasid Samarra and Merv (9th century) and from Umayyad Madinat al-Zahra and Samanid and early Qarakhanid Bukhara (10th century), together with the Islamic plant-ash glass weights from Egypt (11th century), provide reference points from which a chronological pattern emerges, albeit a fuzzy one (Fig. 9.4). In the 9th century, cobalt variants with high zinc and high copper were predominantly used. This agrees with the cobalt pigment identified in Abbasid blue-and-white glazed ware that typically contains some zinc and often also some copper (Wood et al. 2007). In the 10th century, cobalt with high nickel dominated instead. There are a handful of samples containing nickel-rich cobalt as early as the 9th century, but the concentrations of cobalt in these samples are too low to draw any firm conclusions on their origin. None of the samples that can be definitively dated to the 10th century were coloured with the zinc-rich cobalt pigment. All three cobalt variants are present in the 11th century. Unfortunately, there are no accurately dated samples among the glass coloured with the high-arsenic cobalt. Better dated samples are evidently needed to trace the chronological developments in more detail. It is also to be noted that there is a quantitative bias towards the 9th century, from where we have twice as many samples as from the two subsequent centuries combined (Fig. 9.4). It may be relevant that cobalt was used in Abbasid ceramics in the 9th century and only reappeared in the 12th century, after a hiatus of two to three centuries (Porter 1997, 2000). Perhaps the use of cobalt in the Islamic world was largely discontinued for some time. The overall impression from this comparison is, in any case, that the cobalt used in the earliest phases of Abbasid glass production in Iraq was a cobalt associated either with zinc or with copper and that the high-nickel cobalt came into use later. Therefore, the nickel-containing cobalt in early Islamic glass does not simply represent continuous exploitation of a late antique cobalt source, not least because there was apparently a delay in its use.

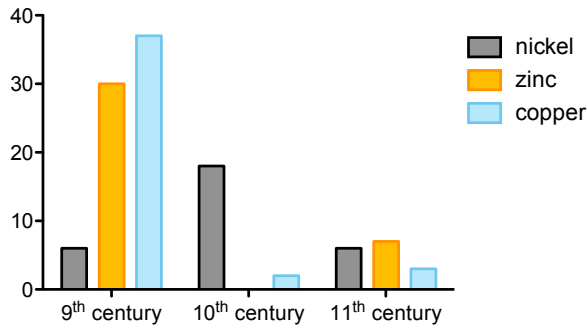

Figure 9.4: Chronology of early Islamic cobalt pigments based on samples dated to a single century.

A break with late antique recipes can also be recognised in the associated impurities. If the nickel content and cobalt content of Islamic cobalt-blue glass are compared with that of Byzantine glass weights coloured with a late antique high-nickel cobalt, both appear at first glance to show a similar correlation between cobalt and nickel (Fig. 9.5a). However, if the zinc concentration is included in the equation, there is a clear difference. It turns out that the late antique Byzantine cobalt-blue glass weights have much lower zinc contents than Islamic ones (Fig. 9.5b). The Byzantine glass weights were chosen for comparison because they can be dated fairly accurately to the 6th and 7th centuries, shortly before the Muslim conquest, and represent both Levantine and Egyptian Foy 2 base glass types (Schibille et al. 2016).

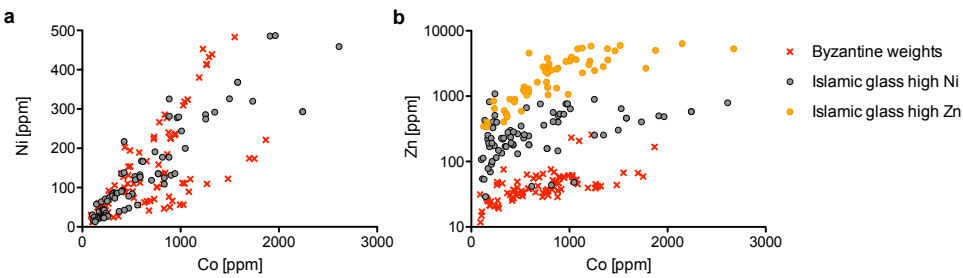

Figure 9.5: Graph comparing the chemical composition of nickel-containing cobalt of Islamic glass with the nickel-rich cobalt found in Byzantine glass weights: (**a**) Ni and Co show a similar trend, whereas (**b**) the Islamic glasses have notably higher Zn concentrations than the earlier, Byzantine samples.

The question then is, where does the zinc come from? Is it associated with cobalt or perhaps with copper? In cobalt-blue glass coloured with a cobalt pigment rich in copper, as well as in copper-blue glass, zinc levels remain much lower than in the cobalt-zinc samples, ruling out copper alloys as a possible source of the zinc in the latter (Fig. 9.6a). What is more, in the cobalt-copper glass, copper and zinc are clearly correlated, which indicates that the zinc here is at least to a certain extent associated with the copper. In the cobalt-zinc pigment, in contrast, the zinc behaves independently of the copper and this pigment clearly represents a different cobalt source and/or colouring technique. In a nutshell, the different cobalt pigments that were used to colour early Islamic glass (and possibly glazes) can be distinguished by a combination of Co/Zn and Co/Ni ratios (Fig. 9.6b). The high-nickel group with low Co/Ni ratios is similar to late antique cobalt, but the two differ in the Co/Zn ratio, which tends to be lower in Islamic glass. Then

there is a high-zinc cobalt that is easily identifiable, because of the strong positive correlation between cobalt and zinc. Finally, there is a high-copper group that separates from the high-nickel group in terms of higher Co/Ni ratios and from the high-zinc group in terms of higher Co/Zn ratios. The high-arsenic cobalt remains an exception in this early period and is primarily characterised by the presence of arsenic that is strongly correlated with cobalt.

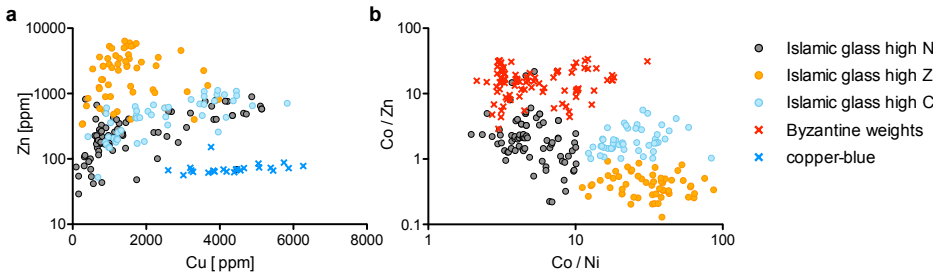

Figure 9.6: Graph showing compositional discriminants: (**a**) Zn and Cu are weakly correlated only in the copper-rich cobalt glass; (**b**) the combination of Co/Zn and Co/Ni ratios can distinguish the three main cobalt pigments (Ni, Zn, Cu) from one another as well as from earlier (Byzantine) nickel-rich cobalt.

A final consideration relating to the nature of the cobalt ore used in early Islamic glass concerns minor accessory elements that may be present. The early Islamic cobalt-blue glasses do not exhibit the correlations between cobalt and aluminium or manganese observed in some contemporary and later Chinese blue-and-white glazes (Jiang et al. 2020; Wood et al. 2007). Cobalt and iron are correlated only in the cobalt-copper group, while lead tends to be somewhat elevated, particularly in the high-nickel cobalt group. None of the samples that come from relatively secure and well-dated archaeological contexts show significant levels of indium, bismuth or uranium. A few samples from Sicily (Schibille and Colangeli 2021) and from Silves and Mertola in Portugal have high indium concentrations, and one glass from Silves has high bismuth values, suggesting these glasses are later intrusions (Cadena-Irizar et al. 2025). A Co-Zn-In signature is linked to the cobalt ore deposits in Freiberg, where mining started in 1168 CE (Gratuze et al. 1992, 1996; Molera et al. 2021). This signature is compatible with that seen in the samples from Sicily, which date to the 13th century and, strictly speaking, cannot be regarded as Islamic glass (Schibille and Colangeli 2021). An association of cobalt with bismuth, arsenic and nickel is known from the 15th century, but occurs more regularly from the 16th century onwards, as seen in data obtained from slag

in the Erzgebirge in eastern Germany (Gratuze et al. 1992, 1996; Molera et al. 2021). This calls into question the early Islamic period dating of the sample from Silves.

Processing and origins of cobalt minerals

Little is known about the processing of cobalt ores or about cobalt deposits that were accessible and exploited during the early Islamic period prior to the 13th century CE (Porter 1997, 2000). A factor that complicates the identification of cobalt sources is the varying solubility of the different elements of cobalt-containing minerals in silica melts. This means that the composition of the glass matrix does not necessarily reflect that of the parental cobalt ore. As was previously shown, cobalt-blue glazes can exhibit pronounced concentration gradients (Jiang et al. 2020; Kleinmann 1991). Based on the morphology of residual cobalt pigments in some 9th-century blue glazes from Samarra, Kleinmann (1991) proposed an elaborate manufacturing process that involved roasting to oxidise the minerals and thus eliminate sulphur and subsequent calcination with a quartz-rich material to obtain a vitreous frit.

The earliest surviving reference to the manufacture of cobalt-blue vitreous material (mīnā) in the Islamic world is the *Javāher Nāme-Ye Neẓāmi* (*Book of Stones for Nezām)* written in Persian in 1196 CE (Porter 2004). It is a compilation of earlier sources and discusses, in Chapter 4, recipes for producing glazes and their colours, including the colour of lapis lazuli (*lâjvard*). According to the author, Mohammad Ibn Abī al-Barakāt al-Jowhar al-Nīšāpūrī, to obtain the brilliant colour of lapis lazuli, 100 *deram* of soaked and washed crystal need to be mixed with 5 *deram* of soaked lapis and some natron and then melted (Porter 2004); folio 155a). By crystal, the author presumably means quartz pebbles (silica), which form the principal material of mīnā (folio 153b). As has been discussed by several authors, the term for lapis lazuli (*lâjvard*) is interchangeable with that for cobalt in early Islamic literature (Al-Hassan 2009; Matin and Pollard 2015; Porter 2000). About a century later, Abu'l-Qasim details the manufacture of differently coloured ceramics in his famous treatise on ceramics, the earliest surviving manuscript of which dates to 1301 CE (Allan 1973). To make a transparent blue glaze like sapphire, one needs to add "one part of *lâjvard* to forty parts of glaze frit", previously produced from "105 parts of shukar-i sang (quartz pebbles) and 110 parts of shakhār (soda)" ground and finely sifted (Allan 1976; §18).

Unfortunately, none of these early Persian sources contain information about the processing of the cobalt ore itself, other than that it had to be crushed, pounded and washed. No roasting of the cobalt minerals is mentioned; in contrast, copper

and silver are repeatedly described as having been roasted (Allan 1973). It is thus uncertain whether cobalt minerals were roasted or whether the ores were merely physically processed. In this context, the term *saffre*, also known as "Damascus blue", which was imported to Venice from the Levant for the glass industry in Murano, may be significant (Hess et al. 2004; Parker and Martlew 2021). Even though the term saffre appears in official Venetian documents only in 1446 CE, cobalt pigments were used in Murano from its very beginnings as a glass production centre in the 13th century CE (Verità and Zecchin 2015, 2016). Saffre refers to cobalt oxide, which results from the roasting of cobalt minerals (Giovanni and Riccardi 2021). Another indication that saffre may have been used for cobalt-blue glass already in the 11th century could be a reference in the *Libellus de consecratione ecclesiae S. Dionysii*, by Abbot Suger of St. Denis (c. 1081-1151 CE). Suger mentions "saphirorum materia" twice in relation to the sumptuous stained-glass windows of the Abbey of Saint Denis (Suger 1867). It has long been surmised that Suger is referring here to saffre/cobalt oxide rather than to sapphire (Bontemps 1868; Seccaroni and Haldi 2016). This would mean that roasted cobalt oxide was known and possibly trade across the Mediterranean long before it was produced in the mines of the Erzgebirge.

Regardless of the exact processing of the cobalt minerals, it is likely that the cobalt ores exploited for the various cobalt pigments used in early Islamic glass were poor in arsenic. Recent laboratory experiments to replicate the saffre production process according to Kunckel (1679) and the silver purification process according to Agricola's *De re metallica* have shown that neither roasting of cobalt arsenide minerals nor a prolonged treatment at high temperatures completely removed the arsenic from the cobalt mineral (Molera et al. 2021). The same results were obtained when the arsenic-rich cobalt ores from Kashan were processed together with borax (Matin and Pollard 2017). It was thus concluded that arsenic-free sources of cobalt must have been used as pigment for glass and glazes that do not contain any significant levels of arsenic (Matin and Pollard 2017; Molera et al. 2021). This appears to rule out the Qamsar cobalt mines, southwest of Kashan (Iran), as a possible source, as the two main cobalt minerals in Qamsar are cobaltite (CoAsS) or erythrite ($Co_3(AsO_4)_2 \times 8H_2O$), and the ore has been shown to contain significant levels of arsenic and iron, but no zinc, copper or nickel (Matin and Pollard 2017).

The cobalt mines in Qamsar are the most commonly cited source of cobalt, presumably because we know from written sources, such as Abu'l-Qasim's treatise on ceramics, that the Qamsar mines were exploited in the 13th or 14th centuries for cobalt used in Islamic and Chinese glazes (Allan 1973; Ma et al. 2022; Porter 1997; Wen and Pollard 2016; Zhu et al. 2015). It is not clear when mining activities

began in Qamsar or which cobalt minerals were mined historically. Abu'l-Qasim describes two variants, one that is "like white silver shining in a sheath of hard black stone" and another type that is "like the red shells of pistachios … very strong but is a fatal deadly poison" (Allan 1973, §8). The latter undoubtedly refers to erythrite ($Co_3(AsO_4)_2 \times 8H_2O$), given its distinctive pinkish colour, while the silvery mineralisation was thought to be either cobaltite (CoAsS; Matin and Pollard 2017) or, possibly, linnaeite ($Co^{2+}Co^{3+}{}_2S_4$; Kleinmann 1991), both of which have a metallic grey-purple appearance with greyish-black streaks (www.mindat.org), matching the description by Abu'l-Qasim. Linnaeite was identified in the mining district of Baytche-Bâgh, in northwestern Iran (Bariand 1963), but it seems generally rare, and there is currently no information about the history of this deposit (Bariand 1963; Porter 1997, 2000). About 200 km east of Kashan, in the Anarak mining district of central Iran's Isfahan province, at the sites of Talmessi and Mes-kani, shallow deposits may have served as an alternative source of cobalt (Henderson 2013; Hill et al. 2004; Jiang et al. 2020; Wood and Hsu 2019). It is not known when the mines in Anarak began to be exploited, and arsenic-rich cobalt minerals predominate here, too. The mining district is famous for its five-element association of Ni-Co-As-Cu-U (Bagheri et al. 2007; Tarkian et al. 1983). If any of these compounds were used as the blue pigment in the early Islamic vitreous materials, arsenic and uranium should accordingly be elevated along with the cobalt. The database of mineralogy run by the Hudson Institute of Mineralogy lists cobalt pentlandite among the mineral species represented at Talmessi, which is a cobalt sulfide (Co_9S_8) that has a yellowish metallic aspect (mindat.org/loc-2011.html).

In essence, it is clear that the cobalt mines in central Iran are historically of great importance, but that the characteristics of their mineralisation, variability and genesis are still not well documented (Bagheri et al. 2007). The Qamsar mines, for example, do not feature among cobalt deposits in the mindat.org database, and while Qamsar may have provided the cobalt rich in arsenic, it is unlikely to be the origin of the other cobalt pigments identified in early Islamic glass. Alternative sources of cobalt must also be considered. For example, the Arabian Peninsula, has been suggested by Jessica Hallett (1999), where carrollite ($CuCo_2S_4$) occurs in the al-Batinah region of Oman and linnaeite is found in the ancient Nuqrah mines in the Medina Region of Saudi Arabia. Similarly, a possible supply from the cobalt deposits of the Caucasus has been proposed for the production of early Islamic glass (Colomban et al. 2021; Porter 2000; Seccaroni and Haldi 2016). Linnaeite is found in the Caucasus Mountain range in the Balakan District in Azerbaijan (mindat.org), whereas cobalt ores in the form of siegenite ($(Co,Ni)As_{3-x}$) are said to occur in Telavi, Georgia (Colomban et al. 2021; Porter

2000), but this could not be independently verified (i.e. there is no entry for this on mindat.org). Ultimately, many questions about the processing, origin and use of cobalt pigments in the early Islamic world remain unanswered, and even in the period after which the first written sources exist, the picture is still unclear.

What we know: Attempt at a conclusion

This comparative study discusses early Islamic cobalt-blue glass from an analytical perspective, considering the properties and origin of the base glass, as well as variations in the pigment signatures. As such, it is an important step towards resolving the complex interplay between glass production and the exploitation of (yet-unknown) cobalt ores. Only a handful of early Islamic natron glasses, in the form of Egypt II, were coloured with cobalt, and no cobalt-coloured glasses have been found among earlier Islamic natron glasses (Levantine II, Egypt I). About 90% of the soda-rich plant-ash glasses in this study have base glass characteristics that suggest a production location east of the Euphrates (e.g. Samarra, Iran, Merv), with the vast majority corresponding to Mesopotamian glass compositions. The new, Islamic base glasses are accompanied by new sources of cobalt. As far as the archaeological dating allows, a chronological evolution can be discerned: initially, cobalt pigments rich in zinc or copper were used, followed by a high-nickel cobalt, which makes up the main pigment in the 10th century and differs from the high-nickel cobalt previously identified in relation to late antique natron-type glasses. This provides compelling evidence that new sources of cobalt were exploited and/or that the processing of the cobalt ores changed in the interim.

Earlier studies have identified the emergence of a zinc-rich variant in Abbasid glass and glazes. The more comprehensive analytical data now available show that four different cobalt minerals were used to obtain cobalt-blue glass in the early Islamic period (8th-12th centuries). Zinc-rich and nickel-rich cobalt were identified also in glazes from the 9th century (Kleinmann 1991; Spataro et al. 2019; Wood et al. 2007). It is noteworthy that in 9th-century Samarra (Iraq), the blue-and-white-glazed ceramics were painted with a nickel-containing cobalt pigment (Kleinmann 1991), whereas the glasses—both the locally produced Samara 2 glass and the imported cobalt-blue flasks—were mainly coloured with a copper-rich cobalt mineral (Schibille et al. 2018). A further observation can be made with regard to the glass from Samarra, namely that the same raw glass (Samarra 2) has different cobalt signatures. However, the other cobalt pigments seem to be the exception, and only three samples each (possibly) represent the zinc-rich and the nickel-rich colourant; there is some doubt about the latter due to low cobalt contents (Co < 150 ppm). At 9th-century Merv, about 2,000 km east of Samarra,

the scenario is different. Here, the base glass of all the cobalt-blue fragments (n = 9) was probably produced in the region around Merv and coloured with a zinc-rich cobalt pigment (Meek et al. 2025). Whether this allows conclusions to be drawn about the origin of the cobalt minerals is uncertain, but it seems safe to assume that cobalt was traded in some form or other (e.g. as saffre, smalt or glass/frit) at least since the 9th century CE.

The sources of ores used for the different cobalt pigments remain obscure; only the arsenic-rich cobalt may eventually be linked to the famous deposits of cobaltite or erythrite in Qamsar. The absence of arsenic in all three of the other cobalt pigments makes it unlikely that they originated from this mining area. If either cobaltite or erythrite were used, at least some traces of arsenic should be detectable in the glass matrix of the early Islamic samples, which is not the case. In order to better understand the extent to which the cobalt signature and its variations calculated from the analysis of the glass matrix reflect the original cobalt ores, the effects of elemental differentiation during heat treatment need to more fully investigated (Jiang et al. 2020). The key to this could be the study of residual pigments that are sometimes present in glazes and glass and which may contain the compositional memory of the original cobalt ore. To fully grasp the technological, chronological and geographical variations, it is essential, as with any archaeometric study, to consider (only) well-dated vitreous material from secured archaeological contexts.

