Christa Hofmann (ed.)

THE VIENNA GENESIS

Material analysis
and conservation
of a Late Antique
illuminated manuscript
on purple parchment

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The Vienna Genesis: Material analysis and conservation of a Late Antique illuminated manuscript on purple parchment

Edited by Christa Hofmann

BÖHLAU VERLAG WIEN KÖLN WEIMAR

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Preface

It is certainly a huge challenge and a great responsibility for a research project to address one of the oldest and most valuable manuscripts in the Austrian National Library. Ever since it was transferred to the Vienna Court Library during the time of Prefect Peter Lambeck (1663–1680), the cimelia later given the name "Wiener Genesis" has, thanks to its outstanding importance, been regarded and admired as a rare testimony of Late Antique art history. Soon after it was acquired, it became the object of scholarly analysis, thus gaining a reputation in the specialist world as a coveted item to be displayed only to select learned visitors as something very special, appreciated as "the greatest piece of antiquity" (Richard Pococke, 1737).

The present publication begins with a methodological and analytical section concentrating on the "materiality" of the manuscript, examining the medium of the text, its purple colouring, the ink, the pigments and dyes and their composition. This is what constitutes the highly innovative element of this research project, underpinning or even putting into perspective the reasoning hitherto based only on palaeographic and art historical aspects.

The second element of this project concentrates on aspects of preservation, and addresses the conservation of the object and questions concerning its future safekeeping.

For the research on this manuscript, the scientific approach certainly means a new impetus that must be exploited, while for those responsible for the preservation of the collection it brings the certainty that a satisfactory solution has been found.

Andreas Fingernagel,
Director of the Department of Manuscripts and Rare Books
at the Austrian National Library

Vienna, December 2018

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Introduction

Christa Hofmann

The Late Antique Codex theologicus graecus 31, the Vienna Genesis, is an iconic manuscript of the Austrian National Library. On 48 preserved pages, the book of Genesis from the Septuaginta is written in Maiuscula biblica in silver ink on purple parchment. 48 miniatures illustrate the slightly abbreviated text. The Vienna Genesis is dated to the first half of the 6th century. The manuscript was presumably produced in a cultural centre in the Near East such as Antioch or Constantinople. It is one of the earliest known cycles of book miniatures from the Old Testament, a rare witness of Late Antique book culture.

Since 1664, the codex has been preserved at the Imperial Court Library, which later became the Austrian National Library in Vienna. Since 1664, the fragile condition of the Vienna Genesis has occupied librarians, curators, bookbinders and conservators. Palaeographers, codicologists and art historians have researched the text and the miniatures. The origin of the Vienna Genesis and its production have kindled a fervent scientific debate. Curators and conservators at the Austrian National Library were concerned regarding the condition and the stability of the famous codex subsequent to the last intervention in 1975. A new effort to conserve the Vienna Genesis and to reconsider the storage situation had to be based on technological and material analysis. So far, the material aspect of the codex has not been in the focus of research. The Austrian Science Fund FWF funded a project that combined the work of conservators and conservation scientists, using scientific analysis and art technological research to investigate the parchment, the purple dye, the silver ink and the miniatures. The objectives were to gain a deeper understanding of the process of manufacture and to discern how many artists participated in the painting of the images. With better knowledge of the materials and their degradation phenomena, we aimed to find the best methods of conservation and preservation.

This publication is a summary of the results. The diversity of authors and themes reflects the different aspects of the project. It is difficult to write and read a multidisciplinary book. Details that are interesting for one reader might be too specialised for another. We have tried to share our results including all questions that remain unanswered. Images illustrate the text and we hope that they make it more vivid and understandable. Many different specialists have created the Vienna Genesis. Many different specialists have researched it in this project. We ask for the patience of the reader to discover the depths and mysteries of this unique artwork that has fascinated us for the last three years and many others for centuries more.

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The history of the Vienna Genesis and former interventions since 1664

Christa Hofmann, Sophie Rabitsch

Introduction

The origins and the history of the Vienna Genesis until 1664 remain for large parts in the dark. By studying the materials, the manufacture and the condition of the manuscript the aim of the project was to complement the conclusions of art historians, palaeographers and codicologists as well as to provide the basis for further studies. This chapter gives an account of the documented history, which starts with the integration of the manuscript in the Court Library in 1664. The following chapters will describe the findings on parchment, inks, colours and treatments in detail.

Origins and early history

The Greek manuscript of the Book of Genesis was written in silver ink in Maiuscula biblica on purple dyed parchment. The codex was probably custom-made for a private owner rather than for liturgical use[1]. 24 folios with 48 miniatures – one on each page – have survived. Otto Mazal assumes that according to the missing sections of the biblical text the original manuscript comprised 96 folios with 192 miniatures[2]. Every page is divided between the text and a narrative cycle of miniature paintings. The slightly shortened text and the miniatures were well adjusted to one another. Precious materials employed like purple-dyed parchment, silver ink and the pigment ultramarine as well as the high quality of manufacture and artistic expression point to a large commission designed for a wealthy patron. Stylistic references, especially the comparison with the Codex Rossanensis, point to an origin in the Eastern Mediterranean. Major cities that could have provided the necessary skills for such an ambitious artistic endeavour were Antioch or Constantinople. Notes by later owners in Italian on folio 1, page 1 and 2, written in Humanist Italic explain the content of the miniatures[3]. On several folios transfers from strips of Latin manuscripts

1 Mazal, 1980, p. 189.
2 Mazal, 1980, p. 27.
3 Mazal, 1980, p. 189.

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Fig. 1: Folio 20, page 39 in UV-light, transfer from a Latin manuscript.

in Italian Rotunda, used to bind the folios, can be seen in normal and Ultraviolet (UV) light, for example on folio 20, page 39 (Fig. 1). On this folio the text can be identified as the beginning of the first letter to the Corinthians by the apostle Paul, verses 1–10[4]. The Italian Rotunda is dated to the late 14th or early 15th century by Mazal[5]. Pieces of parchment that were used for mending showed bills in Italian. These parchment pieces, mentioned by Wilhelm von Hartel, prefect of the Court Library and editor of the first facsimile, were probably removed and do no longer exist[6]. Merchants or crusaders might have brought the codex or parts of it from the Eastern Mediterranean to Italy.

4 Mazal, 1980, pp. 189–190.
5 Mazal, 1980, p. 190.
6 Hartel and Wickhoff, 1895, pp. 99–100.

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In the Court Library 1664–1918

Archduke Leopold Wilhelm of Austria (1614–1662), the second son of Emperor Ferdinand II, acquired the 24 folios of the Vienna Genesis for his important art collection, possibly from an Italian collector in the 17th century. After Leopold Wilhelm's death, his nephew, Emperor Leopold I., inherited the collection. Peter Lambeck, the prefect of the Court Library, discovered a Greek codex with miniatures in the picture gallery of Leopold Wilhelm. Lambeck suggested to Leopold I. that this precious codex be integrated into the Court Library. In a letter to Leopold I. on 23 April 1664, in which Lambeck thanked for the transfer, he described the condition of the manuscript and the deterioration of the silver ink and dated the codex to the 6th century[7] in comparison with the Vienna Dioscorides.

> Fuerunt illae olim coloris argentis, qui tamen injuria temporis ubivis fere evanuit, adeo ut loco literarum nunc sint foramina, qua antiquos styli ductus qualitercumque referent.
> They have once been made in silver colour, which nevertheless by the deterioration in time vanished greatly overall, so that in place of the letters there are now losses, which in some way render the form of the antique style.

The 24 folios had been bound with a Latin codex, which can no longer be identified in the Manuscript Collection. Lambeck probably separated the Vienna Genesis from the Latin codex. The folios of the Genesis were bound together with two pages of the Gospel of Luke from the Codex Purpureus Petropolitanus in a separate pamphlet with the library code Codex theologicus graecus 2. On the lower margin of folio 1 Lambeck wrote in brown ink: "Augustissimae Bibliothecae Caesarae Vindobonensis Codex Manuscriptus Theologicus Graecus Nr. 2" (Fig. 2). Lambeck wrote the page numbering 1–50 in the middle of the upper margin of each page at the same time. The inks used by Lambeck could be identified as iron gall inks of similar composition, see chapter on silver inks. To make the manuscript known, Lambeck initiated the reproduction of the miniatures by the copper prints of Tobias Sadler[8].

Daniel von Nessel, prefect of the Court Library from 1680 to 1700, catalogued the Vienna Genesis under the library code Codex theologicus graecus 31 in his catalogue of Greek manuscripts, which appeared in 1690. This code is still valid today. In the catalogue the commentaries of Lambeck and the prints by Thomas Sadler were reproduced. A new edition of the commentaries of Lambeck by Adam Franz Kollar von Keresztén in

7 Mazal, 1980, pp. 191–192.
8 Mazal, 1980, p. 193.

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Fig.2: Folio 1, page 1, detail with library code by Lambeck.

1776 also contained reproductions of the miniatures in prints by Anton Schlechter[9]. When Napoleon I. occupied Vienna, he had many art works transferred to France, among them manuscripts and rare books from the Court Library. When in 1813 a similar danger was imminent, the Vienna Genesis was brought to Hungary in order to prevent it from being seized by Napoleonic troops[10].

Valuable objects of the library were shown to interested visitors from the 17th century onward. In their travel reports Johann David Köhler[11], Heinrich Sandner[12] and Franz Heinrich Böckh[13] mention that they saw a purple codex in the court library. The German art historian Gustav Friedrich Waagen had the rare opportunity to see and study the codex in 1839. Waagen describes the Vienna Genesis in his book on art monuments in Vienna[14] and comments on the condition:

9 Mazal, 1980, p. 193.
10 Mazal, 1980, p. 193.
11 Köhler, 1762, pp. 20 and 27.
12 Sanders, 1784, p. 505.
13 Böckh, 1823, p. 100.
14 Waagen, 1867, pp. 5–8.

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> Leider haben die meisten Bilder sehr gelitten und ist der Zustand des Pergaments von der Art, sind die Farben so lose, dass gelegentlich einer jeden neuen Beschauung, auch bei der grössten Vorsicht, nothwendig wieder etwas Farbe verloren geht. Da aus diesem Grunde der Codex nur äusserst selten gezeigt wird, so halte ich es für meine Pflicht, die mir von dem Praefekten der Bibliothek, des erst im vorigen Jahr verstorbenen Grafen Moritz Dietrichstein gewährte, ausserordentliche Vergünstigung des Studiums desselben durch eine genaue Rechenschaft darüber einigermassen zu vergelten.

> Unfortunately most of the images have suffered a great deal. The condition of the parchment is such that the colours are so loose that every new inspection, even under utmost care, causes new losses of colour. For this reason the codex is shown very rarely. Therefore I regard it as my duty to compensate the extraordinary privilege of study that the recently deceased count Moritz Dietrichstein granted me with a thorough report.

In the second half of the 19th century cimelia were displayed in the State Hall. Letters in the Austrian National Library archive from 1846 reveal that the library requested showcases for the presentation of its treasures[15]. According to the catalogue printed in 1893[16] folios of the Vienna Genesis were exposed in showcase B. It is not known which pages of the bound folios were shown and for which amount of time. In her 1848 recollections of a journey to Vienna, Therese Bacheracht describes that she was impressed by manuscripts of silver and gold ink on purple parchment from the 6th century in a showcase in the State Hall[17].

At the end of the 19th century, the pamphlet was unbound to reduce damage from use and to produce the first facsimile edition in 1895. Each folio was stored individually between two glass plates[18]:

> Die 24 Genesisblätter, welche bisher ein durch Klebstoff zusammengehaltenes Heft bildeten, litten bei jeder Benützung, indem die Risse sich erweiterten, Bruchstellen sich verschoben und kleinere Stücke abbröckelten. An mehreren Stellen waren Risse und dabei Wörter überklebt; die ungleichen Falten und Schrumpfungen drohten weitere Zerstörung und erschwerten jede photographische Aufnahme. Um diese zu erleichtern und eine bessere Erhaltung und Benützung für die Zukunft zu sichern, entschlossen wir uns, das Heft aufzulösen, die einzelnen Blätter zu reinigen und zu glätten, abgerissene Pergamentstückchen zu befestigen und, so hergerichtet, jedes Blatt zwischen Glasplatten zu legen, eine

15 Austrian National Library Archive, records 196/1846, 223/1846, 126/1847, 133/1847.
16 Gödling von Tiefenau, 1893, pp. 4–5.
17 Bacheracht, 1848, pp. 117–118.
18 Hartel and Wickhoff, 1895, pp. 100–101.

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> lange, mühsame Arbeit, der sich der Custos Chmelarz mit unverdrossenem Fleiss unterzog.
>
> The 24 Genesis folios that where bound with glue to form a booklet suffered at each use. The tears became lager, breaks moved and small particles came off. On several locations, tears were pasted over obliterating words. Uneven folds and shrinkage were an imminent risk for further destruction and complicated the procedure of taking photographs. To facilitate photographic reproduction and to secure better preservation and use for the future, we decided to unbind the booklet, to clean and flatten the folios, to re-adhere torn pieces of parchment and thus adjusted to put each folio between glass plates, a long and tedious work that curator Chmelarz undertook with assidous diligence.

We do not know if the curator Eduard Chmelarz had any kind of training or experience in conservation. The glass plates were fixed with paper adhesive tape as mentioned in a later report[19]. The folios were reproduced with black and white collotypes made by "Erste Österreichische Lichtdruckanstalt" after photographs taken by the "k. k. Lehr- und Versuchsanstalt für Photographie und Reproductionsverfahren", the renowned school for photography and reproduction in Vienna[20]. Lacunae in the parchment remained without infills.

Prefect Joseph von Karabacek started to organise exhibitions in the State Hall in the early 20th century. In 1901 an exhibition was dedicated to miniatures, "Die Miniaturenausstellung der k. k. Hofbibliothek". Folios 7, page 13, and 16, page 31, of the Vienna Genesis were displayed[21]. During the Eucharistic Congress in 1913, folios of the Vienna Genesis were shown in the State Hall. In 1916 two folios (5, page 9, and 16, page 32) were presented in the exhibition on book art, "Buchkunstausstellung"[22]. According to documents in the archive, which report the income, the exhibition was open from 16 April to 19 November 1916[23].

In the Austrian National Library 1918–2018

In 1919, Italian occupying forces took the manuscript to Trento. The Italian government wanted three Estense manuscripts that were private property of the Habsburg family and

19 Austrian National Library Archive, record 775/21.
20 Hartel and Wickhoff, 1895, title page, p. 101.
21 Beer, 1902, pp. 233–238.
22 Katalog der Buchkunstausstellung, 1916, p. 1*.
23 Austrian National Library Archive, record 521/1916.

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could not be delivered. To enforce the seizure the Italians took three of the most valuable objects of the library, one of them the Vienna Genesis, as security. After tedious negotiations and a special contract with Italy, the three manuscripts were returned in March 1921. Prior to their transport to Italy the surface of the glass plates that housed the folios of the Vienna Genesis had been glued with paper adhesive tapes, which served as protection against breaking of the glass. Following their return, the removal of the tape was not completely possible, as the glue had damaged the glass surface. The glue was analysed by the "Landwirtschaftliche-chemische Bundesversuchsanstalt" (agricultural-chemical federal research institute). Director Otto Dafert summarised the findings in a report to the National Library[24]. The glue contained hydrofluoric acid, which damaged and roughened the surface of the glass. During analysis of the glue, a coating covering the inner surface of the glass plates was discovered. It was described as oily droplets with a tendency to crystallization. Investigations revealed that the coating consisted of sodium acetate, but free acetic acid was not detected. Dafert assumed in his report that the glue which was used to hold the glass plates together in the late 19th century contained acetic acid, which later led to the observed coating. A fading of the purple dye was observed since Chmelarz's encapsulation between glass plates. In his report, Dafert states that the glue containing acetic acid could have caused this phenomenon.

The library's director general Donabaum wrote to the federal minister for interior and education to ask for the financial means to buy new glass plates. He refers to the bad condition of the folios and to the frequent use: "… a different storage than between glass plates is not possible considering the bad condition of the folios and the frequent use of the manuscript."[25] The Italian government was asked to pay for 52 new glass plates (2.5 mm thick, 46.5 x 34.5 cm, all four edges polished). The director general's argument was that foreign visitors wanted to the see the manuscript almost daily. The request was granted and the folios were rehoused between new glass plates.

A second facsimile edition was produced in 1931 with a commentary volume by Hans Gerstinger. Kunstanstalt Max Jaffé reproduced the folios as colour collotypes. In the commentary, Gerstinger described different shades of purple on the folios and attributed them to chemical changes and fading of the colorants[26]. These observations led him to the conclusion that the colorant was "artificial purple" rather than shellfish purple, a reasonable assumption as shellfish purple is known to be a rather lightfast natural dye, see chapter on purple parchment. A sample was taken to identify the colorant but without result[27]. Ger-

24 Dafert, Austrian National Library Archive, record 775/21, 1921.

25 Donabaum, Austrian National Library Archive, record 775/21, 1921.

26 Gerstinger, 1931, p. 29.

27 Gerstinger, 1931, p. 187.

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Fig. 3: Folio 1, page 1, detail with silk gauze bridges on tear.

Fig. 4: Folio 1, page 1, in the facsimile edition from 1895.

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Fig. 5: Folio 1, page 1, in the facsimile edition from 1931.

stinger writes that the book conservator Alois Liška thought that the parchment was made from calfskin[28]. The bookbinder and book conservator Alois Liška worked for the Manuscript Collection from 1906 until 1939[29]. He presumably treated the folios of the Vienna Genesis when they were re-housed between new glass plates or before new images were taken for the second facsimile edition. Bridges made from small silk strips on tears can be seen on some folios (Fig. 3) and are visible on the reproductions in the facsimile from 1931. Silk gauze was used for repairs in manuscripts in the early 20th century at the library[30]. Figure 4 shows folio 1, page 1 in the facsimile from 1895 and figure 5 for comparison the same folio in the facsimile from 1931. Some more flattening of the parchment seems to have been carried out. Small bridges of silk gauze have been used to mend the large tear without obscuring text or miniature. Again, losses remain without infills.

28 Gerstinger, 1931, p. 185.
29 Austrian National Library Archive, record 1059/1928; Stummvoll, 1973, p. 119.
30 Smith, 1938, p. 68.

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Fig. 6: Storage between glass plates in the metal container in the Manuscript Collection in the 1950s.

Before the start of World War II, at the end of 1938, cimelia were stored in the basements of the library. The Vienna Genesis was probably among them. When air raids on Vienna became very intense in 1944, valuable objects of the library were transferred to a salt mine in Lauffen close to Bad Ischl[31]. During the last days of the war the National Socialists planned to blow up the salt mines with the stored artefacts from major Austrian collections. In April 1945 August Eigruber, "Gauleiter" of Upper Danube, had eight aerial bombs put into the salt mines with the order to ignite them when the allied troops approached. Art experts and workers at the salt mines jointly decided to resist the order[32]. In the summer of 1946, the objects that were secured in Lauffen were brought back to Vienna with the help of the allied troops[33]. In 1951, the storage areas of the Manuscript Collection were renovated. A special metal container was constructed for the Vienna Genesis[34]. Sandwiched between glass plates, the folios were stored vertically in a wooden cabinet placed inside the metal container (Fig. 6).

Initiated by the observations of the painter Max Weiler an opening of the glass plates was considered by the Manuscript Collection and the Institute of Conservation[35]. After 1945, director general Josef Bick had initiated the establishment of a conservation department at the Austrian National Library. With the support of Josef Bick Hilde Kuhn and Otto Wächter

31 Stummvoll, 1973, p. 119.
32 Bauer, 2017, pp. 399–400.
33 Stummvoll, 1973, p. 208.
34 Stummvoll, 1973, p. 210.
35 Irblich, 1985, p. 24.

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were the first conservators to receive training and to build up a department of conservation. In 1975, the glass plates housing the Vienna Genesis were opened and Hilde Kuhn treated the folios. The silver ink had caused degradation of the parchment support, damage already described by Lambeck in 1664. Hilde Kuhn cleaned the folios, then regenerated and flattened the parchment sheets with the help of parchment glue[36]. Figure 7 shows folio 1, page 1 in the facsimile edition of 1980. In comparison with figure 4 it can be seen that the folio is more even. We assume that parchment glue was sprayed on the folios, a technique frequently used at the Institute of Conservation at that time[37]. It is highly probable that parchment glue, containing acetic acid, was used following a recipe developed by Otto Wächter[38]: parchment glue was prepared from parchment scraps that were cooked at about 50 °C for 24 hours. 7 % wine vinegar was added, one third of the total liquid, followed by ethanol, also one third of the total liquid. With vinegar and ethanol the parchment glue could be used cold. The glue was sprayed with a spray pipe or airbrush. As described by Wächter, the glue was used to soften parchment more and to consolidate paint layers on parchment[39].

The folios were mounted between two 2-mm thick polyacrylate sheets, one of which was drilled with rows of small holes to allow some air exchange (Fig. 8). Between the sheets, the folios were fixed with two small pieces of pressure sensitive adhesive tape on the upper edges. The tape is not yellowed and could be a Filmoplast type. Commercial pressure sensitive tape was used to bind the two polyacrylate plates together. The size of the acrylic sheets was the same as those of the glass plates: 40.6 x 34 cm. The newly mounted folios were stored vertically in the compartmentalised wooden box (Fig. 9) within the closed metal container from 1951. A standing order for daily opening of the container for ventilation was issued[40].

Hilde Kuhn's notes on the conservation treatment of Cod. theolg. gr. 31 in the statistical book of the Institute of Conservation (IfR) give a brief account of the work[41]:

> 1975, Januar: Restaurierung und Umbettung begonnen (9 Blätter)
> Februar: Restaurierung und Umbettung fortgesetzt (17 Blätter)
> März: Restaurierung (Regenerierung und Glätten) und Einbetten in Acrylglasplatten abgeschlossen.

36 Irblich, 1985, p. 24.
37 Verena Flamm, former conservator at the Institute of Conservation, personal communication, April 20, 2016.
38 Wächter, 1982, p. 164.
39 Wächter, 1991, p. 286–287.
40 Irblich, 1985, p. 25.
41 Statistikbuch Institut für Restaurierung 1969–78.

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Fig. 7: Folio 1, page 1, in the facsimile edition from 1980.

1975, January: Restoration and re-housing started (9 folios)
February: Restoration and re-housing continued (17 folios)
March: Restoration (regeneration and flattening) and mounting between acrylic plates completed.

A third facsimile edition with a commentary volume by Otto Mazal was published in 1980[42]. In his commentary, Mazal summarizes previous studies and gives a detailed codicological description of the manuscript. Text and miniatures are studied and described. The chapters in the present book on parchment, silver ink and miniatures refer to Mazal's commentary. As in 1931, Kunstanstalt Jaffé made reproductions in collotypes after conservation. The photographs were taken with the polyacrylate plates opened. Four graphic designers hand-coloured the collotypes from which the facsimile prints were made. Dupli-

42 Mazal, 1980.

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Fig. 8: Folio 24, page 48, mounting between polyacrylate with air holes.

Fig. 9: Compartmentalized wooden box with the 26 folios in polyacrylate mounting.

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cates of the colour transparencies as well as black and white negatives in 13 x 18 cm were stored in the Library's Pictures Archive for documentation[43].

The storage situation was revised in the early 21st century due to concerns about the stability of ink, parchment and miniatures in the closed mounting between polyacrylate sheets as well as about high levels of acetic acid originating from the treatment with parchment glue. A first comparison of the last facsimile from 1980 with the folios did not indicate further losses of ink. The folios seemed to be stable. It was judged necessary to redesign the storage and consider a conservation treatment based on a thorough study of materials and degradation mechanism. The expertise of conservators and conservation scientists should be plumbed to find the best solution for this precious manuscript. In 2011, Maurizio Aceto and Angelo Agostino investigated the silver writing ink, the purple colour of the parchment and the pigments of the miniatures[44] through the polyacrylate sheets with X-ray fluorescence spectroscopy (XRF) and UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS). The ink was identified as silver with low amounts of copper. The following pigments were suggested for the miniatures: carbon black, indigo, ultramarine blue, azurite, vergaut (indigo and orpiment), malachite, madder lake, red lead, red ochre, lead white, orpiment, yellow ochre and shell gold.

The development of conservation and interventions on the Vienna Genesis

The interventions on the Vienna Genesis reflect the development of conservation at the former Imperial Court Library, which became the Austrian National Library. In the 19th century, library books were bound or re-bound by external bookbinders. Very valuable objects seem to have been treated by curators. As well as the Vienna Genesis, the Tabula Peutingeriana (Codex 324), the medieval copy of an Antique map, was also handled by a curator[45]. We have no information on the conservation experience of curator Eduard Chmelarz who treated the Vienna Genesis at the end of the 19th century. After having served as curator at the Museum of Art and Industry, today Museum of Applied Art (MAK), Chmelarz became head of the Court Library's Print Collection in 1885. The description of the treatment shows the growing awareness of conserving valuable objects and of making them available by reproduction or exhibition. On the facsimile from 1895 paper patches and adhesive tape are visible. Chmelarz might have applied them on the folios. No losses were filled. Tapes were applied as small bridges to mend a tear. The historic condition was

43 Irblich, 1985, p. 25.

44 Aceto, 2012, pp. 237–244.

45 Austrian National Library archive, record 113/1863.

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respected in the spirit of Alois Riegl. However, preserving bifolios and the remnants of former bindings was no priority. The folios that originally formed bifolios were separated. The former brochure binding as well as paper or parchment strips of the binding were not preserved, all of which corresponds to the lack of respect for original or historic binding structures that can be observed in the re-binding of medieval manuscripts in the 19th century at the library.

A growing interest in historic bindings can be observed in the early 20th century. The philologist and later director general of the National Library Josef Bick studied historic bindings. Alois Liška, a bookbinder from Ledeč in Bohemia, was engaged on hourly wages since 1906[46], and worked on selected manuscripts under the supervision of curators and Bick. Prefect Karabacek corresponded with Father Ehrle, director of the Vatican Library, who recommended silk gauze from the company Pauly in Lyon for conservation purposes[47]. On the Vienna Genesis, small silk strips were used to bridge tears on many folios, presumably applied by Liška when treating the folios. The strips are very thin and are applied very discreetly without visually disturbing text or miniatures. This corresponds with treatments using silk gauze that can be observed on other manuscripts of the library. Liška was employed as book conservator for the Manuscript Collection in 1920 after several applications and interventions of the directors Karabacek and Donabaum[48]. As Smith writes in his survey on manuscript repair in European archives, the National Library used handmade paper and silk gauze of French manufacture for the manuscript repairs[49], which corresponds neatly with the observations on treatments of the Vienna Genesis in the early 20th century.

In 1948, Josef Bick initiated and supported the installation of a department for conservation. He was well aware of the need for qualified training for conservators. Hilde Kuhn could attend the school for bookbinders in Vienna and worked as an intern at the French National Library. Otto Wächter trained as librarian, bookbinder and conservator. With the support of Bick, Wächter could study conservation at the conservation school of the Academy of Fine Arts in Vienna. Kuhn and Wächter established the department and developed methods for the conservation of books, prints and drawings. By 1968, eight people worked full time in the Institute for Conservation (Institut für Restaurierung, IfR). When Otto Wächter treated the 6th century manuscript the Vienna Dioscorides (Codex medicus graecus 1) in 1960, he refused to apply soluble nylon as advised by experts like Plenderleith and Coremans. Instead, he used parchment glue to regenerate the parchment and to consolidate

46 Austrian National Library archive, record 1059/1928.
47 Austrian National Library archive, record 443/1914.
48 Austrian National Library archive, record 259/1920.
49 Smith, 1938, p. 68.

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Fig. 10: Mending a tear with paper fibres on folio 1, page 1.

the miniatures[50]. Wächter learned about the use of parchment glue during internships in Italy at the institute "Istituto Centrale Patologia del Libro", today ICRPAL, and at the conservation department of the Vatican library. In an article on the conservation of the Vienna Dioscorides Wächter admits that the addition of 1 % vinegar to the parchment glue is controversial. The solution becomes less viscous with the addition of vinegar. The leaves of the Vienna Dioscorides were moistened with ethanol, then rectified by stretching and spraying with parchment glue. Tears were closed with gold beater's skin[51]. When Hilde Kuhn treated the folios of the Vienna Genesis, she probably also sprayed them with parchment glue containing vinegar to flatten the parchment and to stretch deformations. She might have dried the parchment under weights instead of stretching it on a frame. Pressed folds can be observed on some folios. Gold beater's skin was used much less frequently, if at all, than on the leaves of the Vienna Dioscorides. Many folios show mending of tears with paper fibres (Fig. 10). The method of mounting degraded folios of parchment between polyacrylate was also used for the parts of Tabula Peutingeriana (Codex 324) and the folios of the so-called black prayer book (Horarium Galeazii Mariae Sfortiae V. ducis Mediolanensis, Codex 1856).

50 Wächter, 2003, pp. 36–37.
51 Wächter, 1962, pp. 24–26.

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Traces of former conservation treatments and mountings

When studying the condition of the Vienna Genesis, the folios were compared with the images in the three facsimile editions and the photographic images (colour transparencies) from the last edition. It has to be considered that the facsimiles have been retouched and do not show the folios in their exact contemporary state. The found traces were summarized in the following groups:

Parchment patch

On folio 2, an overpainted patch of parchment was used to cover a round hole, see figure 11 in the chapter on parchment. Because of technological aspects, it can be assumed that this repair does not originate from the manufacturing process. The patch is a bit thicker than the rest of the folio and does not cover the hole completely, which might indicate that it was added later. A repair carried out by the parchment maker would have been thinner and more delicate, see chapter on parchment. According to visual observation and analysis of the paint by XRF and FORS, no differences in the paint layers on the patch and the surrounding area can be observed. The painter could have applied the patch while working on the miniature..

Fig. 11: Repair with piece of paper or parchment of folio 11, page 20

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Piece of paper or parchment

On folio 11, page 20, a large tear is bridged at the lower margin with a broad and relatively thick piece of paper or parchment. The adhesive is yellowed. The repair was coloured and now appears brown (Fig. 11). This crude repair can already be seen in the first facsimile from 1895.

Adhesive residues on inks and paint layers

Shiny areas on the folios, glue residues and brushstrokes can be observed on text areas and on the miniatures. They probably originate from efforts to consolidate ink and paint layers. Adhesive residues are visible on some miniatures, e. g. on folio 20 (Fig. 12). Under UV light, additional brushstrokes and a blueish haze on the paint layer can be detected on several paintings, e. g. on folios 20, 22 and 23. The brushstrokes that are visible in normal light can already be seen in the reproductions of the first facsimile. The bad condition of the miniatures as observed by Waagen in 1839 might have led to various consolidation efforts in the 19th century.

Fig. 12: Adhesive residues on folio 20, page 40.

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Strips of silk gauze

Small strips of silk gauze (about 1 x 8 mm) were applied as bridges to gap long tears, e. g. on folio 1, page 1 (Fig. 3). They were also used on most folios on the upper and sometimes lower corners in a former mounting. It is assumed that the folios were mounted with silk strips on the glass plates in the 1920s when the folios were re-housed after their return from Italy. Under UV light, two types of silk gauze can be distinguished: one fluoresces blueish (type 1), the other pinkish (type 2). Both can be seen on the reproductions in the facsimile from 1931. Type 1 was used on corners and on tears, while type 2 was only used on the corners. Differences in adhesive might be responsible for the blueish or pinkish tones under UV-light. It is assumed that Alois Liška applied the strips of silk gauze in the early 20th century.

Paper fibres

Whitish paper fibres are visible on the ink in text areas (Fig. 13) and on tears in the miniatures (Fig. 10) of several folios (folios 1, 15, 16, 17, 20, and 21). Some paper fibres might originate from former repairs with paper that were later removed, as mentioned in the first facsimile edition by Hartel and Wickhoff in 1895. Some tears (folio 1) are mended with paper fibres that seem to originate from thinned paper or Japanese tissue. A similar mending technique can be found in the Vienna Dioscorides, which was conserved in the 1960s by Otto Wächter, as mentioned above. The appearance under UV-light is comparable. We assume that Hilde Kuhn used paper fibres and thinned tissue paper to mend tears in 1975.

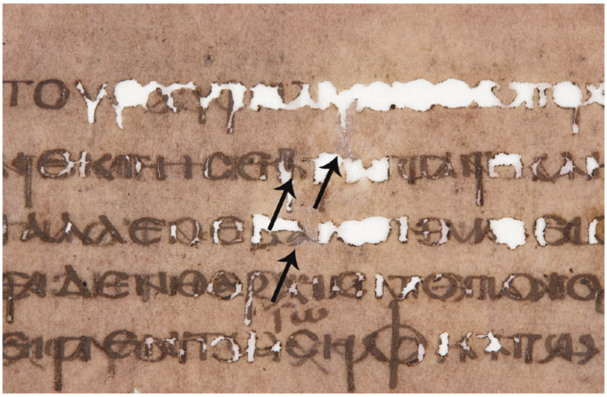

Fig. 13: Folio 17, page 33, detail of stabilising ink with paper fibres.

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Transparent paper

Small pieces of an unidentified transparent paper can be found on folio 20, pages 39 and 40 (Fig. 14). The repair is visible on the facsimile from 1895. Other repairs with paper tapes that can be seen on the facsimile from 1895 do no longer exist (folio 1, page 1, and 16, page 32), but traces of them are still visible. These tapes could originate from Chmelarz' treatment or another unknown one prior to his campaign.

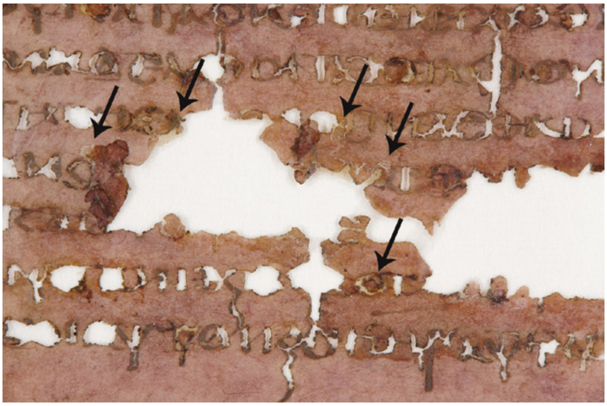

Fig. 14: Reinforcement of ink with transparent paper on folio 20, page 39.

Transparent pressure sensitive tape

Transparent pressure sensitive adhesive tape that looks like Filmoplast can be found on folio 3, page 6, folio 13, page 26, folio 14, page 28, and on folio 16 on both pages. These tapes are first visible on the facsimile from 1980. Small strips of tape (3 x 8 mm) were also used to mount the folios on the polyacrylate plate (the plate without drilled holes). It is likely that Hilde Kuhn applied the tapes for mounting in 1975. The tapes applied as a bridge on a tear (Fig. 15) are very broad. They appear cruder than the other treatments by Hilde Kuhn.

The traces of treatments reflect the history of the Vienna Genesis and the history of conservation at the Austrian National Library. First treatments were probably carried out before 1895 to stabilise the endangered condition of the manuscript. Mending with paper strips, opaque and transparent, was likely carried out in the late 19th century. Silk gauze was used in the beginning of the 20th century. Mending with paper fibres and thinned tissue papers was a common technique at the Institute for Conservation in the second half of the 20th century. Pressure sensitive tapes were used in the 1960s and 1970s. The adhesives used

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Fig. 15: Repair with transparent pressure sensitive tape on folio 16, page 31.

for mending and consolidation could not be analysed with non-invasive methods. It was not possible to date the adhesives employed.

Conclusion

The early history of the Vienna Genesis is not documented. The first hint to its provenience is the notes in Italian of folio 1 indicating an Italian owner in the 15th century. The first written evidence is a letter of prefect Peter Lambeck to Emperor Leopold I. in which Lambeck describes the manuscript and gives a first account of its condition. In 1664, when the Vienna Genesis entered the Court Library, the silver ink already showed signs of corrosion and major losses in the text. By handling the folios bound in a brochure further

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damage to text and miniatures might have occured. The documented treatments were undertaken before facsimiles were produced in 1895, before 1931 and in 1975. Since 1895, the folios have been stored between glass or polyacrylate plates. During the treatments, the parchment was more or less flattened. Tears were mended with strips of paper and silk gauze, thinned paper, paper fibres and pressure sensitive tape. The miniatures were probably consolidated on several occasions, at last with parchment glue in 1975. Losses in the parchment were not infilled. Text, parchment and miniatures were not retouched. The curator Eduard Chmelarz, the bookbinder Alois Liška and the conservator Hilde Kuhn worked with the materials and the knowledge available at their respective time. Their treatments show respect for the original and a considered approach. Despite an eventful history marked by wars, the remaining folios of the Vienna Genesis are surprisingly well preserved. It is the aim of this project to continue with respectful treatment, safe storage conditions and responsible preservation of this unique artefact.

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The parchment of the Vienna Genesis: characteristics and manufacture

Jiří Vnouček, Sarah Fiddyment, Abigail Quandt,
Sophie Rabitsch, Matthew Collins, Christa Hofmann

Introduction

The Vienna Genesis is a rare codex preserved from the 6th century. As such, it is not only a witness of scripture and painting from Late Antiquity but also of the production and use of parchment during this early period. The appearance of parchment in manuscripts before 800 is quite different from the parchment that was produced during the Middle Ages. One of the objectives of this project was to investigate the way in which parchment was made in the 6th century and how its unique properties affect the preservation and conservation of the material. Late Antique parchment is made from sheepskin, has a very smooth surface on both the flesh and hair sides and is usually much thinner than medieval parchment. Inks and paint layers behave and age differently on a smooth and thin support, which was observed in the Vienna Genesis. While no recipes survive, a few early sources contain important clues about the production of parchment. During the project Jiří Vnouček managed to manufacture parchment that replicates the qualities of the material found in Late Antique manuscripts. By close examination of the folios of the Vienna Genesis signs of the production process were investigated. New parchment made in the Late Antique style was used for comparison and for the alteration study of inks, see chapter on alteration study. Identification of the animal species in the original parchment was done by visual and by biomolecular analysis. Using the codicological investigation of Otto Mazal as a guide[1], the scheme of the surviving bifolios was reconstructed by examining the parchment. With both visual and material analysis, as well as the experience gained from recreating an ancient craft, more light could be shed on the process of manufacture of the Vienna Genesis.

1 Mazal 1980, pp. 11–48.

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Characteristics of Late Antique parchment

The parchment of Late Antique manuscripts, which date from the 4th –7th century, is made from sheepskin[2]. It is typically very smooth and thin and has an even surface on both the flesh and hair sides. The production of parchment during this period was distinctively different from the processes used during the Middle Ages. There are no known accounts that specifically describe the methods of manufacture of parchment in the Greco-Roman world. However, hidden within descriptions of historical events and even in some poetical texts, one can find indirect information about the qualities of parchment made during that time and the types of animals from which skins were prepared. The earliest account of the invention of parchment, which is widely repeated in modern texts, is that of Varro (116–27 B. C.) and is noted in Pliny the Elder's (23–79 A. D.) *Historia Naturalis*, (book VII, chapter 21)[3], where the production of parchment in Greek Pergamum (now Bergama in modern-day Turkey) is mentioned:

> Subsequently, also according to Varro, when owing to the rivalry between King Ptolemy and King Eumenes about their libraries, Ptolemy suppressed the export of papyrus, parchment was discovered at Pergamum; and afterwards the employment of the material on which the immortality of human beings depends spread indiscriminately.[4]

It is not clear which kings Varro or Pliny are referring to in this passage. Johnson, like most scholars, identifies them as Eumenes II (197–159 B. C.) and Ptolemy VI Philometor (180–145 B. C.). Johnson recognized that the primary reason for the shortage of papyrus was the threat of war between Egypt and the Seleucid kingdom in the years 173–169, which must have led to a reduction in trade[5]. There is consensus among scholars that leather or slightly tanned parchment were used for several centuries before this date. The method of manufacture of parchment as material for writing was not invented in Pergamum, but it is possible that the techniques were fully mastered there and the process of its manufacture standard-

2 In manuscript catalogues and other scholarly publications, parchment from the Late Antique period is often called vellum. The term is misleading, because this type of parchment is prepared from sheepskin and not from calfskin, from which the word vellum is derived.

3 The production of parchment is only mentioned towards the end of chapter 21, which is focused on the history of papyrus. A description of the manufacture of papyrus and the different types and qualities of "paper" that can be obtained from it, is found in chapters 22 to 26 of book XIII.

4 Plin. *HN* 13.70. The translation is that of H. Rackham, 1938–1963, IV, p. 141, except for two words that were changed by R. G. Johnson (see below): "papyrus" to "paper" and "discovered" to "invented".

5 Johnson 1970, p. 120.

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ized to such a level that it could serve as a regular substitute for papyrus[6]. The same papyrus shortage that struck the Pergamene library also affected Rome. John Lydus, a 6th century Byzantine administrator and writer on antiquarian subjects, claimed that it was the Pergamene King Attalus who was responsible for sending the first parchment to Rome. In 168 B. C., a Pergamene delegation probably headed by Attalus came to Rome. Crates, a leading scholar, accompanied Attalus. They were in Rome at the time when the papyrus shortage had presumably not ended and might have brought some parchment from Pergamum to help supply the Romans. Even if the delivery of papyrus to Rome had resumed by that time, Roman scholars might have been interested in the parchment the delegation had brought, as the demand for writing material would have been very high after years of deprivation.

> Ptolemy, advised by the scholar Aristarchus, first sent off papyrus to Rome and treated them (i. e. the Romans) as friends. Crates, a scholar (serving) with Attalus of Pergamon, became jealous of Aristarchus, produced parchment from hides, and got Attalus to send this to Rome. Thus, in memory of the sender, they still call parchment pergamena.[7]

John Lydus is more precise about the type of the parchment that was being produced during this early period:

> Thus, he [i. e., Crates] sent shaved sheep hides, thin ones, to the Romans, who call them "membrana". In memory of the sender, the Romans still call membrana "Pergamena".[8]

This short sentence is probably the most detailed description that can be obtained from ancient sources and provides at least some characteristics of Late Antique parchment, specifying its quality and the species of animal whose skins were used in the manufacturing process.

Isidore of Seville (around 560–630) contributes some useful information about parchment and especially about its colour in chapter XI of his *Etymologiae* VI: [9]

> 1. Because the kings of Pergamum lacked papyrus sheets, they first had the idea of using skins. From these the name 'parchment' (pergamena), passed on by their descendants, has been preserved up to now. These are also called skins (membranum) because they are stripped from the members (membrum) of livestock.

6 Chahine 2013, pp. 63–46.
7 Boissonade 1962, p. 420.
8 Lydus in Johnson 1970, pp. 121.
9 Barney et al. 2006, p. 141.

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> 2. They were made at first of a muddy (yolk) colour, that is, yellowish, but afterwards white parchment was invented at Rome. This appeared to be unsuitable, because it soils easily and harms the readers' eyesight – as the more experienced of architects would not think of putting gilt ceiling panels in libraries, or any paving stones other than ones of Carystean marble, because the glitter of gold wearies the eyes, and the green of the Carystean marble refreshes them.

Isidore's interesting description of the colours of parchment continues in the fourth and fifth paragraphs:

> 4. Parchment comes in white or yellowish or purple. The white exists naturally. Yellowish parchment is of two colours, because one side of it is dyed, that is yellowed, by the manufacturer[10].

> 5. But purple parchment is stained with purple dye; on which is melted gold and silver so that the letters stand out.[11]

The description of the yellowish colour of parchment that was first produced in Asia Minor is correct, as sheep parchment typically has a yellowish hair side and a white flesh side. However, complaints about the whiteness of parchment that was developed in Rome harming the eyesight raise an interesting hypothesis. It is possible that the author is referring to parchment with equally white hair and flesh sides. The only method of making the two sides of sheep parchment equal in appearance seems to be by peeling off the epidermis layer on the hair side. The resulting material is not only a luminous white colour but also very thin, and these are the two principal characteristics of Late Antique parchment.