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Chapter 10

Smalt and other blues in painting from South Asia and Iran

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Introduction

Technical examination and analysis of artworks from the Middle East and South Asia has been ongoing at the Havard Art Museums and Museum of Fine Arts, Boston, (MFA) since the early 20th century. More recently, technical studies have been integrated into the Mapping Color in History (MCH, https://mappingcolor.fas.harvard.edu) project. The MCH project is developing a digital portal with a searchable online database documenting pigments and their material properties to facilitate the in-depth historical analysis of pigment data in both time and geographical location. At present, the project is focused primarily on materials in works on paper from South and West Asia (the latter often referred to as the Middle East), particularly the Indian subcontinent. The database draws on analyses of more than 200 works in the collections of the Harvard Art Museums; the Museum of Fine Arts, Boston; the Detroit Institute of Art; and the Chhatrapati Shivaji Maharaj Vastu Sangrahalaya in Mumbai, as well as on existing published data. Recent analyses undertaken for this project have generated new information about the pigments used and how these vary both geographically and chronologically. This paper will focus on the use of glassy blue pigments coloured with cobalt in art works dating from the 15th to 18th centuries. Art works in the collection of the Harvard Art Museums are referred to by object number, whereas art works in the collections of the Museum of Fine Arts, Boston, have object numbers prefaced by "MFA".

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Blue is one of the most widely used and important colours in art from the Middle East and South Asia, as discussed by Lazaro (2005) and Kim (2021). Traditionally, artists used primarily ultramarine and indigo, with some azurite. As shown in this study, a glassy blue pigment coloured with cobalt joined the artists' repertoire in the late 15th to 16th centuries. It is tempting to equate this pigment to smalt, particles of potassium-rich glass coloured with cobalt manufactured in Europe as a pigment from at least the early 15th century (Berrie 2015; Mühlethaler and Thissen 1969, 1993; Stege 2004). However, cobalt has been used as a colourant in glass and glaze by many cultures since antiquity (Colomban et al. 2021; Shortland et al. 2006; Tite et al. 2002; Vandiver 1990). Thus, a glassy blue pigment could be derived from crushed blue glass or glaze of varied composition. In his discussion of the invention of blue (and purple) pigments, Berke defined smalt simply as "a substance with a variable composition, a solution of cobalt in glass" (Berke 2007, 20). Whether any blue pigment of crushed glass or glaze coloured with cobalt can be termed smalt or whether this term should be reserved for the potash glass coloured with cobalt produced as a pigment in Europe is debatable. A wider definition would encompass any cobalt-coloured blue glassy material identified as a pigment in art works—the identification of which is obviously far easier than proving such a pigment is truly European smalt. Although the pattern of elements associated with the cobalt acts as a "fingerprint" for the source of the cobalt ores—ore sources in Europe having a characteristic fingerprint that differs from that of ores in Iran or China—cobalt ores and/or products of these ores were widely exported as colourants for glass or glaze. Thus, the use of European cobalt in a glassy pigment does not necessarily prove use of European smalt manufactured in Europe as a pigment and exported as such. For the purposes of this paper, we will refer to all glassy blue pigments coloured with cobalt as smalt, discussing later whether these are actually European smalt.

Production and use of smalt

Since smalt is the best known and most widely used type of glassy blue pigment, any consideration of the materials used in Indian and Islamic art requires an introduction to current knowledge of the production and use of smalt.

Production

Although the history of smalt production in Europe has been extensively studied, the exact origins and details of the early production of smalt are still unclear (Berrie 2015; Colomban et al. 2021; Mühlethaler and Thissen 1969, 1993; Santopadre and Verità 2006; Spring 2017; Stege 2004; Zlámalová Cílová et al. 2020). It is evident,

however, that German cobalt ores were likely used as glass colourants from at least the 12th century onwards, with production of smalt pigment likely starting from the late 14th to early 15th century (Gratuze 2013; Gratuze et al. 1992, 1996; Stege 2004; Zlámalová Cílová et al. 2020). German ores were exported for use in smalt production, particularly to Italy and the Netherlands (Berrie 2015; Columban et al. 2021; Mühlethaler and Thissen 1969, 1993; Santopadre and Verità 2006; Spring 2017; Stege 2004; Zlámalová Cílová et al. 2020). Although most smalt consists of potash glass coloured with cobalt, Renaissance smalt compositions were more diverse and included potassium-rich, sodium-rich and mixed alkali glass (Colomban et al. 2021; Santopadre and Verità 2006; Zlámalová Cílová et al. 2020). Cobalt ores have been shown to have a distinctive fingerprint indicative of their geographical location (Gratuze 2013; Gratuze et al. 1992, 1996). Ores from the Erzgebirge mines of Germany and Bohemia have a characteristic signature of iron, cobalt, nickel, arsenic, and, in some instances, bismuth, with changes in the levels and ratios of elements likely reflecting changes in production processes and exploitation of new veins (Berrie 2015; Columban et al. 2021; Gratuze 2013; Gratuze et al. 1992, 1996; Spring 2017; Spring et al. 2005; Stege 2004; Zlámalová Cílová et al. 2020). This characteristic fingerprint enables smalt produced with cobalt from the Erzgebirge deposits to be readily identified in art works based on elemental analysis.

Use as a pigment

The earliest identification of smalt as a pigment in European artworks comes from polychrome sculpture of the 11th and 12th centuries, and in an anonymous painting dated to around 1400 CE (Stege 2004). Smalt was used sparingly by artists in the 15th and early 16th century—being identified in around 10% of paintings and in a slightly higher proportion of other objects analysed, often combined with other blue pigments (Stege 2004). Use of smalt increased through the mid-16th to 17th century—occurring in around one-third of the artwork investigated (Stege 2004). The popularity of smalt likely owed much to its low cost compared with the other available blue pigments, azurite and, in particular, ultramarine (Stege 2004; Véliz 2010). Smalt degrades in the presence of oil binders, resulting in the loss of alkali, chiefly potassium, from the glass matrix, which in turn results in a dull, grey appearance which was commented on as early as the 17th century (Santopadre and Verità 2006; Spring et al. 2005; Véliz 2010). Use of smalt hence declined through the 18th century, and it was gradually replaced by use of the cheaper Prussian blue, developed in Berlin in 1704 CE and widely used as an artist's pigment soon after its discovery (Berrie 1997).

The earliest reported occurrence of smalt outside of Europe is frequently stated to be on 11th to 13th century wall paintings from Khara-Khoto, Central Asia—now located in Inner Mongolia, China (Gettens and Stout 1966; Mühlethaler and Thissen 1969, 1993). However, although Gettens found smalt on a "fragment of loess wall painting" collected at the site in 1925 (Gettens and Stout 1966; Mühlethaler and Thissen 1969, 1993), the current location of this fragment is unknown. The fragment and hence the use of smalt have traditionally been linked to three wall paintings from Khara-Khoto obtained by Langdon Warner in the first Harvard-Fogg expedition to China in 1924, object 1924.67.1-3. However, the fragment on which Gettens identified smalt appears to have been given to him later and is not related to the wall paintings, which can be dated stylistically. Recent analysis of the three wall paintings identified only azurite and indigo; no cobalt was detected in any area. This raises questions about the dating of the unknown fragment analysed by Gettens and its relationship to other materials from the site. Ongoing analysis of sculptural elements and figures from Khara-Khoto, in conjunction with art historical assessment of the dating, is focused on determining if any smalt is present and on the date of relevant pieces. Khara-Khoto materials have a terminus post quem and ante quem because the site was founded in 1032 CE as the capital of Xixia and was captured by the Mongols in 1226 CE. It is believed to have survived the Mongol takeover but fell into disuse after 1372 CE, not only due to political turmoil, but, probably, also due to water shortage. Initial analysis of the blue pigment on the clay sculpture from the site has found only azurite to date.

Apart from the fragment analysed by Gettens, the earliest certain occurrences of smalt outside western Europe are on Byzantine materials—13th and 14th century manuscripts (Turner and Schmidt Patterson 2017) and wall paintings (Gettens and Stout 1958). Smalt has also been identified on 15th century Armenian manuscripts (Cabelli and Mathews 1982) and a 15th century Venetian manuscript (Ricciardi et al. 2022). A glassy blue cobalt-coloured pigment, termed smalt, occurs with ultramarine on pre-17th century Persian wall paintings (Holakooei and Karimy 2015). However, analysis showed that the smalt grains have significant levels of calcium and lead, appreciable cobalt, arsenic and iron, with no detectable bismuth, which does not match European smalt or cobalt ores and instead suggests local manufacture using cobalt ores from Qamsar, Iran (Holakooei and Karimy 2015). Smalt has only occasionally been identified on Islamic art works prior to this study—a late 17th to early 18th century Ottoman manuscript (Hepworth 2005) and two 18th century Persian manuscripts and an 18th century Persian oil painting (Newman 1998). Although European smalt, confirmed by the characteristic associated elements, is present in a 17th century painting attributed to the Safavid artist Riza Abbasi or his associates, it is thought to be contained in retouching

by the 17th century German collector Gesina ter Borch, who assembled the scrapbook containing the painting (Couvrat Desvergnes et al. 2021). The original blue pigments used by the Safavid artist were instead azurite and ultramarine (Couvrat Desvergnes et al. 2021), consistent with analysis of five late 16th to early 17th century artworks in the collections of the Harvard Art Museums attributed to Riza Abbasi or school of Riza Abbasi that demonstrated use of ultramarine, indigo and/or azurite, with no cobalt detected in any areas. This example highlights the need for careful examination of the artworks to determine whether the pigments detected are original or the result of later intervention. No smalt was identified during previous analysis of over 50 works on paper from Egypt, Iraq, Iran and Central Asia dated from the 13th to 19th centuries at the Harvard Art Museums (Knipe et al. 2018).

In the 17th and 18th centuries, global expansion and colonisation spread European painting styles, techniques and materials across the globe. Smalt has been identified in numerous paintings in South America, brought by European painters who travelled to the New World and imported from Flanders and Italy via Spain (Bruquetas and Presa 1997; Insaurralde Caballero and Castañeda-Delgado 2021; Lazarte Luna et al. 2018; Mahon et al. 2020; Sánchez and Quiñones 2009; Seldes 1994; Seldes et al. 1999; Tomasini et al. 2016, 2018). The glassy blue pigment could result from import of European smalt, from local production by grinding imported Bohemian glass beads, or from local production of glass, glaze or deliberate pigments (Bruquetas and Presa 1997; Insaurralde Caballero and Castañeda-Delgado 2021; Seldes et al. 1999). Smalt has also been identified on late 16th to 17th century paintings from Goa, part of Portuguese India, as a result of European import and influence, which affected both painting styles and materials in Goa (Antunes et al. 2019). Despite this, smalt has rarely been identified on other Indian artwork, with only one confirmed and two possible instances of use on 18th century paintings from Kota (Bowen and Snodgrass 1997) documented prior to the MCH project.

Similarly, smalt was introduced to Japan in the late 16th century when an Italian Jesuit painter founded a painting *seminario* in Japan at the request of the local Jesuit mission, with the aim of producing Christian paintings for the missionaries (Montanari et al. 2021). Smalt has been identified in paintings produced at the *seminario* by European, Chinese and Japanese artists, and in secular and sacred Japanese art from the late 16th century onwards (Montanari et al. 2020, 2021). The association of Fe-Co-Ni-As and Fe-Co-Ni-As-Bi in sacred Buddhist art demonstrates use of European smalt imported by Portuguese and Dutch traders from Italy and the Netherlands (Montanari et al. 2020). Smalt was widely used in China from the 16th century and may have been used as early as the 14th century

(Colomban et al. 2021; Xia et al. 2019). Xia et al. (2019) suggested that European smalt was a cheaper pigment than azurite in the 16th to 19th centuries, as smalt was often used with indigo as a ground layer under azurite.

Analytical techniques and methodology

Paintings, manuscript folios and other artwork from India and Iran in the collections of the Harvard Art Museums and the Museum of Fine Arts, Boston, were studied for the MCH project with a range of techniques, most importantly examination with visible, infrared and ultraviolet illumination, non-destructive XRF, in-situ Raman spectroscopy, and reflectance Fourier-transform infrared (FTIR) spectroscopy. In some instances, small samples were taken from areas of loss or damage for more accurate identification by transmission FTIR, scanning electron microscopy with energy dispersive microanalysis (SEM-EDX) and/or high-performance liquid chromatography (HPLC) to resolve remaining ambiguities. The techniques used for the identification of the blue pigments discussed here were primarily microscope examination, in-situ XRF analysis and SEM-EDX of samples where possible.

X-ray fluorescence with energy-dispersive microanalysis

In-situ X-ray fluorescence with energy-dispersive microanalysis (XRF) was used to determine the elemental composition of different areas and colours on the artworks selected. All analysis was non-destructive; no sampling took place of any areas. As such, the XRF spectra may contain information from multiple layers of pigment and paper and from different phases where mixtures are present.

The XRF system employed at the Harvard Art Museums is a Bruker Artax XRF spectrometer with a Silicon Drift Detector (SDD) and a rhodium (Rh) anode X-ray tube. The primary X-ray beam is collimated to give a spot size of 0.65 mm. Most spectra were acquired for 100 seconds live time at 50kV and 600μA, with a helium flux used to improve detection of elements with low atomic number, from aluminium to potassium. Elements with an atomic number below aluminium, including magnesium and sodium, could not be detected even with use of helium. The XRF system at the MFA is the same type of instrument: a Bruker Artax XRF spectrometer with an SSD detector, a Rh tube and a spot size of about 0.65 mm. Spectra are run for 120 seconds live time at 40kV and 400μA, without the helium flow. In both institutions, multiple analyses were undertaken in each area of interest to assess variability within and between artworks. Longer analyses, with live time of 300 s, were used on blue areas where significant cobalt was detected, to improve detection of all trace elements. The XRF analyses were not quantified, due to the lack of detection of light elements and the potential for multiple particles or phases

to be present in a single point analysis. Semi-quantitative data were obtained from the relative peak intensities of elements of interest.

Scanning electron microscopy with energy-dispersive microanalysis

Although the XRF analysis provided information on the composition of the smalt in the manuscripts and lacquer work, it did not enable us to obtain fully quantified compositions due to the poor detection of light elements and presence of multiple layers and phases within a single analysis point. The possibility of taking samples of the glassy blue pigment for accurate compositional analysis by scanning electron microscopy with energy-dispersive microanalysis (SEM-EDX) was hence investigated by curators, conservators and scientists. In most instances, only micro-samples of a few pigment grains could be removed from rare areas of loss. Samples were placed directly on carbon tape for SEM-EDX analysis. Extensive damage to the edges, and in particular corners, of one manuscript cover, 1984.463, allowed for removal of small samples that included multiple layers. These samples were mounted in resin and polished to produce cross-sections.

SEM-EDX analysis of the loose pigment samples was complicated by the fine particle size and presence of multiple phases in some samples, particularly lead white. The glassy blue pigment was often extremely crumbly and friable even in dark blue areas, suggesting alteration of the particles was likely. Since the samples were unmounted, analysis of the glassy particles was of the surface—the areas experiencing the most alteration. In contrast, the mounted and polished samples from the lacquer manuscript cover allowed for analysis of both the surface and the interior of particles, the latter providing better access to original compositions. Levels of silicon and potassium were extremely variable, both between and within particles in each sample. It was assumed that the highest potassium values likely represent the least altered grains, but this may not be true in all cases. Compositional analyses of smalt particles with variable alteration show that levels of cobalt and associated elements, and the ratios of these elements, are the same for the altered surface and the unaltered interior (Janssens et al. 2016; Spring 2017; Spring et al. 2005; Van Loon et al. 2020). Some difference between the SEM and XRF analyses may be expected, as the former are of individual particles, while the latter combine data from multiple particles to give an averaged result.

A JEOL JSM-IT500LV SEM (tungsten filament) with an Oxford Instruments X-MaxN SDD, 80 mm^2 detector (resolution Mn Kα, 126 eV) running the Oxford Instruments AZtec software (version 4.2 SP1) was used for SEM-EDX analysis. The SEM was operated in low vacuum mode at a chamber pressure of 50 Pa, with an operating voltage of 20 kV, beam current optimised for dead time of analysis, and working distance of 10 mm. The samples were not carbon coated prior to

analysis. Analysis of pigment particles was performed on a flat surface with a live time of 100 s to optimise quantification. Analyses were normalised to 100% and quantified using the following standards: Na, Si: Corning A; K, Ca: Corning D; Pb, Ba: Corning C; Al: albite; Mg: diopside; Fe: forsterite, with internal standards used for other elements.

Raman spectroscopy

Raman spectroscopy was undertaken on selected manuscripts to clarify the pigment mixtures inferred from XRF analysis. The Raman spectrometer utilised at the Harvard Art Museums is a Bruker Optics Senterra dispersive Raman microscope with an Olympus BX51M microscope equipped with 20× and 50× long working distance objectives. The Raman spectrometer has three laser sources, 532 nm, 633 nm and 785 nm. The optimum laser source depends on the pigment analysed, but in general, blue and green pigments were predominantly analysed with the 532 nm laser, at 2 mw or 5 mW power, and other colours analysed with the 785 nm laser, at 10 mW power. The Raman spectrometer at the Museum of Fine Arts is a Thermo Scientific DXR3 dispersive Raman microscope with 10×, 20× and 100× objectives and two laser sources, 532 nm and 785 nm. The typical laser power selection was between 0.1 and 1 mW power. Spectra were compared with reference libraries, particularly the RRUFF database, using the Opus and Omnic softwares, respectively.

Results and discussion: Indian artworks

XRF analysis of more than 200 Indian artworks showed that cobalt was present in blue pigments on a relatively small number of works on paper, as shown in Table 10.1. Microscope examination of areas with cobalt-based blue pigments indicated the presence of glassy blue particles, which will be described as smalt hereafter for simplicity. However, in the absence of other evidence, this use of terminology should not be taken to imply a potassium-rich composition, European origin, or primary production as a pigment. Lazaro (2005) includes smalt, referred to as *asmani*, in his discussion of blue pigments used in the *picchvai (pichwai)* tradition of painting in Rajasthan. Smalt is described as an alchemical pigment from the Middle East that was occasionally used in traditional paintings but is no longer used in traditional studios (Lazaro 2005). It is worth nothing that Lazaro's description of smalt as a pigment from the Middle East is based on the widely accepted but recently questioned presence of smalt on 11th to 13th century Central Asian wall paintings and the historical importance of Iranian cobalt, which was used as a colourant for glass and ceramics from at least the 12th century CE.

Table 10.1: Indian and Persian works on which smalt was identified in the collections of the Harvard Art Museums and Museum of Fine Arts, Boston (abbreviated to MFA). All works are painted folios unless indicated otherwise.