The use of purple-coloured parchment in early manuscripts is mentioned in several ancient accounts[12]. The colour purple, especially when used for whole pages in a book, was a symbol of great wealth, high social status and prestige[13]. Manuscripts written in gold ink on purple parchment had a promotional value symbolizing imperial culture[14]. Saint

10 It is hard to imagine that only one side of the parchment would be coloured with a yellow dye so this description is more likely of the type of sheep parchment that existed earlier, with a yellow hair side and a white flesh side.

11 This is a clear Late Antique reference to purple codices such as the Vienna Genesis.

12 Booker, 1997, pp. 441–477.

13 McKitterick, 1989, p. 143.

14 De Hamel, 1986, p. 46.

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Jerome (347–420) was clearly contemptuous of luxurious decoration, as he repeatedly inveighed against luxurious codices:

> Parchments are dyed purple, gold is melted for lettering, manuscripts are decked with jewels, and Christ (in the form of this poor) lies at their door naked and dying.[15]

> Let those who want them have old texts written on purple parchment with gold and silver letters, or as people say popularly with uncial letters – written burdens I call them, rather than books – as long as they allow me and mine to possess our poor leaves and to cherish emended codices rather than such beautiful ones.[16]

> Let her love the manuscripts of the Holy Scriptures, and in them let her prefer correctness and accuracy to gilding and Babylonian parchment painted scarlet.[17]

These historical texts shed some light on the type of parchment that was produced and used in Late Antiquity. Brief references to parchment and its colours and even to bookbinding can be found in other classical texts including poetry.

It is rather remarkable that the description of Late Antique parchment found in the account by John Lydus, and the note by Isidore about its colour, are so exact and that its major characteristics are properly identified[18]. When compared with the parchment found in manuscripts from this period, the precise nature of these descriptions is even more apparent. In the production of Late Antique parchment, sheepskins are treated in a particular way during the wet part of the manufacturing process, resulting in a smooth, glazed surface. The material is thin and flexible, with a minimum thickness as low as 0.045 mm. It is white overall, with only a small difference in colour and appearance between the hair and flesh sides, making the material suitable for writing on both sides.

This study of the characteristics of Late Antique parchment has relied on the close examination of parchment in manuscripts from the 4th–7th century that were produced in the Mediterranean region, in the territory of both the Western and Eastern Roman Empires. It is possible to say that the quality of the parchment and the technology of its manufacture fluctuates slightly over the span of these centuries and gradually declines towards the end of the 7th century. This phenomenon was observed in some Italian and Greek manuscripts on sheepskin parchment from the later period, which can hardly be

15 Jerome, Epistulae XXII, 32 (ad eustochium) in Labourt, 1949–63, p. 147.
16 Jerome, Preface to Job, in Weber 1975, p. 732.
17 Jerome, epistulae CVII, 12 (ad Laetam) in Labourt, 1949–63, p. 156.
18 Lydus in Johnson 1970, pp. 120–122.

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compared in their overall qualities to the earlier material. It seems that knowledge of the preparation of Late Antique parchment was gradually lost after the fall of the Western Roman Empire[19], in the same way as knowledge of other highly specialized technologies that flourished during Late Antiquity and the Early Byzantine period.

Recreating the manufacture of Late Antique sheep parchment

As no recipes have been preserved, all of the steps of the parchment-making process that are described in this chapter had to be recreated. This was achieved by careful visual examination of the parchment in Late Antique manuscripts, where clues were sought of the manufacturing process, and by repeated practical experiments in reproducing the material. The parchment of about 15 Late Antique manuscripts found in various European libraries was studied by Vnouček as part of his PhD research project at the the University of York[20]. For the purpose of this study it made no difference if the original parchment was left in its natural colour or was dyed purple. The application of purple dye is an independent step in the production of the finished parchment. In the case of the Vienna Genesis it is important to remember that the manuscript is fragmentary and this made the study of its manufacture more difficult. The folios are singletons (single leaves) that were stored for a long period between glass, and later between polyacrylate sheets, which limited the natural movement of the parchment. The folios were also subjected to successive campaigns of restoration that altered the characteristics and behaviour of the parchment. The Vienna Genesis was a luxurious manuscript, for which only the best quality parchment was used. This means that there are hardly any defects or imperfections that could help one understand the various steps in its production. Therefore, this evidence had to be found in more ordinary manuscripts that were produced in the same period and in similar geographic locations. The study of more complete manuscripts turned out to be very fruitful. As some of them consisted of several hundred folios it was also possible to search for the repetition of certain marks that were made during the production of the parchment. Especially useful was the visual analysis of three Late Antique manuscripts[21].

Several steps in the experimental parchment-making process required specialized hand

19 The year 476 is traditionally accepted as the date for the end of the Western Roman Empire.

20 Vnouček, 2019.

21 The Codex Bezae, Cambridge University Library, MS Nn. 2. 41 (406 folios), the Codex Purpureus Rossanensis, Museo dell' Arcivescovado in Rosanno Calabro s. n. (188 folios) (examined at the ICRCPAL in Rome) and the Codex Claromontanus, Biblioteca Apostolica Vaticana, Vat. Lat. 7223 (283 folios).

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skills that could only be obtained with much practice and repetition. Success in the production of the desired quality of parchment depends very much on the selection of the raw material. Parchment from the skins of young or stillborn lambs was easier to work on, while real problems arose with the production of larger parchments from the skins of lambs that were several months old when slaughtered. The new parchment that was prepared in the Late Antique style seems to be comparable in many ways to the original parchment from this period. However, there are still some unanswered questions concerning certain steps in the process, the use of specific tools and especially about efficiency in the workflow of parchment production in Late Antiquity.

Fresh or previously frozen and defrosted pelts of young lambs were first washed in running water to clean them from residues of blood and other debris and then soaked for a couple of days in a lime bath (Fig. 1). Alternatively, a paste of slaked lime was applied directly on the flesh side of the skin[22]. After dehairing and an initial rough cleaning of the flesh side on a wooden beam, the rest of the cleaning took place while the skin was stretched on the frame (Fig. 2)[23]. For a successful result, it was necessary to use the skins of young animals. Selecting the right breed of sheep is also important. Stretching of the skin encourages a natural delamination between the grain and corium layers that is typical for sheepskin. In many ways, it is more a process of splitting or peeling than scraping with a knife. On the hair side, the epidermis is peeled off and then the papillary layer is scraped away underneath (Fig. 3). On the flesh side, residues of fat and other impurities are removed by scraping until the skin is completely clean. The skins of very young animals have no deposits of fat and can be more easily removed from the carcass, leaving the inner surface free of flesh. Epidermal tissue that is removed can be used for patches to repair natural holes in the parchment. After splitting, the colour of the hair side becomes almost equally as white as the flesh side. Any colour spots originating from the pigmentation of the hairs disappear. No chalk is used in the final treatment of the surface. The stretched parchment dries out very quickly as the skin is very thin. When the parchment is dry, nothing else remains to do but to remove it from the frame (Fig. 4). All of the major steps that lead to the final product – parchment for writing purposes – are done during the wet stage of the manufacturing process. This is in great contrast to the steps in the production of medieval parchment especially that made from calfskins[24]. In the medieval process the critical sur-

22 Despite the fact that a standard solution of slaked lime in water (about 5–6 %) was used, the skins were ready to be dehaired in just two or three days. This may have been possible because the lambskins were small and thin and the outside temperature was 20 °C or higher.

23 It is not clear which type of frame was used in Late Antiquity, although it may have been a wooden hoop like the ones that were once used for parchment making in Italy.

24 Vnouček, 2012, pp. 199-229.

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Fig. 1: Fresh skin after skinning (left); sheep pelt soaked in a lime bath (right).

Fig. 2: Dehairing of the skin and stretching it on a circular frame.

face treatment, which includes a reduction in the thickness of the skin, is done when the parchment is dry yet still stretched on the frame.

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Fig. 3: On the left image, peeling off the epidermis layer on the hair side of the sheepskin; on the right image, hair side of dried sheep parchment in Late Antique style (left) and unpeeled parchment with residues of dry peeled epidermis (right).

Fig. 4: The finished parchment on the circular frame (hair side).

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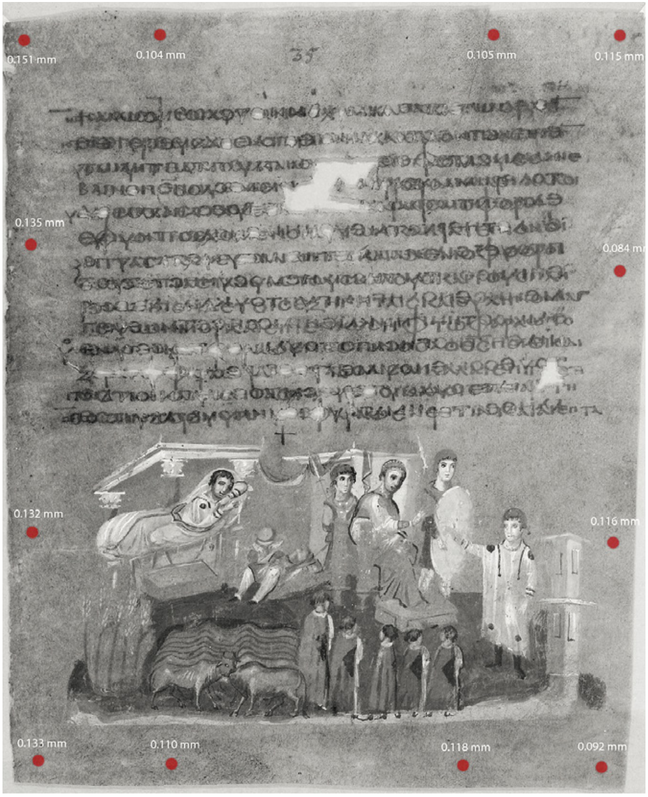

Fig. 5: Thickness measurement points, folio 18, page 35.

The thickness of Late Antique parchment is established during the wet part of the process and cannot be corrected once the parchment has dried out, as any type of abrasives used to thin the skin would spoil its fine and smooth surface texture. Pouncing of the surface is not a normal part of the manufacturing process but scribes could apply the pounce later, while preparing natural coloured parchment for writing. Evidence of pouncing was found, for example, in the 4th century Codex Sinaiticus[25]. A consistent thickness of parchment for the text blocks of Late Antique manuscripts could only be achieved by the careful selection of skins from the same breed of sheep that were slaughtered at approximately the same age. This means that animals from the same herd were likely used. In medieval manuscripts produced from the 8th century onwards parchment that is made from animals of different ages and breeds can often be found. The thickness of Late Antique parchment usually ranges from about 0.070 to 0.170 mm. In certain locations of the skin the parch-

25 Mumford, 2008, pp. 153–171.

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ment is even thinner as low as 0.045 mm, while the thickness rarely exceeds 0.200 mm. The average thickness of the parchment of the individual 24 folios of the Vienna Genesis ranges from 0.108 mm to 0.168 mm[26]. The thickness of each folio was measured at 12 points around the margins (Fig. 5) using a Mitutoyo micrometer (MDC-SX). The average thickness of folios 1–24 is recorded in Table 1. Folio 20 is the thinnest and folio 4 the thickest sheet in the group.

Table 1: Average thickness measurements, folios 1–24.

Folio	Average thickness (12 points were measured on each folio)
f 1	0.148 mm
f 2	0.141 mm
f 3	0.144 mm
f 4	0.168 mm
f 5	0.149 mm
f 6	0.164 mm
f 7	0.157 mm
f 8	0.158 mm
f 9	0.129 mm
f 10	0.119 mm
f 11	0.133 mm
f 12	0.120 mm
f 13	0.151 mm
f 14	0.128 mm
f 15	0.108 mm
f 16	0.118 mm
f 17	0.125 mm
f 18	0.116 mm
f 19	0.120 mm
f 20	0.103 mm
f 21	0.110 mm
f 22	0.113 mm
f 23	0.112 mm
f 24	0.108 mm

26 These measurements have to be considered with caution, as both sides of the Vienna Genesis folios were treated with parchment glue in the past.

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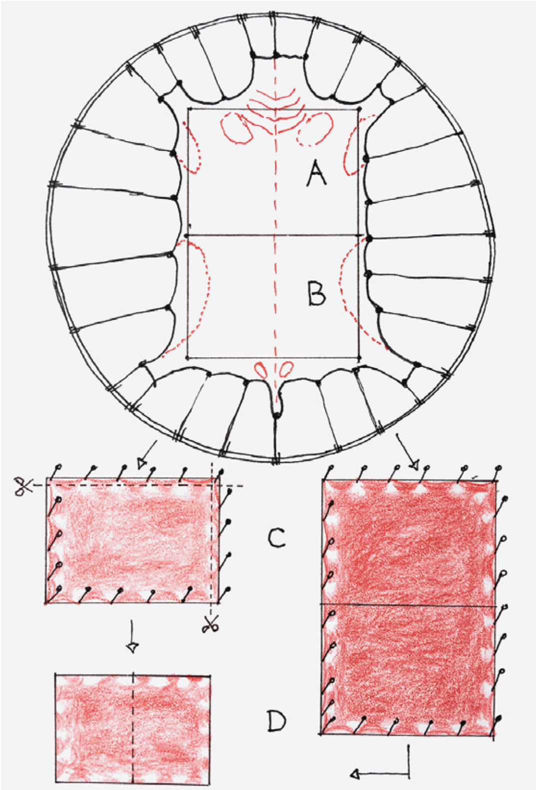

Fig. 6: The dyeing workflow. Newly made parchment is cut off the frame and roughly trimmed. Coloured parchment is stretched after application of purple dye and, after drying, cut to the final dimensions of the bifolio. (Depending on the quality of sheepskin one or two bifolios can be obtained from one skin.)

Thin sheep parchment prepared by the Late Antique method is very suitable for the application of different dyes. Both sides of the parchment accept the colour well. Cross-sections of new parchment dyed with orchil demonstrate that the colorant penetrates the parchment, see chapter on purple dyeing. However, there are noticeable differences between the way that the hair and flesh sides absorb the dye. The hair side has a slightly richer hue while the flesh side is often pale in colour and has a milky appearance (Fig. 11 in chapter on purple dyeing). Purple dye can be applied only to dry parchment that has been completely processed. Most likely, the finished parchment was roughly cut to size in order to avoid wasting precious purple dye on edges that would later be removed (Fig. 6). In this first step, the size of the sheet was kept larger than the final size of the manuscript bifolios. Purple dye can either be applied to the parchment surface in liquid form using a brush or the parchment can be immersed in a vat with the colorant, see chapter on purple dyeing. When the colour is sufficiently saturated, the wet parchment must be immediately re-stretched, otherwise it will become transparent and shrink. It is likely that pieces of dyed

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Fig. 7: Stretching of dyed samples (left) and the traditional way of stretching parchment on wooden board that is still used in Turkey (right).

parchment were stretched and pinned to a wooden board and left to dry (Fig. 7)[27]. After dyeing, no surface treatments were carried out as these would disturb the purple colour. It is surprising that the repair patches in Late Antique manuscripts that were applied over natural holes during the wet treatment of the skin survived the colouring process and stayed perfectly in place. This means that the time spent in contact with the liquid dye must have been relatively short, as the parchment (despite being very thin) did not become so wet that the patches became detached. Colouring only makes these thin patches of epidermal tissue much more apparent compared to similar patches on uncoloured parchment[28]. After dyeing any irregularities in the parchment also become much more visible.

Visual examination of the parchment of the Vienna Genesis

Parchment for a luxurious manuscript is usually very well prepared and selected. In the case of the Vienna Genesis, whose folios range in size from 257 x 238 mm to 328 x 268 mm[29], there ae hardly any visible traces or imperfections resulting from the production of the parchment. On the surviving 24 folios only two holes were found, on folio 2 and folio 11. Both of them are on the lower halves of the folios where the illustrations are located. On the flesh side, a parchment patch that is much thicker than the original parchment covers the hole on folio 2 (Fig. 8). This patch was not applied during the original produc-

27 The stretching and drying of natural coloured parchment on a wooden board is practiced today in Turkey.

28 Observation by Vnouček; Quandt 2018, p. 127 and Fig. 70.

29 For the individual measurements of each folio see the chapter on inks.

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Fig. 8: Repair patch over the hole on folio 2 recto (left) and viewed from verso in transmitted light (right).

tion of the parchment, as in that case it would have been thin and transparent and would have been attached to the hair side of the skin[30]. The patch is oval in shape and does not completely cover the hole, leaving a small gap visible in transmitted light. The edges of the patch were not thinned before the adhesive was applied, and are rather sharp as though they were cut with scissors. It can be assumed that the patch was added later, perhaps during the painting of the miniatures, see the chapter on miniatures. Careful observation has revealed that the edge of the hole is gelatinized (the purple dye makes the edge of the hole look dark). This would not have occurred if the patch had been applied during the wet stage of the process, which would have partially prevented strong gelatinization of the edge of the hole. There is also no evidence that a patch was applied over the hole on folio 11 during the parchment-making process. This hole has a very unnatural shape that was caused by a later deformation of the skin possibly during drying and flattening of the parchment in the process of a conservation treatment. This is confirmed by comparing the present appearance of the hole with a picture from the facsimile published in 1895, where the hole still had its original shape (Fig. 9).

Late Antique parchment has a natural lustre that becomes more pronounced over time, as the surface of the parchment gradually ages. In the case of the parchment of the Vienna Genesis it is difficult to know how the original surface of the parchment looked, since it was greatly affected by various treatments that included overall applications of consolidants by brush or spray. There are many unnaturally shiny areas on almost all the folios, see the chapters on history and conservation. Fine linear wrinkles as well as much larger undulations that are observed on the surface of the parchment are not caused by the natural movement of skin, but by attempts to flatten the folios and by storage between glass or polyacrylate plates.

30 See the later description of patches on the parchment of the Vienna Dioscorides.

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Fig. 9: Comparison of the current condition of the original hole in the parchment (folio 11, page 22; left) with the 1895 facsimile (right).

Another problem is the uneven transparency of some of the folios of the Vienna Genesis. In the course of ageing the surface of thin sheep parchment, as well as other types of parchment, has a tendency to become gelatinized and transparent, especially when it is exposed to liquid water or high humidity. An initial change must have happened when the dry parchment was dyed with the liquid purple solution. A certain amount of transparency occurs even if the sheet is immediately re-stretched after colouring. This is one of the typical characteristics of purple parchment[31]. Nevertheless, the degree of transparency and gelatinization of the parchment bifolios of the Vienna Genesis was made worse by later alterations, which occurred during the long history of the manuscript. The manuscript was probably exposed to high humidity or even liquid water as well as to chloride compounds. X-ray diffraction analysis (XRF) detected chloride in the parchment, see chapter on silver inks.

Fibres that are raised during the cleaning of the flesh side of the parchment create a specific texture, which is more visible on the coloured parchment (Fig. 10). The flesh side of sheep parchment dyed purple can have this appearance. The gradual gelatinization and increase in transparency of the parchment, either through natural ageing or restoration treatments, make it difficult to determine whether the fibrous texture is located on the flesh or the hair side. Evidence of the re-stretching of the parchment after the application of the purple dye is found on certain folios of the Vienna Genesis. The margins of some of the formerly conjoint bifolios show traces of tension lines created during the process of secondary stretching and drying of the parchment sheet after application of the purple dye. These tension lines have a U-shaped appearance similar to the edges of fabric curtains when they are hung (Fig. 11). There are variations in the intensity of the purple colour on the margins, with repeating U-shaped patterns close to the edges. Stretching after dyeing

31 This effect is especially noticeable in the case of purple-dyed calf parchment, which is much thicker.

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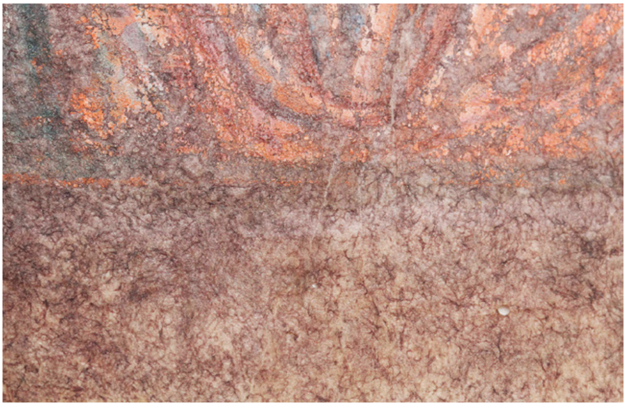

Fig. 10: Fibrous appearance of the flesh side of the parchment on folio 1, page 2.

Fig. 11: Reconstruction of the location of pins (black dots) used for stretching of a coloured bifolio of the Vienna Genesis (above); detail of tension lines from stretching of parchment in transmitted light (below).

likely caused these patterns, which were also observed on new parchment samples, see chapter on purple dyeing. In the upper right corner of folio 2, an original edge of the parchment after re-stretching is preserved (Fig. 12).

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Fig. 12: Original edge of folio 2, which after the application of the purple dye escaped to additional formatting and trimming.

Observation of animal anatomy in parchment and reconstruction of bifolios of the Vienna Genesis

In order to observe and record the anatomical features of the animal skin and determine its original size, it is important to have available as large a part of the original skin/parchment as possible. Since the folios of the Vienna Genesis are now singletons, the first step was to find out whether some of the folios could be reunited into bifolios. This task was surprisingly easy, as the contour of the edges along the former spine folds showed in some cases clear evidence that they were previously conjoint. Some of them fit together perfectly. Others were not so clear, but their original association as bifolios is supported in different ways. Uneven staining on the folios that comes from the application of dye (or was later caused by light exposure) and other irregularities created unique patterns that clearly overlap from one folio to another originally conjoint folio. For some bifolios that were reconstructed, it was even possible to consider that the basic design of the illumination and its preliminary sketch were made on the opened bifolio of parchment. Blind ruling lines or small cracks in the spine fold were seen to continue from one folio to its original conjoint (Fig. 6 in chapter on silver inks). Although the distance between some ruling lines was not exactly the same, these irregularities fit perfectly together when two conjoint folios were placed side by side. The bifolios also matched in the overall hue, tone and saturation of the purple dye. Observation of the folios in transmitted light was very useful for this purpose (Fig. 13). The scheme of the preserved bifolios corresponds with that proposed by Otto Mazal[32]. Only on folio 1 Mazal identified the hair and flesh sides differently[33]. It is generally accepted that the quires of Late Antique codices are made up of four bifolios, starting

32 Mazal, 1980, pp. 25–27.

33 Mazal, 1980, p. 11.

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with the flesh side of the parchment outermost and following Gregory's rule through the whole quire. The reconstruction of the number of missing bifolios was beyond the scope of this project. Identification of the hair and flesh sides of the folios was based on the observation and comparison of three different features. The first is that the hair and flesh sides of purple parchment vary in colour. Because of the differences in texture between the two sides, the colour of the hair side is always more intense, while the flesh side is paler. The second feature is the natural behaviour of the parchment, which is caused by different tensions between the hair and flesh side of the skin. When unrestrained the flesh side of the parchment is convex, while the less elastic hair side is concave[34]. The third feature, and the most commonly used, is the identification of the side that has a hair follicle pattern. None of these methods were easy to use on the parchment of the Vienna Genesis. Due to natural ageing and former treatments the parchment is now so transparent that it is difficult to properly identify the hair and flesh sides of the skin. With the more problematic folios it was helpful to compare the hair and flesh sides of those that were originally conjoint, knowing how the bifolio would have been oriented in the quire. By employing all methods of observation reliable results were obtained that were then recorded in the scheme of reconnected folios (Fig. 14). Folio 1 is a singleton and the only remaining folio of the first quire. Folios 2 and 3 form a bifolio and were part of the second quire. Folios 4 and 5 form a bifolio and are from the third quire, while folios 6 and 7 form a bifolio in the fourth quire. Folio 8 is a singleton again and part of the fifth quire. Folios 9 and 10 were also a bifolio and were from the sixth quire. Folios 11 and 14 and folios 12 and 13 each form bifolios and were part of the seventh quire. Folios 15 and 16 form a bifolio and were from the eighth quire, while folios 17 and 18 form a bifolio from the ninth quire. Folios 19 and 22 and folios 20 and 21 form bifolios and can be traced back to the tenth quire. Quire 11 is missing, while folios 23 and 24 form the last bifolio and are from the twelfth quire. This scheme confirms the scheme of Mazal.

In the case of parchment prepared in the Late Antique style it is almost impossible to identify the type of animal breed that was used, based on observation of the hair follicle pattern. The main reason is that the top layers of the skin, the epidermis and papillary layers, are completely removed during the process of manufacture. With these steps most of the hair follicle pattern is lost as well the pigmentation around the roots of the hairs, and this results in an even texture and colour on both sides of the parchment. The only places where the hair follicle pattern is slightly preserved, and therefore is still visible, are the areas of the former flanks and the belly. Most of the sheepskin (neck, shoulders and posterior) is covered by wool bundles, but on the belly and the axillae (armpits) a different type of hair

34 Bischoff, 1990, p. 9.

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Fig. 13: Reconnected bifolio 4/5 in normal light (left) and in transmitted light (right).

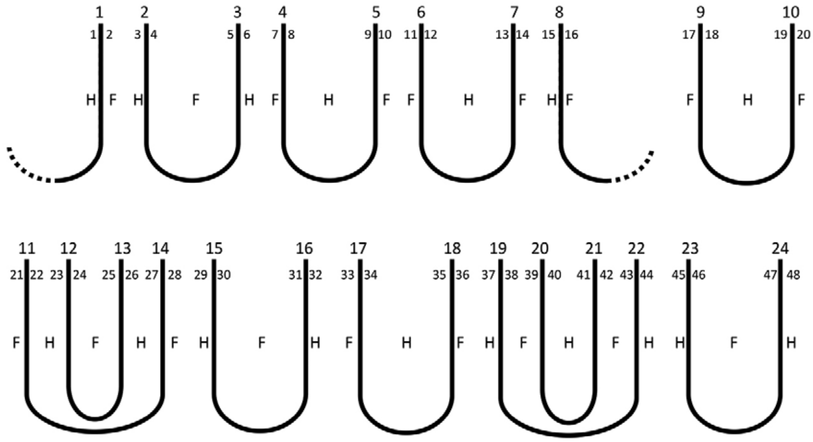

Fig. 14: Scheme of the reconnected bifolios.

is located whose follicle pattern differs from the hairs on the rest of the skin. This is very noticeable when the skin is de-haired during the parchment-making process. Later on, when the skin is stretched and dried on the frame, the area of the belly and axillae can be distinguished more easily. Unlike the rest of the skin where the follicle pattern is removed, the pattern created by this other type of hair is preserved throughout the entire parchment-making process. The application of purple dye makes the area of the axillae and belly on the folios of the manuscript even more visible[35]. The image of the pattern is not sharp

35 After peeling the grain layer of the skin during the preparation of parchment, it is almost impossible to detect any hair follicles or even natural pigmentation of the skin.

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Fig. 15: Traces of the hair follicle pattern preserved in the area of the flank of the sheep on the margin of folio 11, page 22.

and reminds one of spots with a cloudy appearance, as described in the literature[36]. With an experienced eye this pattern can be identified as sheepskin, yet the chance that it could be confused with goatskin is high. As a result, identification of the animal based solely on this feature is problematic. Remains of the hair follicle pattern highlighted by the purple dye can be found on the margins of several folios of the Vienna Genesis, for example on folio 1, folio 11 and folio 15 (Fig. 15). Alois Liška, the bookbinder who treated the Vienna Genesis in the 1920s, assumed that the parchment was made from calf. Both Gerstinger and Mazal refer to his statement in the commentaries to their facsimile editions[37]. It is clear that the follicle pattern is indicative of sheep skin. In combination with the experience from recreating Late Antique parchment, the animal is identified as sheep for all folios of the Vienna Genesis.

36 Federici, 1996, pp. 146–153.

37 Gerstinger, 1931, p. 185; Mazal 1980, p. 11.

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Fig. 16: Comparison of new finished parchment with two bifolios of the Vienna Genesis in transmitted light.

To observe the anatomy of the animal that is recorded in the parchment, it was better to examine the reconstructed bifolios of the manuscript rather than the individual folios. When the bifolios were reassembled, it was possible to asses the approximate size and proportion of the animals used to make the parchment. It seems that the former spine of the animal runs parallel with the original spine fold of each bifolio. Unfortunately, the spine fold of each bifolio was severely damaged and affected by later repairs, so hardly any traces of the animal spine are visible. In addition, with sheep parchment the spine of the animal is rarely apparent, even on well-preserved parchment. During the experimental parchment making, the skin from a two month old lamb was used and its size fits the outer dimensions of two bifolios of the Vienna Genesis (Fig. 16). It was astonishing to see that not only did the proportions of the skin match but even differences in its structure and thicknesses that were visible in transmitted light were the same as in the original parchment. Some of the anatomical features were visible as lighter spots in the area of the shoulders or the axillae. Neck rings characterize the area of the animal's neck. It was interesting to see that, on both the newly produced parchment and on the parchment of the Vienna Genesis, the pelvis bone was not very pronounced[38]. In the case of sheep parchment visibility of the pel-

38 Compared to sheepskin, the pelvis bone on parchment prepared from calfskin is much more visible. This is one of the clear anatomical features that distinguish calf from goat or sheep.

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vis bone changes with the age and probably also the breed of the animal. The pelvis bone can be easily distinguished on parchment prepared from newborn lambs[39], but as the lamb gets older and fat deposits develop under the skin, the pelvis bone and spine of the animal become less visible. However, there could be differences in the sizes of different breeds as well as individual animals, and especially between sheep in modern times and in Late Antiquity. Sheep were probably smaller in the 6th century than the animals that are common today. The growth and anatomy of the traditional breeds are more comparable to those of Late Antique sheep[40].

Identification of the animal species with biomolecular analysis (eZooMS)

In addition to visual examination, biomolecular methods were used to try and identify the animal used to make the parchment of the Vienna Genesis[41].

Evolutionary biologists use DNA to document the history of evolution. DNA is made from four bases (A, C, G, and T) and triplets of these bases encode the 20 amino acids, which comprise proteins. Variations in the sequence of these amino acids will appear in different species allowing us to determine the animal of origin. The predominant protein found in the skin is collagen, a highly conserved biomolecule in all species. Collagen is a structural protein, formed by a triple helix of collagen chains. The three chains of Type I collagen in mammals are coded on two genes, meaning that two of the strands are identical. The robust preservation of collagen in parchment makes it an ideal candidate for species identification through biomolecular analysis, particularly through peptide mass fingerprinting (PMF). Collagen can be imagined as three chains of beads, each more than 1000 beads long. The 20 different beads have different sizes and shapes. Comparing these chains between species, at first glance the chains look identical. On closer inspection, here and there one or more beads are different. This difference may amount to only one bead change in a chain of more than 1000 beads. As these chains are very long they are very difficult to analyse, so we rely on the use of another protein, an enzyme called trypsin, that will cleave the sequence at specific points (it will only cut at two particular types of "bead", the amino acids Arginine and Lysine). These fragments (peptides) of varying length and sequence create what is known as a peptide mass fingerprint. Modern mass spectrometers can rapidly measure the mass of (a subset of) these fragments. If one or more of the frag-

39 The parchment of the Codex Bezae is a very good example of this feature.

40 Gerhard Forstenpointner, Institute for Topographic Anatomy, University of Veterinary Medicine, Vienna, personal communication, June 2016.

41 eZOOMS analysis was done by Sarah Fiddyment at the University of York.

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ments has a different mass, this can be rapidly detected, and therefore the sequence difference and thus the species identified and the animal of origin of the parchment established.

By revealing the animal composition of manuscripts, more can be known about their construction and the craft that went into its production. However, when targeting cultural heritage materials, such as manuscripts, the primary concern is the preservation of the object, making physical sampling very unlikely. In order to circumnavigate this problem, electrostatic Zooarchaeology by Mass Spectrometry (eZooMS) was developed, in collaboration with conservators at the Borthwick Archive at the University of York. eZooMS uses the principle of PMF through ZooMS analysis[42]. However, it has been adapted to cultural heritage objects with the addition of non-invasive sampling based on triboelectric extraction developed by Fiddyment and Collins[43]. The method involves gently wiping the surface of the parchment with a PVC eraser and collecting the resulting eraser crumbs to be analysed (Fig. 17). Fiddyment analysed eraser crumb samples from all 24 folios of the Vienna Genesis and from one folio of the Codex Purpureus Petropolitanus[44]. Eraser crumb samples were extracted in a saline solution with trypsin and incubated at 37 °C for four hours. Samples were then desalted using a C18 filter tip before being spotted onto steel plates for subsequent Matrix Assisted Laser Desorption/Ionization – Time of Flight mass spectrometry (MALDI-TOF) analysis. Resulting spectra were analysed using PMF to determine the species of origin of the parchment (Fig. 18).

Of the 25 folios, Fiddyment identified 17 as a mixture of both sheep and goat, four as sheep, two as either sheep or goat (insufficient resolution of the discriminating peptides to distinguish the species), one as goat, and one as a mixture of sheep and cow. These confusing results highlight the potential and the limitations of the technique. The fact that both sheep and goat were identified in a single sample indicates that there must be a surface treatment on the parchment. All folios were probably treated with parchment glue in 1975, see chapters on history and conservation. According to the conservator Verena Flamm[45], parchment glue was prepared in the conservation department from scraps of parchment. Goat parchment could have been used to prepare the glue in 1975. Folios with more deformation might have been treated with a larger amount of parchment glue in order to flatten them. The signals that were detected come from both the original parchment and the parchment glue. However, at present we are unable to establish which animal is the parchment and which animal is the glue. Nevertheless, by combining biomolecular tech-

42 Buckley et al., 2009, pp. 3843–54.

43 Fiddyment et al., 2015, pp. 15066–71.

44 Extraction protocol, see Fiddyment et al., 2015.

45 Verena Flamm, former conservator at the Institute for Conservation, personal communication, April 20, 2016.

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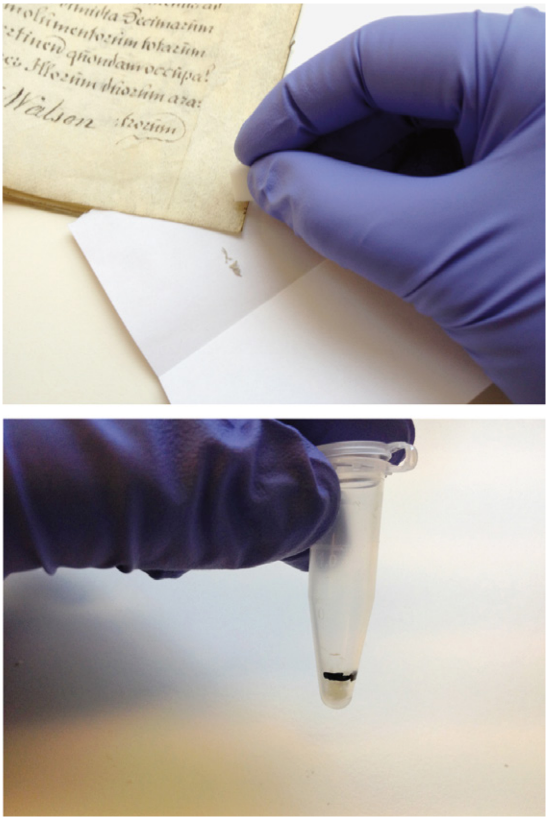

Fig. 17: ZooMS sampling process. Sampling involves using nitrile gloves to use an individual piece of PVC eraser, gently wiped on the surface of the parchment. The eraser crumbs generated are collected on a single use piece of paper and then transferred to a sterile 1.5 ml microcentrifuge tube.

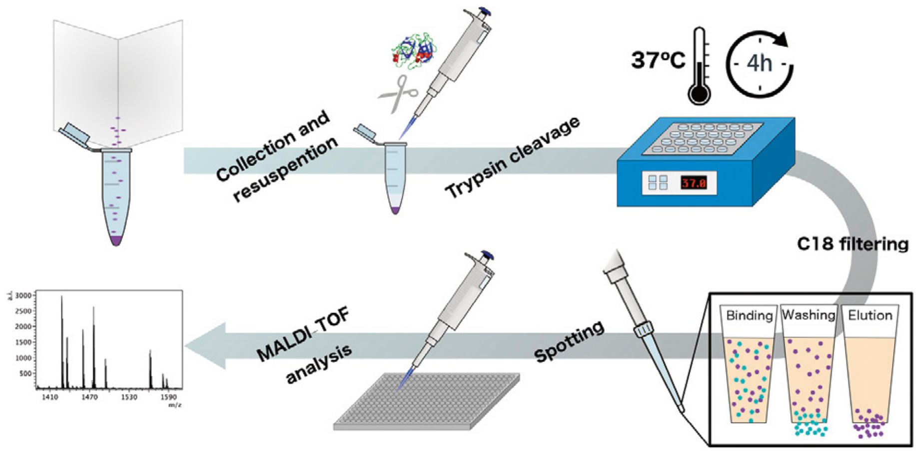

Fig. 18: The extraction process of eraser crumbs for MALDI-TOF analysis (eZooMS).

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niques with visual analysis, we believe that all the folios of the Vienna Genesis are made from sheep parchment. The sheep parchment was treated with glue made from offcuts of parchment. The thickness of the layers of parchment glue probably differ from folio to folio.

Comparison of the parchment of the Vienna Genesis with the Codex Rossanensis, the Codex Sinopensis and the Vienna Dioscorides

The Codex Purpureus Rossanensis[46], a 6th century illuminated Greek Gospel book written in silver and gold ink on purple parchment, is considered to be closely related to the Vienna Genesis. A single bound volume of 188 folios survives from the original manuscript that was in two large volumes; only the Gospel of Mark is complete. The manuscript is kept in the Museo dell' Arcivescovado in Rossano Calabro, Italy. Exposure of the codex to high humidity led to biological damage during the first half of the 20th century[47]. Subsequently, gelatine and cellulose nitrate were applied to the surface of the degraded parchment and the miniatures on the first 20 pages. The last 15 pages, which exhibit severe insect damage and corrosion of the silver ink, were reinforced with silk gauze and gelatine on both sides[48]. While the quires at the front and back of the manuscript were heavily restored, the remaining folios survive in relatively untouched condition. The Codex Rossanensis was recently analysed and conserved at the Central Institute for Restoration and Conservation of Archival and Library Heritage (ICRCPAL) in Rome. During the conservation treatment, Vnouček had the rare opportunity to examine the parchment text block at ICRCPAL in February of 2014[49]. The folios of the Gospels are similar in size to those of the Vienna Genesis, with average dimensions of 307 mm x 260 mm[50]. Surprisingly, almost all of them have survived intact as conjoint bifolios. The thickness of the parchment ranges from 0.05–0.19 mm, which is very close to the parchment thickness of the Vienna Genesis[51]. Over the surface of the folios the purple colour and its hue are more variable than in the Vienna Genesis. This might simply be due to the fact that a larger number of folios are preserved in the Gospels and that this variation in colour is normal for a purple manu-

46 Rossano, Biblioteca del Seminario arcivescovile s. n.

47 Quandt et al., 2020, pp. 46-59.

48 Bicchieri, 2014.

49 Maria Christina Misiti, Lucilla Nuccetelli and Maria Luisa Riccardi kindly granted access to the Codex Rossanesis at ICRCPAL.

50 Both manuscripts have been trimmed, so these are not the original dimensions.

51 These thickness measurements are of the parchment of the unrestored folios of the Codex Rossanensis which make up the bulk of the manuscript.

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script from the Late Antique period. The method of manufacture and dyeing of the parchment appears to be similar to that of the Vienna Genesis. The quality and the physical proprieties of the parchment are also comparable. One notable difference, however, are areas of the Gospel's folios where remnants of the hair roots are preserved. This is rather unexpected for Late Antique parchment, where the epidermis was removed by peeling. Experiments by Vnouček showed that it is not always possible to remove the epidermis as one intact layer. Sometimes the epidermis had to be peeled off in several layers of different thicknesses until the parchment was white overall on the hair side. The parchment of the Codex Rossanensis was identified as sheep by visual and biomolecular analyses (eZooMS), see method described above. The hair follicle pattern is clearly visible as the surface texture of the parchment is well preserved (Fig. 19). The identification of the hair and flesh sides is therefore easier than with the folios of the Vienna Genesis. The parchment for Codex Rossanensis was very well selected. A few imperfections, like flay cuts or little holes, are found on the folios. The network of veins appears rather strong. Repair patches do not seem to have been made during the manufacturing process. The parchment reacts strongly when exposed to fluctuations in the moisture content of the air. In most cases, the animal spine is located along the centrefold of the quires, indicating that two bifolios were cut from a single skin[52]. On some bifolios, however, the animal spine runs horizontally, parallel with the text[53]. This means that the axillae can also be found along the lower margins of the bifolios. On the Vienna Genesis the axillae are always located in the front margin. The sizes of the animals from which the parchment was made are similar for both manuscripts.

The Codex Sinopensis[54] is a fragment of a 6th century illuminated Greek Gospel book that is closely related to the Codex Rossanensis and the Vienna Genesis[55]. Unlike the other Greek uncial manuscripts on purple parchment, however, the text of the Codex Sinopensis is written entirely in gold ink. Assuming that it originally contained all four Gospels the manuscript is estimated to have comprised 490–500 folios[56]. This is not too different from a recent estimate of about 400 folios for the Codex Rossanensis[57]. Only 43 folios of the Codex Sinopensis survive today. These include a large portion of the Gospel of Matthew and five bas-de-page miniatures that illustrate the text of the New Testament. In September of 2018 and January of 2019 Quandt was able to examine the illuminated folios and

52 This assessment was made by Francesca Pascalicchio, who with Anna di Majo made a thorough study of the parchment in the Codex Rossanensis while it was undergoing conservation and analysis at ICRCPAL.

53 Di Majo and Pascalicchio, 2020, pp. 25-38; observed also by Vnouček.

54 Bibliothèque nationale de France, Supplément grec 1286.

55 https://manuscripta.hypotheses.org/530 (accessed 4 February 2020)

56 Cronin, 1901, p. 592.

57 Maniaci and Orsini, 2018, p. 6.

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Fig. 19: Detail of hair residues that are preserved in the parchment of the Codex Rossanensis.

their conjoint folios, and all but six of the text pages[58]. The average dimensions of the folios are 300 x 250 mm yet they were clearly trimmed down, with some folios more irregular in size than others. While the text pages are sandwiched between glass and housed in double-sided wooden frames the illuminated folios and their conjoints (a total of eight folios) are currently housed in paper folders[59]. Given the limited access presented by the housings the thickness of the parchment could only be measured on four folios. The results ranged from 0.08 to 0.16 mm, with an average thickness of 0.13 mm[60]. Although these measurements are not representative of the parchment that comprises the bulk of the manuscript, they are very close to the values obtained for the Vienna Genesis (0.108–0.168 mm) and the Codex Rossanensis (0.05–0.19 mm). Based only upon a visual assessment the parchment of the Codex Sinopensis was identified as sheepskin. It shows all the same characteristics of Late Antique parchment described above: a very smooth and lustrous surface, an even appearance on both the hair and the flesh side, and a tendency for the hair side to curl dramatically upon exposure to air. The purple dye is darker and more saturated on the hair side and paler on the flesh side, although the variation in the intensity of the colour is much greater in the Codex Sinopensis than in the Vienna Genesis[61]. There are many

58 Access to the Codex Sinopensis was generously granted by Dr. Charlotte Denoël, Chief Curator of Manuscripts, and Dr. Christian Förstel, Curator of Greek Manuscripts at the BnF.

59 Two of the bifolios with miniatures are hinged into mats and therefore the thickness of the parchment could not be measured.

60 Although this could not be confirmed, there may be a coating present on both sides of the folios from an early restoration of the manuscript. If that is the case, the thickness measurements that were recorded include the coating.

61 The illuminated folios have clearly suffered from fading of the dye due to exposure to light during exhibition, although many of the text pages that are unlikely to have been displayed show a range of colours.

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random dark streaks across the surface of the folios. These may be knife marks on the flesh side, made during the flaying of the animal skin, that are rough in nature and may have absorbed a larger quantity of dye. In transmitted light one can see very large, translucent veins as well as a fine network of blood vessels that are dark with purple dye. Of those folios that were examined one bifolio (folios 29–31) had a small natural hole measuring 6.0 x 8.0 mm that goes across the centrefold near the bottom edge. The skin is slightly gelatinized around the inside of the hole, indicating that it probably developed as the parchment was being dried under tension on the frame. The axillae are quite prominent along the edges of most folios, showing enlarged and elongated hair follicles within an even thinner area of skin. In the case of both the Vienna Genesis and the Codex Rossanensis there is a consistent practice of cutting the bifolios in one direction or another in respect to the animal spine. With the Codex Sinopensis, however, there is equal evidence of both orientations having been used, with the animal spine running either parallel to or perpendicular with the book spine.

Several folios of the manuscript exhibit small circular patches made with purple parchment[62]. These are not the very thin patches of epidermal tissue seen in other dyed and natural coloured Late Antique manuscripts. Instead the patches are made of a thicker parchment and were likely applied during an early restoration of the Codex Sinopensis. The patches were adhered over naturally thin and fibrous areas of parchment that may have broken through during the manufacturing process, leaving a small hole in the skin[63]. The patches were crudely cut with scissors and the adhesive, probably animal glue, has saturated the thin parchment, leaving a dark stain on the opposite side and causing localized cockling of the original parchment. One of these small patches was glued to folio 30r, directly behind a miniature where oxidized silver paint has stained and perforated the original parchment. It appears as if the silver has partially affected the parchment patch as well, suggesting that the repair was done at an early date. There is other evidence of restoration, including tight, parallel ripples in the parchment and clip marks that may have developed in an attempt to flatten the parchment under tension. A large loss in the upper corner of folio 30 was filled with purple parchment and a long tear extending into the leaf was repaired with a translucent material, most likely goldbeater's skin. The surface of the illuminated folios has a noticeable sheen in raking light. This may be indicative of a coating of gelatine or similar material that was applied in an effort to relax and flatten the parchment. Like the Codex Rossanensis, the parchment of the Codex Sinopensis still retains traces of hair in the roots on many folios. Although the parchment was clearly made in the Late An-

62 Purple-dyed parchment patches were observed on folios 16r, 17v, 28r, 30r and 43v.

63 In transmitted light one can see that the patch does not completely cover the area of damage, leaving a portion of the hole exposed.

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tique style, by peeling away fine layers of tissue from the hair side of the skin, the presence of hair in many follicles indicates that the epidermis was not entirely removed from the surface. A very thin, oval-shaped area on folio 6v (the hair side) resembles the type of rupture that can develop in sheepskin while it is being dried under tension on the frame[64]. It is unclear, however, whether this is a naturally occurring area of delamination or evidence of the work of the parchmenter to produce such a thin product. When compared to the small size of the Vienna Genesis (originally only 96 folios), it may have been difficult for the craftsmen that produced the Codex Rossanensis and the Codex Sinopensis to obtain the required number of skins of sufficiently high quality for these large books of 400–500 folios each, and to prepare all of the parchment to the same standard.

The parchment of the 6th century Vienna Dioscorides (Austrian National Library, Codex Medicus graecus 1) offers another interesting comparison with the Vienna Genesis. This compendium of six pharmacological and zoological works was produced in Constantinople around 512 for Princess Juliana Anikia[65]. 485 folios are preserved with 496 images of plants and animals. One quire consists of four bifolios that are organized in standard Late Antique order according to Gregory's rule starting with the flesh side outermost. The dimensions of the folios vary a lot throughout the text block, going from about 370 to 391 mm in lenght and from 300 to 320 mm in width. The folios have uneven edges due to trimming. The Vienna Dioscorides was conserved by Otto Wächter in 1960[66], see chapter on history. The treatment included the application of parchment glue, the stretching and drying of folios and mending with gold beater's skin. In 1985 the manuscript was newly bound into three volumes. The parchment of the Vienna Dioscorides was produced in the Late Antique style. According to visual (Vnouček) and biomolecular analysis by eZooMS (Fiddyment), the parchment was made from sheep skin. On seven folios, the thickness was measured and ranged from 0.104 to 0.181 mm[67]. The position of the flanks of the animals varies a lot, as large areas of bellies are included. These areas can be found either at the front margin, indicating a vertical position of the spine of the animal, or at the lower margins indicating a horizontal position of the animal spine. Quite unusually, flanks of the animals can be found at the top margins of some folios. This means that the skins of larger and smaller animals of different ages were combined in no special order. The outer dimensions of the folios and their edges are very uneven. The size of the manuscript was probably altered during repair and rebinding campaigns. The quality of the parchment throughout

64 Quandt, 2011, p. 139.

65 Mazal, 1998, pp. 3–11.

66 Wächter, 1962, pp. 22–26.

67 Given the presence of the glue on both sides of the folios these measurements are not those of the original parchment.

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the text block is not very consistent and it seems to have been assembled from different batches of parchment. Probably the most striking feature is the noticeable difference in colour between the hair side, which is more yellowish, and the flesh side, which is very white. This might be explained by the use of skins from different breeds and different sizes of sheep. Parchment prepared from the skins of older and larger animals might result in a more yellowish appearance of the hair side. As older skin contains more fat, the manufacturing process might have included the application of chalk to the flesh side, which would help to reduce the fat content and make the surface very smooth and very white[68]. The parchment of the Vienna Diosocorides was probably prepared by the same Late Antique method described earlier in this chapter. Although the quality of the parchment varies slightly, it has all the major characteristics such as peeled epidermis and holes repaired with parchment patches (Fig. 20). It also includes another very specific type of repair used for holes, namely the belly button repair (Fig. 21). This type of repair is special for the parchment of the Vienna Dioscorides or Byzantine type of parchment, but it appears rather frequently in manuscripts produced during the 6th century in Italy. The belly button repair is another technique for fixing holes in thin parchment. It is undertaken during the wet stage of parchment preparation, before the skin is stretched on the frame. The area around the hole is seized, twisted and secured with a knot made of thread. When the parchment is stretched, a very specific pattern reminiscent of a belly button appears in the area of the former hole. The repair is very often completed by an additional patch placed on the hair side, while a cut from the removal of the actual knot can be seen on the flesh side of the skin. Although patches made from transparent epidermis membrane are the dominant type of hole repair in Late Antique parchment, the Vienna Dioscorides contains several very good and large examples of the belly button repair. Some of the repairs were not made tightly enough and the holes became somewhat loose during the stretching of the skin.

There is no known written account that describes the methods of manufacture of parchment in the Byzantine Empire from the Late Antique period. This is in contrast with surviving descriptions of the preparation of inks and pigments[69]. Parchment is only mentioned in connection with the preparation of the surface for writing or painting in the records from the late and post-Byzantine period. Parchment of later Byzantine manuscripts, and especially Greek manuscripts from the 10th–13th centuries, differs from the quality of the parchment used in early Byzantine manuscripts but shows certain similarities. The parchment is also made from sheepskin. Most of the parchment was prepared in a cruder way, so that the final

68 Use of chalk for the preparation of sheep parchment was common practice in medieval times all over Europe. However, chalk was not generally used for the preparation of parchment in the Late Antique period.

69 Schreiner, 1983, pp. 122–127.

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Fig. 20: Detail of an original patch repair made with peeled epidermis on the hair side that was later covered with paint. The patch was partly infilled and supported by new goldbeater's skin on the flesh side during conservation treatment.

Fig. 21: Belly button repair with a reinforcing patch of peeled epidermis as seen from the flesh side (left) and the hair side (right).

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product is often very thick and oily. However, epidermis membrane is used for the repair of holes in the parchment. Very thin folios can be found in manuscripts containing parchment of irregular qualities. Some steps in the preparation of parchment, including the splitting of sheepskins, appear to be preserved in a modified form in the Late Byzantine period. The quality of these random examples cannot be compared with the high level of production in Late Antiquity. In contrast, the techniques of peeling sheep skin completely disappeared in the preparation of parchment in the Western and Northern part of Europe in early medieval times. Natural holes were not repaired with patches made from the epidermis layer of the skin. As the epidermis layer was not removed, the medieval parchment was thicker and stronger than Late Antique parchment. Holes could be closed by sewing with thread.

The parchment of the Vienna Genesis was manufactured by the same method as most other manuscripts that survive from Late Antiquity, whether they were dyed or remained in their natural colour. The parchment of the Codex Rossanensis and the Codex Sinopensis closely resemble the parchment of the Vienna Genesis. The parchment of the Vienna Dioscorides was also produced using the same technique yet the material was less well selected and shows more differences. The quality of the parchment in the Vienna Dioscorides more closely resembles that of manuscripts of the later Byzantine period.

Summary and conclusions for conservation

The parchment of the Vienna Genesis shows typical features of Late Antique manufacture: thinness, smoothness and an equal appearance of the hair and flesh sides. Similar properties were reproduced during the production of new parchment by removing the epidermis layer from the hair side of sheepskin. The parchment of the Vienna Genesis was carefully selected and shows the expert skills of the Late Antique parchment makers. By visual observation, practical experiments and comparison with other contemporary manuscripts, the writing support was identified as sheep parchment that was made from the skins of young animals. One or two bifolios were cut from a single sheepskin. A comparison of the parchments has confirmed the close relationship of the Vienna Genesis with the Codex Rossanensis and the Codex Sinopensis. The exposure to high humidity, multiple restoration treatments and more than one hundred years of storage between glass and polyacrylate has greatly altered the parchment of the Vienna Genesis. The folios have become more transparent. The application of parchment glue to both sides of the folios and subsequent flattening have changed the surface texture. Finally, the lengthy storage between rigid sheets of glass and polyacrylate has altered the behaviour of the parchment by preventing its natural movement.

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The lessons learned during this study of Late Antique parchment are to avoid the application of moisture during conservation treatment and to keep the use of adhesives to a minimum. All signs of the animal and of the manufacturing process have to be preserved in the Vienna Genesis. The new storage system should allow some movement of the parchment while protecting the surface of the folios.

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Purple dyeing of parchment

Sophie Rabitsch, Inge Boesken Kanold, Christa Hofmann

Purple dyes for parchment

Purple is a colour charged with historical and cultural significance and can be obtained from different natural sources. The term purple covers a range of nuances from red-violet to blue-violet[1].

The most precious and expensive purple dyestuff was shellfish purple, which is a light-fast vat dye produced from the hypobranchial glands of certain marine snails. Antique sources indicate that the origins are located in the Phoenician empire, but it seems that it was already used in earlier times[2]. The dyestuff is mentioned in classical texts, but neither Pliny the Elder, who wrote the most detailed text on it, nor other classical authors such as Aristotle or Vitruvius, offer a completely clear description of its production[3]. Greek papyri mention a variety of sources to produce purple colours, among them plants and lichens. Two Late Antique documents from the 3rd to the 4th century A. D., the Papyrus Leidensis X and the Papyrus Graecus Holmiensis, contain recipes involving vegetable or lichen sources to produce purple dyestuffs[4]. One example is orchil, a lichen dye, which is easier to obtain than shellfish purple and therefore less expensive. It was applied alone or in combination with other organic dyes like madder[5], alkanet, folium, cochineal and indigo for the coloration of textile fibres. According to Pliny, orchil was sometimes used as an initial dye that would then be top-dyed with a small amount of shellfish purple[6]. Throughout history, dyers combined red and blue dyestuffs such as those mentioned above, to achieve purple hues on textiles[7].

The colour purple was a symbol of social status and stood for prestige, especially in Antiquity and Late Antiquity[8]. The use of purple on Antique clothing has been extensively

1 Bogensperger, 2015, p. 157.
2 Bogensperger, 2015, pp. 158–159.
3 Cardon, 2007, p. 553.
4 Bogensperger, 2017, p. 238.
5 Schweppe, 1993, p. 25.
6 Quandt, 2018, p. 122.
7 It is rare for natural dyes to be mixed directly, as each dye requires different conditions to dye successfully. Isabella Whitworth, personal communication, 11 December 2018.
8 Bogensperger, 2015, pp. 155–156.

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researched[9] as it was an important colour in the Persian Empire, in Hellenism as well as in the Roman Empire[10]. Purple was worn by emperors and dignitaries and later by cardinals in the Roman Catholic Church[11]. In the Roman Republic, senators and victorious generals had the privilege to wear purple garments, while in the Imperial era, only the emperor wore purple. Following Commodus (161–192), several emperors had the title Porphyrogennetos (born in the purple), which continued during the Byzantine Empire[12]. The emperors and selected dignitaries of the Byzantine Empire had the privilege to wear purple garments, or certain purple ornamentation on their clothes[13]. Purple played an important role in Judaism[14] and in Christianity[15]. In Judaism, two types of purple, blue and red, were used for the curtains of the Temple and the high priest's vestments[16]. In the Hebrew and Greek bible the colour is mentioned as a sign of human and divine sovereignty[17]. It was a symbol for the suffering of Christ on the cross and his resurrection, as its hues were associated with the blood of Christ[18]. In the early Christian Church, all hierarchical levels of clergy wore dalmatics decorated with two purple stripes. The use of purple on liturgical garments continued in both the East and the West of the Roman Empire. After Constantine recognised Christianity as the state religion, purple signified the empire, in continuity with pagan Rome, as well as the Christian Church, being a symbol for the blood of Christ and the martyrs. Furthermore, Constantine used purple ink in imperial documents[19] and biblical manuscripts were often written on purple coloured parchment in the Byzantine Empire. With the fall of the empire in the 15th century, the demand for purple eventually decreased[20].

Parchment was coloured purple to enhance the worthiness and value of a codex. Only biblical texts were written on purple parchment[21]. These manuscripts, objects of huge pres-

9 Denoël et al., 2018, p. 1.
10 Bogensperger, 2015, p. 160.
11 Zimmermann, 2003, p. 66.
12 Denoël et al., 2018, p. 2.
13 Thiel, 2010, pp. 58–59. An example for this ornamentation is the tablion, a square piece of cloth attached to the cloak. The emperor had a golden one, while the high officials had a purple one. Tablions are visible on some miniatures of the Vienna Genesis as well.
14 Bogensperger, 2015, p. 166.
15 Quandt, 2018, p. 122.
16 Bogensperger, 2015, p. 166.
17 Denoël et al., 2018, p. 2.
18 Quandt, 2018, p. 122.
19 Denoël et al., 2018, p. 2.
20 Boesken Kanold, 2017, p. 67.
21 Trost, 1991, p. 13.

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tige and symbolic value[22], were mostly produced in Late Antiquity and the early Middle Ages, from the 5th to the 11th century. They were commissioned by churches, emperors, kings and other individuals of high status[23]. Purple codices are first documented in written sources in the 3rd and 4th century, while the oldest preserved examples originate from the 5th century[24]. The zenith of their production was in the 6th century[25]. Jerome († 420)[26], one of the early Church fathers, complained about this custom:

> Parchments are dyed purple, gold is melted for lettering, manuscripts are decked with jewels, and Christ (in the form of this poor) lies at the door naked and dying.[27]

As the quotation from Jerome demonstrates, the text was written with silver or gold ink. Few surviving codices like the Vienna Genesis were illuminated[28]. Other valuable examples of purple codices are the Codex Purpureus Rossanensis[29], the Codex Sinopensis[30], or the Codex Purpureus Petropolitanus[31]. Most surviving manuscripts are Greek, Latin (Evangelium Palatinum[32]), or Gothic versions of the Gospels (Codex Argenteus[33])[34]. At the end of the 6th century, the production of purple manuscripts seemed to ebb in the Latin world. Reasons for this could be the decrease of the clientele, scarcity of the necessary materials as well as the decline in technological knowledge. Under the Carolingian dynasty, the production of purple manuscripts was revived, focusing on Gospel books such as the Gospels of Saint-Médard de Soissons[35], the Godescalc Evangelistary[36] or the Vienna Coronation Gospels[37]. Charlemagne represented himself as the new Constantine and defender of Christian-

22 Aceto et al., 2014, p. 54.
23 Quandt, 2018, p. 121.
24 Zimmermann, 2003, p. 65.
25 Denoël et al., 2018, p. 3.
26 Trost, 1991, p. 12.
27 Jerome, Epistulae XXII, 32 (ad eustochium) in Labourt, 1949-63, p. 147.
28 Zimmermann, 2003, pp. 65–66.
29 Mid-6th century, Rossano, Biblioteca del Seminario arcivescovile s. n.
30 Around 550–600, Paris, Bibliothèque nationale de France, ms. suppl. Grec 1286.
31 6th century, Vienna, Austrian National Library, Codex theol. gr. 31, f 25–26. Trost, 1991, pp. 14–15. For further information see: Sörries, 1993..
32 Late 5th century, Trento, Castello de buoncosiglio, Ms. 1589.
33 Around 545–550, Uppsala, Uppsala University Library, DG 1.
34 Trost, 1991, p. 13.
35 9th century, Paris, Bibliothèque nationale de France, MS lat. 8850.
36 781–783, Paris, Bibliothèque nationale de France, lat.1203.
37 Vienna, Kunsthistorisches Museum, Inv. XII. 18. Denoël et al., 2018, pp. 2–4.

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ity by the use of purple[38]. The tradition of purple in liturgical manuscripts continued under the Ottonian emperors[39] (Golden Gospels of Henry VIII[40]). In the high Romanesque and Gothic period, the use of purple is mostly limited to meaningful quotations in liturgical manuscripts. This acts as a way to enhance the importance and value of a text. The use of black colorants to colour parchment in the late Middle Ages seems to continue this tradition and creates an exclusivity comparable to purple manuscripts[41].

In the studies on purple manuscripts, the material and technological aspect has so far received little attention. Surviving Antique written sources are unclear on the purple colorants and their use on parchment[42]. In fact, there is no known surviving written record describing the production of parchment and how it was dyed purple in Late Antiquity. One of the research questions in this project was the identification of the purple dye of the Vienna Genesis and the way it was applied. In the literature[43], it is often assumed that purple manuscripts were dyed with shellfish purple. Until now, there is no analytical evidence that entire folios were dyed with this colorant. Most purple manuscripts analysed so far tested positive for orchil, a lichen-based dye, or folium, a plant-based dye[44]. As mentioned above, these colorants are cheaper and easier to extract than shellfish purple, but are much more light-sensitive. In addition, alkanet and different combinations of orchil, indigo and folium could be identified on parchment manuscripts[45]. Greek papyri[46], medieval and later recipes[47] describe extracts from different berries or combination of dyes like redwood and indigo. These dyestuffs have so far not been detected on purple manuscripts, with the exception of indigo. It is not known how the purple dyes were applied. Crucial for use on parchment is the cold applicability of a dyestuff. A hot dye bath like that often used for textiles would degrade the material, as collagen fibres tend to shrink when being heated in a wet environment[48].

The purple dye of the Vienna Genesis was analysed by X-ray fluorescence spectroscopy (XRF), UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS) and

38 Denoël et al., 2018, pp. 17–18.
39 Denoël et al., 2018, p. 4.
40 977–993, New York, The Morgan Library & Museum, MS M.23. For further information see: Carley. 2013.
41 Andreas Fingernagel, Austrian National Library, personal communication, 21 December 2018.
42 Aceto et al., 2014, p. 54.
43 E. g. Mazal, 1980.
44 Aceto et al., 2016.
45 Aceto et al., 2016.
46 Papyrus Leidensis X (P. Leid. X) and Papyrus Graecus Holmiensis (P. Holm.).
47 E. g. Amberger Malerbüchlein (1492, Provincial Library Amberg, Ms. 77,); Colmarer Kunstbuch (1478, Burgerbibliothek Bern, Cod. Hist. Helv. XII 45); Cod. Pal. germ. 489 (1563, University Library Heidelberg).
48 Larsen et al., 2002, p. 55.

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spectrofluorimetry for a preliminary identification of the dye. For further characterisation microspectrofluorimetry, Raman spectroscopy and surface enhanced Raman spectroscopy (SERS) were performed on micro-samples, see chapter on the identification of the purple dye of the Vienna Genesis[49]. The results of the analyses prove that the parchment of the Vienna Genesis was coloured with orchil, a lichen based dye. The species of lichen could not be identified.

In addition to the identification of the purple dye, the application method on parchment was investigated. Three dyes were selected for the experiments: orchil, folium and shellfish purple. Orchil and folium are the most frequent dyes that have been found on purple manuscripts so far. The tests with shellfish purple aimed to reveal if it is possible to dye folios of parchment with this colorant. The experiments with shellfish purple were based on Inge Boesken Kanold's research and re-creation of the dyeing process. Preparation and application of the three dyes on sheep parchment were examined. Colour, even tone and light fastness were compared with the folios of the Vienna Genesis. Sample sets of parchment were sent to the teams of Maurizio Aceto and Maria João Melo as references for the purple dye identification. The parchment dyed with orchil was used to prepare samples for the ageing experiments, see the chapter on the alteration study of silver inks.

Jiří Vnouček made the sheep parchment which was used for the experiments from the skins of stillborn lambs. It resembles Late Antique parchment, as it is thin and has a smooth surface on both hair and flesh side. The average thickness measures 104 ± 13 µm. The manufacture of the parchment is described in the chapter on the parchment of the Vienna Genesis. For the first experiments, modern lamb parchment made by the Anton Glaser company was used. With an average thickness of 219 ± 32 µm, it is sturdier. The flesh side is not as smooth as the parchment of Vnouček. Experiments by Isabella Whitworth and Cheryl Porter showed that the colour of purple parchment differs depending on the animal source[50]. The preparation of the skin may have an effect as well, as orchil is sensitive to changes in the pH value and can change colour.

Below, an overview is given on each dye. Preparation of the dyestuff and its application are described. The results are interpreted in comparison with the folios of the Vienna Genesis. A simple light-ageing test served to compare the light-fastness of the three dyes.

49 Analyses were carried out by Maurizio Aceto et al. and Maria João Melo et al.

50 Whitworth and Porter, 2013, internal report.

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Orchil

This light-sensitive dye[51] can be extracted from different types of lichen. Orchil (French Orseille[52]) consists of various dye components whose chemical structures were first discussed by Hans Musso in the 1950s[53]. Historical recipes, dating from Antiquity to the 19th century, mostly refer to the use of orchil on textiles. The colour can range from bluish-red, brownish-red to intense purple[54]. The freshly dyed colour has vibrant hues. Orchil dyes protein fibres like wool, silk, or parchment and does not work well on cellulose fibres[55]. A mordant is not required[56], but can be added.

Lichens are organisms consisting of a fungus and a photosynthetic partner, mostly green algae or less often cyanobacteria, growing in a symbiotic association. The fungus provides the physical protection of its cortex and the chemical protection of various products like colorants or precursors of those, while the photosynthetic partner provides carbohydrate and energy for the metabolic process. The fungus is the source of the colorant substances[57]. Lichens grow on solid surfaces like rocks or trees, in various environments. Orchil can be produced from different types of lichens, which can vary a lot in their appearance.

Orchil dyes were produced from sea and land sources:

- A great variety of fruticose lichens, such as the *Roccella* spp. can be used to make orchil. *Roccellae* grow on coasts, often in subtropical or tropical regions[58]. Written sources indicate that different species of *Roccella* were used in orchil making and these include *Roccella tinctoria*, *R. canariensis*, *R. fuciformis* and *R. phycopsis*. These lichens differ in growth and chemical composition and are often difficult to identify with the naked eye[59].
- A large group of crustose lichens grow on the siliceous rocks of European mountains[60]: These include *Lasallia pustulata*, *Ochrolechia tartarea*, *O. parella*, and *Pertusaria dealbescens*[61].

51 Hofenk de Graaff, 2004, p. 278.
52 Cardon, 2007, p. 490.
53 Whitworth and Koren, 2016, p. 6.
54 Schweppe, 1993, p. 25.
55 Whitworth and Koren, 2016, p. 7; Beecken et al., 2003.
56 Schweppe, 1993, p. 25.
57 Cardon, 2007, pp. 485–486.
58 Cardon, 2007, p. 487.
59 Cardon, 2007, pp. 495–505.
60 Cardon, 2007, p. 487.
61 Cardon, 2007, pp. 506–513.

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During the 19th century the trade term for the fruticose lichens was "weed", while the crustose lichens were known as "moss" or "rock moss". It appears that "weeds" were more valuable than "mosses", as lichens such as *Roccellae* are often richer in dyestuff and require less cleaning[62].

To make the dyestuff accessible, a kind of fermentation must take place in order to break down the dye precursors, the colourless polyphenolic depsides and depsidones, such as orsellinic acid precursors. The lichens have to be crushed and left to steep in a container such as a trough or a vat, together with alkaline materials like stale urine, lime or plant ashes. Air should be introduced regularly, for example by stirring. The liquid turns brown and eventually purple. This can take from days to weeks. Keeping it warm can speed up the process[63].

Related dyes, which are also lichen-based, are cudbear (patented in the 18th century) and litmus (already produced in the Middle Ages)[64]. Orchil, cudbear and litmus are colorants produced from the reaction of derivates of orsellinic acid with ammonia[65]. Orchil and litmus are sensitive to changes of the pH value and can change colour in this context. In an acid environment (pH 2.5), the chromophores of orchils and litmus form a bright red cation, while in an alkaline environment they are transformed into a blue-violet anion[66]. Orchil is one of the oldest known natural dyestuffs and was widely used, despite its low light-fastness. It was called *puh* in Akkadian language in the 3rd millennium B. C. Mesopotamia and *puhk* in Hebrew[67]. *Puhk* does not seem to refer to a textile dye, but rather to a cosmetic or medical use[68]. R. J. Forbes assumes that it was also used in Egypt in earlier times[69]. Orchil is mentioned in the Papyrus Graecus Holmiensis and the Papyrus Leidensis X[70] as well as in other written sources.

Theophrastus wrote in the early 3rd century B. C.:

> In Crete there is an abundant and luxuriant growth on the rocks close to land, with which they dye not only their ribbons, but also wool and clothes. And as long as the dye is fresh, the colour is far more beautiful than the purple dye; it occurs on the north coast in greater abundance and fairer, as do sponges and other such things.[71]

62 Whitworth and Koren, 2016, p. 8.
63 Whitworth and Koren, 2016, p. 6.
64 Whitworth and Koren, 2016, p. 7.
65 Cardon, 2007, p. 487.
66 Cardon, 2007, p. 489.
67 Schweppe, 1993, p. 530.
68 Whitworth and Koren, 2016, p. 6.
69 Schweppe, 1993, p. 25.
70 Schweppe, 1993, p. 25.
71 Whitworth and Koren, 2016, p. 5. See: Theophrastus, Enquiry into Plants, trans. A. Hort, vol. 1, bk IV, 6.5: 333.

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In Roman times, the colorant was used for cheaper production of purple textiles and as a lake for paintings[72]. In the 1st century A. D., Pliny the Elder wrote about the dyestuff using the Greek phycos (φύκος) for lichen:

> The phycos which grows on the rocks in the neighbourhood of Crete is used also for dyeing purple; the best kind being that produced on the north side of the island, which is the case also with sponges of the very best quality.[73]

In the 1st century A. D., Dioscorides mention lichens in a pharmacological context[74]. In Post-Roman times, written sources do not talk about orchil until the 13th century in Florence[75]. There are archaeological finds that prove the use of orchil on textiles in the early Middle Ages in Great Britain, Northern Germany and Scandinavia[76]. It was a common dyestuff until the middle of the 19th century, used on its own as well as in combination with other colorants[77].

For the experiments, *Roccella tinctoria* from Lanzarote (Spain) was chosen as an example for sea orchil, and *Lasallia pustulata* from Dartmoor (Great Britain) as example for land orchil.

Preparation

Four different batches from *Roccella tinctoria*[78] and three different batches from *Lasallia pustulata*[79] were prepared (Fig. 1). A recipe provided by Isabella Whitworth was used:

13.24 g of ground lichen, 23.5 ml ammonia and 76.5 ml tap water were mixed in a brown glass jar with a lid[80]. It took about six weeks for the dye to develop. During the first week, the jar had to be shaken four times a day for up to two minutes and the lid was opened at least once a day to allow some air exchange. During the next five weeks, the container was shaken once a day and opened from time to time. In the beginning, the mixture was brown to brownish-green, turning red after a day, and eventually turned dark

72 Schweppe, 1993, p. 56.
73 Whitworth and Koren, 2016, pp. 5–6.; see: Pliny the Elder, The Natural History, trans. J. Bostock and H.T. Riley (London: Taylor and Francis, 1855), bk XIII, 48.
74 Whitworth and Koren, 2016, p. 6.
75 Schweppe, 1993, p. 530.
76 Schweppe, 1993, pp. 66–67.
77 Whitworth and Koren, 2016, p. 7.
78 Kindly provided by Juan Cazorla, collected in Lanzarote, Spain.
79 Kindly provided by Isabella Whitworth, collected in Dartmoor, United Kingdom.
80 The ratio was 1.2:2:6.5 w/v/v.

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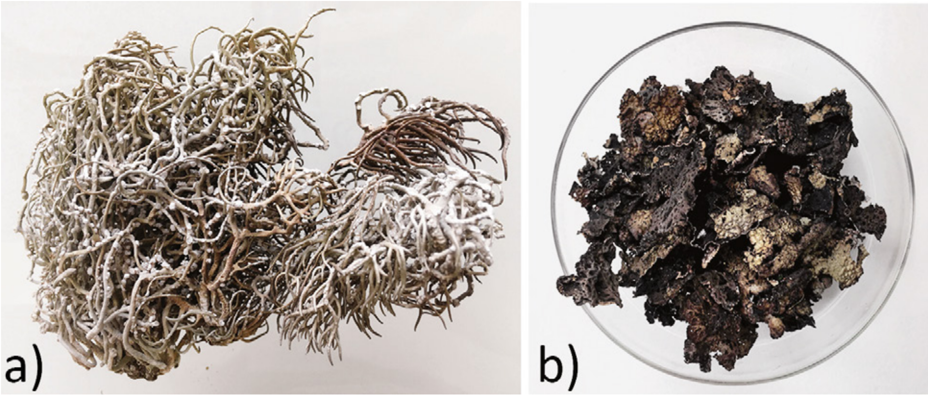

Fig. 1: a) *Roccella tinctoria*, b) *Lasallia pustulata*.

Fig. 2: Change of colour of orchil from green to purple during the fermentation process inside the lid of a glass jar.

purple (Fig. 2). The ground lichens were then removed by filtering the liquid through a nylon filter.

Four batches of orchil made from *Roccella tinctoria* were prepared. The first two batches and the last batch delivered a satisfying result and turned purple. The third batch stayed brownish-red, even after six weeks. The batches were prepared on 19 July 2016, 3 November 2016, 10 March 2017 and 12 Mai 2017. The pH value of the undiluted dye ranged between 10.70 and 10.85[81]. The development of the dye took between five and six weeks. The dye could be used several times. Over a few months and up to one year, the dye spoiled, turned brown and developed a manure-like smell. The pH of the spoiled diluted dye was at 8.27.

81 The pH value was measured with a microprocessor pH meter (WTW, pH 537).

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Three batches were prepared from *Lasallia pustulata*. Two of them resulted in a vibrant purple colour, while the third did not turn purple but stayed brownish. The batches were prepared on 19 July 2016, 03 November 2016 and 12 May 2017. *Lasallia pustulata* developed the dye in about three weeks. The pH value of the undiluted dye was between 9.77 and 11.26. The pH value of the diluted dye was at 10.31.

Application

As there is not much surviving knowledge about the historical methods of dyeing parchment, two different methods of application were tried:
1. application with a tool like a brush and a cotton swab
2. immersion of the parchment into a dye bath

A further method is the application with a cloth, soaked in dyestuff. Parchment is placed between two of those cloths and pressed[82]. This procedure seems to leave marks on

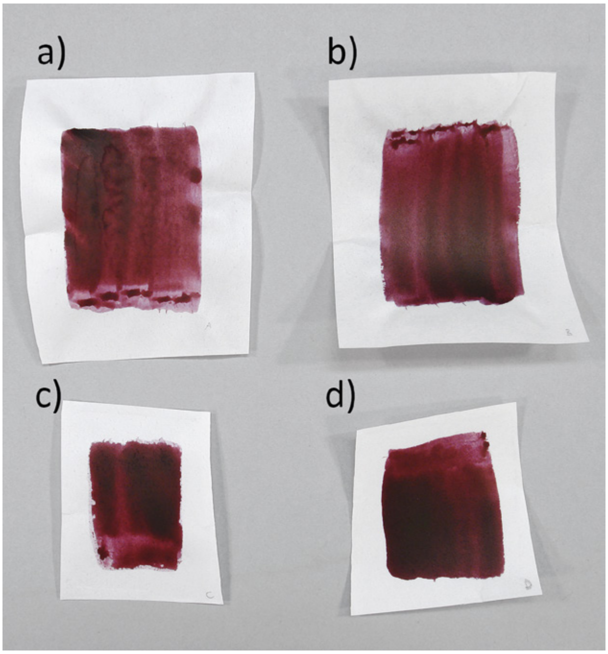

Fig. 3: The application of the dye with a brush gave uneven results: a) flesh side, b) hair side, c) flesh side, d) hair side.

82 Denoël et al., 2018, p. 9.

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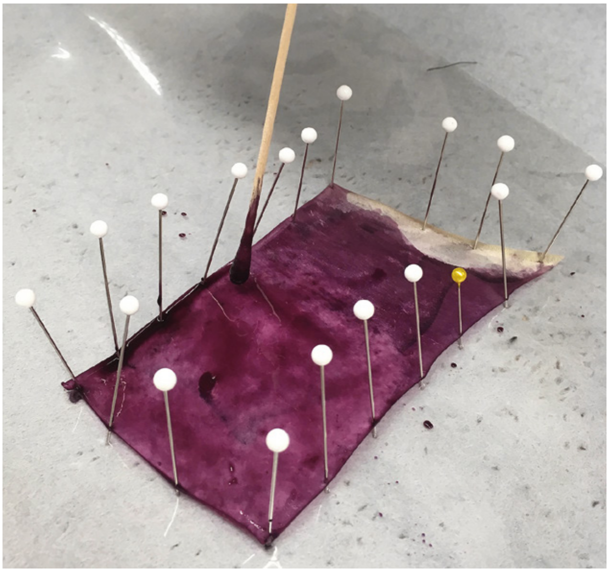

Fig. 4: Application of the dye with a cotton swab on a dry suspended piece of Jiří Vnouček's parchment.

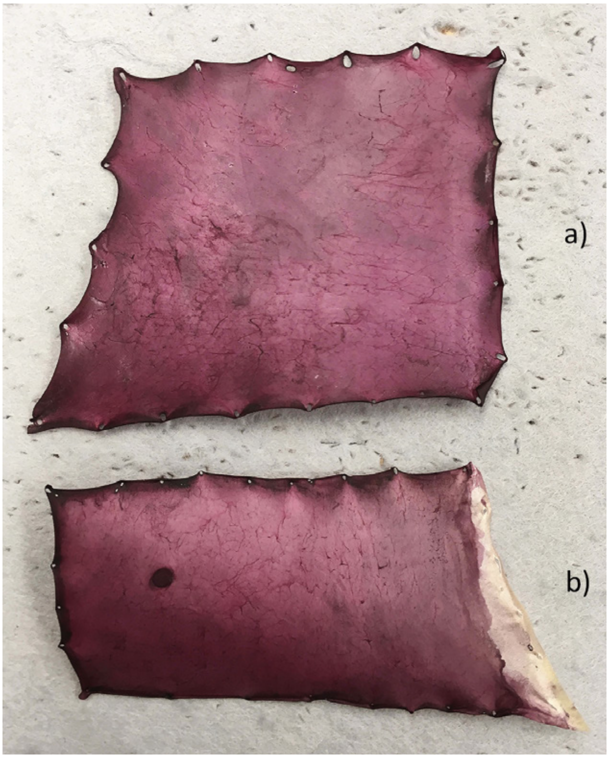

Fig. 5: Comparison of the results: a) dye bath, b) cotton swab; flesh side of the parchment by Jiří Vnouček.

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the parchment[83], which are not, however, visible on the Vienna Genesis. Therefore, this method was not included in the experiments.

In the first small series of tests, the concentrated dye was applied in two layers with a brush on modern lamb parchment (Glaser) that was fixed with clips and awls on a soft fibreboard. One sample was painted on the flesh side, one on the hair side. The results were quite uneven (Fig. 3). The flesh side of the modern parchment does not seem to absorb the dye as well as the hair side.

Application with a cotton swab gave better results than by using a brush. For this experiment, parchment prepared by Jiří Vnouček was used. The parchment was first fixed with pins on a soft fibreboard. Orchil was applied on a dry and on a wet piece of parchment. The dye was dabbed on and spread over the surface with a cotton swab, trying to avoid stains by not over-applying dye (Fig. 4). The colorant can be applied without waiting for the previous layer to dry. The parchment had to be re-stretched after application of the dye, as the wet parchment buckled. The results were good, but seven layers on each side were needed to achieve the same intensity as with dyeing in a bath (Fig. 5). The application with a cotton swab required less dye, but was more time-consuming.

For the second method, a piece of parchment (Glaser) was immersed in a dye bath for about two hours. After removal, the sample was dried stretched. The undiluted dye turned out very dark. A lighter shade was achieved by diluting the colorant with water (Fig. 6). In further tests, one part orchil was diluted with three parts water, which gave good results (Fig. 7). However, we do not know the original colour of the Vienna Genesis folios. Freshly applied orchil has a blueish hue which turns redder when dry. These first tests showed that more even results could be achieved by immersing the parchment into a dye bath. Further tests were done with thinner lamb parchment made by Jiří Vnouček in the Late Antique method. This type of parchment resembles the parchment of the Vienna Genesis more than that from Glaser. The pieces of parchment were placed in a flat bowl and fixed with the help of glass plates to prevent the parchment from curling up. The parchment was covered with the solution and left in the dye bath for one hour. After removing the parchment from the bath, it was stretched with pins on a soft fibreboard (Fig. 8). To avoid stains on the side of the parchment facing the side of the board, the stretched parchment was suspended on the pins. This procedure was used in all of the following experiments. The process of stretching resulted in semi-circular shaped transparent areas along the margins, which are visible on the Vienna Genesis on some folios (Fig. 9). This phenomenon is described in further detail in the chapter on the parchment of the Vienna Genesis. Therefore, we assume that the parchment of the Vienna Genesis was dyed after removal from the frame and was re-stretched after dyeing.

83 Experiments were made by Denoël et al. with Folium.

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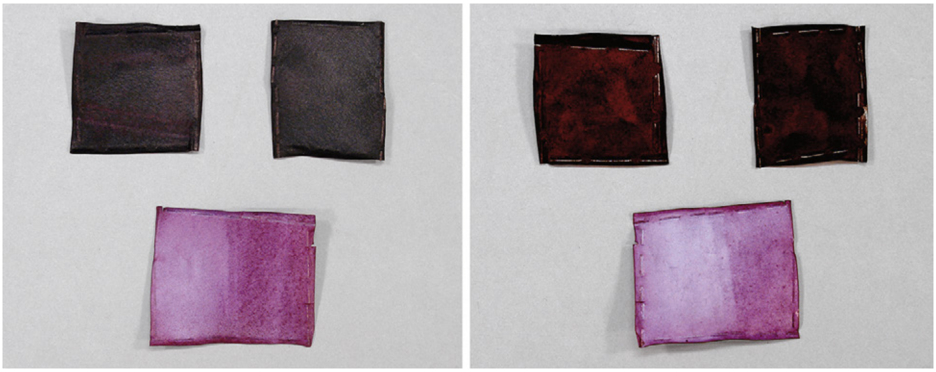

Fig. 6: Results of a dye bath with undiluted orchil (above) and diluted orchil (below), on the left image hair side, on the right image flesh side; parchment by the Anton Glaser company.

Fig. 7: Results of a dye bath with diluted orchil (1:3 v/v with water).

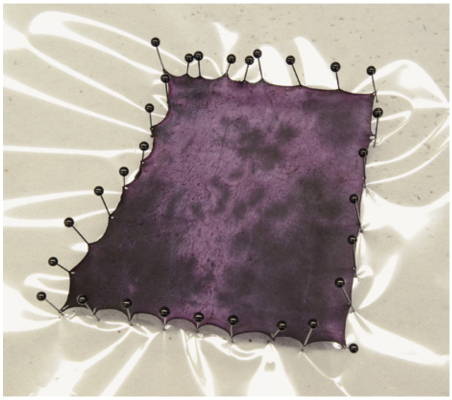

Fig. 8: The parchment was stretched with pins on a soft fibre board and suspended on the pins, while being stretched.

Fig. 9: Semi-circular shaped transparent areas on the test samples and on the Vienna Genesis (folio 4).

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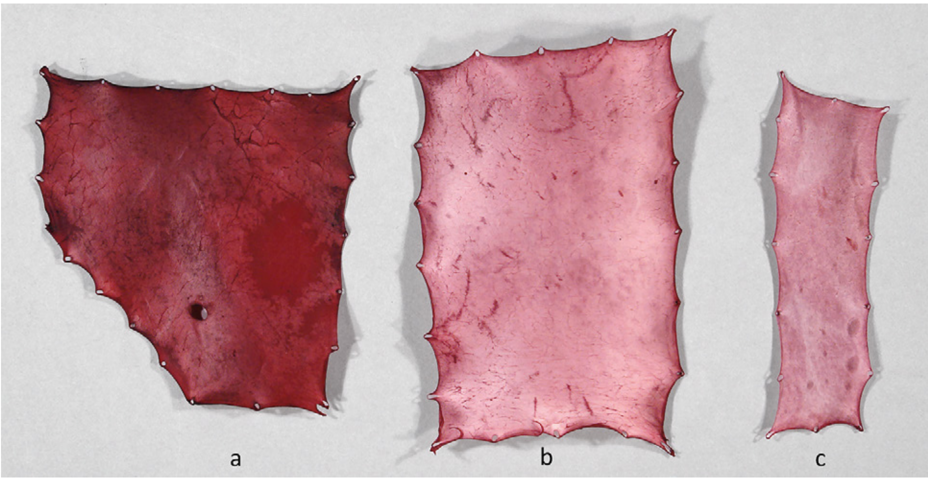

Fig. 10: Parchment dyed with spoiled and brown dye that did not turn purple, but stayed brownish-red. a) undiluted orchil, b) diluted orchil (1:3 v/v with water), c) diluted orchil, rinsed with water after dyeing (parchment by Jiří Vnouček).

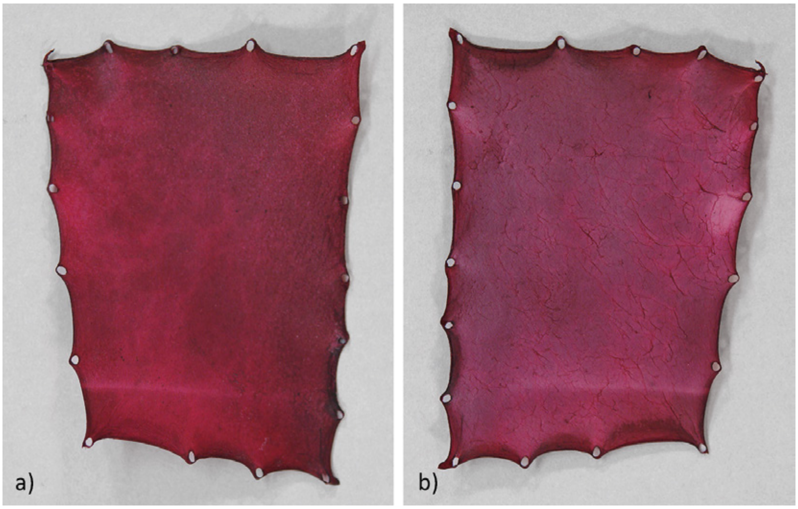

Fig. 11: Comparison of the saturation of colour on a) hair and b) flesh side.

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Results

Parchment can be dyed with orchil obtained from different types of lichens like *Roccella tinctoria* or *Lasallia pustulata*. Preparation of dye from *Lasallia pustulata* was quicker in the experiments, but this is not generally the case[84]. The dye can be applied with a cotton swab or in a bath. For immersion, more dyestuff is needed. The colouration is achieved in one step versus multiple applications by cotton swab. A solution of one part orchil and three parts water proved sufficient for immersion. Dark warm purple colours could be achieved with both *Roccella tinctoria* and *Lasallia pustulata*.