Accession Number	Date	Production Site	Other Blue Pigments	Notes
Jain manuscripts				
MFA 17.2277, folios 1, 10, 13, 44	1497	Gujarat	Ultramarine	Single manuscript, 4 folios analysed
Rajput works on paper				
1995.122	c.1620	Bikaner		
1983.93	c.1678	Bikaner		
1984.458-461	c.1660-80	Bundi	Indigo	Dispersed manuscript, 4 folios analysed
1972.74; MFA 17.2780-2786	c.1660-70	Basohli	Indigo, ultramarine	Dispersed manuscript, 6 folios analysed
1995.76	c.1660-80	Mewar		
1931.16-19	c.1680	Mewar	Indigo	Dispersed manuscript, 4 folios analysed
2009.202.237	c.1720	Kota	Indigo	Attributed to the Kota master
1995.95	c.1730	Kota		Attributed to the Kota master
2015.31	c. 1720-30	Kota	Indigo	
1960.681, 1963.73, 1963.74, 1969.174	c.1756	Malpura	Indigo	Dispersed manuscript, 4 folios analysed, attributed to Jai Kisan
1960.159	c.1760-70	Guler	Indigo	
1974.109	c.1760	Guler	Indigo	
1974.108	18th century	Guler	Indigo	
1971.126	1780	Kangra	Indigo	
1971.139	18th century	Kangra	Indigo	
1972.353	18th century	Mewar	Indigo	
1973.153	18th century	Mewar	Indigo	
1973.155	18th century	Mewar	Indigo	
Safavid works on paper				
1960.48	1632-33	Isfahan	Azurite, ultramarine	Attributed to Mu'in Musavvir
2006.262	1688	Isfahan	Ultramarine, indigo	Attributed to Mu'in Musavvir
15.2015	1658	Iran		
2014.395	1696, 1717	Iran		
Persian lacquer				
1984.463	1685-86	Isfahan	Folios: ultramarine, azurite	Lacquer manuscript cover, black border, blue decoration inside covers
2014.303	1708	Iran	None	Lacquer penbox, black border
2014.399	1784	Iran	Folios: ultramarine, azurite	Lacquer manuscript cover, black decoration on inner cover

Table 10.2: Composition of smalt in art works in the collections of the Harvard Art Museums and Museum of Fine Arts, Boston (abbreviated to MFA). Starred objects were sampled for SEM-EDS analysis.

Accession Number, Collection	XRF Data from Blue Areas	Date/ Century	Site
Jain manuscript folios			
MFA 17.2277, folios 1*, 10, 13, 44	Si, K, Ca, Fe, Co, As, (Ti, Mn, Cu)	1497	Gujarat
Rajput manuscript folios, 17th century			
1995.122*	Al, Si, K, Ca, Fe, Co, Pb, As, (Ti, Mn, Ni, Cu)	c.1620	Bikaner
1983.93		c.1678	
1984.458-461	Si, K, Ca, Fe, Co, Ni, Cu, Pb, As, Bi, (Ti, Mn)	c.1660-80	Bundi
1972.74*; MFA 17.2780, 17.2786*, 17.2792, 17.2793	Si, K, Fe, Co, Ni, Pb, As, Bi, (Ca, Ti, Mn)	c.1660-70	Basohli
1995.76	Si, K, Ca, Fe, Co, Ni, Pb, As, Bi, (Ti, Mn)	c.1660-80	Mewar
1931.16, 1931.17, 1931.18, 1931.19	Si, K, Ca, Fe, Co, Ni, Pb, As, Bi, (Ti, Mn, Cu)	c.1680	
Rajput manuscript folios, 18th century			
2009.202.237	Al, Si, K, Ca, Fe, Co, Ni, Pb, As, Bi, Sn, (Ti, Mn, Cu)	c.1720	Kota
1995.95	Si, K, Ca, Fe, Co, Ni, As, Bi, (Ti, Mn, Cu)	c.1730	
2015.31	Si, K, Fe, Co, Ni, Cu, Pb, As, Bi, (Ca, Ti, Mn)	c. 1720-30	
1960.681*, 1963.73, 1963.74, 1969.174	Si, K, Ca, Ba, Fe, Co, Pb, As	c.1756	Malpura
1960.159	Si, K, Fe, Co, Ni, Pb, As, Bi, (Ca, Ti, Mn)	c.1760-70	Guler
1974.109	Fe, Co, Ni, Pb, As, Bi, (Si, K, Ca, Cu)	c.1760	
1974.108	Si, K, Ca Fe, Co, Ni, As, Bi, (Mn, Cu, Pb)	Late 18th	
1972.353	Si, K, Ca Fe, Co, Ni, Pb, As, Bi, (Cu)	Mid-18th	Mewar
1973.153	Si, K, Ca Fe, Co, Ni, Pb, As, Bi, (Cu, Zn)	18th	
1973.155	Si, K, Ca Fe, Co, Ni, Pb, As, Bi, (Cu, Zn)	18th	
Safavid manuscript folios			
1960.483	Si, K, Ca Fe, Co, Ni, Pb, As, Bi, (Cu, Zn)	1632-33	Isfahan
2006.262	Si, K, Ca, Fe, Co, Pb, (Ni, Cu, As)	1688	
15.2015	Si, K, Ca, Co, Ni, As, Bi, (Ti, Mn, Pb)	1658	Iran
2014.395	Si, K, Ca, Co, Ni, As, Bi, (Ti, Mn, Pb)	1696, 1717	Iran
Safavid and Zand lacquer work			
1984.463*	Si, K, Fe, Co, Ni, As, Bi, (Ca, Mn, Cu, Pb)	1666-86	Isfahan
2014.303	Si, K, Fe, Co, Ni, Pb, As, Bi, (Ca, Cu, Au)	1690-91	Iran
2014.399	Si, K, Fe, Co, Ni, Pb, As, Bi, (Ca, Cu)	1784	Iran

The Indian art works on which smalt was detected in this study include folios from a late 15th century Jain manuscript (MFA 17.2277) and several Rajput and Safavid works dating from the 17th and 18th centuries. In many of these, smalt was used in specific areas, with ultramarine and/or indigo also used in the same artwork. The qualitative elemental compositions of the smalt based on the XRF analysis are shown in Table 10.2. Elements such as silicon, potassium, calcium and titanium

are likely associated with the glass matrix, while elements such as iron, arsenic, nickel and bismuth are likely inherited from the cobalt ore source. Manganese and copper may be associated with either the glass or the original cobalt ore. The results are discussed below in groups based on their art-historical attribution.

15th to 16th century Jain manuscript folios

The earliest of the works on paper in which cobalt was detected by XRF analysis was a Jain manuscript dated to 1497 CE, MFA 17.2277.1-78, an example folio of which is shown in Figure 10.1a.

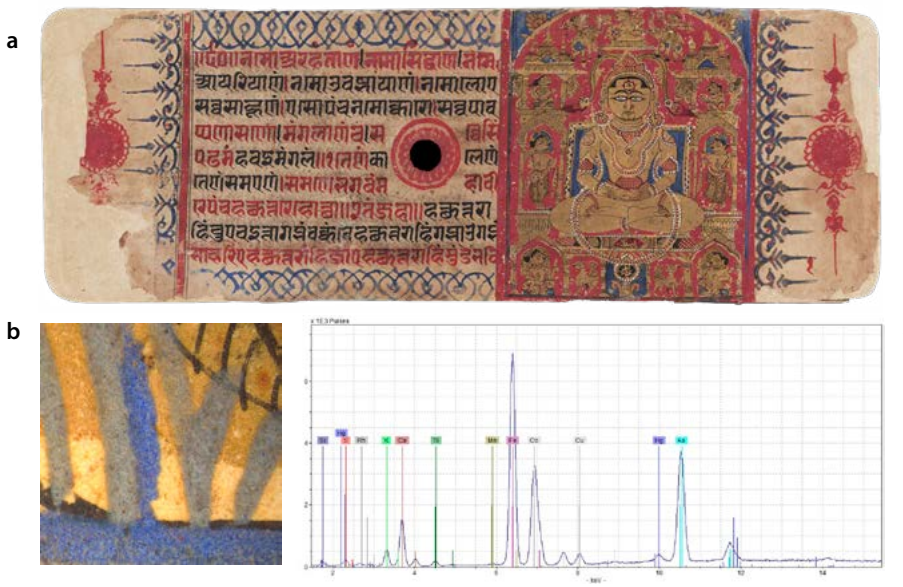


Figure 10.1: (**a**) MFA 17.2277, folio 1 from the manuscript of the Kalpasutra and Kalakacarya Katha, 1497 CE, ink, opaque watercolour and gold on paper, Ross-Coomaraswamy Collection, Museum of Fine Arts, Boston; photograph © Museum of Fine Arts, Boston; (**b**) photomicrograph of MFA 17.2277 fol.44; greyish blue lines are smalt, brighter blue lines are ultramarine; (**c**) XRF spectrum from a folio of 17.2277 showing the presence of Ca, Fe, Co and As, with some K and trace Ti, Cu and Hg (from the adjacent red pigment, vermilion).

Cobalt was present on all four of the folios analysed from this manuscript, and microscope examination confirmed the presence of glassy blue and greyish particles, shown in Figure 10.1b, in areas where cobalt was detected. The larger blue particles visible in the matrix of greyish blue are also smalt. Ultramarine is present on these same folios and is sometimes layered as a separate line of paint

on top of the greyish smalt, perhaps added later to intensify the blue colour. The XRF spectra show significant levels of calcium and potassium, with high iron, cobalt and arsenic but no detectable nickel or bismuth, as shown in Figure 10.1c.

Analysis of other Jain manuscripts dated to the 15th and 16th centuries identified mixtures of ultramarine and/or indigo. In some instances, different pigments are used within a manuscript, for example in one Jain manuscript dated to 1576 CE, MFA17.2280, some folios were painted with indigo only, while others were painted with both ultramarine and indigo. Indigo and ultramarine are the main blue pigments found in traditional Indian art works (Bowen and Snodgrass 1997; Fitzhugh 1988; Gill et al. 2014; Isacco and Darrah 1993; Kim 2021; Lazaro 2005).

SEM-EDX analysis of a sample from MFA 17.2277 folio 1 revealed glassy particles with variable composition and a variety of associated materials. All glassy particles have low levels of alkali and significant iron, cobalt and arsenic, with no detectable nickel or bismuth, as shown in Table 10.3. The low alkali contents suggest chemical alteration, with loss of alkali having occurred at the surface of all particles.

Table 10.3: SEM-EDX analyses of smalt grains in samples from Indian manuscripts, showing average compositions of samples from art works in the collections of the Harvard Art Museums and Museum of Fine Arts, Boston (abbreviated as MFA).

		Na_2O	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	NiO	As_2O_3	PbO	Bi_2O_3	BaO
Jain													
MFA 17.2277	Average	0.8	1.0	78.3	2.1	1.7	1.7	8.0	n.d.	3.4	n.d.	n.d.	n.d.
Bikaner													
1995.122	Average	4.5	10.4	49.0	6.6	5.5	6.5	6.4	n.d.	1.1	1.6	n.d.	n.d.
	Standard deviation	2.5	2.7	12.0	2.5	2.1	3.8	5.2		1.4	1.8		
Basohli													
MFA 17.2786	Average	1.0	1.4	72.2	11.5	0.8	4.5	2.3	0.9	4.8	n.d.	1.3	n.d.
	Standard deviation	<0.1	<0.1	0.7	0.2	<0.1	0.1	<0.1	0.1	<0.1		<0.1	
1972.74	Average	0.7	1.0	76.1	8.2	0.9	2.8	2.7	0.8	3.8	n.d.	2.0	n.d.
	Standard deviation	0.2	0.2	1.0	0.9	0.1	0.3	0.5	0.2	0.5		0.1	
Malpura	**Average**												
1960.681	Standard deviation	0.8	2.6	72.4	7.4	0.5	1.9	0.8	0.7	4.0	0.7	0.0	7.2
		0.3	0.6	2.2	0.1	0.6	0.2	0.3	0.2	1.7	0.6	0.0	0.5
1960.681	Average	0.1	2.6	68.2	5.7	0.5	3.2	1.7	1.0	2.3	1.0	0.0	12.0
	Standard deviation	0.2	<0.1	0.4	0.5	0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	0.1

17th century Rajput manuscript folios

XRF analysis of 17th century Rajput manuscript folios showed that smalt was used mainly in the latter half of the century. Cobalt was found on only one work from the early 17th century, a Ragamala folio from Bikaner stylistically datable to c. 1620, 1995.122, shown in Figure 10.2a.

Figure 10.2: (**a**) Manuscript folio from Bikaner, c. 1620, Kakubha Ragini, or Lady with Three Peacocks (painting, recto), possibly from a Ragamala (Garland of Melodies) Series, Harvard Art Museums/Arthur M. Sackler Museum, Gift in gratitude to John Coolidge, Gift of Leslie Cheek, Jr., Anonymous Fund in memory of Henry Berg, Louise Haskell Daly, Alpheus Hyatt, Richard Norton Memorial Funds and through the generosity of Albert H. Gordon and Emily Rauh Pulitzer; formerly in the collection of Stuart Cary Welch, Jr., Photograph © President and Fellows of Harvard College, 1995.122 (**b**) manuscript folio from Basohli, 1660-80, a *Nayika and Her Lover: Page from a Dispersed Rasamanjari Series (Blossom Cluster of Delight)*, Harvard Art Museums/Arthur M. Sackler Museum, Gift of John Kenneth Galbraith, Photograph © President and Fellows of Harvard College, 1972.74.

All other folios on which smalt was found date from 1660 or later. These later examples include folios from Bikaner, Bundi and Mewar, located in Rajasthan in western India, and from Basohli (an example of which is shown in Figure 10.2b), located in Himachal Pradesh in the Punjab hills.

In some instances, smalt was the only pigment used as a true blue, although indigo was often mixed with other pigments in the same painting, most commonly with Indian yellow to create a variety of green shades but occasionally with white and grey pigments to produce a light blue-grey. In contrast, smalt has not been observed mixed with yellow in any of the paintings examined to date. This may be due to the difference in textures, the fine-grained indigo mixing better with the fine Indian yellow to produce a more homogeneous green than is possible using the coarser-grained smalt. In some paintings, indigo was used in a concentrated form to create black, particularly for the night sky. In other instances, however, indigo or, occasionally, ultramarine was used for other blue areas (see Table 10.1). Within the Rajput paintings, smalt was often used to paint Krishna's skin, which was traditionally depicted as blue in Hindu art, as discussed by Lazaro (2005) and Kim (2021). Smalt may have been chosen for its deep-blue colour and lustrous sparkle, clearly seen in the detail of the face of Krishna from 1972.74 in Figure 10.3a and b.

Figure 10.3: (**a**) Detail of the face of Krishna shown in Figure 10.2, bottom; (**b**) photomicrograph of the glassy blue pigment particles in the face of Krishna.

Although smalt was occasionally reserved for use for Krishna, in most paintings it was also used for other areas, including the sky and clothing, even if indigo (or, more rarely, ultramarine) were also present in the same painting. In addition, smalt was certainly not the only blue pigment used by 17th century Rajput artists to depict Krishna, with indigo or ultramarine used to portray Krishna in other paintings from the same site and from nearby sites. Use of smalt appears to occur in specific

series—for example Table 10.1 lists multiple paintings from a Rasamanjari series made in Basohli 1660-1670 CE, a Rasikapriya series produced in Bundi 1660-1680 CE, and a Ragamala series created in Mewar around 1680 CE. The choice of blue pigment may be due to the preference of the artist or workshop as well as to availability, since both ultramarine and indigo were available and used together with or as alternatives to smalt.

Comparison of the XRF analyses of smalt shows some difference between those in the early Bikaner folio stylistically datable to c.1620 CE and folios from 1660 CE onwards, which can be seen in Figure 10.4a-b. In the earliest painting, 1995.122, the blue areas contain high levels of both potassium and calcium, as well as detectable (and, hence, likely high) aluminium, shown in Figure 10.4a.

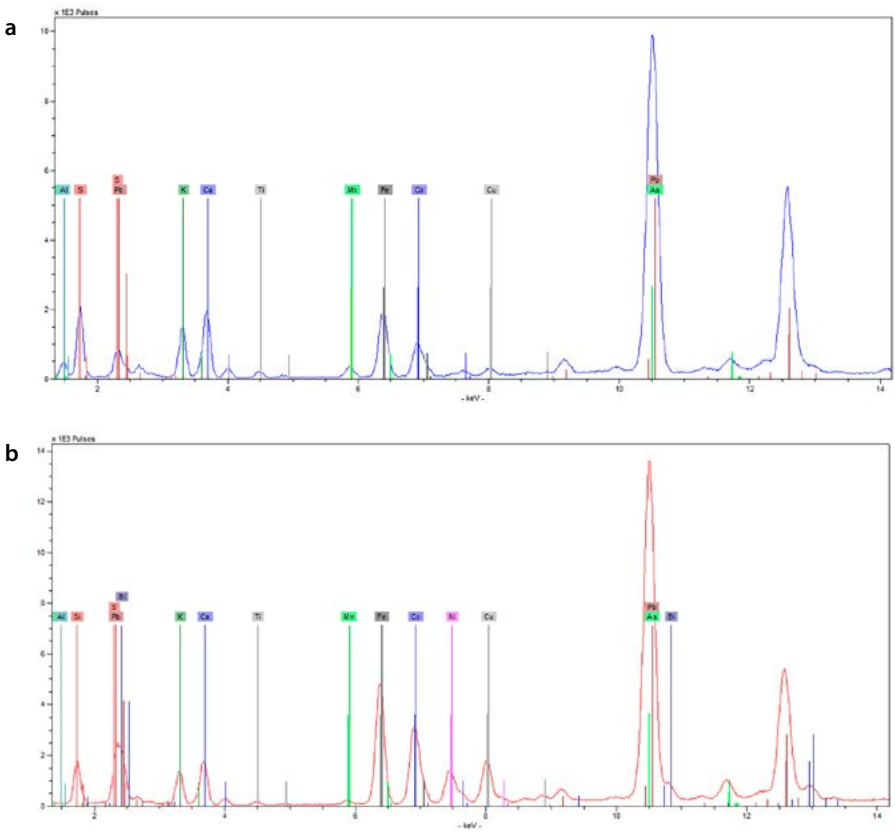


Figure 10.4: X-ray fluorescence spectrum from the blue of (**a**) Rajput manuscript 1995.122, Bikaner, c.1620, showing high levels of Al, Si, K, Ca, Fe, Co, As and Pb with trace Ti and As; (**b**) Rajput manuscript 1983.93, Bikaner, 1678, showing high levels of Si, K, Fe, Co, Ni, As and Bi with trace levels of Ca and Pb.

The XRF spectrum in Figure 10.4a has high levels of cobalt and iron but only traces of arsenic and no detectable nickel or bismuth. In contrast, analyses of glassy blue pigment in mid- to late 17th century Rajput manuscripts show high levels of potassium; low levels of calcium; and high levels of iron, cobalt, arsenic, nickel and bismuth, with no detectable aluminium, seen in the spectrum from a manuscript produced in Bikaner in 1678, 1983.93, in Figure 10.4b.

XRF analyses of manuscripts dating to the second half of the 17th century show a positive correlation between levels of cobalt, iron, arsenic, nickel, potassium, and, to a lesser extent, bismuth.

SEM-EDX examination of a sample from the early Rajput folio 1995.122 showed that the sample contains variety of particles, many of which have high levels of aluminium, silicon, potassium and/or sodium but lack detectable cobalt. Glassy particles in which cobalt was detected have variable composition: significant levels of alumina, soda, lime and potash, and high levels of iron and cobalt, with some arsenic but no nickel or bismuth detected (see Table 10.3). The ratio of iron to cobalt in all particles is similar, but the ratio of arsenic to iron or cobalt is highly variable.

SEM-EDS examination of samples from the 17th century Rajput manuscripts showed angular particles up to 20 microns in diameter with visible conchoidal fracture surfaces, characteristic of glassy pigments. Although BSE images show little obvious difference in average atomic weight, analysis shows that a wide range of potassium and silicon contents are present, with a strong negative correlation between these two elements. Grains with the highest potassium contents are assumed to be the closest to original compositions. Samples from the Basohli manuscripts—1972.74, MFA 17.2781, and MFA 17.2786—showed that the least altered particles have average potash levels of around 9 to 12% and only trace levels of calcium. As noted by other studies on smalt composition and degradation, the levels of cobalt and associated elements are unaffected or only minimally affected by the alteration, with consistent levels in altered and unaltered areas of the smalt particles. As shown in Table 10.3, all particles have significant levels of cobalt, iron, arsenic, nickel and bismuth, with similar ratios of cobalt to iron and nickel but highly variable ratios of cobalt to arsenic and bismuth.