Three pieces of parchment were dyed in a bath of the batch of *Roccella tinctoria* that had not turned purple, but stayed brownish-red. The first piece was dyed with undiluted orchil, the second one with diluted orchil and the third one with diluted orchil as well, but washed with water after dyeing (Fig. 10). The results appear similar to the colour of the Vienna Genesis today. Regardless of the application method, the hair side absorbs more of the dye and turns out to be more saturated and darker than the flesh side (Fig. 11). Tissue remnants presumably originating from blood vessels, nerves, lymphatic vessels and different layers of skin also appear darker, as they absorb more dye.

Folium

Folium (also called Tüchleinfarbe[85], tournesol en drapeaux or morella[86]) is extracted from the fruits and parts of the plant *Chrozophora tinctoria*[87]. *Chrozophora tinctoria* is mainly found in the Mediterranean region and Central/South Asia[88]. Theophilus mentions three different types: folium rubeum (brownish red), folium purpureum (vine red) and folium saphireum (blueish violet). Next to the colour of the fruits those hues depend on the pH value and additives like wood ash, urine or slaked lime. The chemical structure of this dyestuff has not been entirely identified.

Folium, which was used for illumination in Medieval manuscripts and dyeing of parchment[89], is mentioned in different written sources like in Theophilus‘ De diversis artibus, the Mappae Clavicula, the Heraclius treatise, the Neapolitan Codex de arte illuminandi,

84 Isabella Whitworth, personal communication, 11 December 2018.
85 http://www.kremer-pigmente.com/media/pdf/36018.pdf (accessed 5 December 2018).
86 Cardon, 2007, p. 492.
87 Schweppe, 1993, p. 529.
88 http://www.kremer-pigmente.com/media/pdf/36018e.pdf (accessed 2 August 2018).
89 Cardon, 2007, p. 493.

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the Göttinger & Berliner Musterbuch, the Trierer Malerbuch, Le Begues Tabula and the Illuminierbuch of Boltz von Ruffach[90].

The shades of folium are often light and delicate. The colorant is also very light sensitive. In order to preserve and store the colour, small pieces of linen cloth were soaked in the sap of the plant parts. They were hung to dry above containers with dung or stale urine, in an ammoniac atmosphere to achieve blue hues. This process was repeated until the fabric had the desired intensity[91]. The dry cloth could be wetted again to extract and use the colorant. Anne-Marie Brunet, Nathalie Poulain Siloe and Patricia Roger Puyo conducted experiments with damp sheets coloured with folium that were brought in contact with parchment by pressing[92]. From the transfer, visible marks remain on the parchment, which could be observed on the pages of St. Riquier's Gospels[93]. By the end of the 14th century, folium seems to disappear from recipes of colour treatises, while madder, kermes and Brazil wood occur more often[94].

Preparation

Prof. Luigi Menghini[95] kindly provided dried fruits of *Chrozophora tinctoria*, collected in Sardinia, Italy. The fruits have to be processed while still fresh or, if this is not possible, have to be dried for later processing. A recipe provided by Maurizio Aceto was used. First, the dried ripe purple fruits, which result in shades of purple, were separated from the unripe blue and green ones, which result in a blue colour. The purple fruits were further processed (Fig. 12). After removing the seeds, 4.5 g of the fruit husks were placed in a glass filled with 60 ml of tap water and stirred for about half an hour on a magnetic stirrer. The water turned deep red immediately. The liquid was poured into a petri dish and left to dry until the following day. As the extract did not evaporate overnight, the petri dish was warmed in order to dry the extract. The result was a dark red deposit (Fig. 13).

90 Roosen-Runge, 1988, p. 81.
91 Cardon, 2007, p. 493.
92 Denoël et al., 2018, p. 9
93 Abbeville, MS004.
94 Denoël et al., 2018, p. 8.
95 Prof. Luigi Menghini, Università G. d'Annunzio, Dipartimento di Farmacia, 66100 Chieti, Italy.

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Fig. 12: Dried purple fruits of *Chrozophora tinctoria*.

Fig. 13: Dry extract of *Chrozophora tinctoria*.

Application

0.23 g of the dry folium were mixed with the same amount of alum in 48 ml of tap water. A weight ratio of 30 % w/w with respect to the weight of parchment was used, which measured 0.78 g. The pH value of the liquid dyestuff was at 3.37. The parchment, prepared in Late-Antique style by Jiří Vnouček, was immersed for 24 hours in the dye bath while being kept flat. For drying, it was stretched on a soft fibreboard, using pins. The parchment behaved very differently than in the dye experiments with orchil or shellfish purple. It was stiffer, tore very easily and showed no tendency to curl and buckle. This could be a reaction to the low pH value of the dyestuff.

Results

The parchment dyed with folium has a light rose colour, very different from the folios of the Vienna Genesis. As with the previous experiments, the hair side absorbed more dye and appears therefore darker in colour than the flesh side (Fig. 14). The use of folium prepared from fresh fruits by Rita Araújo gave very similar colours as the use of folium prepared from dry *Chrozophora* fruits. The same type of parchment was used for both experiments. On the folios of the Vienna Genesis, no evidence of the use of a fabric for colour transfer has been detected. If the dyers of the parchment of the Vienna Genesis' parchment

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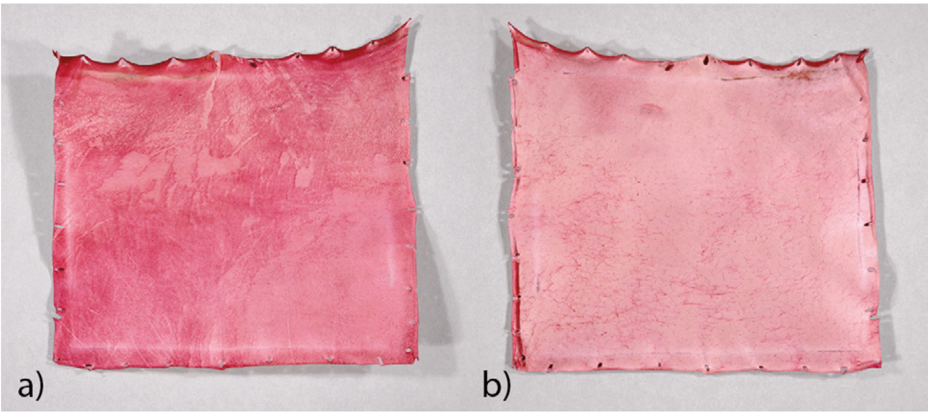

Fig. 14: Result of the dyeing with *Chrozophora tinctoria*; a) hair and b) flesh side.

used folium, they were limited to the season of harvesting fresh fruits and to the immediate supply of the fruits. The process of dyeing with folium seems more complicated than with orchil dyes.

Shellfish purple

Shellfish purple can be produced from different species of molluscs from the *Muricidae* family, which occur in rather warm oceans all over the world. Throughout Antiquity, it was considered the most stable and beautiful colour. The nuances have an obtainable range from purplish-red to various shades of violet up to blue. Shade and quality were difficult to predict as the results are influenced by many factors[96]. Shellfish purple is chemically closely related to plant indigo[97]. Both are vat dyes and very lightfast[98]. The technique used to dye with those two colorants is called vat dyeing, while the dye-baths are called vats as well[99]. The precursors of the purple colorant, also called chromogens, are concentrated in the hypobranchial gland of the mollusc[100]. When the shell is cracked open and the gland comes in contact with oxygen, the colorant undergoes a transformation and turns from transparent to yellow, lime green, green blue and eventually purple. In this state, the

96 Boesken Kanold, 2017, p. 67.
97 Cardon, 2007, p. 553.
98 Quandt, 2018, p. 122.
99 Cardon, 2007, p. 4.
100 Cardon, 2007, p. 555.

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colour can be directly used for painting, but not for dyeing, as it is water-insoluble[101]. In order to process and make it useable for dyeing, time consuming processes of reduction and oxidation have to take place[102]. The glands have to be fermented and the colorant has to be reduced in alkaline conditions in order to achieve its soluble form. The dye can then be absorbed by textiles or, in this case, parchment. In this state, the dyestuff is lime-green. When the dyed material is removed from the vat and exposed to the air, the contact with the oxygen reconverts the lime-green compounds into their purple water-insoluble form, which is then bound to the fibres[103].

Antique sources indicate that the origins of shellfish purple are located in the Near East, in the Phoenician empire[104]. The city Tyre was so famous for the production and trade of purple that the colour was named Tyrian purple[105], a term still used today. The earliest archaeological traces were found for example in Crete (Greece, 1,900–1,700 B. C.)[106], Ugarit[107] (Syria, 15th–13th century B. C.[108]) and Sarepta (Lebanon, around 1,350 B. C.)[109]. In Antiquity, the marine snails were mainly fished in the Mediterranean Sea[110]. There were different kinds of purple molluscs used by the ancient civilisations of the Mediterranean and the Middle East: *Bolinus brandaris*, *Hexaplex trunculus* and *Stramonita haemastoma*[111]. However, the use of molluscs is not unique to the Mediterranean world. Purple dyes were extracted from molluscs along the Atlantic coasts of Europe, in South and Central America[112] and in several ancient civilisations in Asia[113]. Caius Plinius Secundus, known as Pliny the Elder, described the production of the dye in his Natural History (Plin., HN IX, 38) 4:

> The vein already mentioned is then extracted and about a sextarius of salt added to each hundred pounds of material. It should be soaked for three days, for the fresher the extract,

101 Cardon, 2007, p. 4.
102 Quandt, 2018, p. 122.
103 Cardon, 2007, p. 4.
104 Bogensperger, 2015, pp. 158–159.
105 Schweppe, 1993, pp. 30–31.
106 Carannante, 2011, p. 11.
107 Schweppe, 1993, p. 31.
108 Barber, 1991, p. 229.
109 Quandt, 2018, p. 121.
110 Boesken Kanold, 2017, p. 67.
111 Cardon, 2007, pp. 566–586.
112 Several indigenous peoples in Central and South America dyed their textiles by rubbing the mucus of the living snails directly onto the yarn. The technique is still practiced today. Cardon, 2007, pp. 557–558.
113 Cardon, 2007, p. 553. For molluscs used in other parts of the world, see Cardon, 2007, pp. 586–604.

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> the more powerful the dye, then boiled in a leaden vessel. Next, five hundred pounds of dyestuff, diluted with an amphora of water, are subjected to an even and moderate heat by placing the vessels in a flue communicating with a distant furnace. Meanwhile the flesh, which necessarily adheres to the veins, is skimmed off, and a test is made about the tenth day by steeping a well-washed fleece in the liquefied contents of one of the vessels. The liquid is then heated till the colour answers to expectations.[114]

However, neither Pliny nor other authors described the process sufficiently accurate enough to reconstruct it[115]. After the fall of the eastern Roman Empire in 1453 and with the discovery of different red colorants in the Middle Ages, the purple industry declined and technological knowledge was lost. The so-called cardinals' purple was replaced by scarlet red and the garments were now dyed with kermes, an insect-based dye. Attempts at revival throughout the ages failed, Pliny's observations were not understood and could not be replicated effectively[116]. In 2001, Inge Boesken Kanold succeeded in reconstructing a purple dyeing vat using fresh *marine snails* (*Hexaplex trunculus*) with the help of John Edmond's booklet "Tyrian or Imperial Purple Dye, Historic Dyes Series No. 7", at the Conservatoire des Ocres et de la Couleur in Roussillon, France.

Preparation

In May 2017, Inge Boesken Kanold and Sophie Rabitsch experimented with dyeing different types of parchment with shellfish purple in Boesken Kanold's studio in Lacoste, France. About 200 snails, *Hexaplex trunculus*, were bought at local fish markets (Fig. 15). These snails are frequently fished in the Mediterranean Sea and are sold as "escargot de mer". Two kilograms of medium sized molluscs (about 100 animals) were needed for 1.5 litres of water. The colorant is located in the hypobranchial gland, which is situated in the big spiral of the snail shell. This gland contains the precursor of purple in the form of a colourless secretion[117]. To access the gland, the shells had to be cracked open, using a small stone or little hammer. The molluscs were frozen before the experiments, so they did not have to be crushed while still alive. The dyestuff undergoes a transformation: First, it is transparent, then quickly turns to yellow, then lime green, green blue and eventually purple due to the presence of oxygen. This process can be observed when cracking open

114 Boesken Kanold, 2017, pp. 67–68; Bailey, 1929.

115 Cardon, 2007, p. 553.

116 Boesken Kanold, 2017, p. 67.

117 Boesken Kanold, 2017, p. 69.

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Fig. 15: *Hexaplex trunculus*.

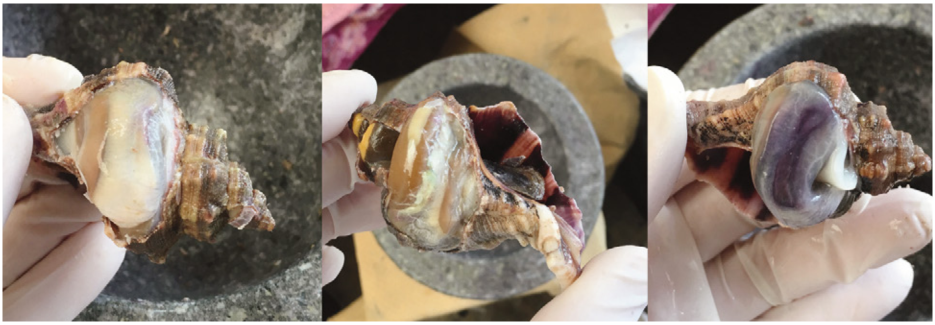

Fig. 16: Change of colour of the dyestuff in the hypobranchial gland from transparent to purple.

the shells (Fig. 16). Together with some adherent tissue, the glands were removed from the animal with the help of tweezers and then put into a glass jar with water. The liquid turns violet within an hour, but the dyestuff has to be reduced to its soluble (leuco) form first, so that it is able to penetrate the (textile) fibres. This process takes time and is achieved in the following days by raising the pH value to 8–9 by adding potash or putrid urine. The vat, kept in a double boiler with lid, was heated to approx. 50 °C, and was kept warm and away from sunlight for at least a week. After a few days, the fermentation process starts. During the first days, the vat is purple coloured, but then changes into blue, blue-green and eventually lime green, meaning the dyestuff is on its way to reduction[118]. This begins normally after three days, but for successful dyeing, one has to wait until the end of one week, as it was done in the described experiments. The liquid should be clear at this time, be-

118 Boesken Kanold, 2017, pp. 69–70.

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Fig. 17: Vat ready to dye in a double boiler.

cause the suspended particles have sunk to the bottom of the container (Fig. 17). The vat has to be kept warm and in a double boiler during the whole process. It is important to constantly protect the vat from larger amounts of oxygen (for example through stirring) and sunlight. If wool or other textiles are dyed, the vat's temperature of 45–48 °C is perfect, but for dyeing parchment, the vat should be at maximum 25 °C. The vats for these experiments consisted of snail glands with some adherent flesh, rainwater and putrid urine. No other chemicals, such as sodium hydroxide or sodium dithionite, were used. With the use of such chemicals, the reduction would be achieved in one hour, whereas the old-style vat takes about a week to produce quality results. Two vats were prepared, one made of frozen glands and one made of fresh glands. Each vat contained about 1.5–2 litres of liquid.

Application

Different types of parchment were dyed: Late Antique style lamb parchment by Jiří Vnouček as well as lamb, adult sheep, hare, calf and deer of unknown origin. To make handling of the pieces easier, cotton strings were attached, so that they could be moved easily inside the vat. Before immersing the parchment into the vat, it was soaked in a mild mixture of vinegar and water to ease the absorption of the dye. To obtain even results, it is important to make sure that the pieces of parchment are not folded or sticking together when immersed in the vat. The parchments were left for about one hour inside the vat, which has to be protected from oxygen and light in this stage. After removing the parchments from the vat, they were soaked in vinegar water again. The oxidation process can be observed within a few minutes (Fig. 18).

The samples of parchment were dried stretched, using pins on a polystyrene board (Fig. 19). The colours turned out intense and even and ranged from an almost pinkish

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Fig. 18: a) Soaking the parchment in a mixture of vinegar and water before dyeing, b) soaking the parchment in a mixture of vinegar and water after dyeing, c) fully developed purple colour.

Fig. 19: Stretched parchment on a polystyrene board using pins.

Fig. 20: Range of colour of the dyed parchment.

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violet to blueish violet. Two pieces of parchment were hung in sunlight during oxidation, which results in a blue colour (Fig. 20). The colour achieved from the vat becomes increasingly blue the more it is used and the older it gets, until finally, only grey shades can be achieved. No differences in colour could be observed between the vat made from fresh glands and the one made from frozen glands.

Results

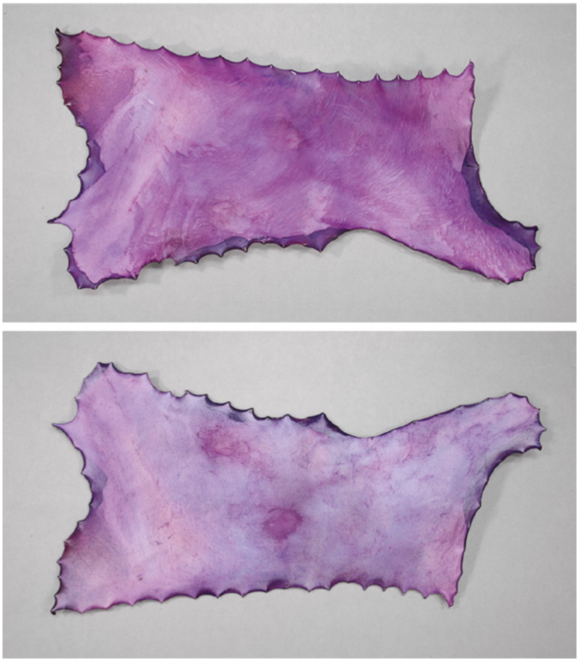

Fig. 21: Comparison of hair (above) and flesh side (below), parchment by Jiří Vnouček.

The experiments showed that it is possible to dye parchment with shellfish purple. The temperature of the vat has to be adjusted to a maximum of 25 °C. As in the case of orchil, the hair side absorbs more of the dye and turns out a little more saturated and darker than the flesh side (Fig. 21). Tissue remnants in the surface of the parchment also appear darker. The dyed parchments have an intense blueish-purple hue. The process of dyeing with shellfish purple is time-consuming and requires considerable experience and knowledge. In comparison, dyeing with orchil seems easier and less expensive.

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Comparison of dyed samples with the parchment of the Vienna Genesis

In order to compare the dyed samples with the aged purple parchment of the Vienna Genesis a simple light-ageing test was performed. Pieces of parchment, partially covered, were exposed to sunlight during the whole month of July 2017. They were placed into a south-west-facing window. The results confirm the light sensitivity of orchil and folium versus the lightfastness of shellfish purple (Fig. 22). The samples dyed with orchil and folium faded strongly, while that dyed with shellfish purple barely altered.

The appearance of the light-aged parchment samples dyed in orchil greatly resembles the hues and nuances of the Vienna Genesis folios (Fig. 23). The vivid colour of freshly dyed orchil samples suggest an originally contrasting and magnificent appearance of a purple manuscript with shiny, silver ink on strong, saturated purple. While the samples dyed with folium from dried fruits are much paler and the purple hues obtained with shellfish appear bluer than the colour of the Vienna Genesis, the parchment samples dyed with orchil resemble the colour found on the Vienna Genesis the most.

Fig. 22: Samples for light ageing experiment, before (above) and after (below).

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Fig. 23: Comparison of the light aged orchil samples with Vienna Genesis, folio 4, page 7 (left) and folio 7, page 14 (right).

Summary and conclusion

The technology of dyeing parchment purple was investigated via practical experiments. Preparation and application methods were tested for orchil, folium and shellfish purple. Parchment can be dyed with all of the three dyes (Fig. 24). A range of vivid hues was achieved with orchil and shellfish purple.

The experiments showed that much knowledge and experience are required to correctly process the dyestuffs. The natural products vary and a successful preparation is not guaranteed, as the orchil batches showed. Furthermore, the results depend on the quality of the parchment. Parchment that seems to be even and perfectly white can turn out blotchy after dyeing (Fig. 25). Different traces of manufacture or individual characteristics of the skin such as scar tissue, spots or patches can be visible and even enhanced on the coloured parchment. The colour varies depending on the species and characteristics of the individual animal.

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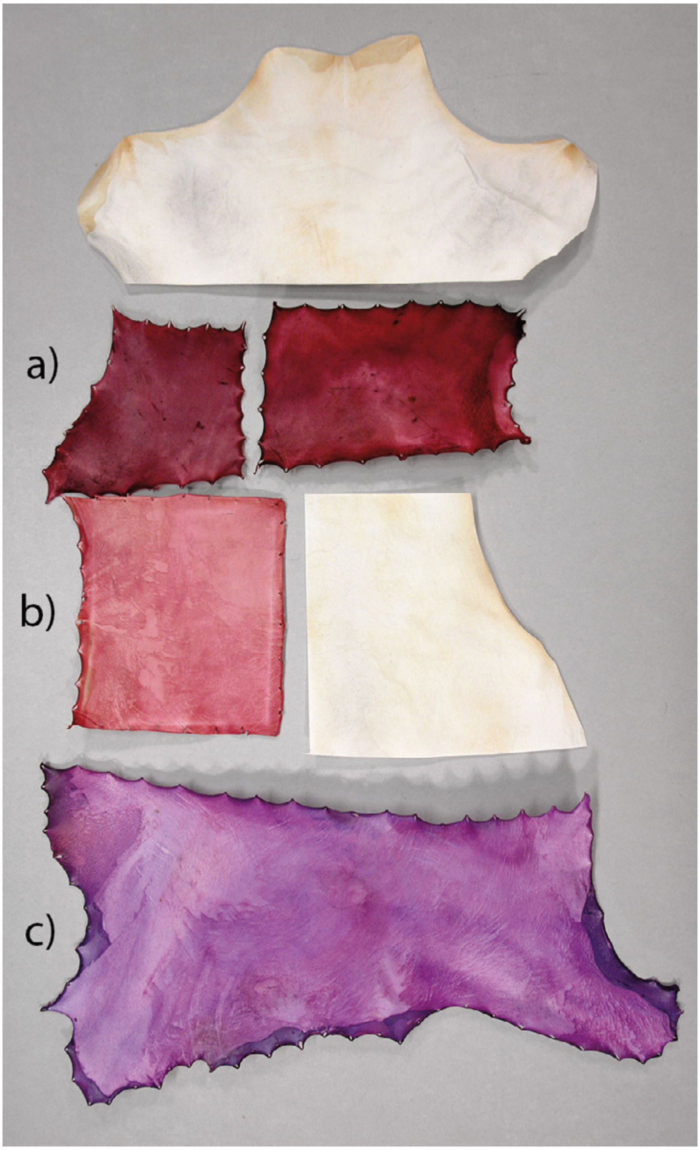

Fig. 24: All three dyes compared: a) orchil, b) folium, c) shellfish purple; hair side of the parchment by Jiří Vnouček.

The experiments with orchil showed that it is possible to dye parchment by immersion in a dye bath as well as by application with a suitable tool like a swab or brush. With a tool, the colour has to be dabbed on in several layers on both sides, which is a time-consuming process. The advantage is that a smaller quantity of dyestuff is needed. A tool like a brush or

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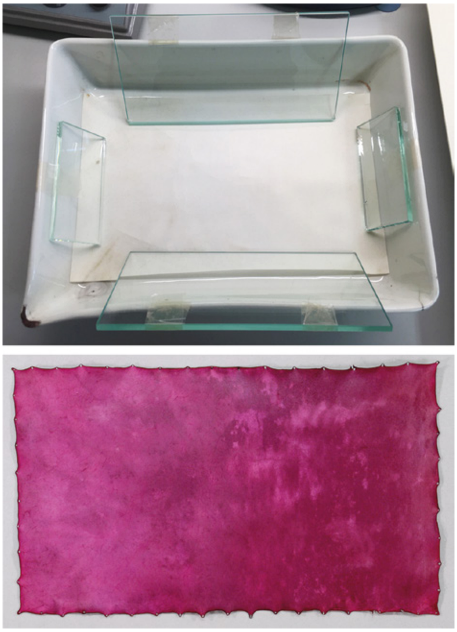

Fig. 25: White piece of parchment before dyeing (above), blotchy appearance after dyeing (below).

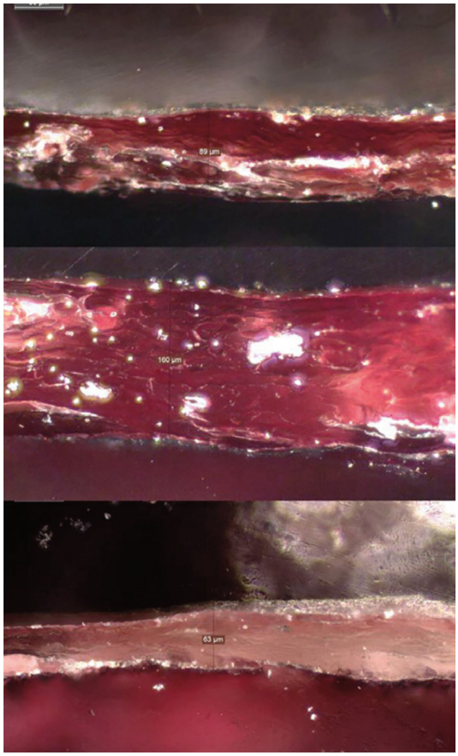

Fig. 26: Cross section of micro samples from the Codex Brixianus (top), a parchment dyed with orchil (middle) and a parchment painted with orchil (bottom).

swab does not necessarily produce visible traces. When using folium, a dye bath seems more practical, because the dye often results in light shades. The method of applying folium via a cloth that is pressed in contact with the parchment was not investigated. If the colorants are freshly processed and used, the addition of a binder is not necessary and the liquid colorant can be directly applied with a suitable tool or in a dye bath. When dyeing with shellfish purple, a bath is necessary to receive even results. If this dyestuff would be applied with a tool, the oxidation process would happen before the contact with the parchment.

The parchment of the Vienna Genesis is completely penetrated by the purple dye. No lighter core section of parchment is visible in cross-section. Colour penetration of a thin parchment can be achieved by immersion as well as by multiple applications of dye with a tool (Fig. 26).

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Semi-circular shaped transparent areas are formed by re-stretching parchment after dyeing. These areas can be observed on some folios of the Vienna Genesis. Therefore, it can be assumed that the parchment of the manuscript was dyed after manufacture and removal of the frame. After dyeing the parchment was dried stretched.

In the experiments described, the purple shades achieved with orchil more resemble the colours found on the folios of the Vienna Genesis than those obtained with folium or shellfish purple. Orchil results in warm saturated purple hues that turn brownish after light exposure. Reddish and brownish purple hues can be observed on the manuscript. The results of the technological experiments confirm the analytical identification of the purple dye on the Vienna Genesis. Orchil and folium are very light sensitive. This disadvantage might have been of less importance in a closed book versus a cloth worn in sunlight. The symbolism of the colour purple was perhaps of higher significance than the source of the dye.

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Identification of the purple dye on the Vienna Genesis

Maurizio Aceto, Maria João Melo, Elisa Calà, Paula Nabais, Rita Araújo

Introduction

The colour of the parchment of the Vienna Genesis is one of its most distinctive features, particularly as the symbolic meaning of purple was typically associated with regality since ancient times. The knowledge of the exact chemical nature of the dye used for purple is a matter of high relevance not only from the perspective of art history but also from that of conservation. In fact, the stability of the dyes to light is very different from one to another. Shellfish purple is considered to be stable and lightfast. Many other purple dyes such as folium from *Chrozophora tinctoria* or orchil (the dye extracted from lichens) are much more fugitive and could fade dramatically with prolonged light exposure (Table 1 a and b). Therefore, knowing what colorant is present on the parchment of the Vienna Genesis is important for decisions on conservation and storage.

The chemical nature of the colorant used for purple parchment has been a matter of speculation among scholars, given its extreme symbolic value. Before scientific analyses were performed in recent years, it has always been taken for granted that shellfish purple, the most prized dye of all times, must have been used for dyeing the parchment[1], despite the lack of any direct analytical evidence. The only indirect clue for shellfish purple was the identification of bromine yielded by X-Ray fluorescence spectrometry (XRF) in few instances, because this element is contained in the structure of 6,6'-dibromoindigotine (Fig. 1), the main molecule of shellfish purple.

Previous research suggested that bromine in a purple area could act as marker for shellfish purple[2], even if this assumption was subsequently criticised, at least with regard to miniature painting[3]. A recent study[4] showed that bromine is contained in significant amounts in many lichen species, used in antiquity for extracting purple dye known as orchil, and in *Chrozophora tinctoria*, the plant from which the folium dye was obtained. Therefore, it is clear that bromine cannot be considered an exclusive chemical marker for the presence of shellfish purple. However, the diagnostic evidence gleaned in recent years

1 Laurie, 1914; Thompson, 1956; Diringer, 1967; Furlan, 1998.
2 Porter et al., 2002; Maravelaki-Kalaitzaki and Kallithrakas-Kontos, 2003.
3 Porter, 2008, pp. 59–64.
4 Aceto et al., 2015.

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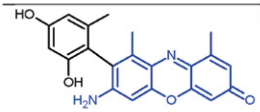
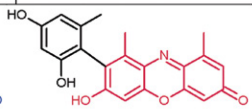
Rocella tinctoria	*Lasallia pustulata*
	
α-aminoorcein	α-hydroxyorcein
	
29.95, 16.38, -1.44	33.31, 11.83, 1.10
	
64.90, 10.84, 19.08	60.98, 10.62, 21.72

Table 1a: Possible sources for purple dyeing in antiquity and molecular structures for the main chromophores: Rocella tinctoria and Lasallia pustulata. In the lichens two type of chromophores may be found, derivatives of amino- or hidroxy-orcein. Dyed parchment samples were irradiated with a Xenon lamp (l_{irr} ffl 320 nm), photographs and L*a*b* colour coordinates for unaged and 310 h irradiation are given.

from scientific methods suggested a completely different story: it revealed that shellfish purple has to date never been directly identified in any purple manuscript, and that other dyes such as folium or orchil were used instead[5]. It is important to keep in mind that it is not possible to detect the indigoid chromophores of shellfish purple admixed with one of these dyes due to the very low quantum yield of fluorescence emission of shellfish purple on one hand, and very low signals in Raman on the other.

The analytical study on the purple dye contained on the parchment of the Vienna Genesis was performed in two phases: 1. non-invasive measurements were carried out in situ with portable instruments at the Austrian National Library. Further measurements were taken in the laboratory on micro-samples (ø 2 mm) of the parchment. The main aim of the non-invasive investigation was to make a preliminary identification of the dye used for

5 See among others Rosi et al., 2013; Aceto et al., 2014; Aceto et al., 2017.

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Table 1b: Possible sources for purple dyeing in antiquity and molecular structures for the main chromophores: Chrozophora tinctoria and shellfish purple (Hexaplex trunculus). Dyed parchment samples were irradiated with a Xenon lamp (I_{irr} ffl 320 nm), photographs and L*a*b* colour coordinates for unaged and 310 h irradiation are given.

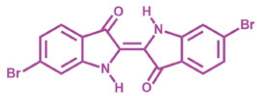
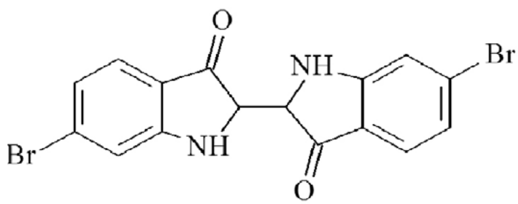
Chrozophora tinctoria	*Hexaplex trunculus*
?	
	
56.79, 15.58, 8.68	50.70, 15.91, -20.59
	
80.99, 5.43, 18.19	69.84, 6.31, -5.44

Fig. 1: Structure of dibromoindigotine.



the purple colour of the parchment. The following analysis enabled the production of a fingerprint identification of the dye.

For the study, four techniques were selected. UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS) was used for the preliminary identification of the dye. Spectrofluorimetry yielded complementary information. Micro-spectrofluorimetry on aged reference samples and on original parchment micro-samples enabled further insight

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on the nature of the chromophores present. Surface enhanced Raman spectroscopy (SERS) made it possible to obtain a definitive fingerprint identification of the dye by analysis of the micro-sample. Finally, X-Ray fluorescence spectrometry (XRF) was used to detect bromine.

For comparison, the same measurements were carried out on a micro-sample of parchment taken from Codex Serius nova 2804 (Cod. Ser. n. 2804) from the Austrian National Library. Cod. Ser. n. 2804 is a fragment of purple parchment without text that is dated to the 6th century.

Methods of analysis

UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS) analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source. Detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5x100 probe. In this configuration, light is sent and retrieved with a single fibre bundle positioned at 45° with respect to the normal surface, in order to exclude specular reflectance. The spectral range of the detector was 200–1160 nm. According to the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectral resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at least at 98 % within the investigated spectral range. Blank correction was not efficient on both the extremes of the spectral range, therefore the regions 200–350 nm and 1100–1160 nm were not considered in the discussion. The diameter of the area investigated on the sample was 1 mm. In all of the measurements, the distance between the probe and the sample was kept constant at 2 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The system was managed by means of AvaSoft v. 8 dedicated software, running under Windows 7.

For Spectrofluorimetry, an Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was used to record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal light source. An FCR-7UV200-2-1,5x100 probe (same as FORS) is used to drive excitation light on the sample and to recover the emitted light. The spectrophotometer works in the range 191–886 nm. According to the features of the monochromator (200 µm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in

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diameter. In all of the measurements, the sample-to-probe distance was kept constant to 12 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 4 s integration time, 3 scans for a total acquisition time of 12 s for every spectrum. The system is managed by SpectraSuite software running under Windows 7.

For Micro-spectrofluorimetry, fluorescence excitation and emission spectra were recorded with a Jobin Yvon/Horiba SPEX Fluorog 3-2.2 spectrofluorometer hyphenated to an Olympus BX51 M confocal microscope, with spatial resolution controlled with a multiple-pinhole turret, corresponding to a minimum 2 µm and maximum 60 µm spot, with 50x objective. Standard dichroic filters used at 45° were used to collect the excitation spectra (570 and 620 nm) and emission spectra (540 and 570 nm). Emission spectra were acquired exciting at 530 and 560 nm, while excitation spectra were recorded collecting the signal at 590 and 630 nm. This enables the collection of both the emission and excitation spectra with the same filter holder. Spectra were acquired on a 30 or 8 µm spot (pinhole 8 and 5, respectively) with the following slits set: emission slits = 3 / 3 / 3 mm, and excitation slits = 5 / 3 / 0.8 mm. The optimization of the signal was performed for all pinhole apertures through mirror alignment in the optic pathway of the microscope, following the manufacturer's instructions. Spectra were collected after focusing on the sample (eye view) followed by signal intensity optimization (detector reading). Emission and excitation spectra were acquired on the same spot whenever possible. Most of the reference samples were analysed in situ. The Vienna Genesis was analysed using micro-samples.

Surface enhanced Raman spectroscopy (SERS) analysis was carried out by Elisa Calà with a high-resolution dispersive Horiba (Villeneuve d'Ascq, France) LabRAM HR model spectrophotometer coupled with a confocal microscope. The instrument was equipped with a 633 nm excitation laser, a 1800 lines/mm dispersive grating, an 800 mm path monochromator and a Peltier cooled CCD detector. The optical arrangement gave a spectral resolution of about 2 cm^{-1}. Spectra were taken by placing the samples on the microscope stage and by observing them with long working distance 50x and 80x objectives. The sampled area was identified and focused using either a video camera or the microscope binoculars. Laser power at the sample was kept very low (30 µW) by means of a series of neutral density filters, in order to prevent any thermal degradation of the molecules. Exposure time was 1–30 s according to needs, with 3 accumulations for each spectrum. The system was managed with LabSpec 5 software running under Windows XP. For the preparation of the sample, silver colloidal pastes were synthesised according to the procedure described by Lee and Meisel[6], based on reduction of silver nitrate with citric acid. Analysis was per-

6 Lee and Meisel, 1982.

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formed directly on the sample, by pouring 1 µl of silver colloidal paste on it and waiting for the mixture to dry before exposing it to the laser beam.

SERS analysis were undertaken by Maria J. Melo et al. using a Labram 300 Jobin Yvon spectrometer, equipped with a HeNe laser operating at 632,8 nm (17 mW). Spectra were recorded as an extended scan. The laser beam was focused with 50x and 100x Olympus objective lens. The laser power at the surface of the sample varied with the aid of a set of neutral density filters (optical densities 0.6 and 1). It was between 4.25 and 1.7 mW. No evidence of sample degradation was observed during spectra acquisition. More than three spectra were collected from the same sample and a silicon reference was used to calibrate the instrument. Silver colloids for SERS were prepared by chemical reduction of silver nitrate with sodium citrate, following the synthetic protocol published by Lee and Meisel[7]. SERS analysis was performed after deposition of 0.8 µL of the silver colloid and 0.1 µL of 0.5 mol L^{-1} KNO_3 aqueous solution onto the micro-sample. All spectra were collected by focusing the laser beam onto the microaggregates that formed inside the dye-colloid droplet a few seconds after the deposition of the silver nanoparticles and KNO_3. Spectra were acquired continuously until the droplet dried out.

X-Ray fluorescence spectrometry (XRF) measurements were taken with a handheld EDXRF Thermo (Waltham, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with a Ag tube (max. 50 kV, 100 µA, 2 W), large area SDD detector, energy resolution of about 136 eV at 5.9 keV. The spot analysed had a diameter of 3 or 8 mm and was focused by a CCD camera, with a working distance of 2 mm. The point of analysis and the size of the irradiated sample are visualised by means of a CCD camera. The instrument was held in position with a moving stage allowing millimetric shifts, in order to reach the desired probe-to-sample distance; the stage was laid on a tripod. The total time of analysis was 240 seconds divided into 4 fractions, in which the operating conditions were modified in order to optimise the instrumental responses at different energy ranges (high: 50 keV, 50 µA, Mo filter; main: 40 keV, 50 µA, Fe/Al filter; low: 20 keV, 95 µA, Cu filter; light: 6 keV, 95 µA, no filter). The spectra obtained were processed with the commercial software WinAxil, derived by the academic software QXAS from IAEA.

Results and discussion

All previous analytical studies on purple codices indicated that orchil or folium, but not shellfish purple, were used for colouring parchment. The Vienna Genesis is no exception.

7 Lee and Meisel, 1982.

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In fact, FORS and spectrofluorimetry non-invasive measurements indicate that all pages were coloured with orchil, the dye extracted from different species of lichens. The results of the analyses are shown in the following figures. The FORS spectrum taken at folio 1, page 1 of the Vienna Genesis, representative of all other folios, is compared in figure 2 with standard purple dyes: alkanet, cochineal/kermes, folium, madder, orchil and shellfish purple. Alkanet, cochineal, folium and madder were prepared in the laboratory. Shellfish purple was obtained from Kremer pigments. The spectra are shown in Log(1/R) coordinates. From the comparison orchil seems to be the main dye of the Vienna Genesis, according to the two maxima at approx. 546 and 588 nm (Fig. 2). The shellfish purple is ruled out as dominant dye by lack of any absorption at approximately 526 nm. The identification of folium is also possible, since its maxima are close to those of orchil. Folium has been previously identified on a few purple codices such as the 6th century Codex Brixianus[8], the 8th century Evangiles de Saint Riquier[9], the 8th century Évangéliaire de Godescalc[10], and a 13th century section inside the 8th century Evangiles dits de Saint-Denis[11]. Thomas and Flieder[12] claimed to identify folium in the parchment of the Codex Sinopensis, but their result is questionable. In 2018 further measurements on the manuscript revealed that orchil was the dye present[13] as the overall shape of the FORS spectrum is closer to that of orchil than to folium. Figure 3 shows the comparison between spectra from the Vienna Genesis (folio 1, page 1), Cod. Ser. n. 2804 (fragment of purple parchment) and the spectra registered on the samples prepared by Sophie Rabitsch after dyeing with orchil from *Roccella tinctoria* and from *Lasallia pustulata* (see chapter on purple dyeing): the spectral features are similar.

The spectrofluorimetric analysis confirmed the identification by FORS. It reinforces the identification of orchil over folium, as the two dyes have different fluorescence maxima. In fact, the spectral features arising from the Vienna Genesis and Cod. Ser. n. 2804 were again similar to those of orchil and appeared as a fluorescence band located at approx. 623 nm (Fig. 4). A comparison is provided with the parchment samples dyed with orchil from *Roccella tinctoria* and from *Lasallia pustulata.* Very similar spectral features were also found on Cod. Ser. n. 2804.

Micro-spectrofluorimetry (8–20 micrometers in diameter) results show the presence of two chromophores in the Vienna Genesis sample, yet we do not know if these are of the same chemical family, of different families or the result of degradation. Emission and excit-

8 Biblioteca Queriniana, Brescia; Aceto et al., 2014; Idone et al., 2017.
9 Bibliothèque municipale, Abbeville, ms. 4; Roger, 2007.
10 Bibliothèque nationale de France, Paris, ms. NAL 1203; Roger Puyo, 2013.
11 Bibliothèque nationale de France, Paris, ms. Latin 9387; Aceto, 2018.
12 Thomas and Flieder, 1980.
13 Aceto, 2018.

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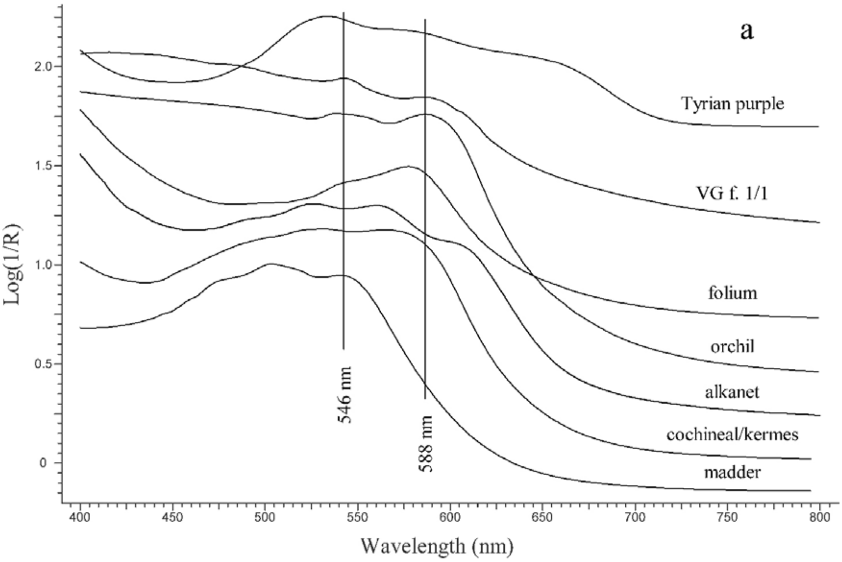

Fig. 2: FORS spectra of the parchment of the Vienna Genesis (folio 1, page 1) and of standard purple dyes. The spectra are shown in Log(1/R) coordinates.

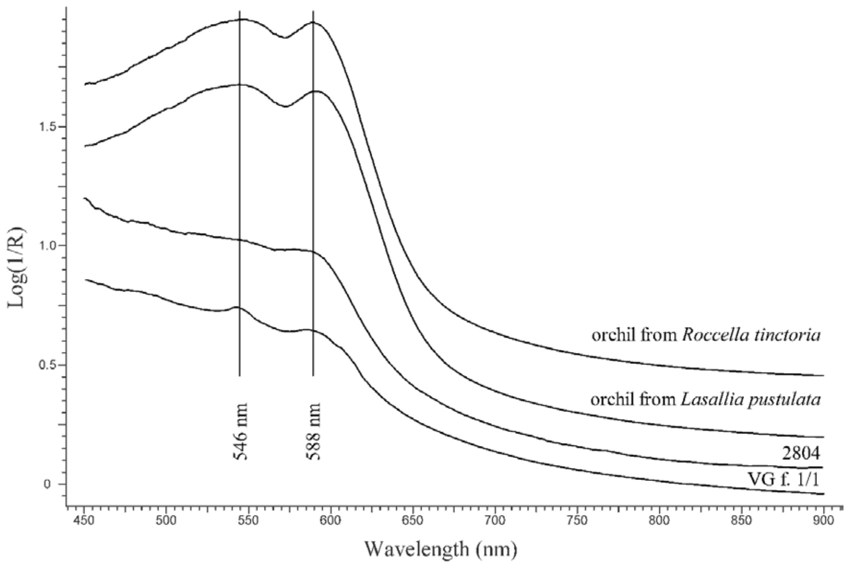

Fig. 3: FORS spectra of the parchment of the Vienna Genesis (folio 1, page 1), Cod. Ser. n. 2804 and of reference parchment samples dyed with orchil from *Roccella tinctoria* and from *Lasallia pustulata*. Spectra are shown in Log(1/R) coordinates.

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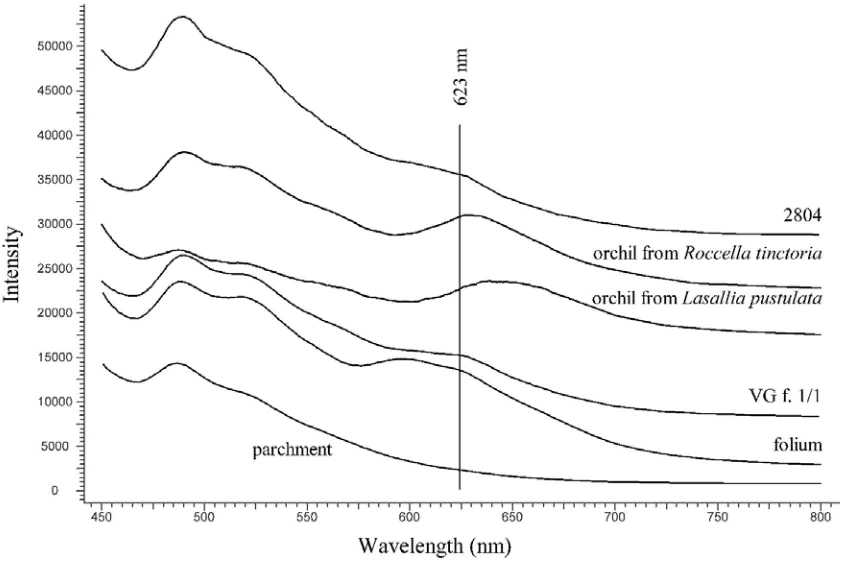

Fig. 4: Spectrofluorimetry spectra of folium, orchil, the parchment of the Vienna Genesis (folio 1, page 1) and of Cod. Ser. n. 2804. The spectrum of undyed parchment is included.

ation spectra were obtained. The latter may simulate the absorption spectrum. One of the species is characterised by an excitation spectrum with a maximum at 535 nm whereas the second species displays a maximum at 590 nm (Fig. 5). On the other hand, the emission maxima are similar, 595 and 600 nm, respectively (Fig. 6). When compared to artificially aged samples of *Lasallia pustulata*, we find a very good match with the chromophore characterised by excitation (Fig. 7) and emission maxima (Fig. 8) at 590 and 600 nm (chromophore #2), respectively. The same was observed for parchment dyed with *Rocella tinctoria* (results not shown). Compared to unaged orcein-treated samples, a 5 nm shift to longer wavelengths was observed in the emission spectrum (Fig. 8). In summary, a very good match was obtained with representative spectra found in the original purple parchment (chromophore #2) and an aged reference sample dyed with *Lasallia pustulata*.

The results of SERS analysis on the samples from the Vienna Genesis and Cod. Ser. n. 2804 are shown in figure 9. Raman microscopy could disclose the molecular fingerprint for the fundamental orcein structures, shared by all the amino and hydroxy derivatives, Table 1. The main assignments are described next[14]; bands 517 cm^{-1} ascribed to δ(COC), 619 cm^{-1} attributed to δ(COO), 798 with a shoulder at approx. 820 cm^{-1} due to ν(CC), ν(CN),

14 Rosi, 2013; Doherty et al., 2014; Melo, 2016.

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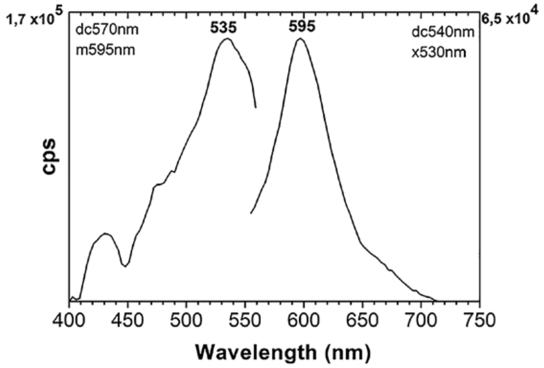

Fig. 5: Representative excitation spectra for the reddish purple colour on parchment in the Vienna Genesis, acquired on a micro-sample.

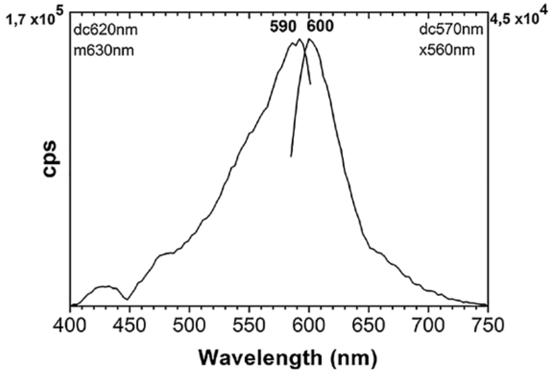

Fig. 6: Representative emission spectra for the reddish purple colour on parchment in the Vienna Genesis, acquired on a micro-sample.

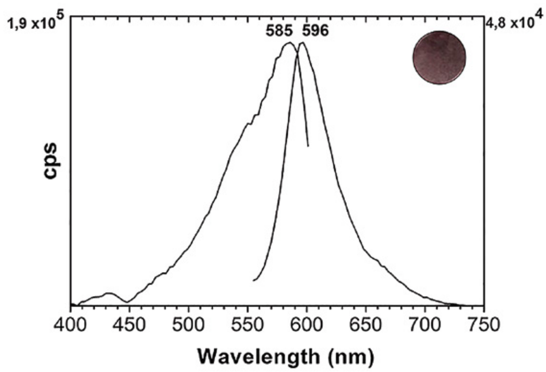

Fig. 7: Excitation spectra of parchment dyed with *Lasallia pustulata*, for 0 h and 167 h irradiation time (Xenon lamp, l_{irr} ffl 320 nm).

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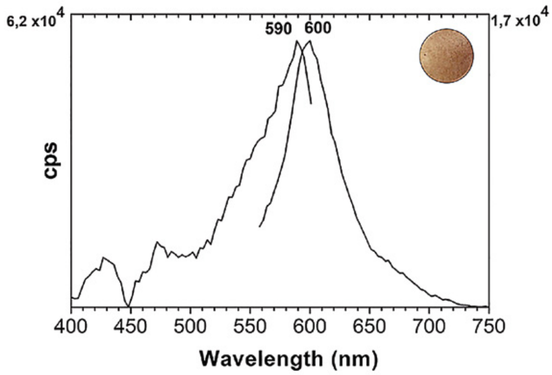

Fig. 8: Emission spectra of parchment dyed with *Lasallia pustulata*, for 0 h and 167 h irradiation time (Xenon lamp, l_{irr} ﬄ 320 nm).

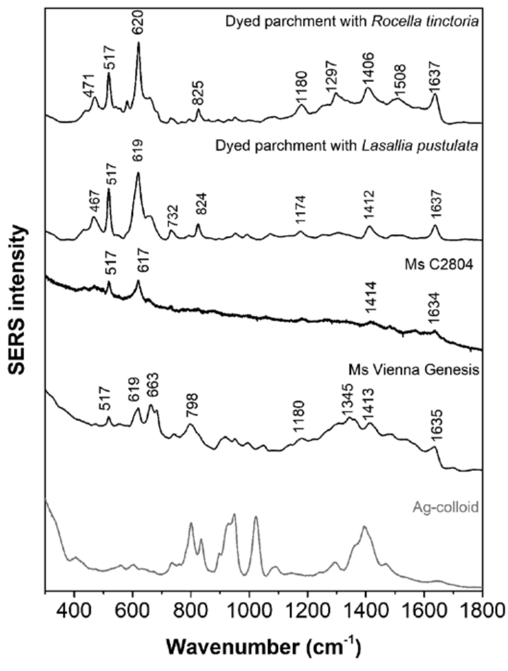

Fig. 9: SERS spectra of the reddish-purple colour, on parchment of the Vienna Genesis compared with the parchment references dyed with Rocella tinctoria and with Lasallia pustulata as well as with the parchment of Cod. Ser. n. 2804. The Ag colloid used in the analysis is also depicted.

δ(CCN) and δ(CNC), 1180 cm^{-1} assigned to ν(C–O), ν(CC) and ν(CN), 1413 cm^{-1} δ(CH_2) and δ(CH_3), 1494–1521 cm^{-1} given by δ(NH) and ν(C=C) aromatic and 1635 cm^{-1} due to ν(C=O), δ(OH) [44, 46]. The Raman spectrum concours with the results obtained for the SERS spectra of the lichen reference samples extracted from parchment dyed with *Lasallia*

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pustulata and with *Roccella tinctoria*, figure 9, thus unequivocally confirming the results obtained with FORS and fluorimetry, figures 2 to 8. A distinctive feature of the SERS mechanism is that it highlights the molecule with the highest affinity for silver nanoparticles, sometimes excluding other molecules. So, while the presence of orchil is definitely confirmed, the presence of other molecules, with lower affinity, cannot be excluded.

One final word can be said regarding the presence of bromine in parchment. As mentioned above, this element was previously reputed to be a marker for shellfish purple, but it is now known to also occur in orchil, particularly from that produced from coastal-sourced lichen species. XRF analysis was carried out in situ with a portable instrument in order to verify the content of bromine in the purple parchment of the Vienna Genesis. The results demonstrated that the amount of bromine is not at all compatible with that expected in the event of the presence of shellfish purple. A further step could be the evaluation of its concentration: it has been suggested[15] that coastal-sourced lichen species could have higher amounts of bromine than inland-sourced species. At low concentration, however, the identification – and therefore the determination of its concentration – is difficult since its peak is very close to the one of mercury (Hg). In addition, given the relative scarceness of available data, at present there are no absolute values to be used for stating whether a sample of orchil comes from a coastal-sourced rather than an inland-sourced species. As an indication, the amount of bromine in the parchment of the Vienna Genesis seems to be very low, suggesting – but this information must be regarded with extreme care – that orchil had been produced from inland-sourced lichen.

Colour of the parchment of the Vienna Genesis

The colour of the parchment folios of the Vienna Genesis appears more brownish-red than purple. The hue is coherent with the use of orchil which is a reddish dye, and similar to the faded orchil samples described in the chapter on purple dyeing. According to the results of non-invasive and micro invasive analysis, all folios were systematically coloured with orchil. This colour is relatively homogeneous throughout the manuscript, but some differences can be noted regarding the tone. The hues can be grouped in three categories, ranging from darker and medium to light purple, see chapter on conservation. Darker and paler zones also occur inside the same page of a folio.

The fact that all folios were coloured with orchil is demonstrated by the FORS spectra shown in figure 10. Spectra are in Kubelka-Munk or F(R) coordinates, obtained through

15 Aceto et al., 2015.

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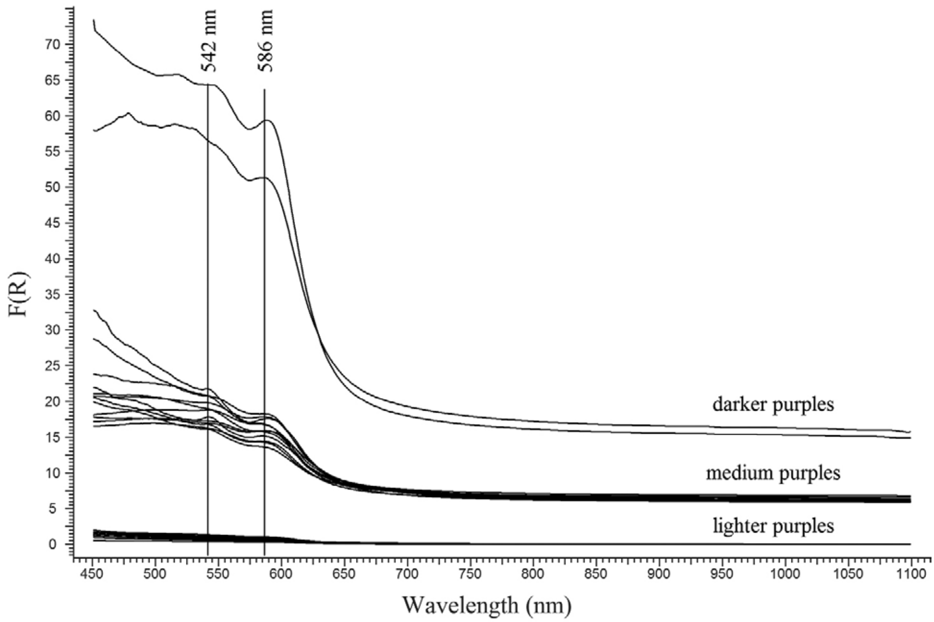

Fig. 10: FORS spectra in F(R) coordinates of light, medium and dark purple folios of the Vienna Genesis.

the transformate $F(R) = (1-R)^2/2R$. The Kubelka-Munk function allows appreciating differences due to the concentration of the absorbing species, orchil in this case. It can be seen that, despite the differences in tone of the respective folios, all FORS spectra show the same features, that is two maxima at approx. 542 and 586 nm, typical to orchil. The differences in the spectra can be explained in terms of residual concentration of the dye on parchment.

After considering the differences potentially introduced by the action of artisans, the effects of the environment must be considered. Orchil is not a lightfast but rather a fugitive dye, i. e. it can fade due to the action of light. In addition, its hue is strongly dependent on pH[16] and redox conditions. Exposure to light, contact with chemical substances (from cleaning products to any kind of chemically active substrate, such as wine, vinegar, etc.) and proliferation of microorganisms are all possible causes for the occurrence of darker and paler areas. A further element of variation could be the preparation of orchil from lichens. As mentioned earlier, this dye was extracted from several species by soaking lichen scraps

16 Consider that a polymeric form of orchil, the so-called *litmus*, is nowadays exploited in litmus paper.

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in ammonia for at least three weeks. The procedure, though managed with expertise by the artisans, was not an industrial process and was therefore subject to some variations from one batch to another, or from one craftsman to another. Finally, the possible use of different lichen species must be considered depending on the availability of raw materials.

Summary and conclusion

Raman microscopy disclosed the molecular fingerprint for the fundamental orcein structures shared by all the amino and hydroxy derivatives, and present in parchment samples dyed with lichens such as *Roccella tinctoria* and *Lasallia pustulata*, table 1a and figure 9. These conclusions were obtained comparing the reddish-purple parchment with unaged reference samples. On the other hand, aged references of dyed parchment presented us with further insights into the lichen species used. Micro-spectrofluorimetry showed that the closest match to the historical parchment was obtained with an aged reference sample dyed with *Lasallia pustulata* (Fig. 7 and 8). Therefore, the lichen used to dye the Vienna Genesis folios would have dyeing properties more like *Lasallia pustulata.* This technique also indicated the presence of another type of chromophore that for the moment could not be characterised by a chemical structure. Overall, the spectroscopic techniques applied in situ indicated the presence of an orchil-dyed parchment, and Raman microscopy (through SERS) provided the dye fingerprint. At this stage, therefore, the identification of orchil on the parchment of the Vienna Genesis is indisputable.

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Contribution of the authors

Prof. Maurizio Aceto carried out FORS and spectrofluorimetry measurements.
Dr. Elisa Calà carried out FORS, spectrofluorimetry and SERS measurements.
Prof. Maria J. Melo carried out micro-spectrofluorimetry and SERS in collaboration with Paula Nabais and Rita Araújo.

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The silver inks of the Vienna Genesis

Sophie Rabitsch, Antonia Malissa, Klaudia Hradil, Rudolf Erlach, Katharina Uhlir, Martina Griesser, Christa Hofmann

Introduction

The use of silver or gold inks in manuscripts was an expression of value and prestige[1]. After the magnificence of the purple-dyed parchment, the silver ink is a symbol for the worthiness and a reflection of the importance of the Vienna Genesis. The term ink refers to coloured liquids used for writing and printing, which are either a pigment dispersion or based on aqueous solutions, penetrating the writing material. There is a large number of different types of ink, ranging from carbon ink, iron gall ink, thorn ink or special coloured ink to ink made from the precious metals silver or gold[2].

The techniques of chrysography[3] and argyrography[4] were already known in Antiquity and continued to be used in the Middle Ages in both East and West[5]. From written sources it can be inferred that they were used in the Hebrew culture during the first and second centuries A. D. and in the Roman Empire since around the first century B. C.[6]. Ovid, Martial and Lucian recorded the use of shiny metal inks on purple parchment, but presumably they were referring to title pages or covers for scrolls and not to entire manuscripts made of those materials[7]. Christian book production started in the 3rd and 4th century A. D. The church fathers Jerome († 420) and John Chrysostom († 407) wrote about preciously equipped codices that were made for sacral use. The latter disapproved of the use of gold ink, but not necessarily the use of dyed parchment[8]. In Byzantine culture, chrysography and argyrography were highly valued and were usually carried out by specialists[9]. Many examples for these techniques survived, mostly in Christian, Jewish and Islamic manuscripts,

1 Trost, 1991, p. 8.
2 Trost, 1991, pp. 1–6.
3 Writing in letters of gold.
4 Writing in letters of silver.
5 Trost, 1991, p. XIII.
6 Trost, 1991, p. 6.
7 Trost, 1991, p. 12.
8 Trost, 1991, pp. 12–13.
9 Oltrogge, 2011, p. 66.

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as well as in certain medieval western documents[10]. The oldest surviving manuscripts with gold or silver ink date from the 4th and 5th century A. D.[11]. The preserved luxurious manuscripts are mostly Greek, Latin or Gothic versions of the gospels, often written on purple dyed parchment. In many cases, the texts are written in silver ink, while the titles, initials, etc. are applied in gold ink. In some cases, gold ink is used for the whole text[12]. Gold and silver inks were mostly used on parchment, especially in Late Antique, insular, Carolingian, Ottonian, Salic and high medieval manuscripts. At the end of the 12th century, codices written with these inks were becoming rarer and almost stopped being produced by the end of the 13th century. Nevertheless, gold and silver were still used for initials and illuminations. During the 13th century, leaf metal became more popular than metal inks[13].

There are numerous surviving historical recipes for metal inks. The most important sources from Late Antiquity to the 13th century are the Papyrus Leidensis X, the Lucca manuscript, Mappae Clavicula, and the Heraclius treaties. More about those sources and the recipes is explained in the chapter on the alteration study. Two types of chrysography and argyrography can be differentiated. The first type, metal ink, such as that on the Vienna Genesis, was common in Late Antiquity and the Middle Ages, while the second type, leaf metal, was more important from the 13th century onwards and was more often used for the background in illuminations[14]. According to Vera Trost, silver inks[15] can be divided into three different categories: the first includes pure silver inks, which contain only silver and some binding medium, while the second category consists of silver inks with additional metallic and non-metallic components. At this point it should be mentioned that Trost not only refers to native metals as metallic components, but also includes salts like copper(II)acetate in this category. The third group of silver inks are so-called substitution inks that do not contain any silver, but various other metallic, vegetable, animal or mineral components that create a metallic gloss. The recipes of the first two categories are always based on powdery gold or silver[16]. If leaf metal is used instead, a number of steps are necessary: the preparation of the writing material, followed by the application of the leaf (with or without a bolus) and burnishing the metal. In the recipes used by Trost, only gold and tin leaves are mentioned as silver leaf tends to tarnish rather quickly[17].

When Peter Lambeck first described the codex, he mentions the alteration of the silver

10 Trost, 1991, p. XIII.
11 Trost, 1991, p. 6.
12 Trost, 1991, p. 13.
13 Trost, 1991, pp. 11–29.
14 Trost, 1991, p. 33.
15 As only silver ink was used on Vienna Genesis, no reference to gold inks is made here.
16 Trost, 1991, pp. 33–35.
17 Trost, 1991, p. 35.

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ink and the losses in the text. One of the aims of this project was to gain more information about the inks of the Vienna Genesis and therefore the possible causes of the deterioration[18]. Whether the scribes used the same or different recipes to prepare silver ink should be investigated. The inks and their application during writing were first examined visually on all folios. Characteristic measurement points were analysed with energy dispersive micro X-Ray fluorescence spectroscopy (µ-XRF) on the inks of all folios. Analysis with X-ray diffraction (XRD and µ-XRD) were aimed to provide insight in the silver corrosion phases. Micro-samples of silver ink from Vienna Genesis were investigated with energy dispersive X-ray analysis in the scanning electron microscope (SEM/EDX). Reference inks prepared for the project as well as other manuscripts held at the Austrian National Library served as comparison.

Visual examination

The inks as well as traces of the writing process of the text were examined in incident and raking light and under magnification with a stereo microscope[19].

The text of the Vienna Genesis is written in Maiuscula biblica. Two scribes have been identified, whose scripts correspond stylistically but can be clearly differentiated. The first scribe, to whom the folios 1–12 (pages 1–24) are attributed[20], had a more advanced style and his handwriting shows characteristics of the scripture of the late 6th century. The second scribe, to whom folios 13–24 (pages 24–48) are attributed[21], had a more archaic style (Fig. 1)[22]. The scribe changes from folio 12 to folio 13, which is unusual[23], as those two folios form a bifolio and the change occurs within a bifolio and a quire, see Fig. 14 in the chapter on the parchment of the Vienna Genesis. Christian Gastgeber assumes in the commentary to the new facsimile that both parts could be written by one scribe. Due to economic pressure, the scribe might have had to hurry which influenced the script[24].

18 Chapters on alteration study and conservation.

19 Wild stereo microscope M 400 (type 126269) at 6.3x–32x magnification.

20 Mazal, 1980, p. 41; personal communication, Prof. Otto Kresten, Academy of Science, 22 February 2017.

21 Mazal, 1980, p. 41; personal communication, Prof. Otto Kresten, Academy of Science, 22 February 2017.

22 Mazal, 1980, pp. 32–33.

23 Personal communication, Prof. Otto Kresten, Academy of Science, 22 February 2017.

24 Gastgeber et al., 2019, p. 40.

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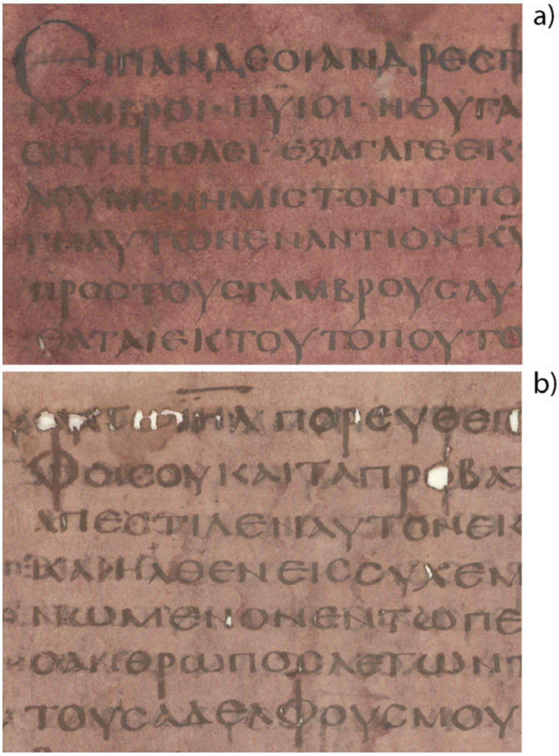

Fig. 1: Details of a) text written by the first scribe, folio 5, page 9, b) text written by the second scribe, folio 15, page 30.

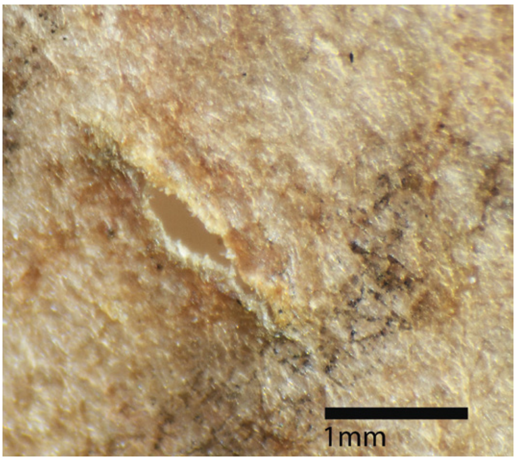

Fig. 2: Microscopic image showing a slit-shaped pricking mark in the corner of a text block, folio 12, 12x magnification, scale bar 1 mm.

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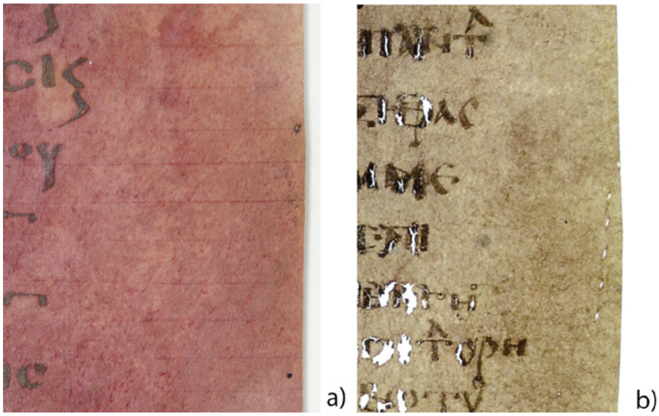

Fig. 3: Details of a) impressed ruling lines, folio 7, page 13, b) impressed ruling lines with pricking marks in transmitted light, folio 3, page 5.

Fig. 4: Detail of vertical impressed lines, folio 12, page 23.

All folios except folio 16 show four pricking marks shaped like small slits or, in rare cases, round holes in the corners of the text block (Fig. 2). Some folios show one additional mark in the middle of the lower edges as well. Impressed horizontal ruling lines, a few times with pricking marks along the margins, are visible on most folios (Fig. 3), except folios 4 and 5. There are also vertical impressed lines that define the margin of the text block (Fig. 4), present on all folios except folios 1, 4 and 5. The ruling has not been carried out consistently and differs from side to side and from quire to quire. According to Otto Mazal[25], there are seven different ruling schemes, which could be confirmed during the observations within the Vienna Genesis project[26] (Fig. 5 a and b). The use of different schemes is rather unusual, according to Otto Kresten[27]. The matching ruling lines on the bifolios indicate that the lines were continued across the centrefold (Fig. 6). In case of some reattached bifolios, it is possible that the basic design of the illumination and its sketch was made on the opened

25 Mazal. 1980, pp. 28–31.

26 Only on folios 2 and 3 Mazal was mistaken regarding the number of vertical lines. He assumed two lines at the inner margin, but there is only one.

27 Personal communication, Prof. Otto Kresten, Academy of Science, 22 February 2017.

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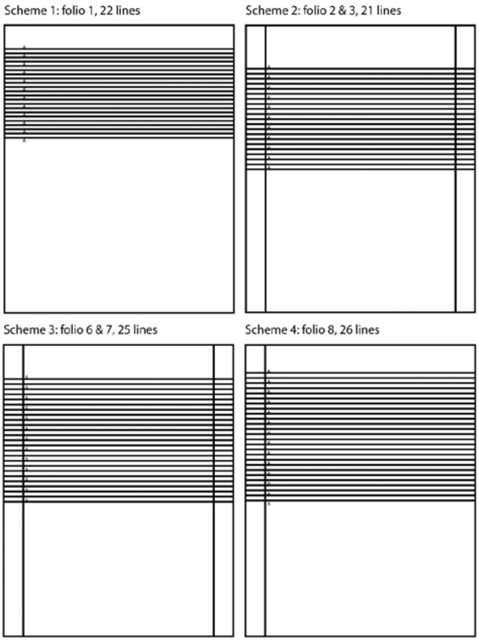

Fig. 5a: Different ruling schemes, 1–4.

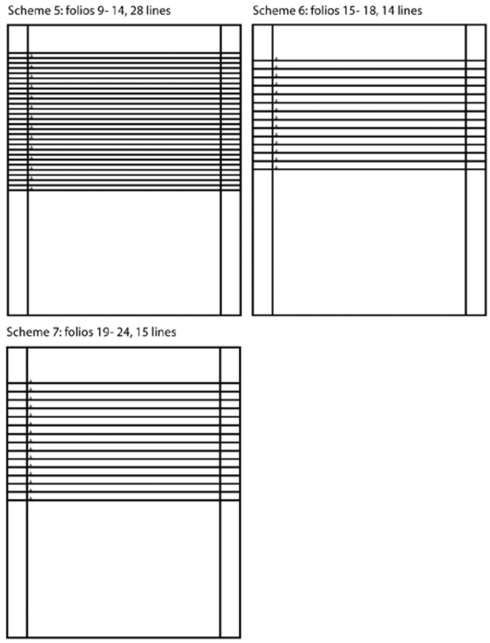

Fig. 5b: Different ruling schemes, 5–7.

bifolio. The scribes used two major schemes of ruling: while the first always skips one line (Fig. 5 a), the second uses every line to write on, (folios 11–14) but sticks to the first scheme in the quire where the scribes changed (Fig. 5 b). Quire 7 was prepared using the ruling scheme of the first scribe, while folio 13 and 14 were already written by the second scribe. It seems that the scribes (or someone else) first prepared the whole quire with ruling marks before writing the text. In the Middle Ages it was common that the scribe himself executed the ruling before writing a text, but the workflow in Late Antiquity is unknown[28]. It can be assumed that the Vienna Genesis was produced in an artistic workshop, which was different from a fully organised medieval European scriptorium[29].

The size of the text block of the Vienna Genesis was not consistent within the whole manuscript, probably due to the different amount of text that had to be adjusted to the illuminations. The text block varies up to 20 mm from quire to quire, and to a minor extent of some millimetres from page to page within one quire as well. The parchment

28 Mazal, 1980, p. 41.
29 Diringer, 1982, p. 275.

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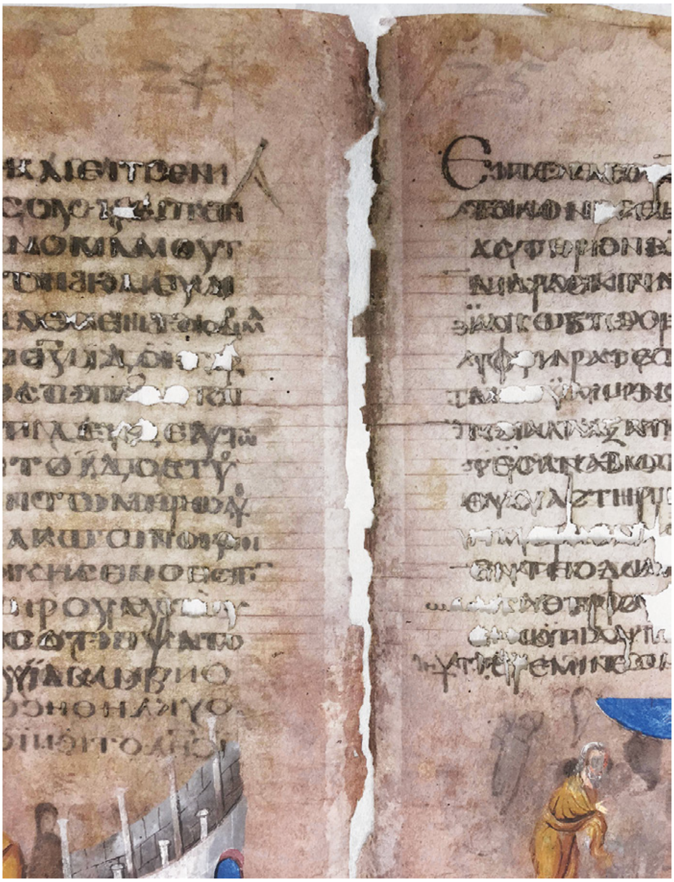
Fig. 6: Detail with matching ruling lines across the centre fold, folios 12 and 13.



presumably changed its dimensions due to ageing, conservation treatments and other external influences and the pricking marks of the single folios do not fit perfectly within one quire or even one bifolio[30]. Cut marks, irregular margins and even cut miniatures and letters indicate that originally the manuscript was larger in size. The current size of the folios ranges from 257 x 238 mm[31] to 328 x 268 mm[32]. The distances between the edge of the parchment and the pricking marks as well as the text and miniature painting of every folio were measured to make suggestions regarding the original size. The largest measurements for the text block in terms of pricking marks in the corners of the text block (and

30 It is assumed that the scribe marked the corners of the text block for a whole quire concurrently once with the pages folded and in place.

31 Length of folio 5, width of folio 1 and folio 17.

32 Length of folio 4, width of folio 9.

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vertical impressed lines between the pricking marks) are 297–300 mm in length (folio 4) and 209–210 mm in width (folio 5). The smallest measurements are 275–279 mm in length (folio 1) and 190–195 mm in width (folio 22). The actual size of the text block is often larger than marked before and can be up to 300 x 242 mm (folio 5). To determine the distance between the two text blocks of a bifolio, folio 20 and 21 were measured. The folios 20 and 21 originally formed a bifolio and still fit together on the inner margins. The distance between the two text blocks on the open bifolio (regarding the impressed vertical line) is 65 mm. The largest distances to the outer edges found are 48 mm (upper margin, folio 3, page 5), 50 mm (lower margin, folio 18, page 31) and 51 mm (outer margin, folio 14, page 27). Folio 2 seems to have an original edge on the upper right margin, the distance to the text is 42 mm (see Fig. 12 in the chapter on the parchment). The original size of the folios of the Vienna Genesis cannot be reconstructed with certainity. The size of the text block was not consistent through the whole manuscript and additionally, the parchment has changed its size due to reasons mentioned above. Regarding the largest measured distances between margin and text (about 50 mm on the upper, outer and lower edges) and assuming that they are the maximum, it is supposed that the folios had a size of 400 x 292.5 mm.

On many folios dark, parallel, horizontal stripes can be seen, see chapter on the conservation. As they only occur in and around the text areas, they could be burnishing marks from the process of smoothing the parchment before writing.

Probably a reed pen known as calamus was used to write the text, as it matches the shape of the ink lines and was the major writing tool in Late Antiquity[33]. Sticks of reed were cut to a point, split and sharpened with a knife[34]. Nevertheless, copper pens are also mentioned at least in the context of chrysography in byzantine texts[35], so this could as well be a possible writing tool. Metal inks are more difficult to write with than iron gall inks or finer pigment inks, as they are relatively coarse-grained and more viscous. According to Doris Oltrogge and Peter Schreiner, copper pens seem to be more suitable for writing with metallic inks[36].

The surface of the ink looks similar on all folios. The scribes probably prepared fresh ink which lasted for writing two pages of text[37]. The colour of the silver ink ranges from dark and medium grey to brownish and silvery grey (Fig. 7). Over time, the inks have darkened in comparison to new silver ink. The silver seems to be finely ground and the ink

33 Personal communication, Prof. Otto Kresten, Academy of Science, 22 February 2017; Sharpe, 2006, p. 165.

34 Diringer, 1982, p. 557.

35 Schreiner, 2001, p. 50.

36 Schreiner and Oltrogge, 2011, pp. 110–111.

37 Personal communication, Prof. Otto Kresten, Academy of Science, 15 March 2017.

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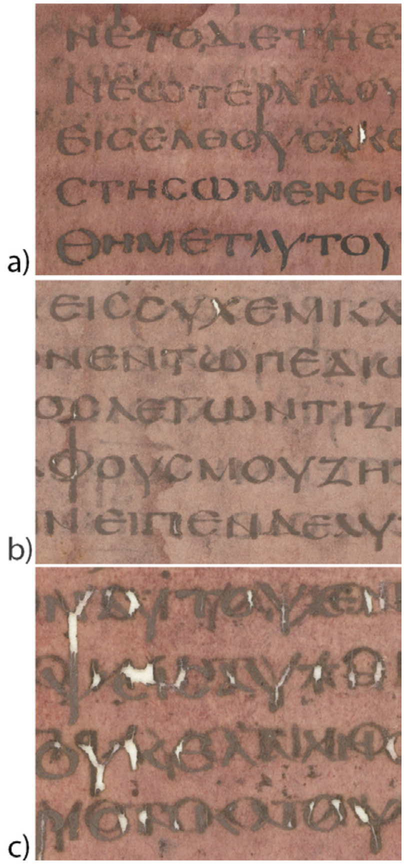
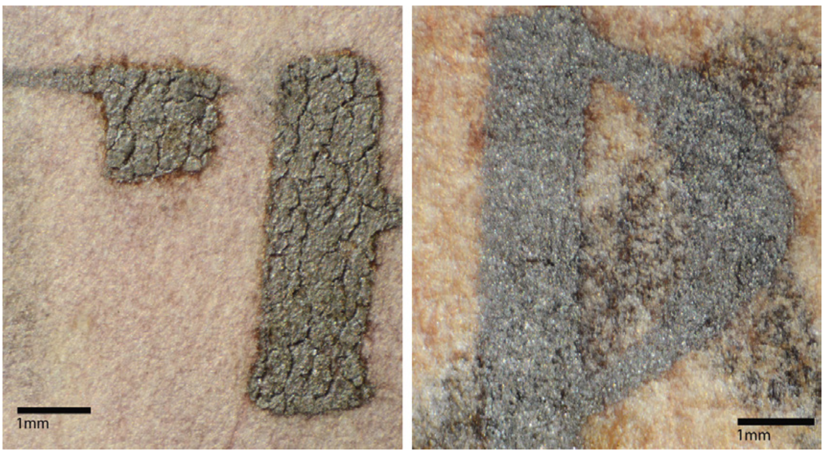


Fig. 7: Details of ink a) dark grey, folio 5, page 10, b) brownish grey, folio 15, page 30, c) silvery grey, folio 19, page 37.

is mostly opaque. The coarse surface often shows small cracks. Under the microscope, it appears shiny and sparkly in many areas (Fig. 8). The ink was probably burnished to enhance the gleam of the silver on the purple background as described in many historical texts.

On every folio, the silver ink has corroded and caused severe damage to the parchment. The extent ranges from small cracks to larger losses in the text area. The deterioration, which differs from folio to folio, is described in detail in the chapter on conservation.

Fig. 8: Microscopic images of silver ink at 12x magnification (scale bar 1 mm), folio 12, page 23.



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Iron gall inks

Different notes and numbers have been added to the folios of Vienna Genesis throughout time. Most of them were inscribed in iron gall ink, as confirmed with XRF[38]. No signs of iron gall ink corrosion are visible. As described in the chapter on the history, transfers from strips of Latin manuscripts, written in Italian Rotunda with dark brown ink and dated to the late 14th or early 15th century, can be seen on several folios. A few transfers of red ink identified as cinnabar[39] were found as well. Italian notes in Humanist Italic were left on folio 1, page 1 and 2 in the 15th century, see the chapter on the history. The brown iron gall ink is rather translucent with very few small dark particles on the surface. The ink lines are relatively thin. In 1664, Peter Lambeck numbered each folio in the centre of the upper margins using iron gall ink (Fig. 9). On the surface of many numerals brown and white glittery particles can be seen, which could be deposits of writing sand. On the first folio Lambeck also added a note in an ink of similar composition, see chapter on the history. The ink is brown, matt and rather translucent.

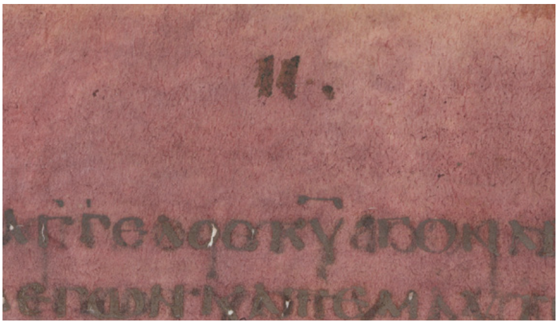

Fig. 9: Numbers added by Peter Lambeck in the middle of the upper edges using iron gall ink, folio 6, page 11.

Pencilled numerals in an unknown hand have been added in the upper outer corners. This might have been done at the end of the 19th century when the pamphlet was unbound. The numbers in pencil are visible on the first facsimile, which was printed in 1895.

Analysis of the silver inks with μ-XRF

In the first year of the project, detailed analysis was performed on the silver inks of Vienna Genesis with micro X-Ray fluorescence spectroscopy (μ-XRF)[40]. On the one hand, the re-

38 XRF, KHM, 2017.

39 XRF, KHM, 2017.

40 The measurments were taken by Antonia Malissa and Katharina Uhlir. Malissa, 2018, pp. 52–54.

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sults of the analysis of the silver inks were used to verify differences in the elemental composition, especially of the silver content, throughout the entire codex. On the other hand, the information obtained about the possible additions of inorganic compounds contributed to a better understanding on the causes of the severe degradation of ink and parchment.

For the analysis of the silver inks with µ-XRF the same instrument as well as identical measuring conditions were used as for the analysis of the miniature paintings, see chapter on miniatures for the detailed description of the instrument and the method. In order to retrace the elemental composition of the silver inks as accurately as possible, measurements of the ink as well as the surrounding blank parchment were recorded on different points of almost every folio (recto and verso).

The spectra obtained from the measuring points of blank parchment and the silver ink from folio 23, page 46 (Fig. 10), show the elemental composition of both the ink and the parchment[41]. The direct comparison indicates that many signals detected arise from the parchment itself, while only a modest number of peaks come from the silver ink. In the parchment, following a very intensive calcium signal which probably results from the use of an alkaline solution of lime ($Ca(OH)_2$) during the manufacturing process, minor signals of chlorine, silicon, phosphorus, potassium and iron were detected. In comparison, the spectrum of the silver ink reveals clearly that silver and copper are the main ingredients of the ink, whereas chromium, gold and mercury are present as trace components. Additionally, an intensive chlorine signal indicates the presence of chlorine, presumably in form of the corrosion product silver chloride (AgCl).

Further evaluation of all spectra generated showed that the elemental composition of the silver ink, which was described above, did not change throughout the entire codex. In particular, the ratio between the K_α-peaks of the elements silver and copper remained without any significant variations for the first as well as for the second half of the codex (Fig. 11). Only in the case of the trace components – chromium, gold and mercury – minor variations of the peak intensities were observed. These differences largely correlate with the variation of the thickness with which the ink was applied. Therefore, the trace components could undoubtedly be detected in correlation with higher silver peaks, whereas especially gold and mercury were hardly found in spectra with overall lower intensities. Due to these observations, we assume that the scribes of the Vienna Genesis used inks with very similar compositions.

Because of the poor condition of the written text passages of the Vienna Genesis, the presence of the transition metal copper as well as the intensive signals of chlorine in all

41 Regarding the detected elements, it has to be pointed out that the peaks resulting from palladium and argon appear in all spectra. Since the palladium signal results from the Pd anode itself and the argon signal derives from the surrounding, they will not be considered in the following discussion.