18th century Rajput manuscripts

XRF analysis of 18th century Rajput manuscript folios and paintings identified smalt in art works produced in Kota, Mewar and Malpura, in Rajasthan, and in Guler and Kangra, in Himachal Pradesh. Mewar is the only location so far where smalt has been identified in paintings from both the 17th and the 18th century. In contrast, no cobalt was detected in 18th century works from Bikaner or Basohli

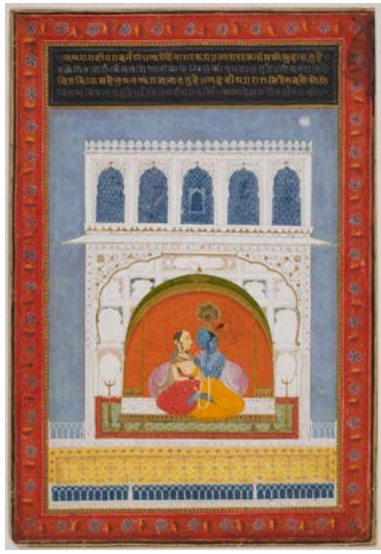
despite the presence of smalt in 17th century paintings from these sites. No cobalt was found in works of any date from nearby Kishnagarh, in Rajasthan. It is, however, important to note that only a limited number of paintings have been analysed to date and that these patterns may change as more data are gathered by the MCH project.

As was the case with earlier works, in these 18th century manuscripts smalt is often used alongside other blue pigments or replaced by them in seemingly similar works and/or works by the same artist. For example, analysis of a late 17th century painting attributed to the Kota Master, 1995.93, revealed that the only blue pigment used was indigo. In contrast, analysis of 18th century paintings by the same artist showed that smalt, indigo and ultramarine were all present in a painting dated to c. 1720, 2009.202.237, whereas only smalt was used in 1995.95, dated to c. 1730 CE. Whether this reflects a change in availability of smalt or a change in the artists' preference cannot be determined without analysis of additional paintings by the Kota Master. Smalt was used exclusively in the decorative borders of two 18th century paintings from Kangra, 1971.126 and 1971.139, with indigo the only blue pigment used for the image. The bright blue smalt border contrasts with the more muted blues in the image. Interestingly, ultramarine was used instead of smalt in a similar border in an early 19th century painting, 1972.67, with Prussian blue used within the image. Smalt has not yet been identified in any 19th century paintings, suggesting that the choice of ultramarine rather than smalt for the border of the later painting might be due to lack of availability of smalt. The presence of Prussian blue demonstrates the continued import of European pigments.

XRF analysis shows that the composition of smalt in the 18th century paintings from Kota, Mewar, Guler and Kangra is very similar to that in the 17th century Rajput paintings: high levels of potassium with generally low calcium, and high levels of cobalt, iron, nickel, arsenic and bismuth. As with the 17th century examples, there is a positive correlation between cobalt, iron, arsenic, nickel and potassium, and a poorer correlation with bismuth.

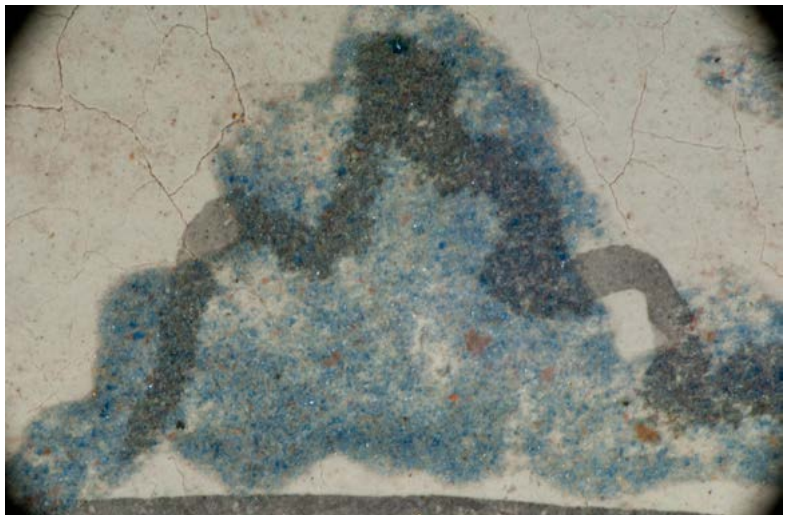
Analysis of four folios produced in Malpura, Rajasthan, in 1756 CE by the artist Jai Kisan as part of a Ragamala picture book, 1960.681, 1963.73, 1963.74, and 1969.174, are unusual in containing smalt mainly in the blue sky. Surprisingly, smalt was not used to depict the gods, Krishna and Shiva, in these folios, who were instead painted using indigo and indigo with lead white, respectively, as shown for Krishna in Figure 10.5a. Raman spectroscopy revealed that the glassy smalt is mixed with lead white and indigo to produce a muted blue in the sky (Fig. 10.5a-b), rather than the painting having the vibrant dark blue colour associated with smalt in other paintings.

a



b

c



d

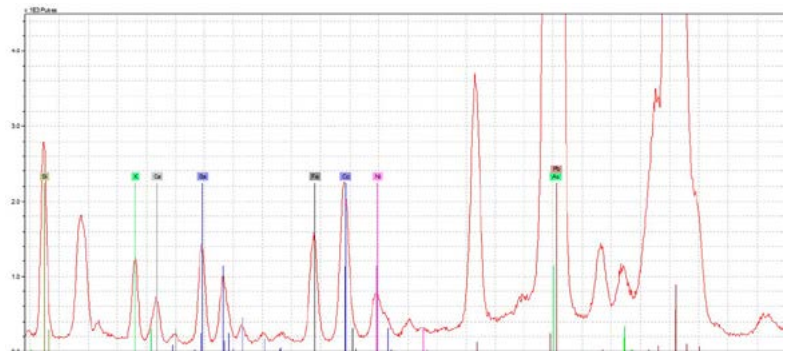


Figure 10.5: (**a**) Folio attributed to Jai Kisan of Malpura, *Dipak Raga (painting, recto), from a Ragamala (Garland of Melodies) Series*, Harvard Art Museums/Arthur M. Sackler Museum, Gift of Eric Schroeder, Photograph © President and Fellows of Harvard College, 1963.73, showing Krishna and other dark blue areas painted in indigo and the muted blue sky painted with a mixture of smalt, indigo and lead white; (**b**) folio attributed to Jai Kisan of Malpura, *Khambhavati Ragini (painting, recto), from a Ragamala (Garland of Melodies) Series,* Harvard Art Museums/Arthur M. Sackler Museum, Gift of Eric Schroeder, Photograph © President and Fellows of Harvard College, 1960.681, showing muted blue sky and blue smalt decoration on the cupola; (**c**) photomicrograph of the decoration on the cupola in 1960.681 showing the glassy blue smalt particles over lines of silver paint; (**d**) X-ray fluorescence spectrum from blue sky of folio 1960.681 showing the presence of K, Ba, Co, Fe, Ni and As, with some Ca; the high Pb levels are due to the lead white mixed with the smalt and indigo to create the desired light blue.

The only other use of smalt on these folios is for occasional decoration on some architectural features, for example on the cupola depicted in folio 1960.681, shown in Figure 10.5b. The lines on the cupola are painted with silver and smalt, shown in Figure 10.5c, giving a sparkling grey-blue appearance.

The smalt used in all four folios has high levels of barium, as shown in the example spectrum in Figure 10.5d. The barium level has a positive correlation with cobalt, iron, nickel, arsenic and bismuth. This suggests that barium is a component of the smalt rather than an additional component in the paint, for example barium sulfate, which was sometimes added as an extender in European painting.

No barium-containing pigments were detected by Raman spectroscopy of the sky in any of the four paintings, confirming that barium is present in the smalt itself. Spectra from the sky have lower levels of cobalt and associated elements and higher levels of lead than those from smalt-containing blues in other manuscripts, likely due to the demonstrated mixing of smalt with lead white and indigo.

The only 18th century manuscript sampled to date is one of the folios from Malpura, 1960.681. SEM-EDX analysis of the smalt particles confirmed the presence of 7-10% barium oxide and the lack of detectable bismuth, as seen in Table 10.3. These particles are smaller than those in samples from the 17th century folios, and the presence of lead white in all samples made analysis difficult. However, overall, particles had a similar ratio of cobalt to barium, iron and nickel, but variable ratios of cobalt to arsenic. Although the composition varies between particles, maximum potash values are 5 to 7% (see Table 10.3). These potash contents are notably lower than those found in the 17th century samples, possibly due to greater surface alteration of the smaller particles. Similar levels of barium occur in smalt particles from historic Chinese sites (Xia et al. 2019), and barium with cobalt occurs in the blue glaze on some 18th century Chinese porcelain

(Giannini et al. 2017). In both instances, the smalt is believed to be European (Giannini et al. 2017; Xia et al. 2019). This is consistent with recent analysis of smalt particles in Dutch paper dated to 1720 CE where a few per cent barium is present. The presence of in smalt on the 18th century Indian manuscripts is hence consistent with export of the pigment from Europe to India.

Results and discussion: Persian art works

17th and 18th century manuscript folios and paintings

XRF analysis of more than 100 Persian manuscripts and paintings found that glassy blue pigment containing cobalt is present in a small number of Iranian artworks dating to the 17th to 18th centuries, as shown in Table 10.1. Ultramarine and indigo remained the predominant blue pigments detected, and there was some use of azurite (Knipe et al. 2018). Surprisingly, despite its use in some Islamic artworks from Iran, smalt has not been detected in any Mughal artworks from Islamic India analysed to date.

Smalt was found in two of six artworks attributed to the 17th century Isfahan artist Mu'in Musavvir (1635-1697 CE) together with ultramarine, indigo and/or azurite, which were used in the other paintings. This use of multiple different blue pigments suggests careful selection by the artist to create the desired shade and effect and implies that availability was not the limiting factor in the use of smalt. Smalt was also used in the fabulously colourful illuminations of two manuscripts dated from the mid-17th to early 18th century. All other 17th century Persian manuscripts analysed contained ultramarine and/or azurite.

XRF analysis showed that the composition of smalt in the manuscript illumination and early 17th century painting by Mu'in Musavvir, 1960.48, dated to 1632-1633 CE, is very similar to that found in the Rajput folios. All analyses of the smalt have high levels of iron, cobalt, nickel, arsenic and bismuth, and significant potassium and silicon. High levels of lead in some analyses are attributed to the frequent presence of lead white. In contrast, the smalt used in the later painting by Mu'in Musavvir, 2006.262, dated to 1688 CE, has much lower levels of nickel and arsenic relative to cobalt and iron, with bismuth barely detectable. In all examples, there is a correlation between cobalt, iron, nickel, arsenic and potassium. Despite the difference in composition between the two paintings by Mu'in Musavvir, both are consistent with use of a potash-based European smalt and may reflect differences in processing or the specific deposits.

17th and 18th century lacquerwork

One of the most interesting uses of smalt occurs in Persian lacquerwork from the late 17th to late 18th century. Lacquer was used to decorate manuscript covers, mirror cases and penboxes in Iran from the 15th century, and was particularly popular in the 18th and 19th centuries (Robinson 1982, 1989; Diba 1994; Farhad et al. 2017). XRF analysis of more than 80 examples of Persian lacquerwork showed high levels of cobalt with associated nickel, arsenic and bismuth in black areas of lacquer decoration on two manuscript covers—one dated to 1685-1686 CE, 1984.463 (Eremin et al. 2024) and the other from the late 18th century, 2014.399—and one early 18th century penbox, 2014.303, as shown in Table 10.1. Within both manuscripts, azurite and ultramarine were used extensively in the text and illuminations, in preference to the smalt found on the covers. The role of smalt in the Persian lacquerwork is unclear—smalt occurs over a layer of silver and is often covered by multiple layers of coloured and clear lacquer, as well as by additional silver and gold layers. The layers can be seen clearly in damaged areas at the corners of the covers of a highly decorated cover to the late 17th century Safavid manuscript 1984.463, shown in Figure 10.6a. Although the lacquer is now black, this may be due to discoloration, with the original colour being very dark blue. In damaged areas of manuscript cover 1984.463, the mixture of smalt and lacquer is extremely degraded and has a dark grey, crumbly appearance, as shown in Figure 10.6b. The use of dark blue lacquer originally is, however, contrary to the widely assumed artistic scheme of gold text and decoration on a black background. The inside of manuscript cover 1984.463 also has decorative panels of blue smalt, which retain the bright blue colour of the original pigment, shown in Figure 10.6c-d.

In all the Safavid lacquer work containing smalt, XRF analysis shows cobalt is associated with high levels of potassium, iron, nickel, arsenic and bismuth and low levels of calcium, as shown in Figure 10.6e for the manuscript cover. There is a positive correlation of cobalt with the other elements. This pattern of elements is very similar to that seen for most of the 17th and 18th century Rajput folios.

Samples from manuscript cover 1984.463 were the only ones that could be mounted and polished for optical microscopy and SEM-EDX analysis, revealing multiple layers of lacquer, metal and pigment (Fig. 10.7a-d).

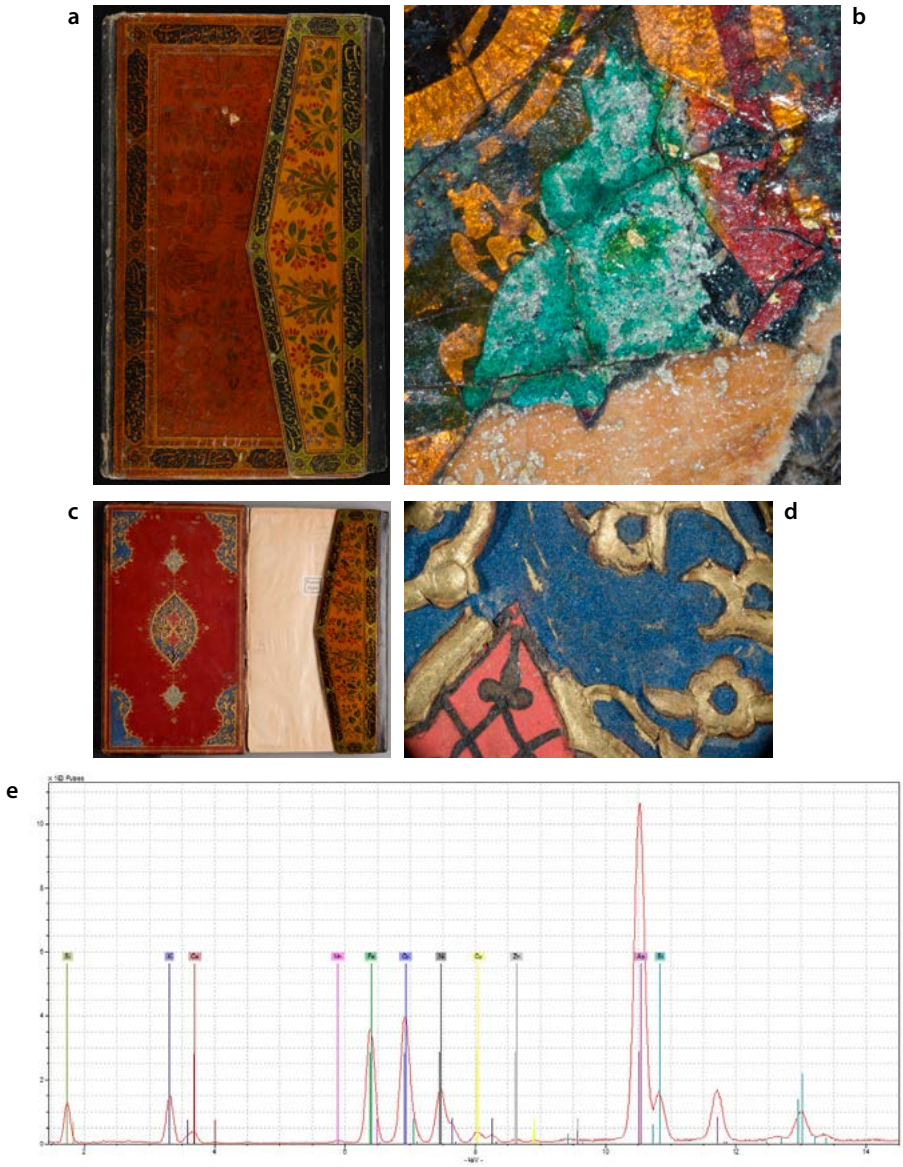


Figure 10.6: (**a**) Back cover with flap folded over of *Illustrated Manuscript of a Compendium of Knowledge (Jung), made for Shah Sulayman*, Harvard Art Museums/Arthur M. Sackler Museum, Gift of Philip Hofer, Photograph © President and Fellows of Harvard College, 1984.463; (**b**) detail of damaged corner of cover 1984.463 showing layers of paper, lacquer, dark smalt, green lacquer over silver and red lacquer over gold; (**c**) front inside cover and flap of *Illustrated Manuscript of a Compendium of Knowledge (Jung), made for Shah Sulayman,* Harvard Art Museums/Arthur M. Sackler Museum, Gift of Philip Hofer, Photograph © President and Fellows of Harvard College, 1984.463, showing the blue pigment use as decoration; (**d**) detail of the blue pigment showing granular particles; (**e**) XRF spectrum from 1984.463 blue pigment inside back cover, showing K, Fe, Co, Ni, As and Bi.

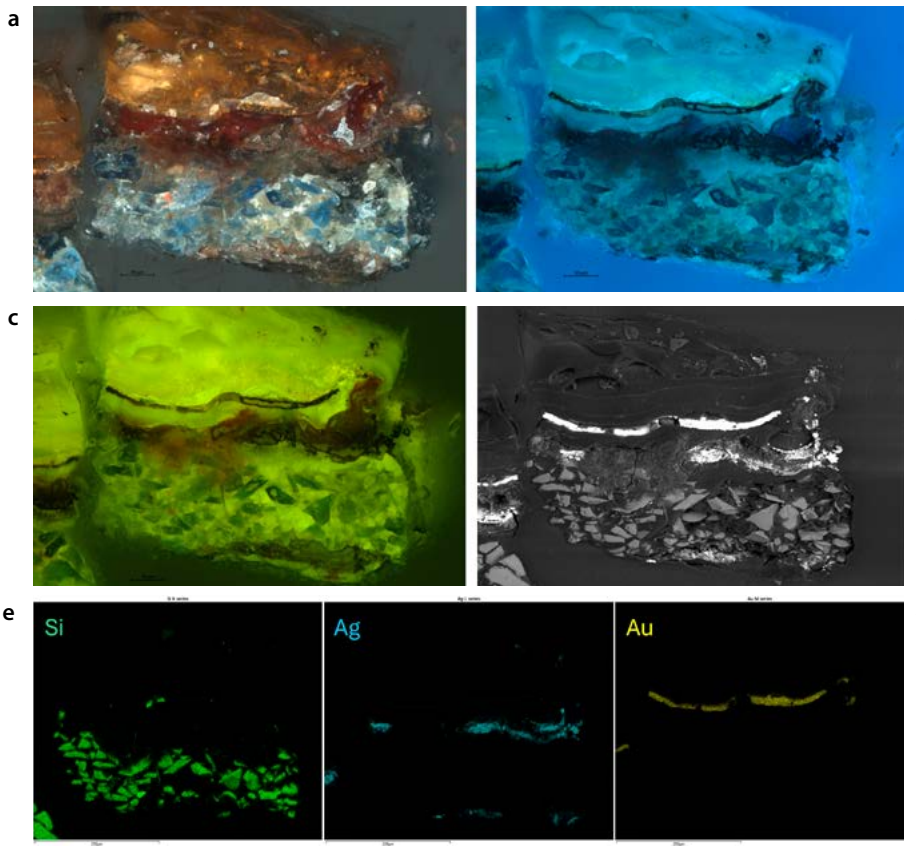


Figure 10.7: Optical and scanning electron microscopy images of a cross section of lacquer sample from the cover of Safavid manuscript 1984.463, showing the complex layering and discoloration of the smalt layer. (**a**) to (**c**) are optical images with differing illumination and filters; (**d**) is a back-scattered electron image from the scanning electron microscope, the lacquer in (**b**) and (**c**) can be seen clearly from the fluorescence; (**e**) to (**g**) are elemental maps from cross section showing location of layers of smalt (**Si map**), silver (**Ag**) and gold (**Au**) maps.