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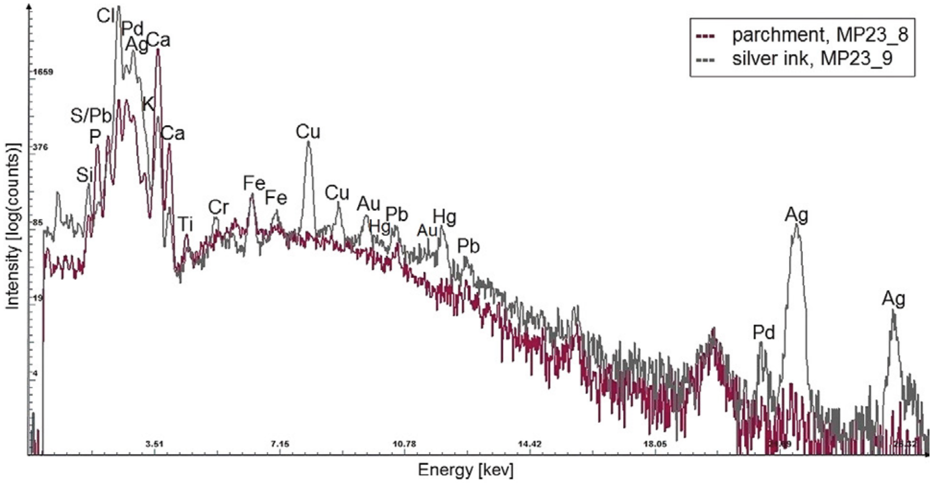

Fig. 10: XRF spectra of the parchment (MP23_8, purple) and the silver ink (MP23_9, grey) on folio 23v.

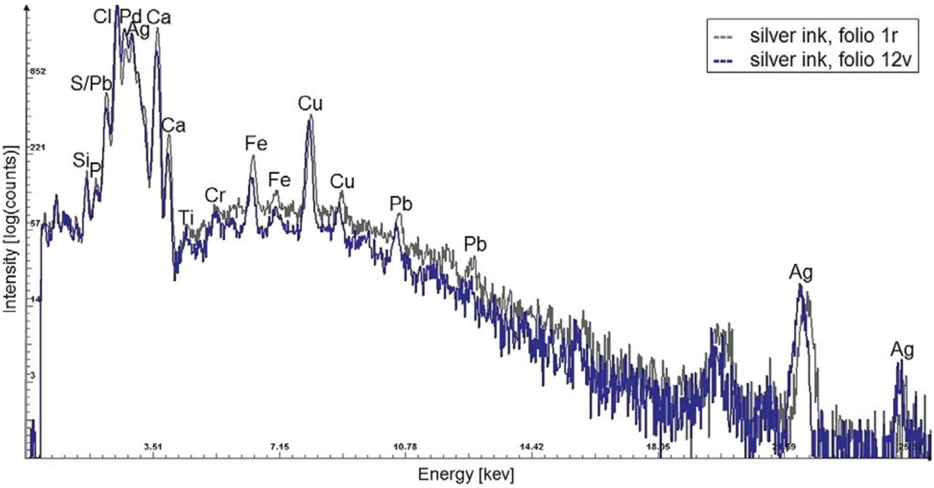

Fig. 11: Comparison of the XRF spectra of the silver ink on folio 1r (MP1_2, grey) and the silver ink on folio 12v (MP12_9, blue).

spectra of the silver inks were of greater interest. Therefore, further characterisation of the silver inks of the codex was undertaken by a comparison with several reference inks. As it will be described in greater detail in the chapter on the alteration study, a series of 13 samples was prepared. 14 different reference inks (ST1-ST14, according to historic recipes)

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were applied onto purple-dyed parchment and were then artificially aged using high temperature and varying relative humidity. One of the 14 inks could not be used since its components did not mix[42]. For the purpose of comparison with special regard to the amount of copper and chlorine, the artificially aged inks were analysed with XRF, see chapter on the alteration study.

In order to be able to estimate whether copper was a trace element of the ink, for example as an impurity in the used silver, or if it was an intended component, the silver inks of the original codex were compared with four reference inks. These inks contained different amounts of copper in the form of copper(I)oxide (copper hair, Cu_2O) or copper(II) acetate (verdigris, $Cu(CH_3COO)_2$). The direct comparison of the spectra of the reference inks ST1, which contains 4.55 wt% of Cu_2O, and ST6, to which no copper was added during the sample preparation, reveals a clear difference regarding the intensity of the copper K_α-peak (Fig. 12). The spectrum of reference ink ST1 shows a distinctive copper signal, while the low intensity of the copper K_α-signal in the spectrum of ST6 indicates the presence of copper only in traces, presumably due to impurities of the silver used.

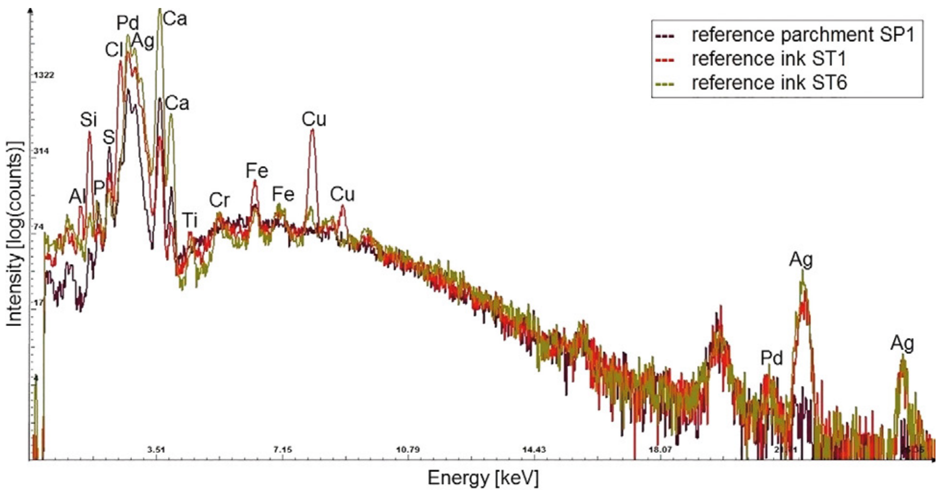

Fig. 12: Comparison of the XRF spectra of two reference inks, ST1 (red: copper containing) and ST6 (green: without added copper), and a spectrum of the corresponding parchment (purple) showing the detected background signal.

42 As described in the chapter on the alteration study, reference ink ST8 was produced by amalgamation of silver chips. Since the resulting silver powder did not stay in a homogenous mixture with the binding medium, the ink could not be applied to the parchment.

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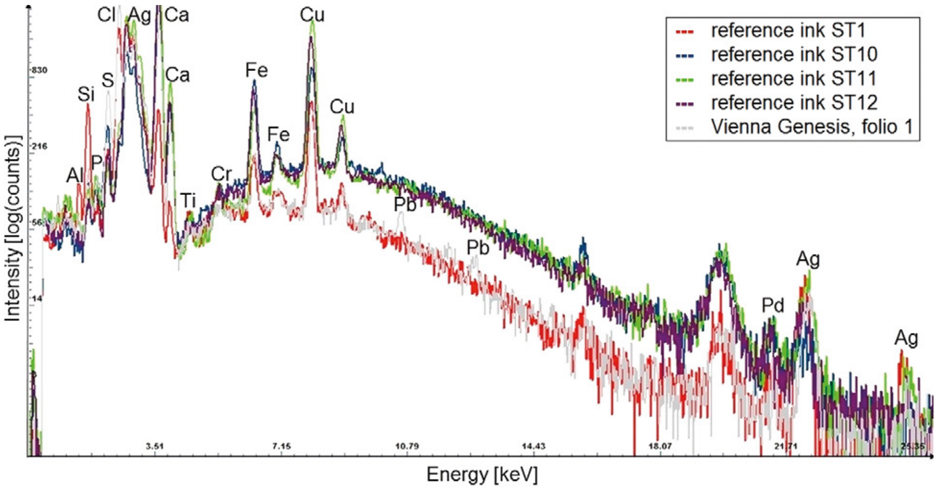

Fig. 13: Comparison of the XRF spectra of four copper containing reference inks: ST1 (red), ST10 (blue), ST11 (green) and ST12 (purple) and a silver ink of Vienna Genesis on folio 1r (MP1_2, grey).

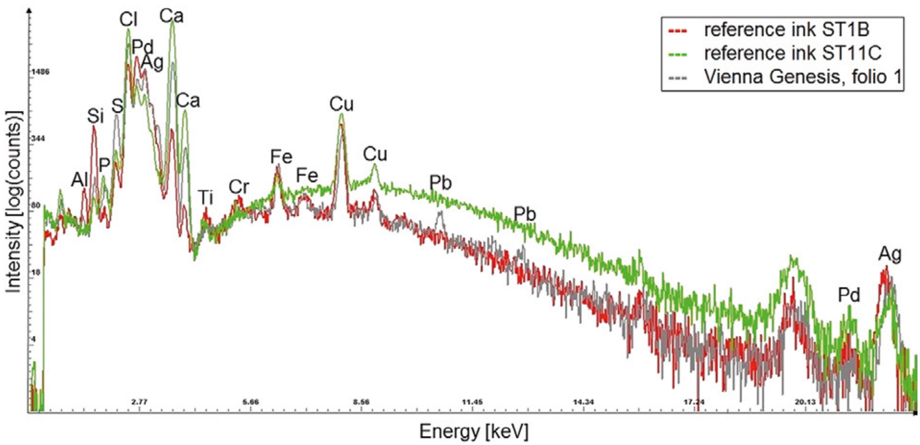

Fig. 14: Comparison of the XRF spectra of two reference inks – ST1B (red), to which NaCl was added during the production process, and ST11C (green), which does not contain any NaCl, but was later prepared with a solution of NaCl (3,5 %) – and a silver ink of Vienna Genesis on folio 1r (MP1_2, grey).

Therefore, a comparison of a spectrum of the silver ink of folio 1 of the Vienna Genesis and the four spectra of the copper-containing reference inks ST1 (4.55 wt% Cu), ST10 (20.70 wt% Cu), ST11 (25.32 wt% Cu) and ST12 (25.32 wt% Cu) is depicted in figure

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13. However, it should be mentioned that parchment with a thickness of approximately 104 µm was used for the production of the samples of reference ink ST1, whereas a different parchment with a thickness of approximately 190 µm was used for the preparation of the other three reference samples (ST10, ST11 and ST12). Compared to this, thicknesses between approximately 100 and 160 µm were measured for the folios of the Vienna Genesis, see the chapter on the parchment. Additionally, the parchments analysed were not completely flat, but had an uneven surface. The impact of the different thicknesses of the parchment matrices as well as the geometric effects due to the uneven surface of the samples on the spectra can be seen in figure 14 and should be factored into the interpretation. Considering these facts, the spectrum of the silver ink of Vienna Genesis shows the greatest congruity with the spectrum of reference ink ST1 (4.55 wt% Cu).

The intensive chlorine signals in the spectra of the Vienna Genesis, which were attributed to the corrosion product silver chloride (AgCl), led to the question of whether the inks used contained chlorine themselves or if the inorganic compound resulted from environmental influences. Therefore, sodium chloride was added to one reference ink (ST1) during the production process of the ink in accordance to a historic recipe, in order to imitate an internal source of chlorine. Furthermore, additional samples of each reference ink were produced and moistened with a solution of sodium chloride (3.5 wt%) in the course of the ageing study, in order to reproduce the impact of an external (environmental) source.

The comparison of the spectra of the sodium chloride containing reference ink ST1_B, reference ink ST11_C, which was moistened with a solution of sodium chloride, and the silver ink of folio 1 of the Vienna Genesis is shown in figure 14. All three spectra reveal intensive chlorine K_{α}-signals, without significant variations of the peak intensities.

Considering the fact that an external source of chlorine, for example in the form of air pollutants, would not have only had impact on the silver ink, but on the parchment as well, the spectra of the related parchments of sample ST1_B, ST11_C and folio 1 of the Vienna Genesis are compared in figure 15. While intensive chlorine signals are present in the spectra of reference sample ST11_C and of folio 1, only a peak of low intensity can be seen in the spectrum of reference sample ST1_B. Due to these observations, we presume that the intensive chlorine peak in the spectra of the inks of Vienna Genesis results at least partially from an environmental chlorine source. Nevertheless, as can be seen from figure 10, the chlorine peak in the ink is much more intense than in the parchment. Therefore, an additional internal origin, or an accumulation of the corrosion product in the ink might both be possible.

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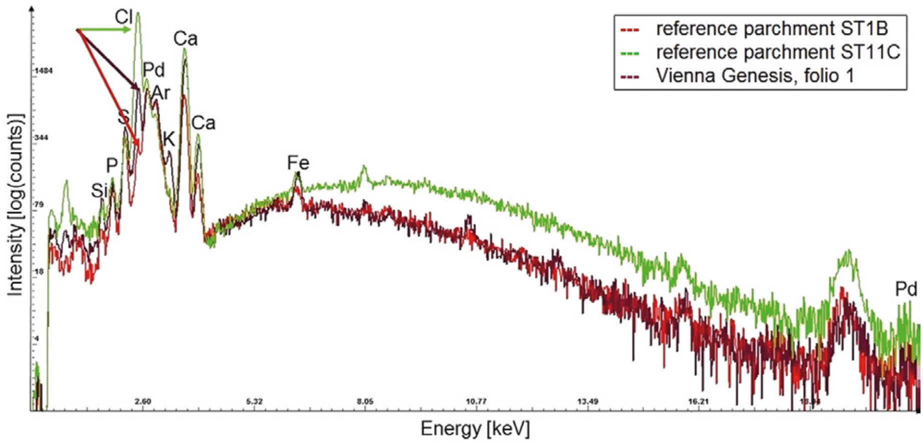

Fig. 15: Comparison of the XRF spectra of measuring points on the parchments belonging to the reference inks ST1_B (red) and ST11_C (green) and the spectrum of the parchment of folio 1 (MP1_3, purple).

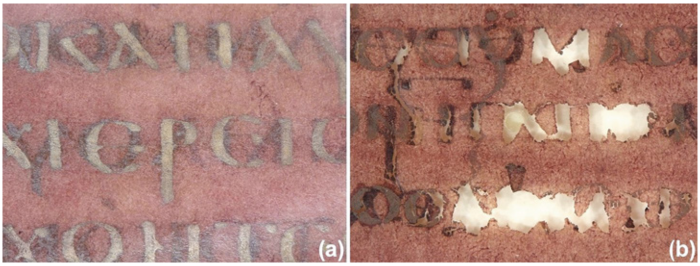

Fig. 16: Detail of the silver ink and the parchment of (a) the Codex Purpureus Petropolitanus and (b) the Vienna Genesis.

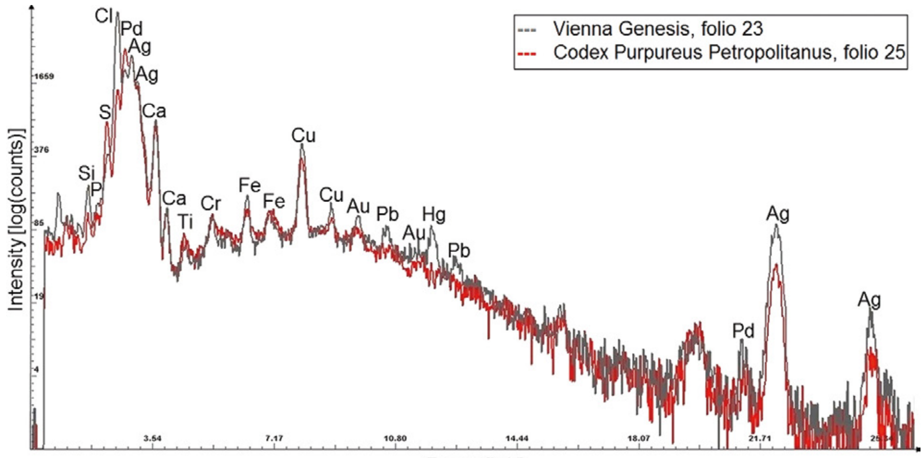

Fig. 17: Comparison of the XRF spectra of silver ink of the Vienna Genesis on folio 23v (MP23_8, grey) and silver ink of Codex Purpureus Petropolitanus on folio 25 (MP25_1, red).

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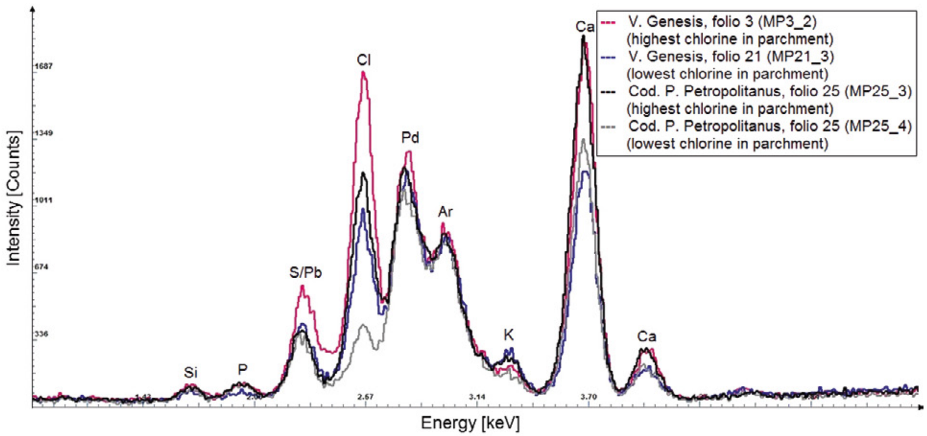

Fig. 18: Comparison of the XRF spectra of measuring points on the parchment of the Vienna Genesis on folio 3 (purple), on folio 21 (blue) and of Codex Purpureus Petropolitanus on two points on folio 25 (grey and black).

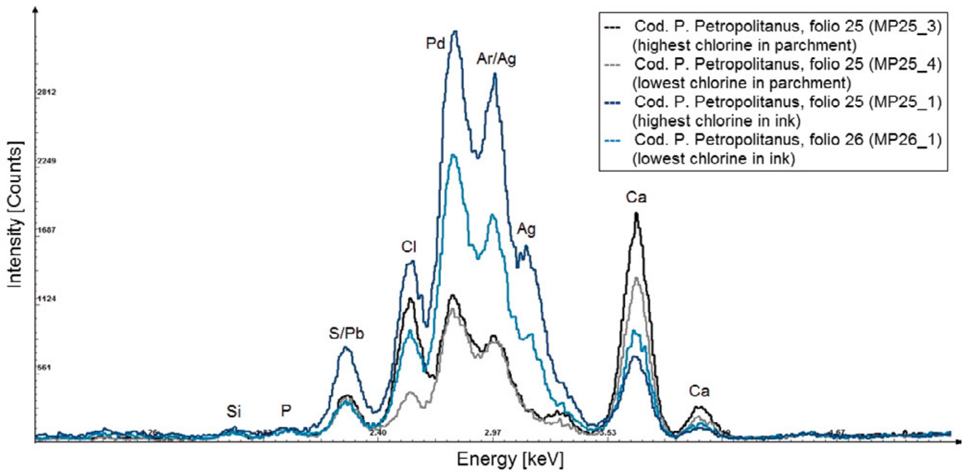

Fig. 19: Comparison of the XRF spectra of measuring points on silver ink on folio 25 (dark blue) and on folio 26 (light blue) as well as on the parchment on folio 25 (grey and black) of Codex Purpureus Petropolitanus.

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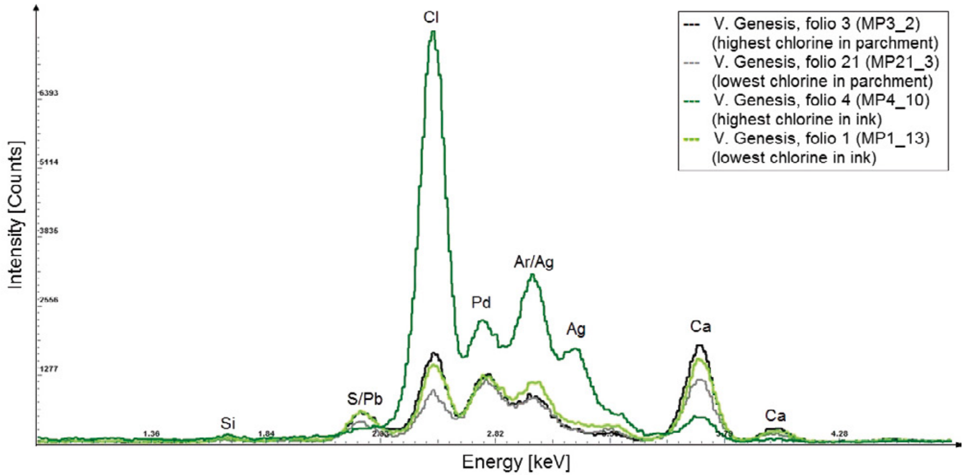

Fig. 20: Comparison of the XRF spectra of measuring points on silver ink on folio 1 (light green) and on folio 4 (dark green) as well as on the parchment on folio 3 (black) and on folio 21 (grey).

The silver ink on the two folios of the Codex Purpureus Petropolitanus[43] (6th century), preserved at the Austrian National Library, was used for comparison (Fig. 16). The ink of the Codex Purpureus Petropolitanus still has a silver colour and a metallic gloss and has caused less damage to the parchment carrier. The XRF spectra of the silver inks of both codices reveal almost identical inorganic components: both spectra show intensive signals of the elements silver, copper and chlorine, the chlorine K_α-peak being more intensive in the case of the Vienna Genesis (Fig. 17). Additionally, chromium and gold are present in traces in both spectra, while mercury is only a trace component of the silver ink of Vienna Genesis. Due to the accordance of the detected elements as well as the almost identical ratio of the peak intensities of the copper and silver K_α-peaks it is presumed that comparable silver inks were used for the two codices. Nevertheless, regarding the question of a deliberate addition of a chlorine containing component during the production process of the silver ink used for the Vienna Genesis, the comparison of the parchments of the Vienna Genesis and of the Codex Purpureus Petropolitanus seems to be interesting. As shown in figure 18, the spectra of the parchments of both codices are very analogous, especially considering the elements in the lower energy region (Si–Ca). Additionally, the intensity of the chlorine peak of the ink in the Codex Purpureus Petropolitanus (Fig. 19) is quite comparable to the intensity of chlorine in the parchment. In contrast, considering the Vienna Genesis, the chlorine signal has a much

43 Codex theologicus graecus 31, folios 25–26.

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higher intensity in the ink than in the parchment (Fig. 20). As a possible reason for the worse condition of the silver ink on the Vienna Genesis, two explanations may be considered:

Firstly, the scribes might have used a recipe containing a chlorine component on the Vienna Genesis. In the preparation of silver, sodium chloride could have been added as a grinding aid, see chapter on the alteration study. Secondly, the Vienna Genesis was probably exposed to a chlorine containing atmosphere (e. g. the Mediterranean Sea). Chlorine is expected to be much more concentrated in the ink containing silver, leading to the formation of the previously mentioned corrosion product silver chloride (AgCl).

X-ray diffraction (XRD) experiments

Micro-samples were taken from the silver ink of the Vienna Genesis to further investigate the corrosion products. The analysis of the silver corrosion phases was performed by micro-X-ray diffraction (μ-XRD), i. e. with beam diameters of about 100–300 μm in contrast to the beam sizes in the mm-range for conventional X-ray diffraction techniques[44]. For the investigation a Malvern/PANalytical B. V. powder diffractometer EMPYREAN in θ-θ-geometry was used together with a 2-dimensional GaliPIX photon detector.

A focusing reflection mirror, mounted in the primary beam, provided a monochromatic X-ray beam of a copper anode at the sample position with a wavelength of 0.15405 and 0.15443 nm, $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$, respectively. The energy of the X-ray beam allowed a penetration depth in the range of a few 10 μm, dependent on the material under investigation and the incident X-ray beam angle. Hence, the phase analysis was restricted to the near surface region in contrast to the bulk analysis by e. g. neutron diffraction methods with penetration depths about one order of magnitude higher. A 300 μm slit in horizontal direction ensured a small beam on the sample position (Fig. 21). Thus, in principle a locally restricted phase analysis on the sample is possible. The xyz-table of the instrument allowed a scan range of +/- 28 mm in two directions, parallel to the sample surface, and 20 mm perpendicular to the sample surface to cover the different measured positions on the samples without remounting and re-adjusting of the whole sample set-up. Technically the entire parchment folios could be screened by scanning the μm-beam parallel to the surface in a nondestructive way. Since the Vienna Genesis could not leave the Austrian National Library, micro-samples were taken by scraping the surface of inked areas with a scalpel. Therefore, only a very restricted number of original samples were at hand for the analysis of the crystallographic phases.

44 The analysis was carried out by Klaudia Hradil and her team at the X-ray centre of the Technical University Vienna.

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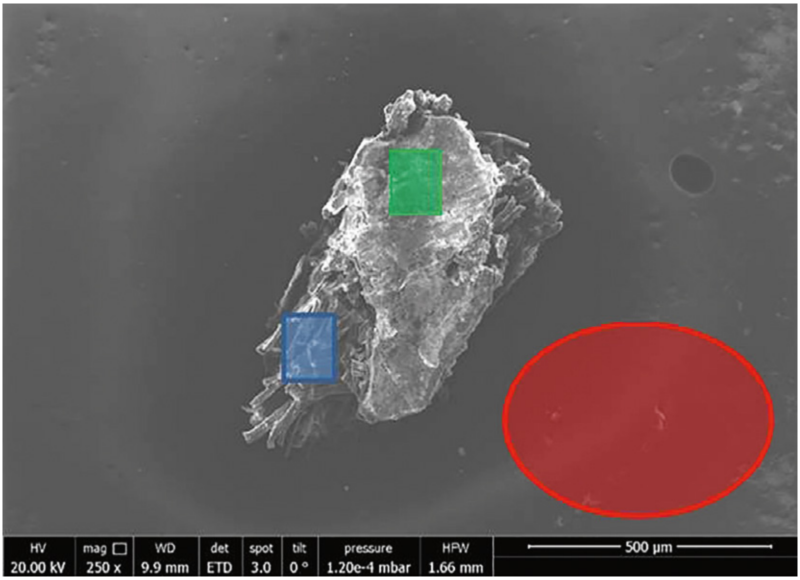

Fig. 21: Scanning electron microscope image of sample T1 from the Vienna Genesis. The red ellipse represents the size of the µm–beam, the blue and green rectangles the areas of mainly parchment (blue) and ink/corrosion (green).

The analysis of crystalline phases by X-rays as a probe is based on the physical principle of the diffraction of individual electromagnetic waves, which arises by the scattering process at the individual electrons within atoms during the interaction of the sample with the X-ray radiation. The X-ray wavelengths used for these types of experiments are within the range of $0.05 < \lambda < 0.3$ nm and thereby correspond to the range of inter-atomic distances in crystals. Together with a strict long-range order of atoms present in the crystallites, i. e. periodicity, the latter is subject to the observation of a diffraction spot on a detector. The diffraction angle yields the information of the lattice parameters and bond lengths based on the lattice plane distances. The intensity implies the amplitude of the resulting wave after the diffraction at the atomic arrangement and therefore contains the information on the atomic type and position within the arrangement. Both parameters are structure phase intrinsic and can be considered as a fingerprint for a phase present within a sample[45].

The qualitative analysis of the crystallographic phases was done by comparison of the observed intensity and positions of detected reflections to either crystalline phases in the data base or to theoretical positions from structure modelling using the PDF-4+ data-

45 Bragg and Bragg, 1913, pp. 428–438.

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base[46]. The quantitative amounts of the phases were analyzed by fitting the diffraction pattern using the Rietveld method based on the crystallographic structures within the PANalytical B. V. HighScorePlus program[47].

For the analysis a main issue arose due to the minute size of the micro-samples, resulting in a highly-restricted number of crystallites illuminated during the experiment with X-rays, and the analysis is, therefore, influenced by a reduced orientation distribution of crystallites. Consequently, the relative intensity distribution within the diffraction diagram can be changed and the database search of fitted phases can be considerably hampered. In figure 21 a scanning electron microscope (SEM) picture of a typical sample from the Vienna Genesis is presented, which was used for the μ-X-ray diffraction (μ-XRD) phase analysis. The red ellipse indicates the X-ray beam size given by the experimental method: due to the sample extraction by chipping a miniscule fragment from the ink on parchment, it is composed from ink/corrosion product combined with tiny parts of the parchment. This is consistent with the XRF analysis where the bluish marked region shows mainly the elements Ca, K, Si, Al and O (parchment) whereas the greenish marked area displays the main elements Ag and Cl (ink area).

In the best case, the standard phase analysis by X-ray diffraction methods uses samples typically in the mm^2 range with randomly distributed crystallites. This guarantees a statistically balanced orientation distribution of the crystallites present, resulting in an optimal quality of the diffraction pattern, allowing direct comparison with the theoretical diffraction patterns within the database.

Typical diffraction patterns are presented in Fig. 22 (sample T1 from folio 4, page 8) and Fig. 23 (sample T9 from folio 18, page 35) taken of the manuscript. Table 1 presents the results for the crystalline phase analysis on the Vienna Genesis samples.

46 Soorya et al., 2002, pp. 333–337.
47 Degen et al., 2014, pp. 13–18.

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Table 1: Phase analysis of the diffraction patterns of the investigated samples of the Vienna Genesis; the table contains the crystalline phases with the corresponding PDF-4+ data base number, the mineral names and the quantitative amount of the crystallographic phases.

sample # V.G.	data base (PDF-4+) #	Phase	mineral name	Amount wt.%
T1: folio 4, page 8				
	04-007-8790	Ag	Silver	Only qualitative analysis possible due to sample amount
	01-071-5209	AgCl	Chlorargyrite	
	00-001-0856	AgNO3	Silver Nitrate	
T7: folio 8, page 15				
	04-007-8790	Ag	Silver	Only qualitative analysis possible due to sample amount
	01-071-5209	AgCl	Chlorargyrite	
T8: folio 13, page 25				
	04-007-8790	Ag	Silver	37
	01-083-3289	CaCO3	Calcit	18
	01-071-5209	AgCl	Chlorargyrite	45
T9: folio 18, page 35				
	04-007-8790	Ag	Silver	23
	01-071-5209	AgCl	Chlorargyrite	76
	04-005-4923	Ag2O	Silver(I)Oxide	1
T10: folio 20, page 40				
	04-007-8790	Ag	Silver	70
	01-071-5209	AgCl	Chlorargyrite	30
T11: folio 25, page 50				
	04-007-8790	Ag	Silver	Only qualitative analysis possible due to sample amount
	01-071-5209	AgCl	Chlorargyrite	

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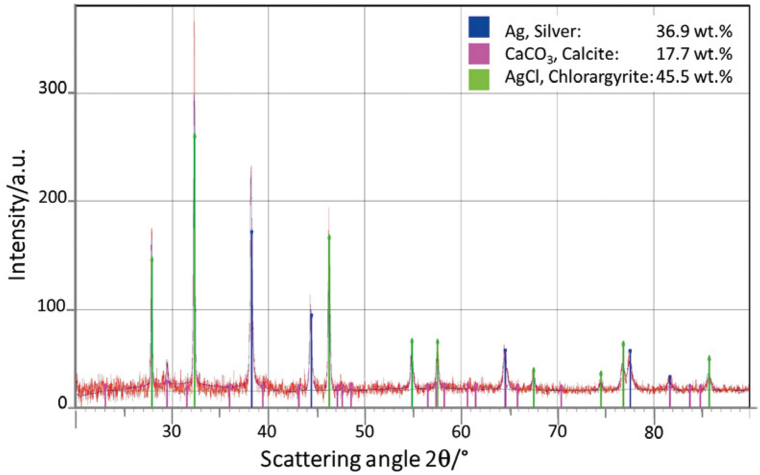

Fig. 22: Diffraction diagram of the sample T1 from the Vienna Genesis.

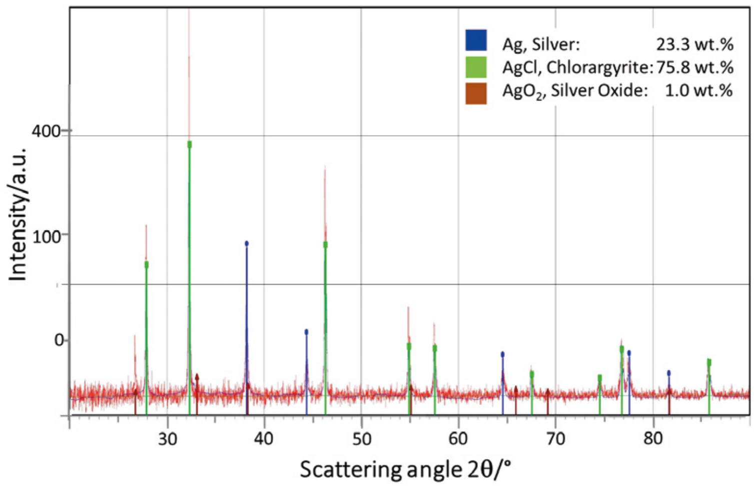

Fig. 23: Diffraction diagram of the sample T9 from the Vienna Genesis.

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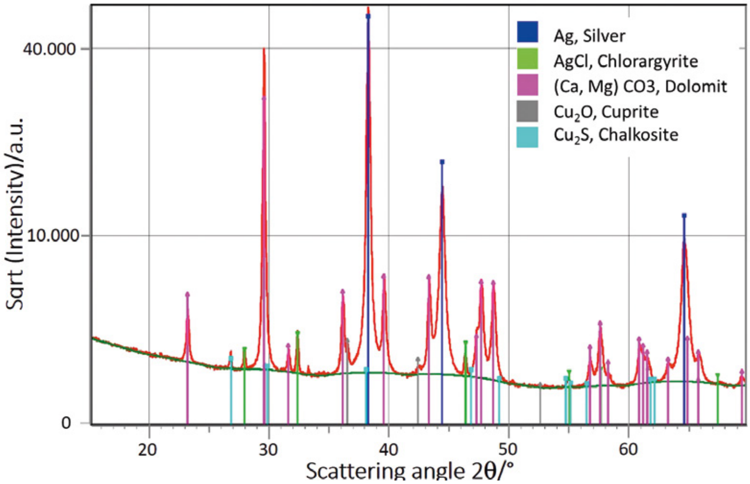

Fig. 24: Diffraction diagram of the sample from reference ink ST1.

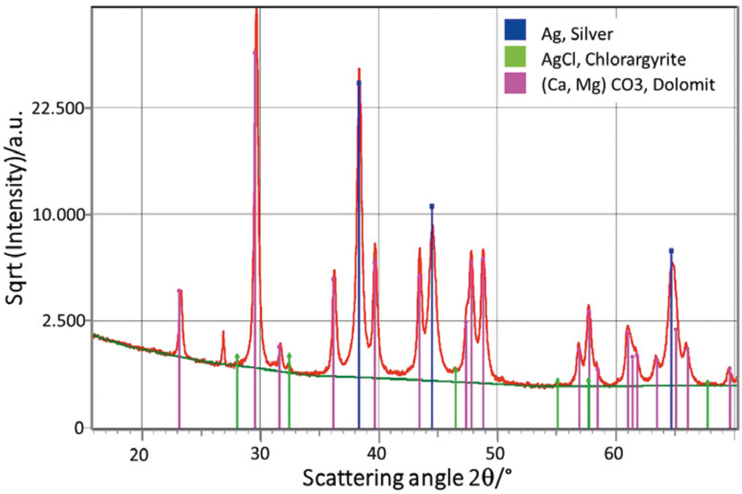

Fig. 25: Diffraction diagram of the sample from reference ink ST2.

Besides the main crystalline phase silver dedicated to the ink itself, various corrosion products, i. e. silver chloride (AgCl; chlorargyrite), silver oxide (Ag_2O) and silver nitrate ($AgNO_3$) can be detected. The amounts vary considerably. Since the sampling for the

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XRD analysis was by chipping, the calcite can be assigned most likely to the parchment. The main corrosion product of the ink is silver chloride consistent also with the XRF analysis of the chemical elements. No crystalline copper compounds were detected on the original Vienna Genesis samples by XRD.

A selection of reference silver inks, unaged and artificially aged, were analysed with the μ-X-ray diffraction phase analysis. The analysis of samples from the reference inks ST1 and ST2 are illustrated in figure 24 and 25, respectively. Besides the pure silver phase (ST1, ST2) and the hair copper phase used within the ink mixture for ST1, we found a considerable amount of calcite and/or dolomite phase, which also explains the high calcium content within the XRF analysis. It can be assigned most likely to the sample preparation procedures or the treatment of the parchment, for example grinding of silver in a mortar or preparing the animal's skin with lime. We can find a tiny amount of a corrosion product for both ink samples, i. e. silver chloride (AgCl; chlorargyrite) even in the unaged and untreated sample. The aging procedures and the different treatments yielded additional corrosion products as silver oxide (Ag_2O) and silver chlorate ($AgClO_3$). Their relative amounts vary considerably in the different samples. Based on presence of chlorargyrite as the main corrosion product and the assumption of a contact with seawater for the parchment, in-situ ageing experiments within a reaction chamber using seawater aerosols and temperatures up to 300 °C were performed during the XRD measurements to follow the phase development during these treatments. The details of the analysis of the aged reference inks and the in-situ investigations are discussed in a further publication[48].

Analysis of the silver ink with SEM/EDX

Energy dispersive X-ray analysis in the scanning electron microscope (SEM/EDX)[49] was employed for additional characterisation of the silver ink. Micro-samples of silver ink from Vienna Genesis and the reference ink ST1 from the alteration study were investigated by SEM/EDX. The samples are listed in Table 2 (chronological order as provided for analysis). Samples T2, T5, T6 and T11 were taken by slightly scratching the surface of inked areas on the Vienna Genesis with a scalpel. Sample T17 was taken as one cross-section from an inked area on folio 22 with a loss. The samples contain ink and parchment. Sample Pe1 was taken from parchment without ink on the inner edge of folio 22. For comparison, samples were taken from reference ink ST1, unaged and aged. ST1 is a silver ink which contains sodium chloride and copper(1)oxide, see chapter on the alteration study.

48 Hradil et al., to be published.

49 SEM/EDX analysis was carried out by Rudolf Erlach.

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Table 2: Samples for SEM/EDX.

Sample number	Origin	Description
T2 a–c	Vienna Genesis	Silver ink, f4
T5	Vienna Genesis	Silver ink, f4, page 8, line 1 right
T6a, b	Vienna Genesis	Silver ink, f5, page 9, line 4 right
T11	Codex Purpureus Petropolitanus	f25, page 50, last line
T17	Vienna Genesis	f22, page 43, cross-section: parchment with silver ink
Pe1	Vienna Genesis	f22, page 43, parchment without ink from inner edge
P1	Reference ink ST1_B	LA-parchment, purple dyed, silver ink with sodium chloride and copper(1)oxide, polished, aged
P2	Reference ink ST1_B	See above
P3	Reference ink ST1	See above, polished, unaged

All samples were investigated in a FEI Quanta FEG 250 SEM in high vacuum mode (if not specified otherwise). X-ray micro analyses were performed with an EDAX system equipped with an Apollo X SDD detector. The samples were investigated in their state as delivered, no sample preparation was applied. Since in all samples from the Vienna Genesis the surface of the silver ink was contaminated with material consisting mainly of organic matter mixed with mineral particles, only point analyses were performed on spots where the surface of the silver ink appeared to be clean in BSE images.

Results of EDX analyses containing all elements detected from three samples are presented in Table 3 (normalized to 100 wt%, all figures are given in percentage by weight), the element patterns of these samples are representative of all other samples. The EDX results, which are only partly listed in Table 3, show that chlorine is present at each sample position in a percentage ranging from about 1 % to 20 %. Sulfur is present only at about 2/3 of total positions and in half of these positions with a percentage of less than 1 %. Therefore, it seems reasonable to assume that the corrosion of the silver ink is predominantly of chloridic nature.

Table 3: EDX results containing all detected elements for three samples (point analyses), percentage per weight, normalised to 100 wt%.

Pos	C	N	O	Na	Mg	Si	S	Cl	Ag	Ca	Fe	Cu	Au
T2 b 1	7.24	1.00	5.20	1.04		0.86	0.33	7.04	73.84	2.09		0.83	
T2 b 2	8.74	1.44	5.82	1.09		0.30	1.35	4.12	75.07	0.55		0.66	0.64

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Pos	C	N	O	Na	Mg	Si	S	Cl	Ag	Ca	Fe	Cu	Au
T2 b 3	8.37	1.51	4.36	0.50		0.11	0.44	7.76	75.42			0.73	0.81
T2 b 4	17.54		2.74	0.40		0.35	0.14	14.42	63.78	0.38			
T2 b 5	3.52	0.91	1.84	0.64				15.69	77.05	0.35			
T5 1	3.63							9.62	86.75				
T5 2	4.38							8.22	87.40				
T5 3	5.48		2.50				0.24	11.59	80.19				
T5 4	7.40		0.83					12.55	79.23				
T5 5	5.99		4.74			0.54	0.87	10.91	75.56			0.84	
T5 6	6.25	1.46	5.09	0.68		0.97	3.15	5.07	72.53	2.01		1.22	0.94
T5 7	2.28							8.61	89.11				
T5 8	2.76		0.72			0.22		13.04	83.27				
T5 9	2.30		1.07					8.46	88.17				
T5 10	2.26		1.17					9.17	87.40				
T5 11	1.78							6.92	91.30				
T5 12	4.20		0.71				0.31	14.39	80.40				
T5 13	4.88		8.90				0.31	8.77	69.50	7.64			
T5 14	7.11	1.08	4.65			0.48	0.23	9.07	76.87				
T5 15	4.78		2.17					9.41	83.64				
T6 a 1	4.33		1.59			0.92	6.32	5.71	80.61				
T6 a 2	7.01		1.69			0.44	6.54	2.29	80.92	0.52		0.58	
T6 a 3	4.91	0.89	1.65		0.82	0.30	4.58	5.02	79.82	0.31		0.87	0.51
T6 a 4	5.99	1.36	5.08			0.68	7.17	2.19	74.68	1.54		0.71	0.60
T6 a 5	3.61		2.70			0.39	7.62	2.08	80.39	0.97		0.76	1.49
T6 a 6	7.08	1.61	4.18		1.06		5.43	4.94	73.85	0.94			0.50
T6 a 7	3.24		1.12					10.89	84.75				
T6 a 8	7.91		1.93			0.53	5.42	2.95	80.81	0.45			
T6 a 9	5.75		2.42				0.61	11.94	79.28				
T6 a 10	3.99		2.71					10.75	81.86	0.69			
T6 a 11	4.89		2.08			0.36	4.66	6.64	79.26	0.57		0.67	0.45
T6 a 12	4.89	1.28	2.42			0.53	6.41	5.12	77.34	0.84			
T6 a 13	3.76		1.57				0.66	10.97	83.04				
T6 a 14	11.71		2.14	0.25			1.04	20.00	64.65	0.21			
T6 a 15	7.04	1.91	3.33			0.67	7.80	3.50	73.69	1.76			

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To evaluate the composition of an alloy possibly used in the production of the silver ink, the EDX analyses were recalculated excluding all elements that are not potential alloying partners of silver; the corresponding results for all sample positions are listed in Table 4 (normalized to 100 %). The potential alloying partners of silver – copper (Cu) and gold (Au) – are present only in some of the analyses (in 14 of 72 point analyses both Cu and Au, in 9 only Cu, in 7 only Au). All EDX analyses of silver ink up to now are surface analyses on samples whose surfaces are not clean but more or less contaminated by dust and organic matter. It seems likely that the presence of copper and gold might be due to contamination at the location of the respective analysis position. If a silver-copper alloy with low copper content was used for preparing the silver ink, the copper as the less noble metal could have been removed from the alloy by the corrosion process.

Table 4: EDX results recalculated using only potential alloy partners of silver, percentage per weight, normalised to 100 wt%.