The different layers can be seen clearly in elemental maps from the SEM, with smalt particles shown by the silicon (Si) map, and metallic layers by silver (Ag) and gold (Au), as shown in Figure 10.7e-g.

The glassy blue pigment particles between the silver layers are extensively altered from interaction with the organic lacquer matrix, and optical images show the degradation of both the lacquer and the glassy particles, with the latter altering to grey rather than the original blue. The large, angular grains allowed for multiple analyses within each sample and of individual grains. Analysis showed a wide

range of potassium and silicon values between and within particles—surprisingly not reflected in the appearance of the grains in the back-scattered electron (BSE) image. The normalised analyses show a negative correlation of silicon and potassium, consistent with loss of alkali from the pigment particles as degradation increases. The values of cobalt, iron, arsenic and bismuth show no variation with potassium or silicon, confirming that these are largely unaffected by alteration, as found by other studies (Janssens et al. 2016; Spring 2017; Spring et al. 2005; Van Loon et al. 2020). Hence, while only those analyses with high levels of potassium were used to calculate the likely original glass compositions, all data were used to calculate the average values of the heavy elements. This shows a constant ratio of cobalt to iron but variable ratios of cobalt to bismuth, arsenic or nickel.

Table 10.4: Averaged compositions of smalt particles in samples from the cover of Safavid manuscript 1984.463.

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	CoO	NiO	As_2O_3	Bi_2O_3
Main group: particles with 15 ≤ K2O ≤ 17											
Average	0.9	0.1	0.9	68.3	15.8	0.5	2.8	2.6	0.6	5.2	1.4
Standard deviation	0.1	0.1	0.1	1.1	0.7	0.1	0.3	0.2	0.2	0.3	0.3
Main group, including altered particles											
Average						0.6	2.8	2.6	0.7	5.3	1.6
Standard deviation						0.2	0.4	0.3	0.2	0.3	0.3
Group 2: particles with K2O>20											
Average	0.8	0.0	0.8	69.9	21.2	0.5	0.8	0.7	1.8	1.8	0.9
Standard deviation	0.0	0.0	0.0	0.8	0.6	<0.1	<0.1	0.1	<0.1	<0.1	0.0
Group 2, including altered particles											
Average						0.6	0.9	0.7	2.0	1.9	1.1
Standard deviation						0.0	0.1	0.1	0.2	0.1	0.1

The average composition of the smalt grains is shown in Table 10.4. Most unaltered particles contain 15 to 17% K_2O, although a few particles have a distinct composition of over 20% K_2O and lower colourant levels (see Table 10.4). The potassium-rich, colourant-poor particles have very different ratio of nickel, arsenic and bismuth to cobalt than the main group. Examination of a second sample from the cover revealed a distinct particle within the smalt layer, shown in Figure 10.8a-d.

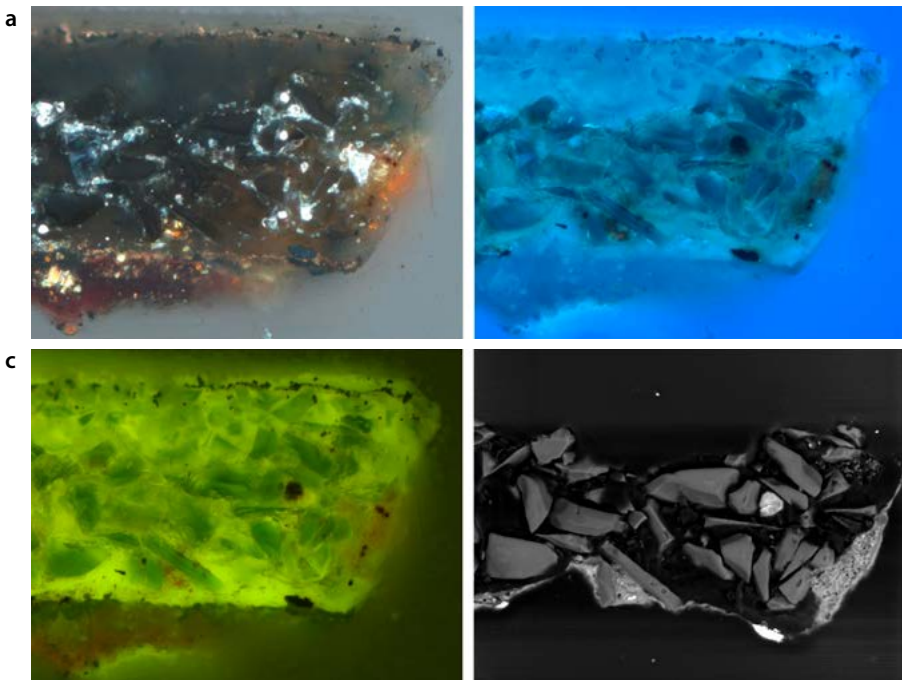


Figure 10.8: Optical and scanning electron microscopy images of a cross section of another lacquer sample from cover of Safavid manuscript 1984.463; (**a**) to (**c**) optical images; (**d**) BSE image from the scanning electron microscope, in which the bright particle in the BSE image (a dark particle in the florescence images) has very high Ni, As and Bi and low Si, K, Co and Fe. The images show the extensive discoloration of the upper lacquer and smalt layer.

The composition of this particle is highly variable, with very high levels of nickel and arsenic; variable bismuth; and low silica, potash, cobalt and iron, as shown in Figure 10.9a-e. This variation in particle composition and particularly in the relative values of heavy elements is not seen in the XRF analyses, likely due to the larger analysis volume of the XRF resulting in averaged analyses.

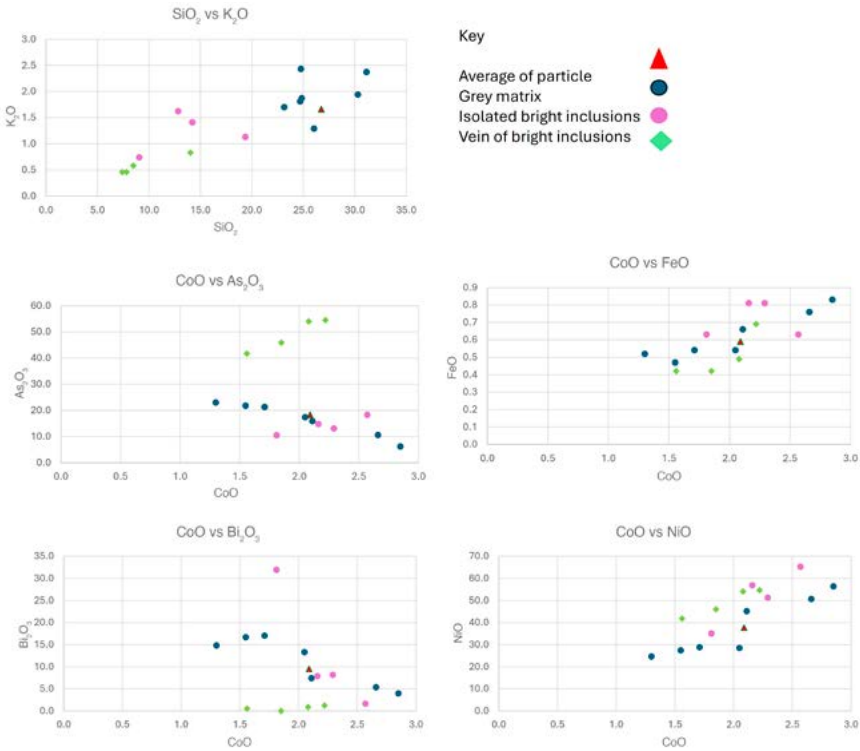


Figure 10.9: Composition of the bright particle seen in the scanning electron microscopy image in the smalt sample from the cover of Safavid manuscript 1984.463, showing variations within the particle.

Discussion

Analysis has shown that the blue glassy pigments used in mid-17th to late 18th century artwork from both Iran and India have high levels of potassium with little calcium and are characterised by significant cobalt, iron, nickel, arsenic and bismuth, with barium present in folios from Malpura. These compositions are very similar to those reported for smalt in 16th and 17th century Dutch paintings and other artefacts. SEM analysis shows some variation in smalt composition within a single object and/or for manuscripts in a series, consistent with observed variations within European paintings (Janssens et al. 2016; Panighello et al. 2016; Spring 2017; Spring et al. 2005; Stege 2004; Van Loon et al. 2020). The pigment used is these objects is hence believed to be imported European smalt.

Although export of cobalt ores and/or smalt from Europe to China and the Middle East may have occurred from the 14th century (Stege 2004), there is as yet no direct evidence for this trade. In particular, there is no evidence in the records of the Dutch East India Company for shipments of smalt (Couvrat Desvergenes et al. 2021). Despite this, it is likely no coincidence that the appearance of European smalt in 17th century Iranian and Indian artwork coincides with the opening of trading posts by the Dutch East India Company in Iran and India in the 17th century, just as the appearance of smalt in Goan paintings coincides with the establishment of Goa as the centre of Portuguese India (Antunes et al. 2019). At the beginning of the 18th century, Dutch traders were already deeply embedded in textile trades in Gujarat (the adjoining state to Rajasthan), and European traders were actively seeking to engage the Rajput courts. Later European pigments such as Prussian blue (produced from 1704 CE onwards) and Emerald green (produced commercially from 1814 CE onwards) have been found in many 18th and 19th century Indian and Iranian art works at the Harvard Art Museums, attesting to import of pigments from Europe. Although use of smalt currently appears to be somewhat limited, this may reflect import of smaller quantities by artists rather than of large amounts of trade goods by merchants.

In contrast, glassy blue pigment from the 15th century Jain manuscript and the early 17th century Rajput manuscript has a more variable composition, with no detectable nickel or bismuth. The lack of nickel and bismuth in both manuscripts and the high levels of alumina, soda and lime in the early 17th century manuscript are very different from the compositions reported for European smalt. These pigments may instead be derived from crushed blue glass or glaze of more local origin, with glaze more likely, based on the high alumina content. Similarly, local manufacture using Iranian cobalt ores was proposed for glassy blue pigment on pre-17th century wall paintings in Iran based on the significant levels of calcium and lead and lack of detectable bismuth (Holakooei and Karimy 2015).

Studies of Safavid and Mughal ceramics and of Mughal enamel indicate soda-rich compositions with minor potash, lime and alumina (Gill 2023; Gill and Rehren 2011, 2017; Gill et al. 2014; Gulzar et al. 2013; Wypyski 2008). Such compositions are closer to those obtained from the glassy blue pigment used in the early 17th century Rajput manuscript than the composition of European smalt, although they are not identical to the glassy blue pigment in the Rajput manuscript. The cobalt used as colourant in the dark blue Mughal glaze and enamel is compositionally distinct from European ores, and proposed sources include Kashan or Qamsar, in Iran, and Khetri, in Rajasthan, India (Gill 2023; Gill and Rehren 2011, 2017; Gill et al. 2014; Wypyski 2008). Although further investigation is required to confirm this, it seems that similar sources could have been used for the blue glassy

pigment in these earlier Jain and Rajput manuscripts that lack detectable nickel or bismuth.

Conclusion

Analysis and examination of many artworks from Iran and South Asia shows the use of a glassy cobalt-blue pigment in a small number of 15th century Jain manuscript folios; in several 17th and 18th century Rajput manuscript folios; and in some 17th and 18th century Iranian manuscripts, lacquer manuscript covers and lacquer penboxes. Analysis so far suggests that the use of smalt was limited and that most artists used the traditional blue pigments ultramarine, indigo, and, to a lesser extent, azurite. A survey of published studies on Iranian and Indian works included in the MCH database supports this suggestion. However, it should be stressed that only a small number of works have been analysed to date compared with the vast corpus of art produced in Iran and South Asia from the 15th to 20th centuries and that the observed patterns of pigment use may change as more data become available.

The composition of the glassy blue pigment found in Iranian and Indian art works from the second half of the 17th century is very similar to that of European smalt of the same date, and the pigment was likely imported from Europe. The appearance of European smalt coincides with the opening of trading posts in Iran and India by the Dutch East India Company and with increasing interest in the Rajput courts by European traders. The apparently rather limited use of smalt may be due to import by European artists, both professional and amateur, rather than by merchants as deliberate trade goods.

Much further work is required to determine how and in what quantity smalt was imported from Europe, and the extent to which local blue glass or glaze was used. We should, however, be careful about what is meant by the term smalt, particularly where this is based solely on XRF analysis. The definition of smalt purely as a pigment composed of crushed blue glass coloured with cobalt acknowledges that different types of smalt may be found and does not necessarily imply import of European smalt.

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Chapter 11

The use of cobalt on Chinese ceramics from the 7th to 20th centuries CE

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Introduction

Cobalt gives ceramics a very elegant dark blue colour. The five Chinese dynasties —Tang, Song, Yuan, Ming, and Qing, from the 7th to 20th centuries—witnessed the origin, boom and bust of blue-decorated ceramics, known as blue Sancai and blue-and-white porcelains. Blue Sancai is a kind of Sancai (lead-glazed) ware with cobalt-blue decoration, either alone or in combination with other colours, usually white, yellow and green. The archetypal Chinese blue-and-white porcelain is a porcelain decorated with underglaze cobalt pigment(s) and covered with a transparent lime glaze. A large volume of archaeological research has discussed the kiln sites, production organisation, main users, periods of popularity, distribution, materials and technologies etc., and many studies have included scientific analyses. This paper reviews the production and use of blue-decorated ceramics and the technology of cobalt materials in order to summarise the use of cobalt on Chinese ceramics.

The production of blue-decorated ceramics

Tang dynasty (618-907 CE)

Archaeological excavation has identified six kilns producing Tang Sancai—the Huangbao (also known as Huangbu and Yaozhou) (Xue 2002) and Liquanfang kilns in Shaanxi (Shaanxi Academy of Archaeology 2008); the Gongyi (also known as Gongxian) kiln in Henan (HPICHA et al. 2016); the Xing kiln in Hebei (Jia and Jia 1987); the Hunyuan (or Jiezhuang) kiln in Shanxi (Tian 2002); and the Qionglai (or Qiong) kiln in Sichuan (Li 2013). Apart from the Qionglai kiln,

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which is in southwestern China, all the other Sancai kilns are in north China. The Liquanfang, Huangbao, Gongyi and Xing kiln sites were big ceramic factories in the Tang dynasty (618-907 CE), with abundant products, but only the Gongyi and Liquanfang kilns produced blue Sancai (Fig. 11.1).

Gongyi is situated about 54 km as the crow flies east of Luoyang (Fig. 11.1), the eastern capital city during 664-705 CE and 904-907 CE and the second-largest city of the Tang Empire (Schafer 1963, 46). Gongyi refers to two principal kiln sites, called Huangye and Baihe by Chinese archaeologists, which are about 4 km apart and have similar products, and other related, smaller sites. Archaeological excavation showed that the production in Huangye and Baihe began in the Sui dynasty (581-618 CE) and Wei dynasty (386-534 CE), respectively, and continued to the end of the Tang dynasty (HPICHA et al. 2009, 8; 2016, 304). In the Tang dynasty, Sancai, including blue Sancai, became one of the main products of the Gongyi kiln. More remarkably, Gongyi potters started to make Tang blue-and-white porcelain—the first in China. Six sherds have been found here: two in Huangye and four in Baihe (HPICHA et al. 2009, 11, 2016, 17). The production of blue Sancai started earlier and lasted longer than that of blue-and-white porcelain, with a much larger production. Blue Sancai was made from the 7th to the end of the 9th century CE and blue-and-white porcelain was developed in the late 9th century CE at this kiln (HPICHA et al. 2016, 299-305).

Figure 11.1: Map showing locations of some important kilns in ancient China, with red stars marking the capital cities of China from the Tang to Qing dynasty and orange and blue triangles marking the locations of blue Sancai kilns and blue-and-white porcelain kilns, respectively (modified from https://lbs.amap.com/demo/javascript-api/example/map/map-english).

Song dynasty (960-1279 CE)

After the collapse of the Tang Empire, the production of blue-decorated ceramics in Gongyi stopped. The locations of the capital cities (Fig. 11.1) moved towards the south in the Northern Song (960-1127 CE) and Southern Song (1127-1279 CE) dynasties. Only four blue-and-white sherds have been discovered in the rammed-earth layers of two pagoda foundations in Zhejiang, southern China, dating to the Song period. Three sherds were excavated from the Jinsha Pagoda in Longquan (Ruan 1990; Zhu 1980) and one sherd from the Huancui Pagoda in Shaoxing (Zhu 1990). These towers were constructed in 977 and 1265 CE, respectively, which suggests that these blue-and-white porcelains were produced at or before these dates. However, as yet, no kilns have been confirmed as the source of Song blue-and-white. Two blue-and-white sherds and one plate were found in the Jizhou kiln in southern China by an early archaeological survey (Tang 1980). Their date was inferred to be Song or early Yuan. However, no more evidence of Song blue-and-white has been found by recent excavation at this kiln (Zhang et al. 2014). There are, however, many debates about the existence and provenance of Song blue-and-white ceramics (Feng 2001, 455; Li 1995).

Yuan dynasty (1271-1368 CE)

From the Yuan dynasty, Jingdezhen became the centre of porcelain production in ancient China, especially for blue-and-white porcelain. Before that, the mainstream product of Jingdezhen was Qingbai porcelain (white body with a pale blue, transparent glaze) (Jiang 2015a). Kublai Khan, the first emperor of the Yuan dynasty, ordered the establishment of Fuliang Ciju (Fuliang Porcelain Bureau; Chinese: 浮梁磁局) at Jingdezhen in 1278 CE to produce various porcelains for the central government (Jiang 2013). Fuliang (浮梁) is the name of the county which governed Jingdezhen. However, Fuliang Ciju was directly controlled by the central government in Beijing. According to the historical accounts and current excavations (Cao and Xu 2009; Chen 2019; Jiang 2013; Lin 2018; Yu 2016), during this period, the "imperial kiln" (or "official kiln", referring to the kiln that produced and offered ceramics to the imperial family), producing porcelains for the central government, did not refer to a specific kiln with one location. It was more likely to be an official administrative organisation. Some high-quality folk kilns (established by the common people, with a production targeted to the civilian market) in Jingdezhen were selected to receive the orders from the central government. Such production processes were under surveillance by the officials of the central government. This system may have lasted 74 years, until 1352 CE (Chen 2019; Jiang 2013). Yuan blue-and-white porcelain was one of the products and orders in Jingdezhen. Many folk kilns contributed to the official orders,

and dozens of sites have been found in Jingdezhen, such as the Xiaogangzui, Luomaqiao, Zhushan, Liujianong, Daijianong and Shibaqiao kilns (Cao and Xu 2009).