Pos	Ag	Cu	Au	Pos	Ag	Cu	Au	Pos	Ag	Cu	Au
T2 a 1	100.00			T5 9	100.00			T6 b 3	100.00		
T2 a 2	100.00			T5 10	100.00			T6 b 4	98.30		1.70
T2 a 3	100.00			T5 11	100.00			T6 b 5	98.28	0.80	0.92
T2 a 4	98.19	0.75	1.07	T5 12	100.00			T6 b 6	98.72	1.28	
T2 a 5	100.00			T5 13	100.00			T6 b 7	97.93	0.88	1.19
T2 a 6	100.00			T5 14	100.00			T6 b 8	100.00		
T2 b 1	98.85	1.15		T5 15	100.00			T6 b 9	100.00		
T2 b 2	99.09	0.91		T6 a 1	100.00			T6 b 10	100.00		
T2 b 3	98.11	0.95	0.94	T6 a 2	99.26	0.74		T11 2	97.82	0.35	1.84
T2 b 4	100.00			T6 a 3	98.26	1.10	0.64	T11 3	100.00		
T2 b 5	100.00			T6 a 4	98.24	0.96	0.80	T11 5	100.00		
T2 c 1	97.70	1.37	0.93	T6 a 5	97.22	0.95	1.84	T11 6	97.40		2.60
T2 c 2	98.16	0.92	0.92	T6 a 6	99.31		0.69	T11 7	100.00		
T2 c 3	98.52	1.48		T6 a 7	100.00			T11 8a	98.63		1.37
T2 c 4	97.77	0.84	1.38	T6 a 8	100.00			T11 8b	100.00		
T2 c 5	100.00			T6 a 9	100.00			T11 8c	96.70		3.30
T5 1	100.00			T6 a 10	100.00			T11 8d	99.01		0.99
T5 2	100.00			T6 a 11	98.55	0.87	0.58	T11 9	100.00		
T5 3	100.00			T6 a 12	100.00			T11 10	100.00		

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Pos	Ag	Cu	Au	Pos	Ag	Cu	Au	Pos	Ag	Cu	Au
T5 4	100.00			T6 a 13	100.00			T11 11	98.46		1.54
T5 5	98.85	1.15		T6 a 14	100.00			T11 12	100.00		
T5 6	97.06	1.66	1.27	T6 a 15	100.00			T11 13	100.00		
T5 7	100.00			T6 b 1	100.0			T11 14	100.00		
T5 8	100.00			T6 b 2	97.47	0.83	1.70	T11 15	100.00		

To check for any differences in composition between the surface layer and the inner layers of the silver ink areas, cross sections were produced of samples T17 (Fig. 26) and T6 a (Fig. 29) from the Vienna Genesis and of samples P1 (Fig. 31) and P3 from the reference silver ink ST1. The polished cross sections were covered with a conductive layer of carbon prior to examination by SEM.

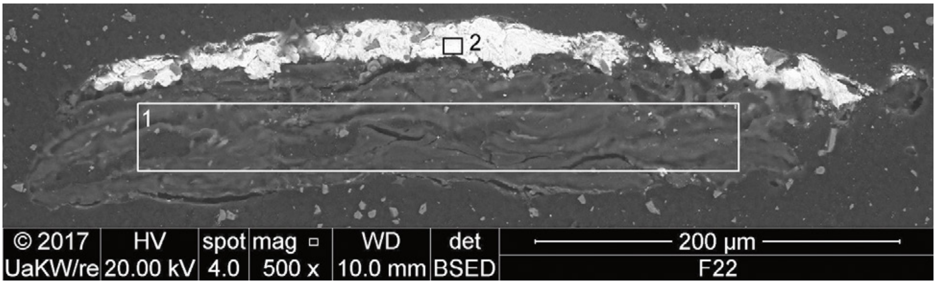

Fig. 26: BSE image, at 500x magnification, of cross section from sample T17 (folio 22, page 43).

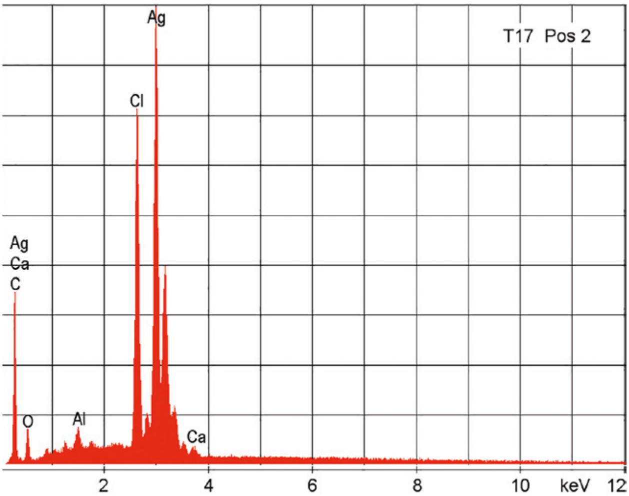

Fig. 27: EDX spectrum of cross section from sample T17 (folio 22), position 2 in fig. 26.

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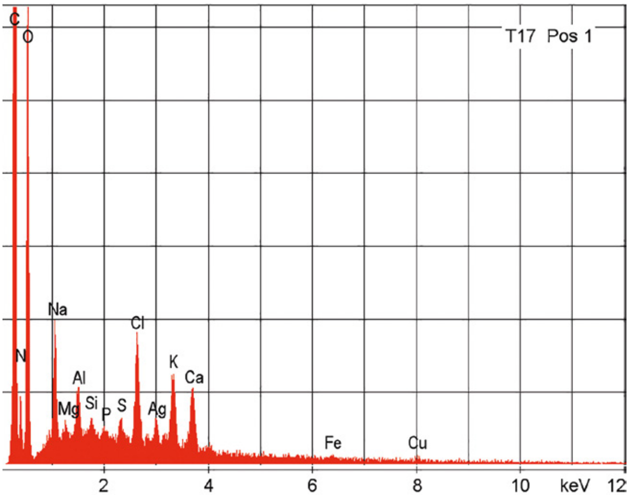

Fig. 28: EDX spectrum of cross section from sample T17 (folio 22), position 1 in fig. 26.

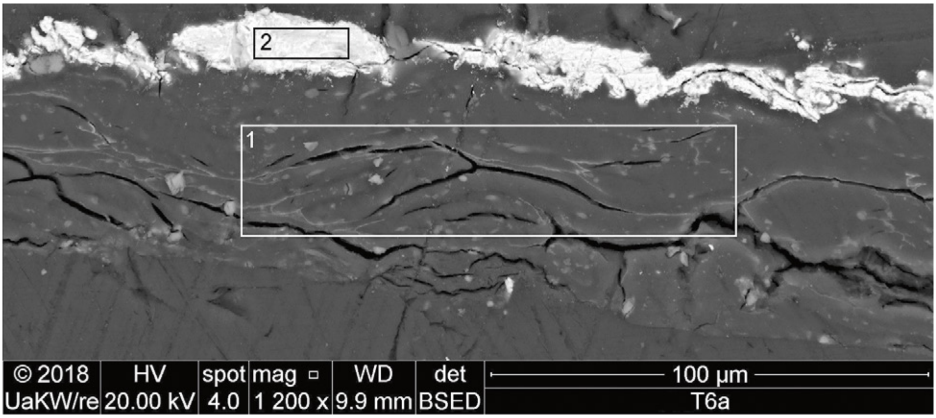

Fig. 29: BSE image, at 1,200x magnification, of cross section from sample T6a (folio 5, page 9).

Sample T17, cross-section of ink and parchment, from folio 22, page 43:
Copper and gold could not be detected in the silver ink area, neither in position 2 (see EDX spectrum in figure 27) nor in other positions (not shown in figure 27) in the silver ink. However, a small amount of copper was detected in the parchment (0.49 wt%, see figure 28).

Sample T6a, ink from folio 5, page 9:
As with sample T17 no copper could be detected in the silver ink layer, but a small amount

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of copper in the parchment (0.57 wt%, EDX spectra are similar to spectra in figures 27 and 28).

Sample Pe1, parchment from folio 22, page 43:
Parchment sample Pe1, which was taken for comparison far off from the areas with silver ink, at the inner edge of folio 22, also showed a small copper peak in the EDX spectrum corresponding to 0.26 wt% copper.

Samples from reference silver ink ST1:
Surface analysis of the silver ink layers on the samples from the reference silver ink ST1 prior to cross sectioning shows that the ink consists of a mix of some silver particles, quite a lot of silicates and a few particles containing copper (Fig. 30 and 32). Cross section of P1 (ink ST1 aged) in figure 31 shows that the ink layer is quite different to that in the samples from the Vienna Genesis (figures 26 and 29) – very thin, with only a few silver particles (bright spots in figure 31) compared to the approximately 10 µm thick silver packages in the Genesis samples. The parchment contains no copper, the particles at the bottom of the parchment are most likely calcium carbonate. Similar results are found for samples P3 (ink ST1 unaged) and P2 (ink ST1 aged).

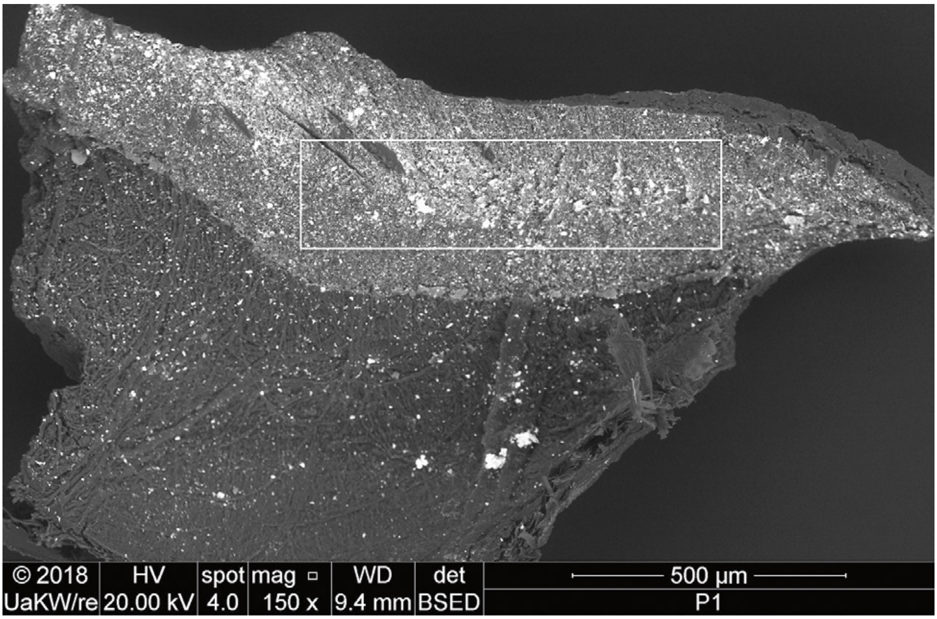

Fig. 30: BSE image, at 150x magnification, of the surface of sample P1, silver ink ST1, parchment with aged silver ink on top.

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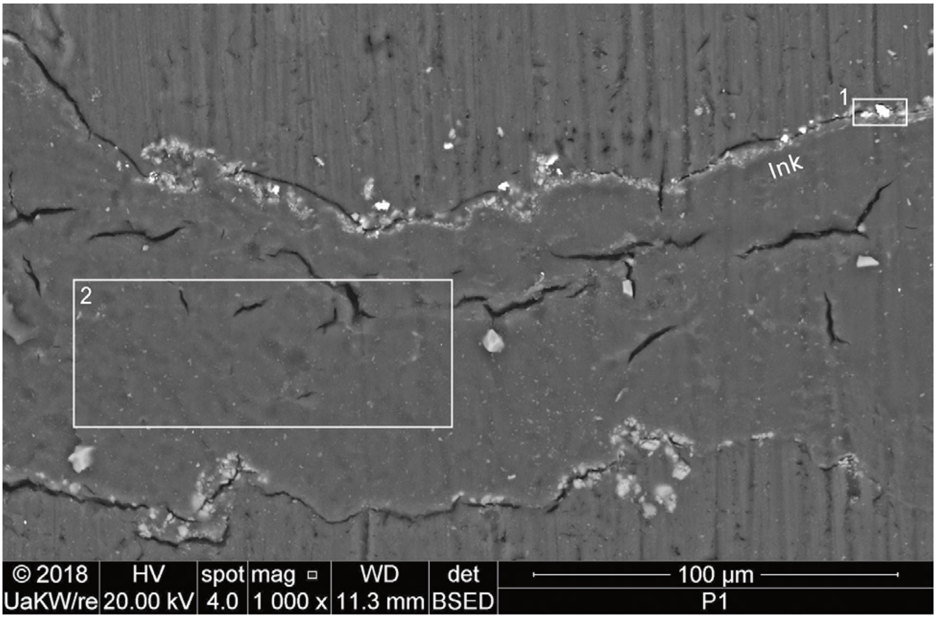

Fig. 31: BSE image, 1,000x magnification, of cross section from sample P1 (aged ink ST1 on parchment).

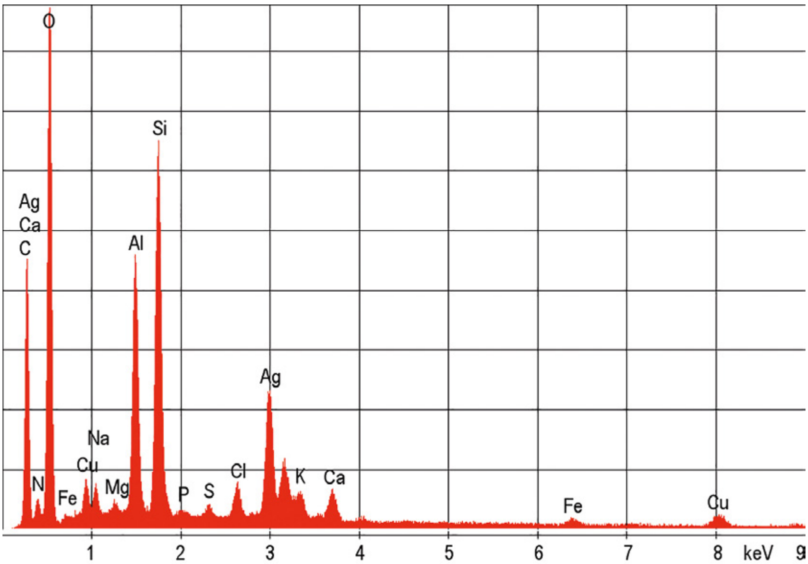

Fig. 32: EDX spectrum of the silver ink ST1 in the rectangle in figure 30.

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The metal used for the production of the silver ink may have been pure silver, at least no contradicting indications were found. If small amounts of copper had been present in the metal originally, this would most likely have been removed due to the corrosion process. No metallic silver has been found in the remnants of the silver ink, silver is always accompanied by chlorine, most likely as silver chloride. The copper detected in the parchment below the inked area in the cross-section of T17 could result from copper compounds in the ink that migrated into the parchment carrier. Studies on copper pigments on paper showed that copper ions migrate into surrounding areas especially under high humidity[50].

Summary and conclusions

The folios of the Vienna Genesis were cut and resized at least once. Measurements of the text blocks and the margins suggest a maximum folio size of 400 x 292.5 mm. XRF analyses revealed that the elemental composition of the silver inks is consistent on all folios of the Vienna Genesis. The presumably two scribes used a similar ink recipe. According to XRF, XRD and SEM/EDX silver is the main component of the ink. Significant copper peaks were detected by XRF on all folios with a constant ratio of silver to copper intensities. The XRF spectrum of reference ink ST1 with a copper content of 4.55 wt% compares well with XRF spectra of the silver ink on the Vienna Genesis. On one cross-section of a micro-sample, low amounts of copper were detected in the parchment by SEM/EDX. The results of XRF, XRD and SEM/EDX confirm the presence of silver chloride as main corrosion product. XRF detected chlorine in the parchment and in the ink with higher intensities in inked areas.

In comparison with reference inks and the ink on two folios of the 6th century Codex Purpureus Petropolitanus, we assume that the scribes of the Vienna Genesis used a silver ink which contained copper. Due to several limitations, XRF analysis does not allow an exact quantification of the concentration of copper in the ink. Besides environmental influences, the corrosion product silver chloride could also originate from the production process of the ink itself, for example the use of sodium chloride as a grinding aid for silver. The enhanced presence of chloride in the parchment could be an additional hint for contact of the manuscript with chlorine containing media, for instance with salty seawater or Mediterranean climate. We assume that the corrosion of the silver ink and the degradation of the parchment of Vienna Genesis are caused by a combination of internal and external factors:

50 Hofmann et al., 2015, p. 175.

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1. The silver ink contained copper and additionally chlorine compounds.
2. The manuscript was exposed to high humidity or even liquid water. External chlorine compounds, which were transported by water or other sources, affected ink and parchment.

In its current aged and altered condition, it is not possible to identify all components of the original ink. Therefore, the deterioration process cannot be completely reconstructed and explained. In the alteration study, the effects of copper and chlorine containing compounds as well as of parchment glue containing acidic acid have been further investigated.

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Alteration study of silver inks on parchment

Sophie Rabitsch, Antonia Malissa, Katharina Uhlir, Martina Griesser, Christa Hofmann

Introduction

Since the corrosion of the silver ink of the Vienna Genesis is very pronounced and has caused severe damage to the parchment, a study of the accelerated ageing of silver inks on parchment was carried out in the first year of the project. The aim of the study was to achieve a better understanding of different factors that probably contributed to the present condition of the ink and the parchment. Conservation methods and storage conditions should be chosen based on the conclusions of the study. Accordingly, the impact of different organic and inorganic components, like sodium chloride (NaCl, salt), sodium hydrogen carbonate ($NaHCO_3$, soda), or potassium nitrate (KNO_3, saltpetre), as well as the metallic component copper (Cu) were tested. Additionally, the influence of environmental conditions in the earlier history of the object, like salty sea air, and the contribution of conservation treatments with parchment glue containing acetic acid in the 1970s were investigated. Studies by Verena Flamm[1] indicate deformation of parchment due to the application of parchment glue that contains acetic acid. The visual appearance of the samples was evaluated before and after accelerated ageing under the microscope. The reference inks were analysed with micro-X-ray fluorescence spectroscopy with energy dispersive detection (µ-XRF), the fibre morphologies of the parchments under the microscope and the shrinkage temperatures of the parchments with the Micro Hot Table method (MHT method), respectively.

Literature and categories of silver inks

Important art technological treatises contain a number of historical recipes for silver inks. The alteration study described in this chapter is based on sources from Late Antiquity to the 13th century. The recipes are taken from Vera Trost's book on gold and silver inks[2], which investigated Antique and medieval ink recipes using art technological studies. Many written sources are based on each other, great parts are correlating and therefore, several

1 Flamm 1994, pp. 56–65.
2 Trost, 1991.

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recipes are contained in different treatises. For the production of the reference inks for this study recipes were followed which have their origin in the Leiden papyrus X, the Lucca manuscript, the Mappae Clavicula and Heraclius' treatises. Among these four manuscripts the eldest is the Leiden papyrus X, which was found in the course of excavations in Thebes in 1828, being dated to the end of the 3rd or the beginning of the 4th century A. D. Many of its recipes are included in the Lucca manuscript, which has its origins in the 7th and 8th century in Lucca. The Mappae Clavicula, which is dated to the 12th century and was presumably written in Great Britain or Normandy, contains parts of both manuscripts. The Heraclius treatises, which consist of a collection of recipes named Libri Eraclii de coloribus et artibus Romanorum, are closely related to the Mappae Clavicula. The eldest known fragmentary version is dated to the 11th century, while the most completely preserved one is from the 13th century[3].

While metallic silver is part of most silver ink recipes in these four treatises, a great variety of other organic and inorganic as well as metallic additives and different kinds of binding media are mentioned in the texts. Depending on whether an ink contained only an organic binder next to silver or if other additional organic, inorganic or metallic components were added, Trost divided silver inks into three categories: first, there is the group of pure silver inks, which contain only a transparent or slightly coloured binding medium next to powdered silver; second, there are silver inks with non-metallic or metallic additives, which contain components like saffron, orpiment, mercury, copper(I)oxide and copper(II)acetate. Finally, there is a third group of silver inks that do not contain any silver at all, but different metallic, animal, herbal or mineral additives that imitate a metallic gloss[4].

Reference samples of silver inks on parchment

In order to study the influence of a great diversity of components, the severely damaged silver ink of the Vienna Genesis was compared with 14 different reference inks, which were prepared in the course of the entire alteration study. While the preparation and artificial ageing of the reference inks ST1–ST9 were covered by a first sub study, the reference inks ST10–ST14 were produced and aged in the course of a second sub study during the second year of the project. The 14 reference inks included pure silver inks as well as silver inks with metallic and non-metallic additives.

The selection of recipes used for the first and second sub study was based on analyses of the silver ink of the Vienna Genesis. The recipes chosen for sub study 1 were based on

3 Trost, 1991, pp. 36–48.
4 Trost, 1991, pp. 33–35.

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preliminary investigations of micro samples of the original silver ink with energy dispersive X-ray analysis in the scanning electron microscope (SEM/EDX) performed by Rudolf Erlach and with micro-X-ray diffraction (µ-XRD) performed by Klaudia Hradil, see chapter on silver inks. Micro samples were taken by slightly scraping the surface of the ink with a scalpel. According to the results of SEM/EDX, the metal used for production of the silver ink may have been pure silver. If small amounts of copper had been present in the metal originally, this would most likely have been removed due to the corrosion process. The detected silver is always accompanied by chlorine, a clear hint for the presence of silver chloride. µ-XRD detected the main crystalline phase silver and various corrosion products, i. e. silver chloride (AgCl; chlorargyrite), silver oxide (Ag_2O) and silver nitrate ($AgNO_3$). The results of these measurements indicated that the ink analysed is a pure silver ink with silver chloride as the main corrosion product. Due to these preliminary results, recipes for the production of pure silver inks as well as for silver inks with metallic and non-metallic additives were chosen for the first sub study. The selection of recipes used for sub study 2 was based on the results of further analysis of the Vienna Genesis' silver ink using µ-XRF in the second year of the project, see chapter on silver inks. Representative measurement points were chosen on different folios of the manuscript. The XRF spectra generated indicated a more significant amount of copper than it was initially presumed due to preliminary analyses, with copper being more likely a minor component of the ink. Additionally, an almost constant ratio between silver and copper could be observed for the silver ink of the entire codex. Whereas sub study 1 mainly focused on the corrosive impact of different inorganic and organic ingredients, the effect of copper was investigated within the second sub study. An overview of the reference inks and the exact name of the recipes according to Trost as well as a summary of the categories of silver inks and the additives used are given in Table 1.

Table 1: Overview of the reference inks, the exact name of the recipe templates according to Trost, a summary of the different categories and the used additives.

Reference ink	Recipe	Group	Additives
ST1	CL N 3–13	Silver ink with additional components	Sodium chloride (NaCl), copper(I)oxide (Cu_2O, copper hair)
ST2	MC LXXXXII d	Pure silver ink	-

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ST3	MC CCXLVIII	Silver ink with additional components	Sodium hydrogen carbonate ($NaHCO_3$, soda)
ST4	MC CCXLVIII	Silver ink with additional components	Potassium nitrate (KNO_3, saltpetre)
ST5	H III, XLIII	Pure silver ink	-
ST6	CL M 24–29	Silver ink with additional components	Sodium hydrogen carbonate ($NaHCO_3$, soda)
ST7	LP X 8ª /3–4	Pure silver ink	-
ST8	CL α 11–20	Pure silver ink	-
ST9	H I, VII	Pure silver ink	-
ST10	CL δ 29–34	Silver ink with additional components	Copper(II)acetate ($CuAc_2$, Verdigris)
ST11	MC L a (1. paragraph)	Silver ink with additional components	Copper(II)acetate ($CuAc_2$, Verdigris)
ST12	MC L a (1. paragraph)	Silver ink with additional components	Copper(II)acetate ($CuAc_2$, Verdigris)
ST13	MC CCXLVIII	Pure silver ink	-
ST14	MC CCXLVIII	Silver ink with additional components	Potassium nitrate (KNO_3, saltpetre)

Preparation of silver inks

The production of all reference inks and the further preparation of the reference samples followed four major steps[5] (Fig. 1):

1. production of powdery silver
2. addition of further components
3. addition of a liquid binder
4. application of the inks on the parchment samples and burnishing of the dried ink with an agate polishing stone

5 The experiments were carried out by Sophie Rabitsch and Antonia Malissa in the Institute of Conservation of the Austrian National Library and the Conservation Science Department of the Kunsthistorisches Museum Vienna from November 2016 until January 2017 (sub study 1) and in April 2017 (sub study 2).

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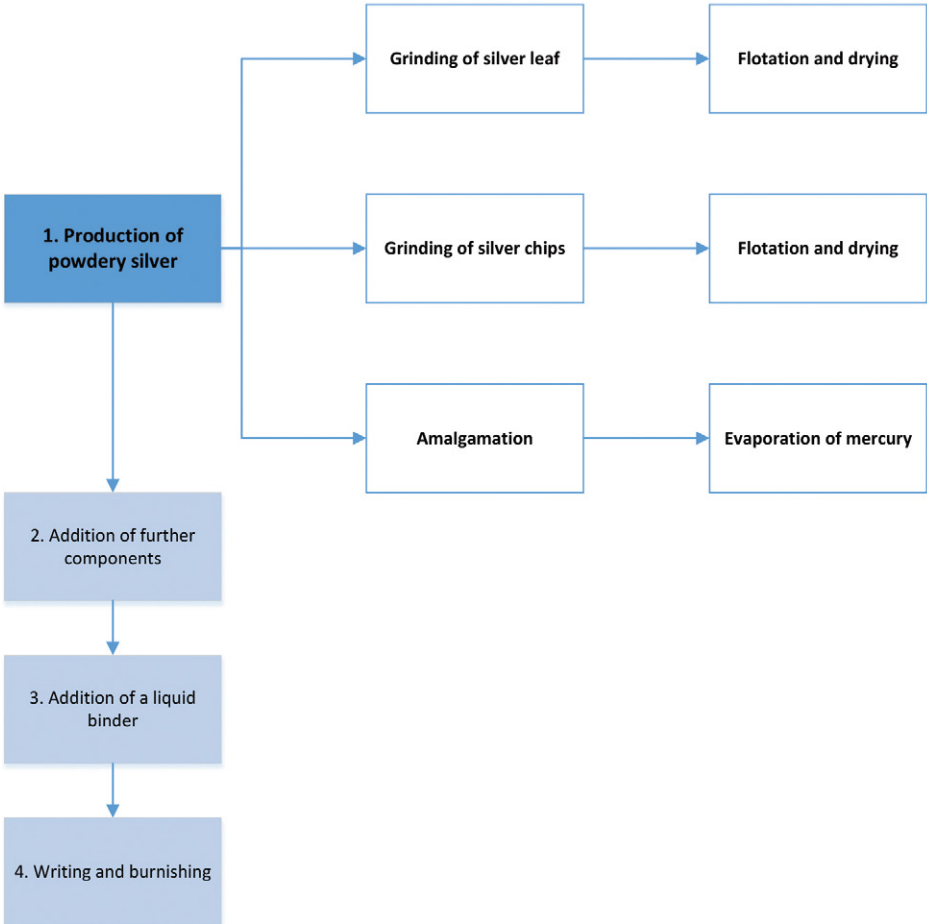

Fig. 1: Scheme of the preparation process of the reference samples.

According to the historical recipes, two forms of silver were used for the experiments:

1. Silver leaf[6] that is used as silvering coating in decorative arts. The leaves measure about 0.5 µm in thickness. They are produced by mechanically flattening silver foils.
2. Pieces of rolled silver[7] (silver foil of 0.21 mm in thickness) were filed with a small iron file to obtain fine silver chips.

As illustrated in the workflow (Fig. 1), the silver leaves or silver chips were further processed to powdered silver by three different methods:

6 Obtained from Alois Wamprechtsamer GmbH, Blattgoldschlägerei, Vienna.
7 Obtained from Advent Research Materials Ltd.

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1. Silver leaves were ground by hand in a porcelain bowl or with a pestel in a mortar. A grinding aid (e. g. sodium chloride, honey, gum arabic, glue) helped to finely disperse the silver.
2. Silver chips were ground with a pestel in a mortar with the addition of a grinding aid (as above). Coarse silver chips cannot be ground by hand in a porcelain bowl.
3. Silver leaves or silver chips could be used for the third method employing amalgamation. The silver was ground in a mortar together with mercury while being heated.

The first possibility to achieve silver powder is by the mechanical grinding of silver leaves by hand or with a suitable tool like a mortar and a pestle. The use of a grinding aid is recommended in the literature: grainy additives like salt help to achieve a homogenous powder[8]. Sodium chloride was detected on different silver inks by analysis[9]. During the process of grinding with sodium chloride, silver can easily react with it forming silver chloride. Viscous materials like honey, gum or glue are mentioned in the Late Antique Greek Leiden and Stockholm papyri for helping to disperse the metal powder[10]. Additionally, a small amount of water can be added as a lubricant[11].

Mechanical grinding by hand (using the index finger) was executed in a large, smooth porcelain bowl without any inside edges, using highly viscous gum arabic as a grinding aid. The technique, still used in oriental book illumination, was demonstrated by Cahit Karadana[12]. After the silver leaves were mixed with gum arabic, they were ground with circular movements starting from the bottom of the bowl for up to two hours. During this process the mixture of gum arabic and silver was thoroughly dispersed to the rim of the bowl. The process was continued while single drops of water were added from time to time, until no coarse particles were visible (Fig. 2). Trost cites recipes calling for salt, red wine and vinegar to be used as grinding aids.

The second way to obtain silver powder is by grinding silver chips in a mortar. A marble mortar and pestle were used. Similar to the first method, coarse grinding aids like salt were added. Water, red wine or vinegar were added dropwise as lubricants, depending on the recipe (Fig. 3). The grinding process took between 10 and 20 minutes.

In the case of both methods, grinding aids as well as larger particles and possible impurities had to be removed after the refining process, by flotation, the thorough washing of the silver powder. Therefore, the silver powder was transferred into a porcelain bowl, if it had not already been ground in one, then finely dispersed in a great volume of water (Fig.

8 Oltrogge, 2011, p. 66.
9 Schreiner and Oltrogge, 2011, p. 107.
10 Oltrogge, 2011, p. 66.
11 Schreiner and Oltrogge, 2011, p. 107.
12 Cahit Karadana, book conservator at the Institute for Conservation, Austrian National Library.

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Fig. 2: Grinding silver leaves by hand together with gum arabic in a porcelain bowl, until the silver is finely dispersed.

Fig. 3: Grinding silver chips together with vinegar in a mortar.

Fig. 4: Flotation – washing of the sedimented silver in the bowl.

Fig. 5: Drying of the powdered silver in the water bath.

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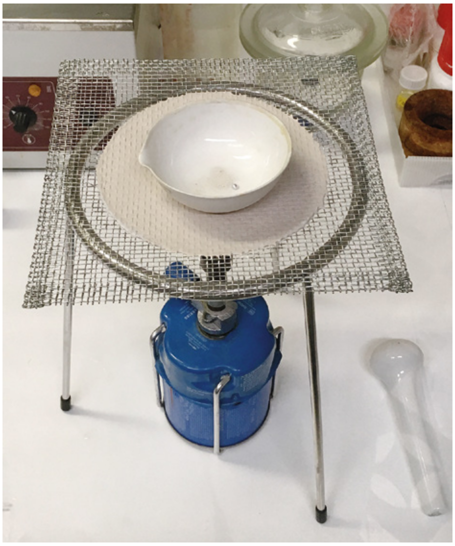

Fig. 6: Formation of an amalgam with the help of the flame of a Bunsen burner.

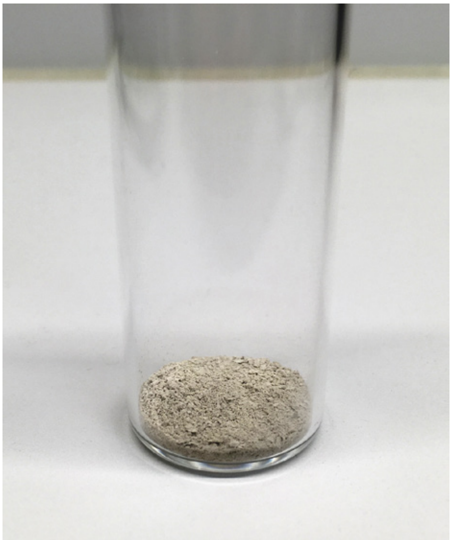

Fig. 7: Silver powder in a small glass bottle.

Fig. 8: Self-prepared bamboo pens, similar to the Late Antique calamus.

4). In order to prevent the silver powder from being contaminated with dust particles, the bowl was covered. As soon as the powder deposited at the bottom of the bowl, which could take up to several hours or even a day, the water was changed by pouring it out quickly, so that the powdery silver sediment remained inside the bowl. This process was repeated up to six times[13]. The final residue was dried in a small porcelain bowl in a water bath, which was heated slowly (Fig. 5).

13 Schreiner and Oltrogge, 2011, p. 107. One could also use a fine cloth as a filter. Those methods work with silver, gold and copper.

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The third process to obtain fine silver powder is by the formation of silver amalgam[14]. Silver leaves or chips are ground with mercury in a porcelain bowl while being slightly heated. When the temperature is raised, mercury evaporates while a fine silver powder remains. In the course of the sample preparation, silver chips were ground with mercury in a porcelain mortar while being heated with a Bunsen burner[15](Fig. 6). After one hour of grinding the silver powder seemed to be fine enough and the silver amalgam was further heated for 30 minutes.

After the refinement of the silver, the required amount of silver powder was transferred into a small glass bottle (Fig. 7) and mixed with the additives and a liquid binder, immediately before the application of the inks on the parchment samples. Different types of parchment were used, which is explained below. Parchment was dyed purple with orchil (obtained from *Roccella tinctoria*) and cut to a sample size of between 2.5 x 2.5 cm and 3 x 3 cm in sub study 1 and 5 x 4 cm in sub study 2[16]. For writing, hand carved bamboo pens[17], replicating the Late Antique calamus, were used, see chapter on the silver ink (Fig. 8). In order to avoid contaminations of the inks by each other, individual pens were used for each ink. Greek letters were written on the purple parchment samples. During the final step of the sample preparation, the silver inks were burnished with an agate polishing stone under low pressure[18].

In the course of the experimental preparation of the reference inks some of the recipes taken from Trost's book had to be modified in order to improve their usability. The ingredients and the qualities of the 14 reference inks are described below.

Sub study 1: ST1–ST9

Reference ink ST1

For the production of ST1, recipe CL N 3–13 (variation V, model 40)[19] by Trost was used. The recipe originates from the Lucca manuscript and therefore can be dated to the 7th or 8th century. The reference ink is categorised as a silver ink with metallic and non-metallic

14 Schreiner and Oltrogge, 2011, p. 137.

15 This part of the experiments was executed under the fume hood in the laboratory, considering the required safety measures.

16 The samples were larger in sub study 2, as more parchment was available at that time.

17 The technique was kindly demonstrated by Cahit Karadana.

18 In the literature, hematite, sardonyx, wolf or dog teeth are mentioned. One could also put a piece of textile like silk for protection in between. Schreiner and Oltrogge, 2011, p. 111.

19 Trost, 1991, p. 117.

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additives, as it contains copper in the form of copper(I)oxide (Cu_2O, copper hair), as well as sodium chloride (NaCl). Ox gall was added in the function of a binder. This recipe was chosen in order to investigate, if the influence of NaCl as a component of the ink itself was comparable with the impact of sodium chloride from the surrounding atmosphere.

To prepare the silver powder, 112 mg of silver leaves were ground in a marble mortar, using 31.2 mg of uniodised NaCl in total[20] as a grinding aid. After one hour of grinding, the fine silver powder was washed three times with 200 ml of a solution of NaCl in water[21] and then dried using a water bath[22]. The dry powdered silver was then mixed with 4.981 mg of Cu_2O and five drops of ox gall[23]. The ink wrote smoothly but smeared a bit during the burnishing with the agate polishing stone. When the ink was freshly applied to the purple parchment, it showed a red cast but appeared more yellowish after drying (Fig. 9).

Fig. 9: ST1_A; the left sample is made using the Glaser parchment, while the right sample is made with the Late Antique parchment by Jiří Vnouček.

Reference ink ST2

In order to produce ST2, recipe MC LXXXXII d (variation I, 1, 2; model 112, 113)[24] by Trost was used. The ink recipe originates from the Mappae Clavicula and thus can be dated to the end of the 12th century. The reference ink is categorised as a pure silver ink.

20 The amount of the grinding aid recommended by Trost had to be increased during the grinding process, since the recommended 11.2 mg of sodium chloride were already finely ground after a few minutes. Therefore, another 20 mg of sodium chloride were added step by step. Furthermore, 12 drops of a saturated solution of sodium chloride had to be added as a lubricant.

21 500 mg of sodium chloride were diluted in 200 ml of tap water.

22 In the case of this recipe a drying step was not included by Trost. The authors dried the silver anyway, as it would have contained to much liquid for further processing.

23 The amount of ox gall had to be increased from two drops (as it was recommended in the recipe), since the ink would have been too pastry to use it for writing otherwise.

24 Trost, 1991, p. 215.

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It contains only a mixture of isinglass and gum arabic as a binder in addition to powdery silver.

For obtaining a fine silver powder for reference ink ST2, 98 mg of silver leaves were ground in a mortar using water as a lubricant, which was added dropwise. As soon as the silver powder seemed to be fine enough the grinding process was stopped and the powder obtained was washed three times. After drying, the silver powder was mixed with 13 drops of a 3:1 mixture of isinglass (5 %) and gum arabic (20 %), as described by Theophilus[25]. The obtained ink was rather viscous and therefore not easy to write with. Additionally, it smeared during the burnishing process. The dry ink ST2 had a golden-greenish hue on the purple parchment (Fig. 10).

Fig. 10: Samples ST2_A; as described in fig. 9.

Reference ink ST3

For the production of reference ink ST3, recipe MC CCXLVIII (variation II, 1, 2; model 130, 131)[26] was followed. As it was the case for ST2, the recipe of ST3 originates from the Mappae Clavicula (end of 12th century). The reference ink is categorised as a silver ink with a non-metallic additive. Sodium hydrogen carbonate ($NaHCO_3$), soda, was added to the powdery silver. The aim was to investigate the impact of this inorganic ingredient on the corrosion of silver by artificially ageing ST3.

Since the recipe required silver chips for the production of silver powder, 100 mg of silver was filed off a thin silver plate using a fine iron file. The gained silver chips were ground in a marble mortar with ten drops of wine vinegar (5 %) as a grinding aid for 20 min, leading to the formation of a brownish paste, which was washed six times and subsequently dried. The powdery silver obtained was mixed with 0.094 mg of $NaHCO_3$

25 The recommended amount of two drops of binding medium had to be increased to 13 drops, since the ink was not usable otherwise.

26 Trost, 1991, p. 236.

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and 21 drops of a 3:1 mixture of isinglass (5 %) and gum arabic (20 %)[27] as a binder. Due to the fact that the fine silver particles slowly filled up the lines of binder, which had been created with the bamboo pen, ST3 was not an easy writing medium. Therefore, the ink had to be dabbed on with the pen repeatedly to achieve the desired coverage. After the ink had dried, it appeared in a light greyish to whitish hue and tended to powder off during burnishing (Fig. 11).

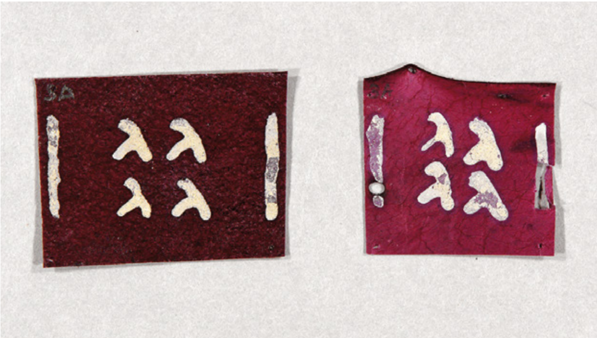

Fig. 11: Samples ST3_A; as described in fig. 9.

Reference ink ST4

For the production of reference ink ST4, the same recipe (MC CCXLVIII: variation II, 1, 2; model 130, 131)[28] was used as for ST3. It is also a silver ink with a non-metallic additive. The difference lies in the interpretation of the term nitrum, which is used in the original recipe in the Mappae Clavicula. In the case of ST3, nitrum was interpreted to be sodium hydrogen carbonate ($NaHCO_3$). Additionally, the term is interpreted as potassium nitrate (KNO_3) in literature. Therefore, KNO_3, saltpetre, was added to reference ink ST4 in order to evaluate its effect on the corrosion behaviour.

The preparation of the silver ink was performed almost identically with that of ST3. Instead of 0.094 mg of $NaHCO_3$, 0.096 mg of KNO_3 as well as 20 drops of binder were added. Due to the formation of small lumps, the ink could not be applied easily with the bamboo pen. Like ST3, it tended to smear when burnished with the agate polishing stone (Fig. 12).

27 The amount of binder had to be increased from the recommended two drops to 21 drops, since the ink was not processable otherwise.

28 Trost, 1991, p. 236.

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Fig. 12: Samples ST4_A; as described in fig. 9.

Reference ink ST5

In order to obtain reference ink ST5 the recipe H III, XLIII (model 150)[29] was used. The original recipe comes from the Heraclius treatises and can be dated to the 11th century. Due to the fact that it only contains a mixture of egg white and artificial urine as a binding agent, ST5 is categorised as pure silver ink.

For the production of the reference ink 110 mg of silver chips were scraped off a thin silver plate using a fine iron file. The silver chips obtained were then ground in a marble mortar for 10 minutes without the addition of any grinding aid. During this process the silver turned black. The refined silver was then washed six times and dried using a water bath. Afterwards two drops of egg white[30] and two drops of artificial urine[31] were added.

Fig. 13: Samples ST5_A; as described in fig. 9.

29 Trost, 1991, p. 258.

30 Egg white was beaten stiff and stored. After some time liquid separated from the stiffed egg white. Only the liquid part, which was collected at the bottom of the vessel, was used for the ink.

31 For the preparation of artificial urine 0.064 g $CaCl_2$, 0.114 g $MgSO_4 \times H_2O$, 0.820 g NaCl and 2 g urea were dissolved in 100 ml of water.

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ST5 could be applied smoothly to the parchment samples with the bamboo pen. It could be burnished without any smearing or powdering-off. As soon as the ink was dry, it appeared to be dark brownish-grey and glittery (Fig. 13).

Reference ink ST6

Reference ink ST6 was produced using recipe CL M 24–29 (variation III 1 b, model 32)[32]. The recipe has its origins in the Lucca Manuscript and can therefore be dated to the end of the 7th or the beginning of the 8th century. Since sodium hydrogen carbonate ($NaHCO_3$) was added to the silver powder, ST6 is categorised as a silver ink with non-metallic components. Cherry gum was used as a binder. Silver was refined by grinding silver leaves by hand using gum arabic as grinding aid. The aim was to investigage whether the method used for refining silver had an impact on the corrosion behaviour of the ink compared with that of ST3.

In order to obtain a fine silver powder, 100 mg of silver leaves were ground by hand using gum arabic as grinding aid. Afterwards the powdery silver generated was washed three times and then dried. The fine silver powder was mixed with ten drops of wine vinegar (5 %) and ground in a mortar for five minutes causing the silver to turn blackish. After this second grinding process the silver was washed six times and then dried, whereby the colour of the powder changed to dark grey. 0.047 g $NaHCO_3$ as well as seven drops of cherry gum (5 %) were added before use. ST6 could be applied to the parchment samples easily with the bamboo pen but smeared a little bit during burnishing. The dry reference ink appeared in a dark greenish-grey colour on purple parchment (Fig. 14).

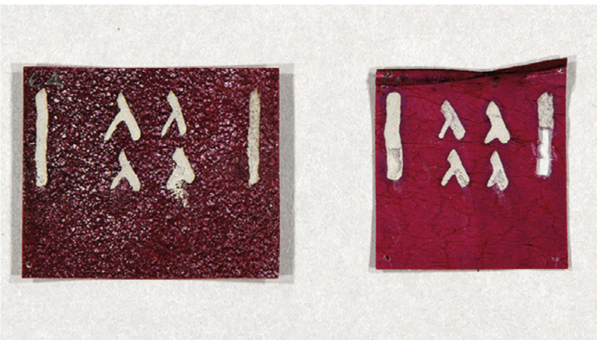

Fig. 14: Samples ST6_A; as described in fig. 9.