Ming and Qing dynasties (1368-1912 CE)

At the beginning of the Ming dynasty (1368-1644 CE), Zhu Yuanzhang (Hongwu), the first emperor, ordered the establishment of a physical imperial kiln in Jingdezhen for the central government, especially for the royal family (Wang 2009). The imperial kiln site is located in Zhushan (Zhu Mountain, Chinese: 珠山) which is the centre of modern-day Jingdezhen city. This establishment fixed the imperial kiln system from the early Ming until the end of the Qing. The imperial kiln produced porcelains, including blue-and-white, until 1911 CE (Jiang 2015a). Notably, the production of the imperial kiln was not continuous. As a consequence of a close connection with the political situation, the imperial kiln experienced boom and bust along with the stability and turbulence of the country. Three periods—the Hongwu to the Xuande period (1368-1435 CE); the Jiajing to the Wanli period (1522-1620 CE); and the Kangxi to the Qianlong period (1662-1795 CE)—witnessed the peaks of imperial porcelains. The imperial kiln experienced its last glory from the Tongzhi to the Xuantong period (1862-1911 CE).

In contrast, the production scale and technology of folk kilns in Jingdezhen developed uninterruptedly. There were approximately 200-300 folk kilns, with hundreds of thousands of potters, in the Qing dynasty (1636-1912 CE) (Jiang 2015b). This flourishing of folk kilns in the Qing dynasty could not have existed without some key innovations in the Ming dynasty (1368-1644 CE). In the early Ming, proficient potters were strictly controlled by the central government. They had to work in the imperial kiln, with no freedom of independent employment. From 1485 CE, potters were allowed to sell some of their labour for money (Li et al. 2012). Some imperial expert workers could join in at some folk kilns, even though they did not have full freedom (until 1698-1726 CE, in the Qing dynasty, when imperial kilns transferred to an employment system and potters legally had freedom of employment, Li et al. 2012). Because the demand for porcelains from the central government exceeded the maximum production of the imperial kiln, some collaboration between the imperial kiln and folk kilns was accepted in the late Ming. Some orders from the central government were assigned to some folk kilns (Wu et al. 2012). When the quality of some products made by folk kilns was below the imperial standard, those porcelains could be sold by the folk kiln after paying a fine (Wu et al. 2012). All these innovations in the Ming dynasty allowed advanced techniques, royal tastes and some products similar to "imperial

porcelain" to be produced by the folk kilns and sold to the local market. In 1728 CE, the emperor Yongzheng agreed to the sale of excess imperial products by the imperial kiln (Jiang 2015b).

The production and technology of porcelain, including blue-and-white, was at its peak in the Ming and Qing periods. Besides the kilns in Jingdezhen, many other kilns in China also produced blue-and-white porcelain—for example, the Yaozhou and Chengcheng kilns in Shaanxi (Du and Gao 2006; Gao and Du 2010); the Longtan and Jizhou kilns in Jiangxi (Lu 1995; Zhang et al. 2014); the Yangwuling and Liling kilns in Hunan (Yang et al. 2021; Zhang et al. 2009); the Dali, Yuxi and Jianshui kilns in Yunnan (Ge 1990; Yang et al. 2001; Zheng and Hao 2020); the Xiaji, Dehua, Anxi, Zhangzhou, Dongji and Yongfu kilns in Fujian (Li and Yang 2016; Ma et al. 2009; Yang and Liu 2015; Ye and Liu 2014); the Chaozhou kiln in Guangdong (Zheng and Hao 2020); and the Meiyang kiln in Hainan (Jiang et al. 2020) (Fig. 11.1). Additionally, some new porcelains were created based on the blue-and-white porcelain—Doucai (Fig. 11.2a) and Wucai (Fig. 11.2b). They were both decorated with underglaze cobalt-blue pigment and some overglaze pigments, such as iron red and copper green. The key difference between them is that all motifs of Doucai porcelain were outlined by underglaze blue pigment and the other colours were applied to the designated areas and that Wucai porcelain did not show this characteristic (Lv 2005; Ye 1997). Another interesting product relating to cobalt material in the Ming and Qing is Jilan (sacrificial blue) porcelain (Fig. 11.2d). It is a high-fired porcelain covered with a cobalt-blue lime glaze. Although a few blue-glazed porcelains had been produced in the Yuan dynasty (Fig. 11.2c), their production boomed in the Ming and Qing periods. There is no doubt that the Ming and Qing dynasties were the golden time for the production of blue-decorated ceramics.

Figure 11.2: Photographs of four ceramic vessels in the collection of the Palace Museum: (**a**) Ming dynasty Doucai porcelain jar (H 12.6 cm), from https://www.dpm.org.cn/collection/ceramic/227398.html; (**b**) Ming dynasty Wucai porcelain jar (H 33.2 cm), from https://www.dpm.org.cn/collection/ceramic/227384.html; (**c**) Yuan dynasty blue-glazed porcelain plate (D 16 cm), from https://www.dpm.org.cn/collection/ceramic/227131.html; (**d**) Ming dynasty Jilan plate (D 20.1 cm), from https://www.dpm.org.cn/collection/ceramic/227662.html.

The use of blue-decorated ceramics

Tang Sancai: The beginning of the use of cobalt on Chinese ceramics

As the earliest ceramic decorated with cobalt-blue decoration in China, blue Sancai had a very different use from blue-decorated ceramics in subsequent periods. Most of the Tang Sancai ceramics, including blue Sancai wares, were buried in tombs, and only a few blue Sancai objects were collected and dedicated by Buddhist temples. For example, a blue Sancai plate was excavated from the chamber of Dagoba in the Qingshan Temple in Lintong, near Xi'an (Zhao 1985). Also, a sherd with blue decoration of a figure of the Buddha was unearthed from the hall site in Qinglong Temple in Xi'an (Institute of Archaeology CASS 1974). The most notable characteristic of funerary Sancai is the use of various vivid, modelled figures (Fig. 11.3a-c), especially large figures.

Figure 11.3: Photographs of blue Sancai ceramics: (**a**) female figure (H 45 cm) excavated from the Zhongbaocun tomb in Xi'an, taken by the author; (**b**) figure of a camel carrying musicians (H 58.4 cm) found in Xianyu Tinghui tomb (Ma and Zhang 1958), from https://content-static.cctvnews.cctv.com/snow-book/index.html?item_id=7600625431161816985&t=1652798299100&toc_style_id=feeds_default&share_to=wechat&track_id=b7c70d1c-ff7b-4c02-b253-83b59344b83d; (**c**) figure of an acrobat (H 40.8 cm) contained in tomb M31 on the southern outskirts of Xi'an, published by Sun et al. (2004), reproduced with permission from https://www.xabwy.com/showtwo.html?id=291&type=39&num=2 (Xi'an Museum); (**d**) pot (H 14.7 cm) unearthed from the Yangjia Weiqiang Tomb, reproduced with permission from Guan et al. (2012); (**e**) blue *deng* (lamp) (H 33.6 cm) unearthed from Gongling, reproduced with permission from Wang (2011).

Tang blue-and-white porcelain: The origin of Chinese blue-and-white porcelain

Tang blue-and-white porcelains have been found in five places—the Gongyi kiln, the cities of Zhengzhou and Yangzhou in China, Siraf in Iran, and a shipwreck off Belitung Island, in Indonesian waters (Zhang and Pollard 2022). Gongyi is the only provenance known for Tang blue-and-white porcelain, and six sherds have been found there (Fig. 11.4a-f). Some 19 km east of the kiln site, a tomb was discovered in Zhengzhou containing two intact pagoda-shaped jars (Fig. 11.4i and j) (Wang et al. 2009). This tomb is the only one containing Tang blue-and-white porcelain as burial wares. Yangzhou, which contains the greatest number of Tang blue-and-white sherds of all the five places in China (n = 27), was the busiest trading port in southern China and was the main port of exchange of commodities between northern China and overseas (Benn 2004, 46; Schafer 1963, 17). Scientific analysis found that the provenance of the Tang blue-and-white excavated in Yangzhou was the Gongyi kiln (Chen et al. 1996; Cheng et al. 2005a and b, 2016; Zhang et al. 1986, 1989).

Another port city and the richest port on the Persian side of the Gulf, the city of Siraf, in Iran, also yielded one Tang blue-and-white sherd made in the Gongyi kiln (Spataro et al. 2019; Wood and Priestman 2016). The other discovery of Tang blue-and-white on the Maritime Silk Road concerned three plates in the Tang dynasty Belitung shipwreck (Flecker 2001). The archaeological finds in ports in China and the Middle East, as well as along the maritime trade route, confirm the close connection between blue-and-white porcelain and international trade in the Tang dynasty.

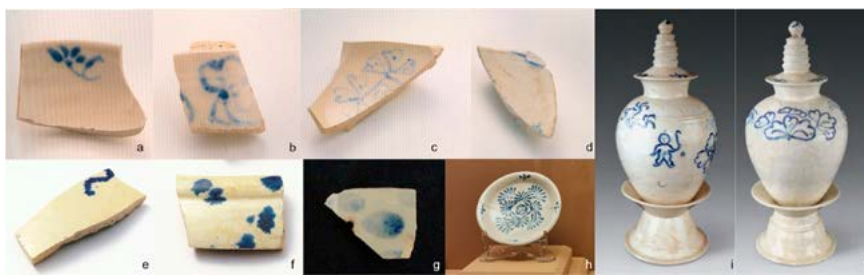

Figure 11.4: Photographs of Tang blue-and-white ceramics: (**a**)-(**f**) sherds found in the Gongyi kiln, China, reproduced with permission from HPICHA et al. (2005, 145, 2009, 165-167); (**g**) sherd unearthed in Siraf, Iran, reproduced with permission from Spataro et al. (2019); (**h**) plate uncovered from the Belitung shipwreck in the collection of the Asian Civilisations Museum in Singapore, taken by the author; (**i**) and (**j**) Tang blue-and-white pagoda-shaped jars, reproduced with permission from Qi (2017).

Song blue-and-white porcelain: The fading of the use of cobalt pigment

The use of cobalt on high-fired ceramics was not common in northern China or outside China after the Tang period. No Song blue-and-white porcelain has been found on the Silk Road or in the international market, and only four Song sherds have been found in southern China—three sherds unearthed from the Jinsha Pagoda in Longquan (Fig. 11.5) (Ruan 1990; Zhu 1980) and one sherd from the Huancui Pagoda in Shaoxing (Zhu 1980). The location of these four Song-blue-and-white sherds in the pagodas of two temples indicates that the use of blue-and-white porcelain probably related to Buddhism in the Song dynasty.

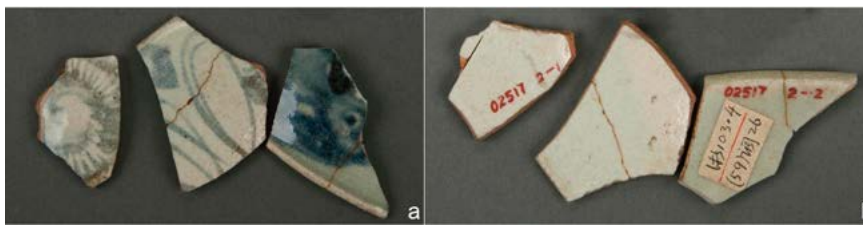

Figure 11.5: Photograph of Song blue-and-white sherds excavated from the foundation of Jinsha Pagoda in Longquan, southern China, reproduced with permission from https://www.zhejiangmuseum.com/cn/#/Collection/ExcellentCollection/27566 (Zhejiang Provincial Museum). This image only shows both sides of two sherds from two bowls. The two fragments on the left are regarded as one joint sherd because they belong to the same bowl (Ruan 1990; Zhu 1980)

Yuan blue-and-white porcelain: The glory of archetypal blue-and-white porcelains

The use of blue-decorated ceramics was much more widespread from the 13th to 20th centuries CE than it had been before. Archetypal blue-and-white porcelains from the Yuan to Qing dynasties were, among other things, funerary objects, sacrificial offerings, daily wares—storage tools, furniture, and ornaments (Fig. 11.6)—and export porcelain (Lin 2018; Wang 2009). The correspondence between production and use was complicated. For example, large Yuan dynasty blue-and-white porcelains were produced in the Hutian kiln at Jingdezhen and were targeted at the royal families and nobility in West Asia and South-East Asia. The Luomaqiao kiln in Jingdezhen made blue-and-white porcelains as ordinary merchandise for the local market and for South-East Asia (Jiang 2013). Furthermore, the elites', the nobility's, and especially the emperors' tastes affected the use of blue-and-white porcelain for all classes.

Figure 11.6: Photographs of archetypal blue-and-white porcelains from the Yuan to Qing dynasties from the collection of the Palace Museum: (**a**) Yuan blue-and-white pot (H 27.5 cm), from https://www.dpm.org.cn/collection/ceramic/227179.html; (**b**) Ming blue-and-white porcelain flask (H 46 cm), from https://www.dpm.org.cn/collection/ceramic/226869.html; (c) Qing blue-and-white porcelain vase (H 39.3 cm), from https://www.dpm.org.cn/collection/ceramic/226791.html.

The technology of cobalt minerals

Origins and characteristics of cobalt materials

Regarding the origins and characteristics of cobalt ores used in the blue-decorated ceramics from the Tang to Qing dynasties, there are many relevant scientific analyses. Here we re-analyse published data on 13 Tang blue Sancai, 12 Tang blue-and-white, 2 Song blue-and-white, 12 Yuan blue-and-white, 47 Ming and 45 Qing blue-and-white porcelains in terms of Fe_2O_3/MnO ratio (Fig. 11.5a); MnO/CoO and Fe_2O_3/CoO ratios (Fig. 11.5b); and the proportional relationship of Cu, Fe, Mn and Cu (Fig. 11.5c) in their cobalt pigments (Table 11.1).

Table 11.1: Chemical compositions of cobalt-blue decorations on blue-decorated ceramics (wt%). Most data are obtained from XRF analysis through the glaze, which is subject to differential absorption of characteristic X-rays. The cobalt remains of blue-and-white porcelains are at the bottom of the clear glaze, and the analysis depths for Mn, Fe and Co, etc., are generally smaller than the thickness of the clear glaze. Therefore, these data and ratios of cobalt pigment have analytical limitations. Since the imported and Chinese cobalt ores show significant differences in Fe and Mn, the ratios between Mn, Fe and Co can be used to differentiate between those cobalt ores (Ma et al. 2021). b&w = blue and white.

Reference	Category	Sample Identifier	MnO	Fe2O3	CoO	CuO
Li et al. (2017)	Huangye blue Sancai	16-6		1.09	0.78	0.5
	Huangye blue Sancai	16-7		0.27	0.43	0.16
Cheng et al. (2005a)	Huangye blue Sancai	4	0.04	1.21	1	
	Huangye blue Sancai	5	0.05	0.6	0.74	
	Huangye blue Sancai	6	0.01	0.81	1.46	
	Huangye blue Sancai	7	0.02	0.81	0.5	
	Huangye blue Sancai	8	0.01	0.7	0.6	
	Huangye blue Sancai	9	0.03	0.64	0.6	
Li et al. (2017)	blue Sancai (Gongyi, Baihe)	C070		0.48	0.3	0.25
Zhang et al. (1986)	blue Sancai (Gongyi)	T-5	0.03	1.05	1.92	0.22
	blue Sancai (Gongyi)	T-6	0.02	0.7	0.56	0.24
	blue Sancai (Gongyi)	T-7	0.02	1.1	0.47	0.19
Chen et al. (1978)	blue Sancai (Gongyi)	T-1	0.03	0.99	1.03	0.38
	blue Sancai (Luoyang)	T-2	0.03	1.1	1.09	0.25
Lu et al. (2016)	Tang b&w (Gongyi, Huangye)	21-1	0.1	2.04	8	0.11
Cheng et al. (2005a)	Tang b&w (Gongyi, Huangye)	1	0.08	1.36	1.56	
Lu et al. (2016)	Tang b&w (Gongyi, Baihe)	C301	0.09	1.75	1.39	0.03
	Tang b&w (Gongyi, Baihe)	C303	0.39	1.59	2.62	0.04
	Tang b&w (Gongyi, Baihe)	C304	0.12	1.83	0.42	0.05
Cheng et al. (2005a)	Tang b&w (Yangzhou)	2	0.08	1.34	0.38	
	Tang b&w (Yangzhou)	3	0.11	1.56	0.4	
Chen et al. (1995)	Tang b&w (Yangzhou)	TY1	0.18	1.04	0.57	0.22
Zhang et al. (1989)	Tang b&w (Yangzhou)	TB-W-2	0.07	1.3	0.42	
	Tang b&w (Yangzhou)	TB-W-4	0.1	1.4	0.32	0.06

Reference	Category	Sample Identifier	MnO	Fe2O3	CoO	CuO
Zhang et al. (1984)	Tang b&w (Yangzhou)	TB-W	0.07	0.82	0.32	0.09
Spataro et al. (2019)	Tang b&w (Siraf)		0.06	0.82	0.28	
Chen et al. (1978)	Song b&w	S-1	1.19	2.54	0.24	
Chen et al. (1980)	Song b&w	S-3	1.23	1.14	0.1	
Chen et al. (1978)	Yuan b&w	Y-1	1.73	0.09	0.37	
	Yuan b&w	Y-2	2.91	0.13	0.77	0.01
	Yuan b&w	Y-5	1.84	0.11	0.5	
	Yuan b&w	Y-6	2.47	0.12	0.58	0.01
	Yuan b&w	Y-7	4.26	0.12	1.14	0.03
Wen et al. (2007)	Yuan b&w	y4-l	1.84	0.07		
	Yuan b&w	y4-d	8.79	0.11		
	Yuan b&w	y7-l	2.48	0.08		
	Yuan b&w	y7-d	7.47	0.11		
	Yuan b&w	y10-l	1.41	0.07		
Zhang et al. (1986)	Yuan b&w	Y-3	1.56	1.3	0.13	
	Yuan b&w	Y-4	1.64	2.9	0.27	
Wen et al. (2007)	Early Ming b&w	hw10	2.43	0.08	0.15	
	Early Ming b&w	hw1	0.79	0.07	0.12	
	Early Ming b&w	hw2	1.06	0.07	0.1	
	Early Ming b&w	yl11	1.66	0.12	0.17	
	Early Ming b&w	yl14	2.5	0.17	0.61	
	Early Ming b&w	yl15	1	0.09	0.15	
	Early Ming b&w	yl3	1.13	0.09	0.08	
	Early Ming b&w	yl6	1.01	0.09	0.11	
	Early Ming b&w	yl7	2.38	0.16	0.41	
Wen et al. (2007)	Mid-Ming b&w	xd2	0.82	0.66	0.15	
	Mid-Ming b&w	xd3	0.59	0.24	0.01	
	Mid-Ming b&w	xd4	1.1	1.1	0.1	
	Mid-Ming b&w	xd9	0.63	0.67	0.04	
Chen et al. (1978)	Mid-Ming b&w	Xuande	2.17	0.25	0.24	
Zhang et al. (1986)	Mid-Ming b&w	M-6 xd	1.69	0.23	0.34	0.02

Reference	Category	Sample Identifier	MnO	Fe2O3	CoO	CuO
	Mid-Ming b&w	zt3	0.69	0.28	0.02	
	Mid-Ming b&w	zt5	0.9	0.56	0.07	
	Mid-Ming b&w	zt6	0.7	0.58	0.09	
Wen et al. (2007)	Mid-Ming b&w	zt8	1.01	0.81	0.22	
	Mid-Ming b&w	ch12	0.96	0.63	0.09	
	Mid-Ming b&w	ch14	0.72	0.13	0.05	
	Mid-Ming b&w	ch7	0.88	1.27	0.19	
Chen et al. (1978)	Mid-Ming b&w	M-1 ch	1.14	0.44	0.19	
	Mid-Ming b&w	hz2	1.01	0.51	0.09	
	Mid-Ming b&w	hz6	0.92	1.13	0.17	
Wen et al. (2007)	Mid-Ming b&w	hz7	0.86	0.41	0.05	
	Mid-Ming b&w	hz8	0.94	0.49	0.06	
	Mid-Ming b&w	hz9	0.82	1.32	0.25	
	Late Ming b&w	zd11	1.01	0.28	0.05	
	Late Ming b&w	zd4	0.49	0.06	0.01	
	Late Ming b&w	zd5	0.73	0.09	0.06	
Wen et al. (2007)	Late Ming b&w	zd6	1.04	0.31	0.04	
	Late Ming b&w	zd7	0.77	0.08	0.02	
	Late Ming b&w	zd9	0.62	0.09	0.04	
Chen et al. (1978)	Late Ming b&w	M-2 zd	0.9	3.35	0.53	
	Late Ming b&w	jj1	0.32	0.09	0.05	
	Late Ming b&w	jj12	0.96	0.12	0.16	
Wen et al. (2007)	Late Ming b&w	jj5	0.65	0.16	0.23	
	Late Ming b&w	jj8	1.31	0.17	0.34	
Chen et al. (1978)	Late Ming b&w	M-4 jj	0.86	2.25	0.75	
Zhang et al. (1986)	Late Ming b&w	M-7 jj	1.06	0.46	0.42	0.04

Reference	Category	Sample Identifier	MnO	Fe2O3	CoO	CuO
Wen et al. (2007)	Late Ming b&w	wl10	1.35	0.42	0.42	
	Late Ming b&w	wl6	1.63	0.28	0.29	
	Late Ming b&w	wl8	1.78	0.24	0.33	
	Late Ming b&w	wl9	0.86	0.16	0.21	
Zhang et al. (1986)	Late Ming b&w	M-8 wl	0.98	2.22	0.28	
	Late Ming b&w	M-9 wl	1.36	0.56	0.32	
Chen et al. (1978)	Qing b&w (Jingdezhen)	C-1	0.96	2.29	0.32	
	Qing b&w (Jingdezhen)	C-2	0.91	2.11	0.32	
	Qing b&w (Jingdezhen)	C-3	1.1	4.11	0.7	0.01
Zhang et al. (1986)	Qing b&w (Jingdezhen)	C-4	0.93	2.34	0.36	0.01
	Qing b&w (Jingdezhen)	C-5	0.92	2.28	0.45	0.01
Zhang and Gethin (2021)	Qing b&w (Jingdezhen)	K1	2.16	0.83	1.82	
	Qing b&w (Jingdezhen)	K2	2.17	0.94	1.22	
	Qing b&w (Jingdezhen)	K3	1.47	0.89	2	
	Qing b&w (Jingdezhen)	K4	0.98	0.71	0.56	
	Qing b&w (Jingdezhen)	K5	4.45	0.88	2.07	
	Qing b&w (Jingdezhen)	Y1	3.19	1.05	0.56	
	Qing b&w (Jingdezhen)	Y2	1.61	0.69	0.5	
	Qing b&w (Jingdezhen)	Y3	3.68	1.37	0.89	
	Qing b&w (Jingdezhen)	Y4	2.83	1	0.55	
	Qing b&w (Jingdezhen)	Y5	2.02	0.98	0.89	
	Qing b&w (Jingdezhen)	Q1	0.86	0.92	1.06	
	Qing b&w (Jingdezhen)	Q2	3.2	1.07	1.59	
	Qing b&w (Jingdezhen)	Q3	0.76	0.98	0.77	
	Qing b&w (Jingdezhen)	Q4	2.05	1.05	2.19	
	Qing b&w (Jingdezhen)	Q1	0.8	0.62	0.34	
Yu et al. (2020)	Qing b&w (Yunnan)	YXY1	2.34	1.35	0.6	
	Qing b&w (Yunnan)	YXY2	1.52	1.38	0.36	
	Qing b&w (Yunnan)	YXY4	2.02	1.31	0.46	

Reference	Category	Sample Identifier	MnO	Fe2O3	CoO	CuO
Li et al. (2020)	Qing b&w (Zhejiang)	LT1	0.76	1	0.09	
	Qing b&w (Zhejiang)	LT2	2.09	0.55	0.2	
	Qing b&w (Zhejiang)	LT3	1.81	1.35	0.15	
	Qing b&w (Zhejiang)	LT4	1.99	0.96	0.26	
	Qing b&w (Zhejiang)	LT5	2.04	1.06	0.15	
	Qing b&w (Zhejiang)	LT6	1.92	0.68	0.21	
	Qing b&w (Zhejiang)	LT7	0.42	0.65	0.05	
	Qing b&w (Zhejiang)	LT8	2.21	1.46	0.19	
	Qing b&w (Zhejiang)	LT9	2.03	1.41	0.3	
	Qing b&w (Zhejiang)	LT10	1.74	1.33	0.2	
	Qing b&w (Zhejiang)	LT11	3.24	1.73	0.26	
	Qing b&w (Zhejiang)	LT12	1.39	0.9	0.18	
	Qing b&w (Zhejiang)	LT13	0.3	0.58	0.03	
	Qing b&w (Zhejiang)	LT14	1.01	1.33	0.12	
	Qing b&w (Zhejiang)	LT15	1.92	1.8	0.29	
	Qing b&w (Zhejiang)	LT16	1.34	1	0.14	
	Qing b&w (Zhejiang)	LT17	1.45	1.56	0.17	
	Qing b&w (Zhejiang)	LT18	2.99	1.48	0.38	
	Qing b&w (Zhejiang)	LT19	2.06	2.5	0.33	
	Qing b&w (Zhejiang)	LT20	1.3	1.94	0.17	
	Qing b&w (Zhejiang)	LT21	0.94	0.73	0.07	
	Qing b&w (Zhejiang)	LT22	1.44	0.49	0.13	

As the very first scholars who analysed Tang blue-decorated ceramics, Chen et al. (1978) demonstrated that the colourant of blue Sancai glaze was cobalt, and Zhang et al. (1986) proposed that blue Sancai and Tang blue-and-white shared the same cobalt material, based on scientific comparison between them. Figure 11.7a and b proves this point. Sancai and blue-and-white porcelain in the Tang dynasty both show low MnO/CoO and high Fe_2O_3/CoO. In other words, a high-iron-low-manganese cobalt ore was used to produce Tang dynasty cobalt pigment. This characteristic is very similar to the imported cobalt pigment used in the Yuan and early Ming dynasty at the imperial kilns. The other notable characteristic of

Tang cobalt material is the existence of copper. Zhang and Pollard (2022) point out that cobalt material coexisting with copper was applied to Tang blue-decorated ceramics, and the same blue pigment was used in subsequent Yuan and early Ming blue-and-white, probably from the Middle East.

The chemical characteristics of Song blue-and-white are distinguished from those of Tang blue-decorated ceramics by very low Fe_2O_3/MnO and high MnO/CoO (Fig. 11.7a and b). Chen et al. (1978, 1980) analysed two Song blue-and-white sherds unearthed in Zhejiang and compared them with local cobalt ore. They found that the MnO/CoO ratio of the Song sherds is very close to the ratio of fired local asbolite in Zhejiang, but quite different from the imported pigment. This indicates that the source of Song cobalt pigment is Zhejiang, which matches the distribution of Song blue-and-white porcelain. This viewpoint has been accepted as a key observation, and no further analytical work has been done on Song samples.

Wen et al. (2007) considered scientific studies and literary evidence to reveal the types and provenance of cobalt pigment used in Jingdezhen from the Yuan and Ming dynasties. Sumali pigment, which is rich in iron and poor in manganese, was probably imported from the Middle East and used on blue-and-white porcelain during the Yuan and early Ming (1368-1424 CE). The pigment used in the mid-Ming (1426-1505 CE) is mainly native Chinese pigment. The ratio of pigments for the late Ming (1506-1620 CE) lies between the ratio for the early and the mid-Ming periods, which suggests that a mixture of imported and domestic pigments was used. Figure 11.7 a and c shows these changes clearly. An exception is the two samples represented by the red triangles near the horizontal coordinate in Figure 11.7a and near the two green squares in Figure 11.7b. These two blue-and-white porcelains used high-manganese cobalt ore and were produced in Zhejiang and Yunnan, also in China, instead of in Jingdezhen (Zhang et al. 1986). They have the same characteristics as the Song blue-and-white samples, which supports the idea that Song blue-and-white, as well as a few Yuan wares, employed native cobalt ore(s).

In the Qing dynasty, the origin and types of cobalt pigment varied. Zhejiang, Yunnan and Jiangxi and others supplied abundant cobalt ores to blue-and-white kilns in Jingdezhen and other places. The shared characteristic of these Chinese cobalt ores is low iron and high manganese (Fig. 11.7a and c). Potters mastered the selection and processing of the cobalt pigment. Some Qing dynasty literature offers precious and reliable records. For example, Pu Lan (蓝浦), who was born and lived in Jingdezhen, did a lot of investigation and experiments at his hometown to write a book—Jingdezhen tao lu (景德镇陶录)—which was published in 1815 CE (Lan 2004, 26). He stated that the blue pigment from Zhejiang was the top

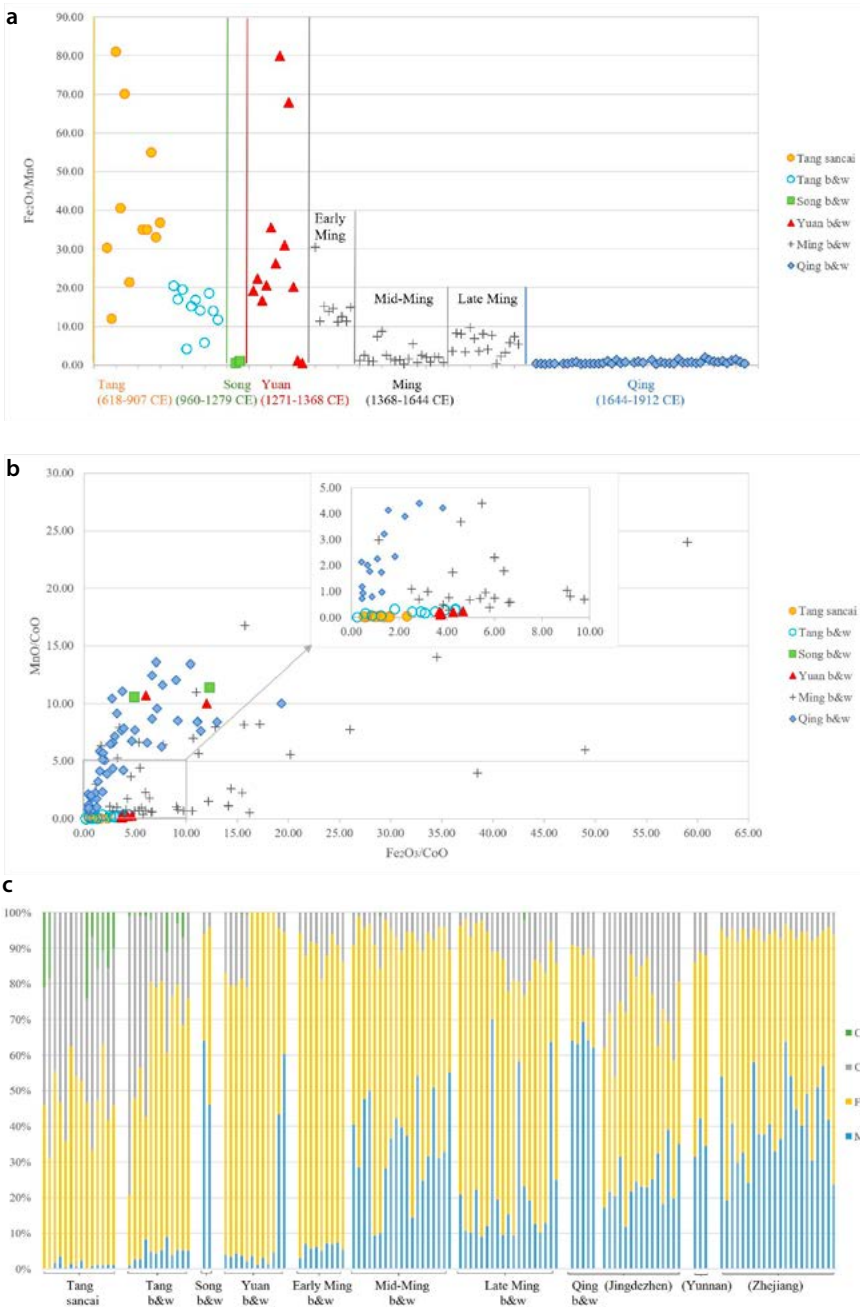

Figure 11.7: Scatter diagrams of (**a**) Fe_2O_3/MnO values; (**b**) MnO/CoO and Fe_2O_3/CoO values of the blue glaze and pigment used in Sancai and blue-and-white porcelains (underglaze instead of overglaze enamels); (**c**) the percentage relationship of Co, Fe, Mn and Cu of cobalt materials used in Sancai and blue-and-white porcelains.

cobalt material and that Yunnan, Guangdong and Jiangxi also provided the blue pigment. Traders selected the biggest and roundest stones to sell, which might be regarded as the best products. He said the black ore with gloss was top quality and that cobalt-blue pigment was also applied to enamelled Chinese porcelain. Giannini et al. (2017) were the first to establish that the overglaze blue enamels of the Famille Verte and Famille Rose wares and the underglaze blue on the Qing dynasty blue-and-white porcelain were from different sources. Pigment was imported from Erzgebirge in Germany in the form of smalt, a cobalt glass, for use in the overglaze enamels, for a better shade of blue. But this pigment was not used in the underglaze wares, where the colour might be susceptible to running.

Processing method of the pigment

The description of the processing methods of cobalt pigment given in historical accounts is rather simplified. To reveal details of the method, Zhou and colleagues, in the first half of the 20th century, did fieldwork at "old" kilns in Jingdezhen to record the traditional methods and then detailed the procedures of cobalt pigment making (Zhou et al. 1958). The process is as follows:

Step 1: Washing

Place 15 kilograms of cobalt ore in a bamboo dustpan, put the dustpan in a wooden basin, and pour clean water into the basin. Then, place the wooden basin on a bench inclined at an angle of 15-18 degrees to the ground. Sit at one end of the bench, wearing four iron finger covers on the left hand, excluding the thumb, and three finger covers on the right hand, excluding the thumb and the index finger. With both hands, continuously lift the cobalt ore that is partially immersed in water and vigorously rub it downwards (Fig. 11.8a). Continue this process for 30-40 minutes. Afterward, remove the dustpan from the wooden basin and pour the tinted water into a wooden barrel to allow it to settle. This precipitate (铁骨泥 Tiegu paste) is the raw material for black cobalt-iron glaze. The crushed material that falls from the dustpan into the wooden basin is called Ya material (牙料 rough material). After draining the tinted water, transfer this crushed material back to the dustpan with the remaining cobalt ores in the basin, add clean water, and repeat this process seven or eight times until the water remains clear.

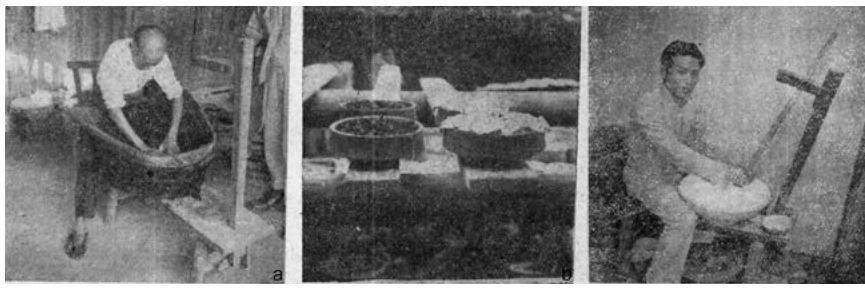

Figure 11.8: Photographs of some procedures of cobalt making in Jingdezhen, China, in the early 20th century: (**a**) washing the cobalt ores; (**b**) filling bowls with selected cobalt ores; (c) grinding the cobalt pigment, reproduced with permission from Zhou et al. (1958).

Step 2: Filling bowls

Place a small porcelain dish at the bottom of each bowl. Take the cleaned ore (excluding the rough material) and pack it wet into several large, circular boxes (with a diameter of approximately 16.5-17.5 cm), filling the bowls to the rim (Fig. 11.8b). Then cover it with a sheet of yellow straw paper and seal the top with a yellow clay cake.

Step 3: Firing

Place the bowls filled with cobalt material into the kiln and dig a rectangular pit approximately 20 cm deep beneath the kiln chimney. The size of the pit is determined by the number of bowls, and the depth of the pit is determined by the temperature of the kiln. If the temperature is high, the pit is deep, and if the temperature is low, the pit is shallow. Once the pit is prepared, put the bowls inside the kiln and cover them with coarse soil. Then fire them all at once.

Step 4: Selection

Take the bowls out of the kiln and place them on the ground to cool down. The next day, remove the clay cakes, pour the cobalt material into a wooden basin, and use a nested series of a large-aperture sieve and a medium-sized-aperture sieve to sift the cobalt material (the mesh size of the large-aperture sieve is approximately 1 cm, that of the medium-size-aperture sieve is 0.7 cm, and that of the small-aperture sieve is 0.2 cm). The cobalt material left on the large sieve is categorised as type I, and the cobalt material left on the medium-sized sieve, as type II. The cobalt material that passes through the medium-sized sieve is referred to as Xiao material (小料 small material). Use a small-aperture sieve to remove impurities,

such as sand and clay particles. What remains is categorised as type III. Take out the cobalt material remaining on the large sieve (type I) and the medium-sized sieve (type II) and place it on a lacquer table for grading. Material with a bright colour, high density, and a metallic sound when tapped is graded as top-grade material. Conversely, grade material with a dull colour, low density, and a muted sound as graded as lower-grade material.

Step 5: Grinding

The top-grade cobalt material selected from the residue on the large- and medium-sized-aperture sieves (type I and II), when ground in equal proportions, becomes top-grade blue colourant for blue-and-white porcelain. The remaining by-products, Xiao material (small material) and Ya material (rough material), become ordinary and lower-grade blue colourants for blue-and-white porcelain. Grind the pigment using porcelain bowls and porcelain hammers (Fig. 11.8c). The finer the pigment is ground, the better. Some pigments may require several months of grinding.

Conclusions

In the beginning of the use of cobalt on Chinese ceramics, the material was imported from overseas, probably from the Middle East. It contains high iron, low manganese and trace copper. This material was made into blue glaze to decorate the wares either on its own or in combination with other colours, such as brown, green or white. Only two kilns—Gongyi and Liquanfang in northern China, near the capital cities—produced this blue ceramic. Gongyi produced it throughout the Tang period, but Liquanfang only made it from 730 CE to 760 CE. The royal family and ordinary people could both use blue Sancai as their burial objects in tombs. In the late Tang, around the 9th century CE, Gongyi potters created the earliest blue-and-white porcelain. Compared with blue Sancai, Tang blue-and-white was targeted to a niche but distant market. These blue-and-white porcelains were produced in Gongyi and transported south to Yangzhou, the busiest port in the southern China. From there, these blue products were shipped to the Middle East, such as Persian Gulf.

However, these two blue-decorated ceramics did not flourish in the Song dynasty. Also, the import of cobalt materials seems to have stopped. An unknown kiln or kilns made a few Song blue-and-white porcelains using local cobalt ore from southern China. This blue pigment contains high manganese and low iron. When the Mongol Empire was established across Asia and Europe, Jingdezhen dominated the production of blue-and-white porcelain, using cobalt pigment from West Asia and the Middle East. From then on, Jingdezhen became the centre

of porcelain production in China and fine Yuan blue-and-white porcelains were mainly exported.

The production and use of blue-and-white porcelain continued throughout the Ming dynasty. Specifically, the organisation of the imperial kiln was confirmed by Zhu Yuanzhang, and many folk kilns were built in Jingdezhen and other places from northern to southern China. Blue-and-white porcelain was used as daily wares, burial ceramics, sacrificial offerings, and export porcelains, among other things. The nobility and ordinary people in China, as well as people overseas, liked this porcelain very much.

The origins of cobalt pigment can be divided into three periods. The early Ming possibly took over the cobalt materials from the Yuan dynasty, and the imported cobalt materials were still applied to the porcelain. The mid-Ming started to use local cobalt ore widely. The late Ming potters mixed imported and local cobalt ores together to make a blue pigment. After that, the Qing dynasty witnessed the diversification and the last glory of blue-and-white porcelain in ancient China.

The origins of cobalt ores were various, and suitable cobalt pigment was found and exploited in many places in China. The processing method was very elaborate, including multiple physical and chemical reactions. The products, production organisation, use, market, and technology were upgraded. On one level, this china turned China into the country of china.

Acknowledgements

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Chapter 12

Light and dark blue: A non-destructive analysis of blue enamel and underglaze compositions in Fürstenberg porcelains

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Introduction

As a porcelain factory, Fürstenberg was founded approximately 275 years ago, in 1747. It was established by Duke Carl I von Braunschweig-Wolfenbüttel (1713-1780), who inherited the ducal power in 1735. Characteristic for his reign are investments in economy, infrastructure and education. The manufactory is located on the site of the old castle of Fürstenberg, in modern-day Niedersachsen (Lower Saxony), close to the village of Höxter, on the River Weser, in northwestern Germany. The environment of the factory was well suited for this activity, as ample amounts of firewood were present in the nearby Solling forest. Excellent reference works exists on the history and art-historical value of Fürstenberg porcelain, such as Ducret (1965), Lechelt et al. (2016), and Unterberg (2010).

This research forms part of a larger research project conducted at the universities of Leiden (The Netherlands) and Cranfield (United Kingdom) in collaboration with specialists from the Museum Schloss Fürstenberg (Germany). The goal of this project is to document enamel production technologies at historic porcelain factories across Europe. Significant work has been undertaken in the past to document Meissen enamel productions (Casadio et al. 2010; Domoney 2012; Zumbulyadis and Van Thienen 2020), resulting in a reliable reference database. Now this methodological and interpretative framework is expanded upon through

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looking at how 18th and 19th century enamel technology and the factories' resources developed in central and western Europe, with a focus on Fürstenberg. The resulting database will allow—in variable resolutions—dating of the enamel recipes based on their chemical composition and thus attribute decorations to a particular time period. It is the goal to expand this in the future towards more producers.

In this paper, the results the project's analyses on a set of blue overglaze enamels and blue underglaze are presented, specifically focused on the role of cobalt used for the blue decoration.

From the historical records, it is known that several painters connected with blue enamels and glazes worked at the manufactory (Lechelt et al. 2016). Records from 1767 state that 14 blue painters are documented, and those from the 1800s mention 21 in total, including 7 trainees. Notable artisans, with the date of their Fürstenberg association indicated, include Johann Christof Kind (1728-1798), 1751; Georg Friedrich Geisler (1714-1782), 1753; Tobias Hennickel (1731-1776), 1757; Johann Jakob Stemmer (1722-1796), 1758; August Gronau (?-1776?), 1767; Adam Guntersperg (dates unknown), 1767; David Adam Büttner (1721-1769), 1767; and Christian Friedrich Geisler (1742-1811), 1772. Several of these painters travelled and likely developed both their skillset and their recipes along the way. One interesting aspect of this is how these painters where influenced or constrained by access towards either pigments or raw materials. The earliest record of blue painting relates to 1769, to Georg Friedrich Geisler, who worked both in Meissen and in Höchst before arriving in Fürstenberg. Tobias Hennickel, on the other hand, came from southern Germany. He was born in Memmingen and was probably trained in Künersberg. Johann Jakob Stemmer is documented as "trained in Fürstenberg", but there may be misinformation associated with this documentation. Both Gronau and Guntersperg are referred to as trainees. David Adam Büttner was also trained at Meissen and came to Fürstenberg later. Christian Friedrich Geisler, son of G. F. Geisler, was trained in Meissen (1761-1769), subsequently worked in Ansbach, and was at Fürstenberg from 1772 to 1811 as a 'blue painter'.

Methodology

A Bruker Tracer 5g, handheld X-Ray Fluorescence analyser (hhXRF) was used for all analyses at the Museum Schloss Fürstenberg repository (https://www.fuerstenberg-schloss.com) (Fig. 12.1). Due to its fast, non-destructive and mobile characteristics, as well as its capability to identify a wide range of chemical elements, this technique is well suited for porcelain analysis (Bezur and Casadio

2013; Zumbulaydis and Van Thienen 2020). Each analysis was carried out for 45 seconds, following standard operating procedures. The HH-XRF was run under the following two operating condition sets: (1) at 15kV, 21.8μA for 30 seconds with no filter in place for light element detection; and (2) at 50kV, 33.2μA, for 15 seconds with an Al 200 μm, Ti 25 μm; Cu 75 μm filter to optimise heavy element detections. Analysis areas for the enamels measured approximately 3 mm (Fig. 12.2) in diameter. To get enough information from the underglaze decoration, a larger area was examined, requiring a larger beam size. Analysis areas for the underglaze therefore measured approximately 8 mm in diameter. The focus of the study here is on the blue overglaze and underglaze enamels, and especially on their differentiation by means of their composition. Where possible, multiple points were measured as an assessment of variability in these enamels. Net count intensities were calculated through a Bayesian deconvolution approach in Bruker Artax software and were normalised to rhodium, the X-ray target of the instrument used. Data analysis was conducted through qualitative visual peak analysis of the spectra, as well as through plotting peak counts for pairs of elements in bivariate diagrams in order to identify compositional groupings. Significant groups were compared with Cranfield University's database of Meissen enamels (also Domoney 2012; Domoney et al. 2012).

Figure 12.1: Photograph of the Museum Schloss Fürstenberg reference collection, which forms the basis of the Cranfield-Leiden-Fürstenberg Porcelain Project.

Figure 12.2: Bruker Tracer 5g internal instrument camera image of the internal instrument camera example of a 3 mm collimator analysis area of a blue-decorated enamel.

Materials

Several research stays at the Museum Schloss Fürstenberg yielded a current database of 406 enamel and glaze compositions. In this study, both the overglaze enamels and the underglaze blue will be documented (n = 44; 28 objects), specifically in light of determining the potential variability in use of cobalt in these blues. Table 12.1 lists the objects that form part of this study, which includes material from the Museum Schloss Fürstenberg as well as excavated Fürstenberg porcelain sherds derived from excavations at Höxter and reference materials held in the private collection of Jens Storre.

Table 12.1: Inventory list of names and the associated descriptions, remarks and dates for the samples discussed in the text.

Sample Identifier	Item	Remarks	Dating
F002	Plate—flowers	(JS 444)	1760
F003	Plate— Jerome Napoleon	(JS 171)	1805
F004	Plate—small	(JS 224)	1760
F006	Plate early	(JS 273) F Mark in underglaze blue, very dark	1755
1741_3	Plate—flowers	Museum	1785
1741_1	Plate—flowers	Museum	1785
1784	Plate—flowers and birds	Form comparable to F002	1760
1729	Plate—fruits	-	1762
657	Plate—mixed style	-	1820
HX290/301	Shards—Höxter	-	1760
R001	Saucer	Reichmann Collection: Rocaille-black	1755
R003	Saucer—Metzsch	Painted by Metzsch	1753
HX290/272	Shards—Höxter	F Mark	1760
HX290/311	Shards—Höxter	-	1760
425-3	Underglaze blue	-	1765
1227	Underglaze blue	Stones and bird	1785
F009	Plate—underglaze blue	Sample of Christian L	1850
1246	Plate	-	1830
1228	Plate—stone and birds	Underglaze blue F Mark	1765
F007	Saucer—Oettner	-	1767
1741-2	Plate	Underglaze blue F Mark	1785
496	Fruit plate, large	Underglaze blue F Mark	1762
F005	Plate	(JS 229) early Weitsch? also in RM Collection	1758
2325	Sanding device	Underglaze blue	1775
2305	Tray—attrib. to Kind	Underglaze blue	1785
R008	Weitsch—tableaux	-	1767
R009	Plate—copied from KPM	Underglaze blue F Mark	1775

Results and discussion

Overglaze blue enamels

The overglaze blue enamel data consists of 19 measurements on 13 objects, ranging in date between 1755 and 1820. In the early porcelain vessels, the elevated presence of both Ni and Co can be detected in most objects; however, some objects exhibit, in addition, a high Ba peak (Fig. 12.3). Towards the end of the 18th century, the blue enamels change (as illustrated by porcelain dated to 1785), and both Zn-enriched cobalt blue and non-Zn-enriched cobalt-blue enamels were used. In the late 18th century and early 19th century, the Zn/Co ratio increases significantly, to Zn/Co >1.0. These differences seem to be more related to chronological and, by extension, resource and/or technology rather than colour intensity itself. Figure 12.4 demonstrates that the elemental variability between darker or lighter areas of blue (1755-1760) is much less significant than that between the various porcelain vessels. In analyses of the black enamels, higher cobalt values were only attested in enamels attributed to the late 18th century and later. At Meissen (Domoney 2012), two major black enamels were defined: Samuel Stöltzel's 1731 Mn-based black and Höroldt's 1731 "good black" (Mn, Fe, Co). While the blacks at Fürstenberg are Mn based, the absence of Co largely points at an own Mn recipe or Stöltzel's Mn recipe.

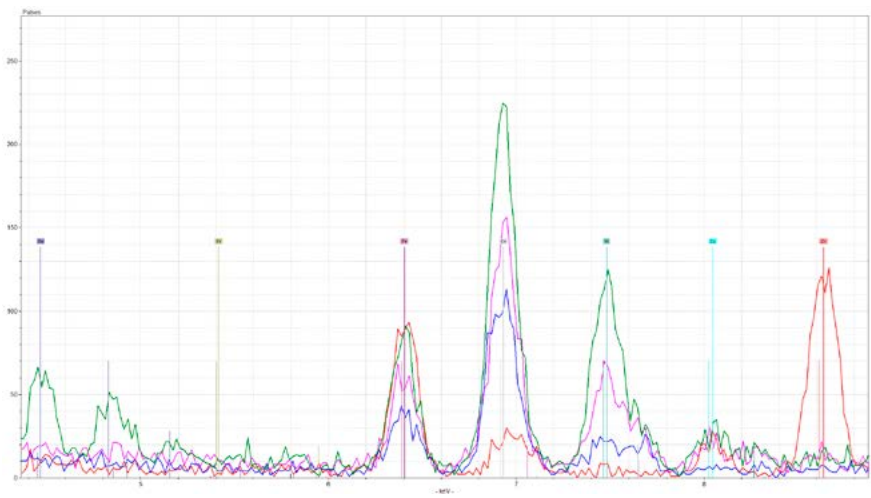

Figure 12.3: X-ray fluorescence spectra of representative compositional differentiations of objects dated to 1753 (pink line), 1755 (green line) and 1785 (blue and red lines).

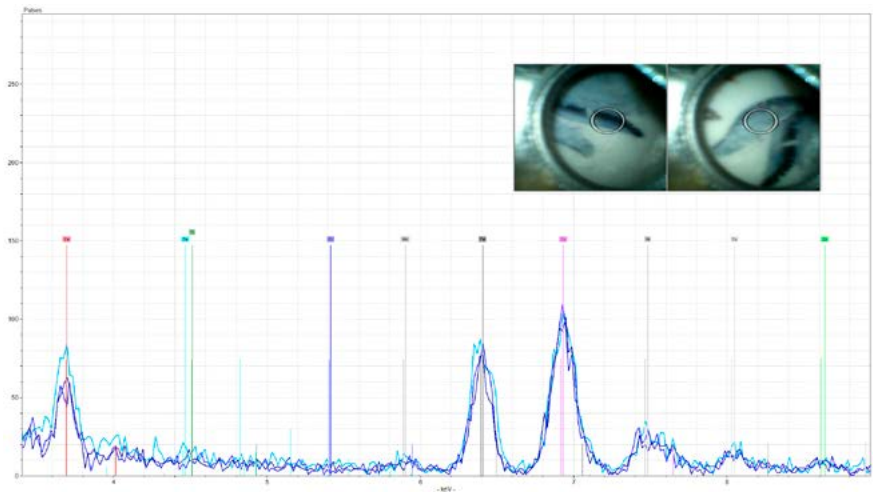

Figure 12.4: X-ray fluorescence spectra showing spectral consistency between light and dark blue decorative patterns.

Underglaze blue enamels

Blue is one the most prevalent underglaze colours, also within the repertoire of Fürstenberg porcelains. This blue is typically based on cobalt blue (involving the use of smalt) and is applied before, and thus located under, a hard glaze coating. The symbol characterising the porcelain manufactory is a stylised letter F, which changes appearance through time. Although the basis for these blues is cobalt, variable compositions can be detected through time. A total of 24 underglaze blue measurements were conducted, for the most part on the F marks at the bottom of 17 porcelain vessels ranging in date between 1760-1830 (with potentially later examples included). Since a glaze layer covers these decorations, these types of materials are harder to measure and use for semi-quantitative approaches. Also, since these underglaze pigments can partially migrate into the glaze layer, they can thereby obscure the XRF spectra. Nevertheless, clear differences can be observed in the formulations used: (1) a high-Ni blue, present on objects from 1755-1785; (2) a high-As blue, only attested on one piece, from 1785; and (3) a consistent cobalt blue, without other significant elements, observed from 1765-1770 as well as from 1805-1830. What is further noteworthy is that with the exception of one object, no Zn or very low Co/Zn ratios were found in in Fürstenberg underglaze blue. This is a remarkable differentiation from Meissen underglazes dating from 1765-1905 (Domoney 2012), which contain significantly higher Zn values. Also

noteworthy is that Bi was not identified in Meissen underglazes until 1772, while a clear Bi presence was detected in Fürstenberg underglaze in a single object, dated to 1755 (Fig. 12.5), which needs further contextual documentation.

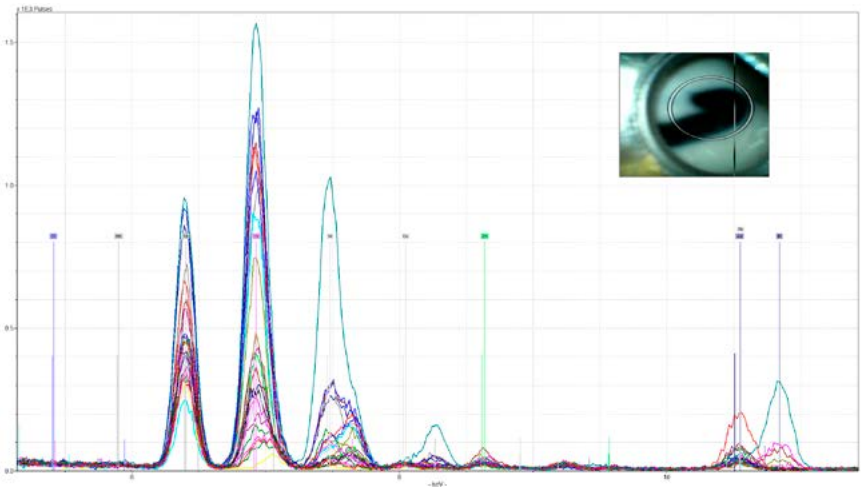

Figure 12.5: X-ray fluorescence spectral identification of Bismuth in an underglaze blue factory mark consisting of the letter F, dated c. 1755.

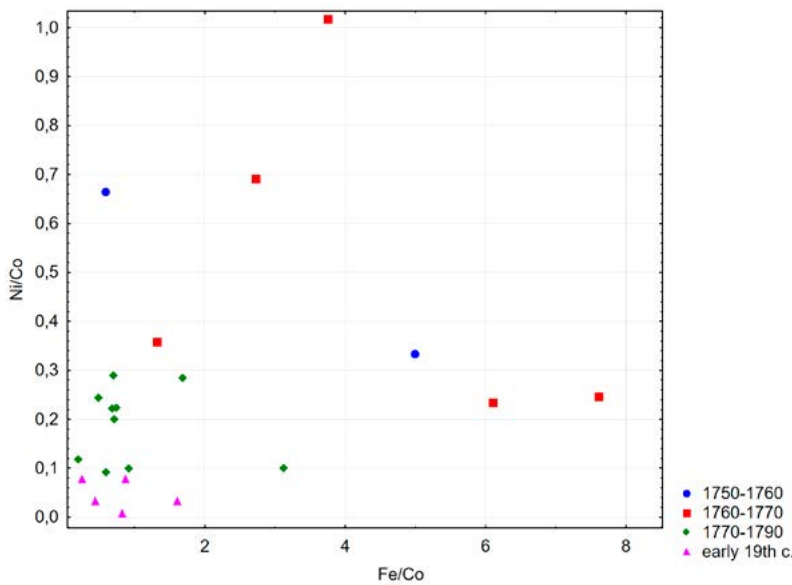

Figure 12.6: Bivariate plot of Ni/Co versus Fe/Co ratios according to the expert eye dating of the porcelain.

A clear pattern can be observed in the Ni/Co and Fe/Co ratios of the cobalt-blue formulations, and based on this pattern, it can be suggested that both Ni and Fe are source impurities. Underglaze blues related to the early 19th century do exhibit very low ratios of Ni/Co and Fe/Co (Fig. 12.6), which point to a decrease in these elements, likely due to the implementation of new technologies. On a chronological scale, higher Ni/Co ratios can be observed in the period 1770-1790 and, especially, earlier, in 1750-1770.

Conclusions

Based on the dataset presented here, a few systematic observations can be made. The developments in Fürstenberg blue enamel formulations seem to run largely parallel with developments at Meissen. However, small but important compositional differences in blue over- and underglaze enamel can be observed between the early phases of development (that is, prior to c. 1760), on the one hand, and the late 18th century and the early 19th century, on the other. All the early Fürstenberg blue overglaze enamels contain Ni, with some also enriched in Ba, whereas the late 18th century and early 19th century enamels are characterised by increasing Zn/Co ratios, although they also show continued use of non-Zn enamels.

In none of the spectral data can substantial proportions of Zn can be identified in the underglaze F marks and other decorative aspects until the late 18th century. It seems likely that the variable quantities of Ni and Fe in these different blues are resource impurities, as over time the presence of both elements in the enamels decreases. However, it remains to be verified whether the quantities of Ni and Fe also relate to production recipes and thus may constitute deliberate additions.

The results presented here provide the first analyses of the blue-coloured materials that are part of Fürstenberg porcelain, as part of a larger-scale porcelain analysis project. Future research will involve analysis of the porcelain bodies, multi-colour overglaze enamels and more 19th century materials.

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Cobalt: named after goblins, allotted to gods.

Cobalt and its compounds have had a long and important part to play in history. Metallic cobalt is a modern innovation, vital in the green energy transition. However, cobalt compounds have been used for 3,500 years to create deep-blue pigments, featuring in many important works of art and religious artefacts, associated with heaven, eternity and the divine. Cobalt ores are rare, and their exploitation is a dangerous pursuit. Their co-occurrence with arsenic has led to severe health consequences for workers, which were blamed on supernatural spirits and goblins, "kobolds", from which the name cobalt is derived. *Of Goblins and Gods* discusses the state-of-the-art of the extraction and use of cobalt ores through history, alongside the technology involved in making and applying cobalt pigments in many man-made materials across all regions and periods, from the Death Mask of Tutankhamun and pre-Islamic tiles to Indian manuscripts and the windows of Canterbury Cathedral.

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