32 Trost, 1991, p. 107.

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Reference ink ST7

The recipe used for the production of reference ink ST7 was based on LP X 8ᵃ/3–4 (model 9)[33]. The recipe has its origins in the Leiden papyrus X and can be dated to the end of the 3rd or the beginning of the 4th century A. D. Since the binding medium cherry gum is the only component of the ink next to powdery silver, ST7 is categorised as a pure silver ink.

80 mg of silver leaves were ground by hand using gum arabic as a grinding aid. The obtained fine silver was then washed three times and dried. The powdered silver was heated, mixed with 10 mg of cherry gum as well as with 0.5 ml of water and was further ground in a marble mortar for 10 minutes. The resulting ink was easily applied to the parchment samples using the hand carved bamboo pen and could be burnished without any smearing. The dry ST7 has a light grey to whitish hue (Fig. 15).

Fig. 15: Samples ST7_A; as described in fig. 9.

Reference ink ST8

For the production of reference ink ST8, Trost's recipe CL α 11–20 (variation II, model 49)[34] was followed. The recipe originates from the Lucca manuscript and is dated to the end of the 7th or the beginning of the 8th century. Like reference ink ST7, it contains only cherry gum as a binding medium next to powdery silver and thus can be categorised as pure silver ink. Since the powdered silver is obtained by the process of amalgamation, the recipe was chosen to investigate possible effects due to this method.

For the preparation of the silver powder, 100 mg of silver chips were filed off a thin silver plate, using a fine iron file. The gained silver chips were then ground in a porcelain mortar together with 300 mg of mercury (Hg) under high temperature, above the flame of a Bunsen burner. After 15 to 20 minutes small silver flakes formed. They were ground for

33 Trost, 1991, p. 70.
34 Trost, 1991, p. 129.

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another 25 to 30 minutes until the silver powder appeared fine enough for further processing. In order to evaporate as much mercury (Hg) as possible the powder was ground under high temperature for another 35 minutes. The fine silver powder was mixed with 10 drops of cherry gum (5 %). Since the silver particles did not form a homogenous mixture with the binding medium, but instead stayed separated, it was not possible to write with the ink[35] (Fig. 16). Therefore, the ink had to be excluded from the ageing study.

Fig. 16: Ink ST8_A in a glass. The ink could not be used for writing.

Reference ink ST9

Trost's recipe H I, VII (variation I 1 b, model 137)[36] was used to produce reference ink ST9. Since the recipe has its origins in the Heraclius treatises, the recipe can at least be dated to the 11th century. As only ox gall was added to powder silver, ST9 is categorised as pure silver ink. Red wine was used as grinding aid. The aim was to evaluate, if wine, as an internal acidic source, influenced subsequent corrosion.

For the refinement of the silver, 180 mg of silver leaves were ground by hand, using gum arabic as a grinding aid. According to the recipe, the obtained pasty silver was transferred into a marble mortar adding a little amount of water and was then ground for 15 min with 0.5 ml of red wine. Afterwards the silver was washed eight times and dried before being mixed with 13 drops of ox gall[37]. Reference ink ST9 could be applied easily with the

35 The reason may be that the particles were still not fine enough.

36 Trost, 1991, p. 243.

37 Only 0.1 ml of ox gall were used by Trost. Since the ink was not usable with this small amount of binder, further drops of ox gall were added stepwise until the ink had a better consistence.

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bamboo pen but could not be burnished due to powdering off. In a dry condition ST9 appeared in a light grey, almost white colour (Fig. 17).

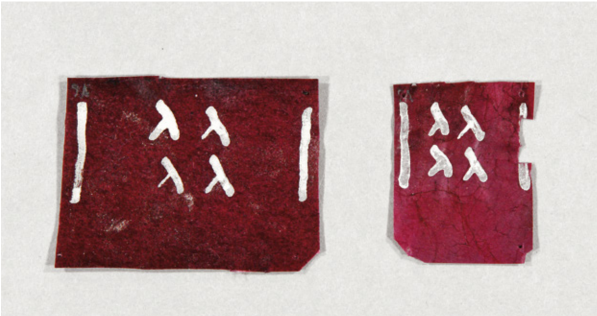

Fig. 17: Samples ST9_A; as described in fig. 9.

Sub study 2: ST10-ST14

Reference ink ST10

Reference ink ST10 was produced following recipe CL δ 29–34 (model 55)[38] by Trost. The recipe originated from the Lucca manuscript and thus can be dated to the end of the 7th or the beginning of the 8th century. Since the reference ink contains copper in the form of verdigris, copper(II)acetate ($CuAc_2$), it is categorised as a silver ink with an additional metallic component[39]. Since no binder was mentioned in the recipe, the silver powder was mixed with water. One reason for choosing this recipe was to investigate the impact of copper (Cu) on the corrosion. Additionally, the intention was to evaluate a possible impact of the refinement method of amalgamation again, since the production of ST8 had failed.

A fine silver powder was obtained by filing off 100 mg of silver chips from a thin silver plate using a fine iron file. The chips were then ground in a porcelain mortar together with 300 mg of mercury for 30 minutes under high temperature produced by a Bunsen burner. As soon as the silver seemed to be fine enough, the grinding process was stopped and the metal heated for another 20 minutes. During that process matt silver plates formed. 130 mg of silver powder, probably containing residues of mercury, remained and was mixed with 65 mg of $CuAc_2$ in a mortar. 2 ml of water were then added and the mixture was stirred. Since the components silver and $CuAc_2$ tended to separate after a few minutes, the mixture needed to be stirred frequently during use. The reference ink was of very thin consistence and when it was applied to the parchment the silver particles subsequently

38 Trost, 1991, p. 139.

39 Following the categories defined by Trost, see chapter on silver inks.

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slowly flowed into the water line which had been drawn with the bamboo pen. The ink could be burnished without being damaged by the agate polishing stone. When ST10 was dry, it had a dark greenish-grey colour (Fig. 18).

Fig. 18: Sample ST10_A, the sample is made using the medieval style parchment by David Frank.

Reference ink ST11

The recipe of reference ink ST11 is based on Trost's recipe MC L a (paragraph 1) (variation 1, model 82)[40] which has its origins in the Mappae Clavicula and can be dated to the 12th century. Since ST11 contains copper(II)acetate ($CuAc_2$) next to silver powder like ST10, the reference ink is categorised as silver ink with an additional metallic component.

In contrast to reference ink ST10, the silver powder was obtained by grinding 80 mg of silver leaves by hand using gum arabic as grinding aid. After the refinement of the silver, it was washed three times and then dried. The gained silver powder was transferred into a mortar and ground together with 79.5 mg of $CuAc_2$ and 1 ml of water for five minutes. As was the case for ST10, silver and $CuAc_2$ repeatedly separated into two phases and had to be stirred frequently to obtain a homogeneous ink. The ink could be applied to the parchment by the bamboo pen easier than ST10. It was more opaque, but it tended to smear when it was burnished. The colour of the dry ink was light silver to grey (Fig. 19).

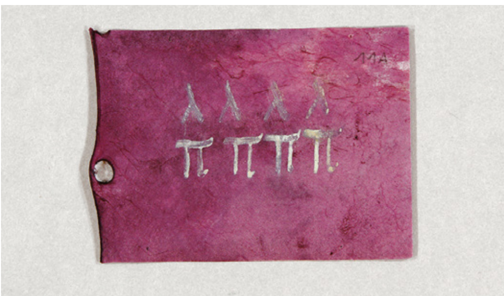

Fig. 19: Sample ST11_A, as described in fig. 18.

40 Trost, 1991, p. 182.

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Reference ink ST12

The production of reference ink ST12 is based on recipe MC L a (paragraph 1. variation 1, model 82)[41], which also was followed to prepare reference ink ST11. In contrast, gum arabic was added instead of water in order to investigate a possible stabilizing influence of the binding medium on the corrosion process.

78.2 mg of fine silver powder were mixed with 78.8 mg of $CuAc_2$. Eventually, 1.5 ml of gum arabic (8 %) and 0.5 ml of water were added. The ink was easier to write with than ST10 and ST11, but tended to smear during burnishing. The colour of the dry ink was light silver to grey (Fig. 20).

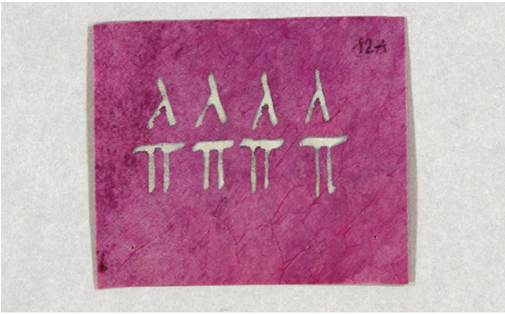

Fig. 20: Sample ST12_A, as described in fig. 18.

Reference ink ST13

The preparation of reference ink ST13 is based on the same recipe as for ST4 (MC CCXLVIII: variation II, 1, 2; model 130, 131)[42], which was part of sub study 1. Since the results of the artificial ageing of ST4 had shown severe signs of corrosion, ST13 was prepared in order to investigate whether the corrosion resulted from the addition of wine vinegar as a grinding aid or from the further addition of potassium nitrate (KNO_3). For the preparation of ST13 no KNO_3 was added.

For the production of fine silver powder, 104.5 mg of silver chips were ground together with 10 drops of wine vinegar (5 %) in a marble mortar for 20 minutes. The ground chips were then washed six times and dried. The obtained silver powder was mixed with 20 drops of isinglass (5 %). As it had been the case with ST4, reference ink ST13 could not be easily applied to the parchment using the hand-carved bamboo pen and could not be burnished. The dry ink had a brownish to greyish colour (Fig. 21).

41 Trost, 1991, p. 182.
42 Trost, 1991, p. 236.

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Fig. 21: Sample ST13_A, as described in fig. 18. Fig. 21: Sample ST13_A, as described in fig. 18.

Reference ink ST14

Reference ink ST14 is another variation of reference ink ST4. It is based on the same recipe (MC CCXLVIII: variation II, 1, 2; model 130, 131)[43] by Trost. In contrast to ST4 and ST13 the silver chips used for the preparation of silver powder were ground adding water as grinding aid instead of wine vinegar.

102.3 mg of silver chips were ground in a marble mortar together with 10 drops of water for 20 minutes. The obtained silver powder was washed six times, dried and mixed with 0.098 g of potassium nitrate (KNO_3). 20 drops of isinglass (5 %) were added. The reference ink showed the same problems regarding its further use as ST13. It seemed to be a bit translucent and had a brownish colour (Fig. 22).

Fig. 22: Sample ST14_A, as described in fig. 18.

43 Trost, 1991, p. 236.

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Sample preparation on parchment

The chosen reference silver inks were applied on the flesh side of the parchment samples. The parchment has been dyed with orchil made of *Rocchella tinctoria*, see chapter on purple dyeing of parchment. Greek letters were written with bamboo pens on pieces of purple parchment of sample sizes 2.5 x 2.5 cm and 3 x 3 cm in sub study 1. In sub study 2 the samples measured 5 x 4 cm. At the time the study took place, only a limited amount of parchment was available, especially parchment that was produced based on Late Antique techniques, see chapter on the parchment of the Vienna Genesis. Therefore, three different types of parchment were used.

For sub study 1 each sample-set was produced twice, using two different types of lamb parchment:

1. modern lamb parchment from the company Anton Glaser (NP, new parchment)[44] with an average thickness of 219 µm
2. lamb parchment produced in Late Antique style by Jiří Vnouček (LP, Late Antique parchment 1) with an average thickness of 104 µm, see chapter on the parchment of the Vienna Genesis

The samples of sub study 2 were all prepared on lamb parchment produced by David Frank according to medieval methods (MP, medieval parchment)[45]. Frank's parchment is very smooth on flesh and hair side, with an average thickness of 190 µm. The average thickness of the parchment folios of the Vienna Genesis measures 100–160 µm.

For sub study 1, one half of the parchment was burnished with an agate polishing stone prior to the application of the silver inks. The influence of this finishing step on parchment and inks was intended to be evaluated after ageing. For sub study 2, the entire parchment was burnished in advance. Each reference sample-set of both runs was produced in quadruplicate and marked with the labels A–D (Fig. 23):

A: unaltered as reference sample
B: artificially aged
C: sprayed with water in sub study 1; sprayed with a 3.5 % solution of sodium chloride (NaCl) in sub study 2; aged.
D: sprayed with parchment glue containing acetic acid[46], according to Wächter[47]; aged.

44 The exact methods and substances used in the production of the parchment are unknown.

45 The surface of the parchment was scraped and not split, as it was presumably done in Late Antiquity; see chapter on the parchment of the Vienna Genesis.

46 Therefore, 60 ml of a 20 % parchment glue were prepared and mixed with 20 ml ethanol and 20 ml 5 % wine vinegar.

47 Wächter, 1982, p. 164.

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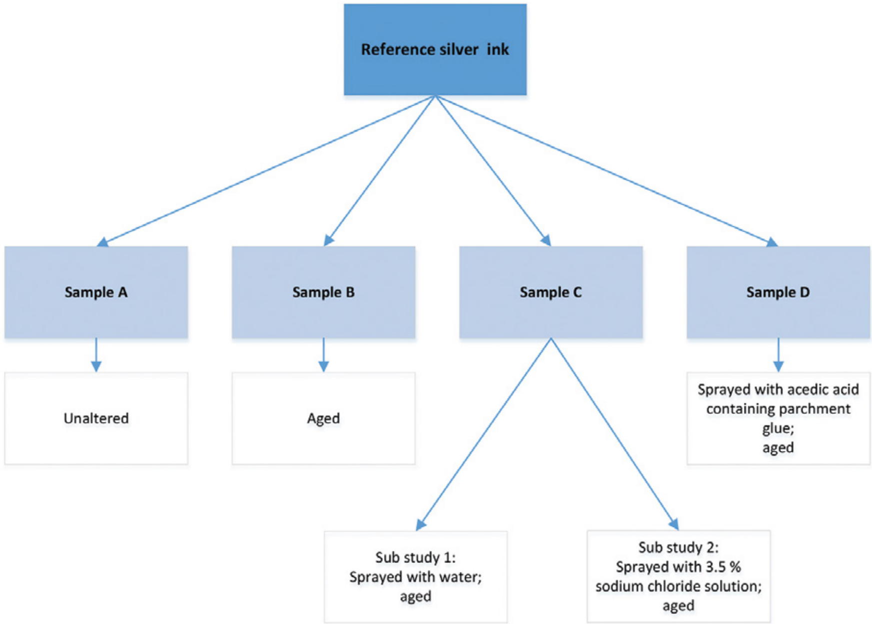

Fig. 23: Flowchart showing the treatments applied to the four sets of samples (A, B, C, D).

Water, the solution of sodium chloride and parchment glue were applied with a commercial plastic spray. In sub study 1 water was sprayed four times on the surface of the samples. The samples were covered in the spray mist; the distance between the spray bottle and the samples was approximately one meter. The bottle was held straight and the samples were placed flat on the table, fixed with pins on a soft fibre board in order to prevent them from curling up. In sub study 2, the solution of sodium chloride was sprayed six times, until a wet film formed on the surface of the samples. This treatment was meant to replicate severe water damage with salty sea water. The parchment glue was sprayed six times as well, until drops formed on the samples. According to Verena Flamm[48] parchment glue was applied with a spray pipe on parchment objects in the Institute of Conservation. The amount of glue depended on the application. For consolidation the glue was sprayed once, for moistening folded parchment the glue was applied several times.

Sample set C replicates the influence of water and of seawater, while sample set D replicates the influence of the conservation treatment with parchment glue in 1975.

The samples of sub study 1 were mounted on their upper edge with Japanese tissue

48 Verena Flamm, paper and parchment conservator, who worked with Otto Wächter at the Institute of Conservation of the Austrian National Library, 2016, personal communication.

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and wheat starch paste on museum matboard (Fig. 24). The samples of sub study 2 were mounted on all four edges in order to prevent them from curling up in the climate chamber (Fig. 26).

Since the purpose of the artificially aged samples was to contribute to a more detailed characterisation of the different materials of the Vienna Genesis, they were analysed with the same methods and the same measuring conditions as was the original manuscript. The inks were investigated visually with the naked eye and under magnification, using a stereo microscope[49]. Non-destructive analysis with µ-XRF was performed on the written letters in the middle of the samples as well as on the surrounding blank parchment. For the determination of the shrinkage temperature with the Micro Hot Table method (MHT–method) samples of blank parchment were taken at the bottom side of the reference samples prior to, during and after their artificial ageing periodically.

Ageing Conditions

In order to create a degree of degradation of the collagen structure of the parchment which was comparable to that of the Vienna Genesis' parchment in a small amount of time, the right conditions regarding relative humidity, temperature and time needed to be chosen for the accelerated ageing[50]. Therefore, the degree of degradation of the collagen structure was characterised by the determination of the shrinkage temperatures of reference samples and samples of the Vienna Genesis with the MHT–method according to Larsen[51], respectively.

For the analysis of the parchment of the reference samples, small pieces of 1 x 2 mm were taken from the flesh side with a scalpel, while some fibre samples of the Vienna Genesis were taken from the inner margin areas of the folios 2 and 9[52]. Sampling of parchment from the Vienna Genesis was kept to a minimum. In the course of the sample preparation, the parchment samples were placed on a circular glass slide and conditioned in one drop of deionised water for 10 min. The wet collagen fibres were then separated under a stereo microscope (Stemi 2000-C, Zeiss) with preparation needles using 60x magnification. After another drop of deionised water had been added, the collagen fibres were covered with another glass slide, then transferred into the sample chamber and placed on the heat-

49 Wild stereo microscope M 400 (Type 126269); at 6.3x–32x magnification.

50 Malissa, 2017, pp. 42–44.

51 Larsen et. al., 2002, pp. 55–56.

52 The researchers refrained from taking fibre samples from the more intact and closed surface of the middle parts of the parchment.

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ing block of the heat stage TMHS 600 (LINKAM). In order to determine the shrinkage temperature the heat stage was connected to an electronic temperature controller TP93 (LINKAM). According to Larsen, samples were heated with a heating rate of 2 °C/ min and the shrinkage activity of the fibres was observed and documented with the digital microscope KH-7700 (HIROX) using 100x and 150x magnification[53], respectively. As soon as no further shrinkage activity could be observed, the measurements were stopped. According to Larsen, five different shrinkage intervals are defined: A1, B1, C, A2 and B2. They are distinguished by the shrinkage activity, with interval C being the main shrinkage interval. The activity increases from the first interval, A1, where single fibres are shrinking with pauses in between to the main shrinkage interval C, where it reaches is maximum. In the following, the activity decreases again until no movements are observed anymore in interval B2. The characteristic shrinkage temperature Ts marks the starting point of the main shrinkage interval C[54].

At first, the shrinkage temperatures of a fibre sample of the Vienna Genesis and the unaged reference parchment (NP) provided by the company Anton Glaser[55] were determined. While three-fold measurements were performed in the case of the reference samples, only a single-fold measurement could be carried out for the fibre sample of the Vienna Genesis, due to the minimal amount of sample available. Table 2 gives an overview of the results of the measurements which were carried out. The fibre sample from the Vienna Genesis showed a shrinkage temperature of 28.4 °C, whereas a shrinkage temperature of 54.6 ± 1.3 °C was determined for the unaged reference samples (NP_ref).

53 Dependent on the visual appearance of the fibres, 100x or 150x magnification was used, respectively.

54 Larsen et al. 2002, p. 56.

55 At that time only parchment produced by the company Anton Glaser was available in the required amount.

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Table 2: Mean values for the temperatures of the first observed shrinkage activity (T_{first}), the shrinkage temperatures (T_S), the temperature at the end of the main shrinkage interval ($T_{S,end}$), the length of the main shrinkage interval (ΔT), the temperature of the last observed shrinkage activity (T_{last}) and the length of the entire shrinkage interval ($T_{complete}$) of the following samples: one fibre sample of the Vienna Genesis from folio 2r (Vienna Genesis_S1), an unaged sample of reference parchment of NP (NP_ref), a sample of reference parchment NP after 1 week with 30 °C, and alternating 30 %RH and 70 %RH (NP_30/30/70/1w), after 1 week with 80 °C, and alternating 30 %RH and 70 %RH (NP_80/30/70/1w), after 2 weeks with 80 °C, and alternating 30 %RH and 70 %RH (NP_80/30/70/2w), after 3 weeks with 80 °C, and alternating 30 %RH and 70 %RH (NP_80/30/70/3w), after 1 week with 95 °C, and alternating 30 %RH and 70 %RH, (NP_95/30/70/1w) and after 13 days with 95 °C, and alternating 30 %RH and 70 %RH (NP_95/30/70/13d)

sample	T_{first} [°C]	T_S [°C]	$T_{S,end}$ [°C]	ΔT [°C]	T_{last} [°C]	$\Delta T_{complete}$ [°C]
Vienna Genesis_S1	26,6	28,4	29,4	1,0	30,5	3,9
NP_ref	53,0 ± 1,5	54,6 ± 1,3	56,9 ± 0,6	2,3	58,1 ± 1,0	5,1
NP_30/30/70/1w	52,2 ± 0,7	53,9 ± 0,7	55,6 ± 0,4	1,7	56,9 ± 1,0	4,6
NP_80/30/70/1w	41,0 ± 1,5	43,6 ± 0,8	45,5 ± 1,4	1,9	47,1 ± 1,3	6,1
NP_80/30/70/2w	38,8 ± 0,5	40,3 ± 0,3	42,6 ± 0,3	2,3	43,8 ± 0,5	5,0
NP_80/30/70/3w	34,1 ± 0,3	37,5 ± 0,5	40,2 ± 0,2	2,7	42,0 ± 0,6	8,0
NP_95/30/70/1w	30,4 ± 1,0	34,1 ± 1,5	36,6 ± 2,4	2,5	39,4 ± 3,6	9,0
NP_95/30/70/13d	25,8 ± 1,5	32,6 ± 1,3	37,1 ± 1,1	4,5	37,5 ± 2,8	11,7

Based on these first values the best-suited ageing conditions were developed step by step. Therefore, samples of the reference parchment NP were artificially aged for three weeks at a temperature of 30 °C and relative humidity of 30 % and 70 %, which were each held constant for 12 h. The artificial ageing was undertaken in a climate chamber[56] VCC³ 4034 (Vötsch Industrietechnik), which was controlled by the software SIMPAT 4.0.

Since no changes of the shrinkage temperatures could be observed by the application of these conditions (Table 2), a second run was carried out using slightly different ageing conditions: while the parameters of relative humidity and duration were kept the same, the temperature in the climate chamber was increased to 80 °C. In the course of this run, samples were taken weekly in order to determine the shrinkage temperature. As can be seen in Table 2, the most significant change of the shrinkage temperatures takes place after one week of artificial ageing. Hereby, a decrease of the shrinkage temperature starting at 54.6 ± 1.3 °C down to 43.6 ± 0.8 °C could be observed. Following this first drop of the shrinkage

56 The climate chamber was provided by the Institute of Art and Technology, University of Applied Arts Vienna.

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temperature, a further decrease to 40.3 ± 0.3 °C after two weeks and to 37.5 ± 0.5 °C after three weeks of artificial ageing could be observed.

In order to reduce the experimental time, the temperature was increased to 95 °C, while relative humidity was kept the same in a third run. A sample which was taken after one week showed a shrinkage temperature of 34.1 ± 1.5 °C. Since another determination of the shrinkage temperature after 13 days of artificial ageing showed only a smaller decrease to 32.6 ± 1.3 °C, which was comparable with the shrinkage temperature of the Vienna Genesis, the experimental run was stopped. Therefore, a temperature of 95 °C, a duration of 13 days and relative humidity of 30 % and 70 %, which were each held constant for 12 hours, were used for the ageing study.

The visual appearance of the reference samples before and after accelerated ageing

The visual appearance of all reference samples – inks and parchments respectively – was examined visually with the naked eye (Fig. 24-27) and under magnification before and after accelerated ageing. A Wild stereo microscope M 400 (type 126269) at 6.3x–32x magnification was used to observe colour changes of the dyed parchment samples and their deformation behaviours as well as colour changes of the reference inks and the damage patterns of the inks. The following presents a compact overview of the information gained.

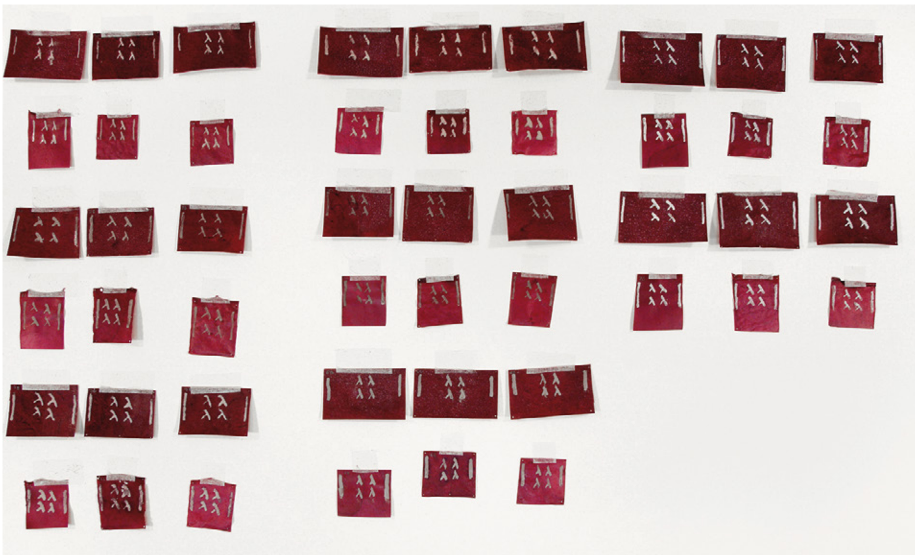

Fig. 24: The mounted samples of sub study 1.

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Fig. 25: The mounted samples of sub study 1 after accelerated ageing.

Fig. 26: The mounted samples of sub study 2.

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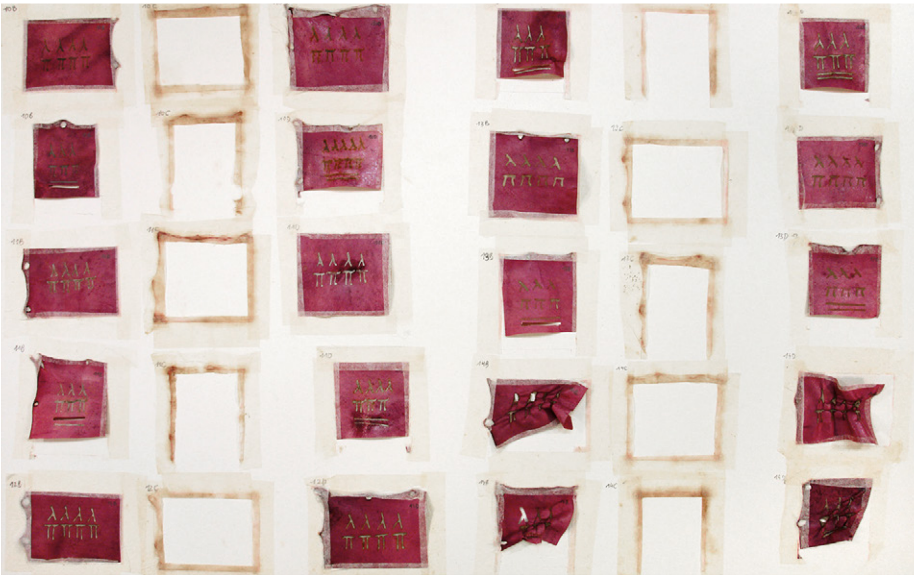

Fig. 27: The mounted samples of sub study 2 after accelerated ageing. In sub study 2 the sample set C was so deformed that the parchment pieces became detached from the mounting board.

Evaluation before ageing

Prior to the accelerated ageing the colours of the reference inks ranged between yellowish, greenish or brownish grey and a very light grey on purple parchment (Fig. 24 and 26). Comparing particularly the copper(II)acetate containing reference inks ST10–ST12, only ST10 had a greenish colour, while the reference inks ST11 and ST12 were silvery. Additionally, the majority of the inks was at least a bit glittery under the microscope (6.3x–32x magnification). Most of the inks showed different degrees of losses of the ink layer after drying, which might be due to the binding agent not being strong enough. Furthermore, fine cracks in the ink layers could be observed on some inks. Inks which were produced using fine silver powder from grinding silver leaves with gum arabic by hand appeared finer under the microscope (6.3x–32x magnification) than those which were produced using silver refined by grinding in a mortar or amalgamation[57] (Fig. 28). In particular, refer-

57 This goes along with observations made during the production of the reference inks which showed that inks which were prepared using silver powder obtained by manual grinding with gum arabic could be applied easier to the parchment samples with bamboo pens than those inks which were produced using silver powder obtained by grinding in a mortar or amalgamation. The finer silver powder mixed better with the binding agent resulting in better flowing inks.

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ence inks made from silver ground in a mortar had a crumblier appearance[58]. After letting the reference inks dry for a few hours, they were burnished with an agate polishing stone, during which process most of the inks tended to smear or started to flake off. Only three inks – ST5, ST7 and ST10 – could be burnished without showing any of these phenomena, which is not congruent with Trost's observations[59]. While the reference inks mostly had a matt greyish colour before burnishing, those burnished had silvery shiny surfaces (Fig. 29).

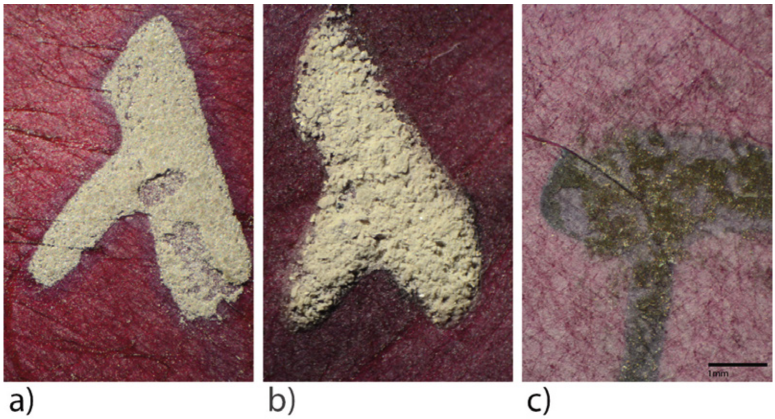

Fig. 28: Microscopic images at 12x magnification (scale bar 1 mm) of ink from silver powder obtained a) by grinding silver leaves with gum arabic by hand, ST7_A, b) by grinding silver in a mortar, ST6_A, c) by amalgamation, ST10_A.

Fig. 29: Greyish colour of the ink before burnishing (above), and silvery shine after burnishing (below) on sample ST1_A.

58 This could either be due to the mortar itself or the grinding process not being long enough.
59 In her thesis most of the inks are described as easy to write with and being burnishable.

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Evaluation of untreated samples after accelerated ageing

Most of the parchment samples of sub study 1 were severely deformed during the accelerated ageing. The samples were mounted only on the upper margin. The parchment turned stiff, curled up and especially the ink areas shrunk strikingly, which complicated analyses and observations (Fig. 30). In contrast, the parchment samples of sub study 2 did not deform to such an extent[60], because they were mounted on four sides. Only the reference samples, which were sprayed with a 3.5 % solution of sodium chloride in water (sample-set C), were severely deformed after the alteration (Fig. 31). They became detached from the mounting during ageing. Additionally, the colour of all parchment samples had turned duller and slightly darker.

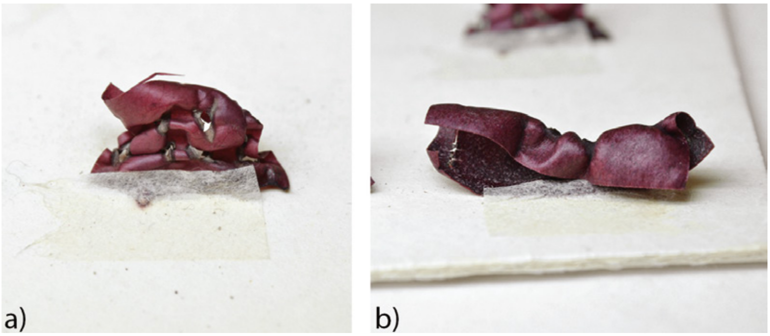

Fig. 30: Samples ST1_B from sub study 1 after accelerated ageing: a) Late Antique parchment, b) Glaser parchment.

All reference inks showed changes in colour and turned brownish in varying degrees during the ageing process. Some samples in both sub studies show signs of corrosion: in sub study 1, samples of the reference inks ST1, ST3, ST4, ST5 and ST6 developed signs of ink corrosion in different degrees in form of cracks, tears or losses in the areas the ink had been applied on (Fig. 32). Reference ink ST1 contains copper in the form of copper(I) oxide, whereas ST5 contains artificial urine and egg white and ST6 contains sodium hydrogen carbonate and was prepared with wine vinegar. In the case of the reference inks ST3 and ST4, the used silver powder was obtained by grinding silver in a marble mortar using wine vinegar as lubricant. While sodium hydrogen carbonate was added as a further component of ST3, ST4 contains potassium nitrate in addition. All of these inks

60 As explained above, the reference samples of sub study 2 were mounted on each side with Japanese tissue and wheat starch paste, while the samples of sub study 1 were only mounted on one side.

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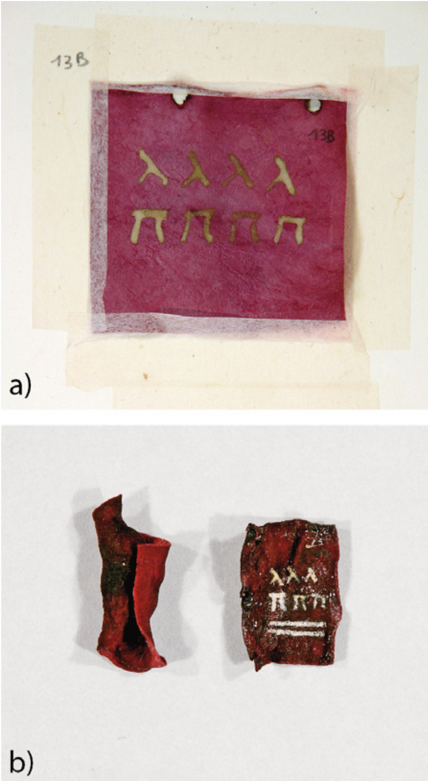

Fig. 31: Samples ST13_C from sub study 2 after accelerated ageing: a) untreated sample, ST13_B; b) sample treated with salt water.

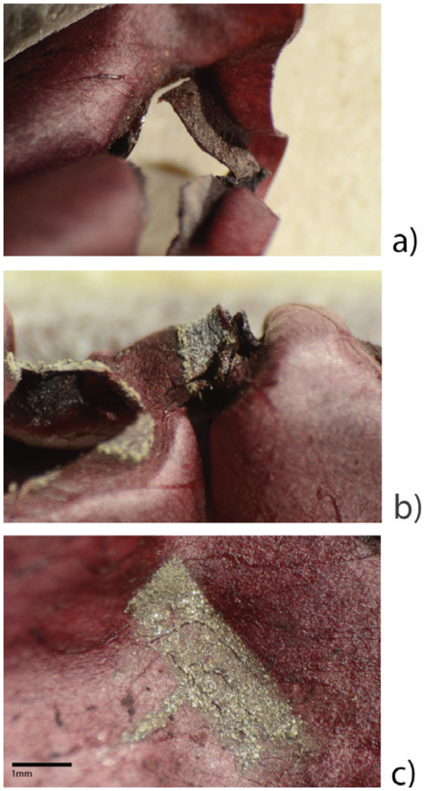

Fig. 32: Macroscopic images (scale bar 1 mm) of samples after accelerated ageing showing the degradation of the inks: a) ST1_B, b) ST4_B, c) ST5_C.

show dark halos around the silver ink lines as well as dark migration on at least one sample. Among these the reference inks ST3 and ST4 show the most pronounced phenomena of ink corrosion, particularly ST4. The ink corrosion and degradation phenomena of dark halos and migration appeared always more pronounced on the thinner Late Antique style parchment (LP).

In sub study 2 the reference samples of the reference ink ST14 showed the most serious signs of damage (Fig. 33). ST14 as well as ST13 were prepared for further investigation of the damage developed by ST3 and ST4. ST3 and ST4 were both prepared with wine vinegar and contain either sodium hydrogen carbonate or potassium nitrate. ST13 was produced solely using wine vinegar as a lubricant for the grinding process and contains no further component. ST14 was not prepared using wine vinegar, but contains potassium

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Fig. 33: Sample ST14_B after accelerated ageing.

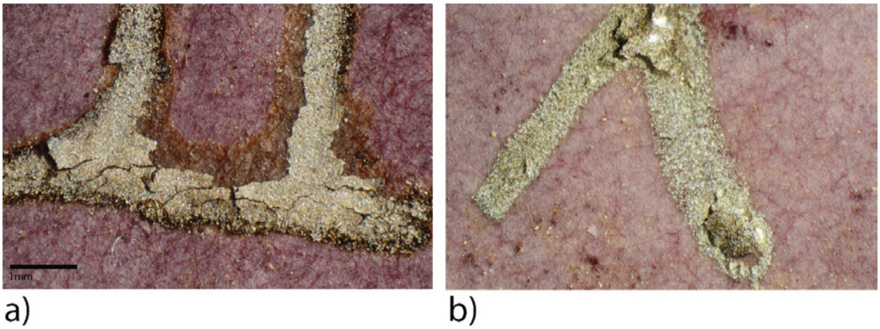

Fig. 34: Microscopic images, 12x magnification (scale bar 1 mm) of a) sample ST12_B, b) sample ST11_B.

nitrate as an additional component. Therefore, the comparison of the visual appearance of the reference samples after ageing shows that the strongly pronounced ink corrosion resulted from the presence of potassium nitrate[61] in ST4 and ST14, rather than from the refinement of silver using wine vinegar.

Comparing the visual appearances of all reference inks of sub study 2 (ST10–ST14) regarding the used binding agent, it seems as if reference inks which particularly contained gum arabic developed more tension in the ink layer than those only mixed with water. For a direct comparison of the impact of the binding medium, ST11 and ST12 were prepared following the same recipe. ST11 contains water and ST12 contains gum arabic. It could be observed that ST11 was more powdery, while the ink layer of ST12 seems to be under tension (Fig. 34).

61 It is therefore assumed that the severe corrosion of reference ink ST3 results from the addition of sodium hydrogen carbonate.

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Evaluation of treated samples after accelerated ageing

In sub study 1, it did not seem as if the treatment with water before ageing (sample-set C) had a large impact on the degradation of the samples. The only special observation made was that the inks of the samples ST2_C, ST4_C and ST5_C were less brownish than the other samples produced with those inks. The reason for this phenomenon remains unclear. However, it can be assumed that the samples were not wetted enough to show any observable phenomena.

In sub study 2, the samples from set C were sprayed six times with a 3.5 % solution of sodium chloride in water. The samples were moistened more than the samples of sub study 1 to imitate severe water damage with salty sea water. This had a huge impact on the parchment, as those samples shrunk dramatically. The parchment curled up, turned stiff and white efflorescence appeared on the surface (Fig. 31). All the samples became detached from the mounting support during ageing in the oven. With most inks, the surface of the samples C seemed to be grainier. Due to the enormous shrinkage of the parchment, most inks showed more losses on those samples.

On the surface of samples from set D which were treated with vinegar containing parchment glue, small shiny droplets are visible. This phenomenon is not visible on the Vienna Genesis, but can be seen on other objects from the Austrian National Library that were treated with this method in the 1960s and 1970s. As mentioned above, the amount of parchment glue depended on the object and the treatment. For at least some inks, the treatment with parchment glue seems to have had an impact, as the samples ST2_D, ST3_D, ST6_D and ST7_D turned more brownish. The reference inks ST2 and ST7 were pure silver inks containing only silver powder and a binder, while ST3 and ST6 were ground with vinegar and contain sodium hydrogen carbonate.

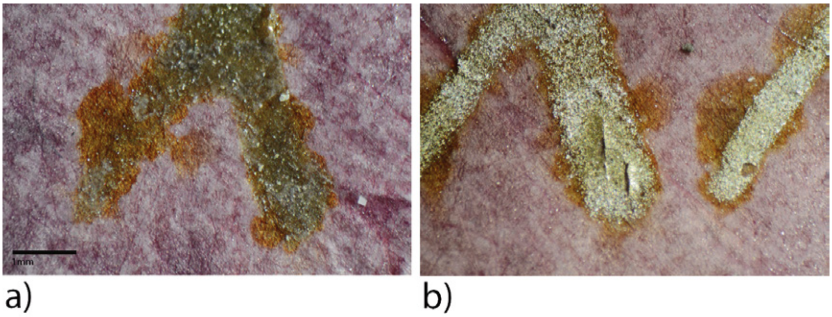

Fig. 35: Microscopic images, 12x magnification (scale bar 1 mm) of rust-like halos, a) sample ST10_D, b) sample ST11_D.

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In addition, all silver inks that contained copper(II)acetate formed rust-like halos on the samples prepared with parchment glue (Fig. 35). It seems that the vinegar in the mixture is responsible for this phenomenon.

Comparison with the silver ink of the Vienna Genesis

Comparing the appearance of the reference inks with the damage patterns of the Vienna Genesis, it is evident that it was not possible to recreate the appearance of the original silver ink, either in damage or optical characteristics. The surface of the original ink is smooth, but also a bit coarse on some folios. The silver seems to be finely ground and sufficiently adherent (Fig. 36). The amount of silver powder and binder appears to be well balanced, which was often not the case with the reference inks. The silver did not flake off like it did with the majority of the reference inks. Many of the reference inks are more crumbly than the original ink. It was not possible to burnish them.

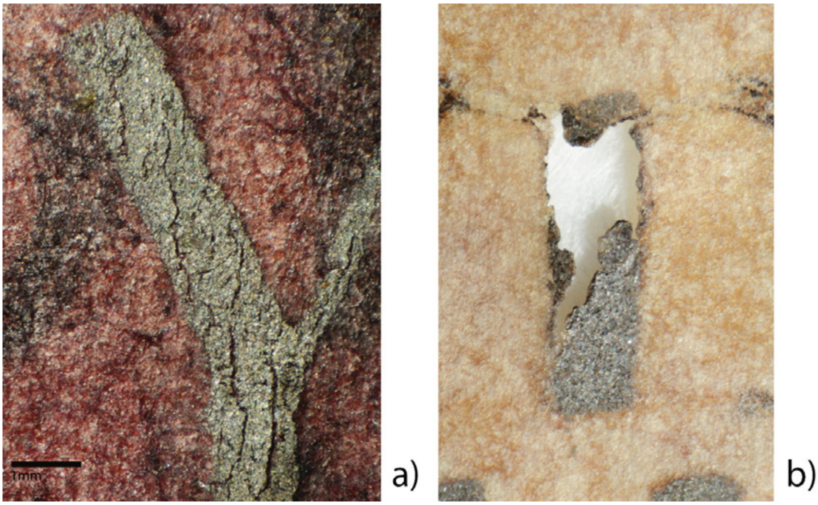

Fig. 36: Microscopic images, 12x magnification (scale bar 1 mm), of the silver ink of the Vienna Genesis a) folio 10, page 19, b) folio 12, page 23.

Considering the degradation of the silver ink of the Vienna Genesis and its multiple treatments, the visual impression of the original ink has probably changed considerably compared to its original appearance. Not all components of the silver ink, nor all later additions like adhesives, could be identified by analysis, see chapter on silver ink. Therefore, it

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was not possible to replicate the aged silver ink of the Vienna Genesis. Visual examination of the reference inks showed how strongly silver inks change due to additives and ageing conditions. Also minor components of the inks like potassium nitrate (saltpetre) or copper(II)acetate can cause degradation of medium and carrier. Water in the form of liquid or vapour accelerates the ageing process. Sodium chloride as a component of the ink (grinding aid) or as an external factor (e. g. seawater) can have a strong impact on the condition and appearance of inks. Also, the treatment with acidic parchment glue is able to alter the appearance of silver inks.

Shrinkage Temperature

In the course of the analysis of the shrinkage temperatures samples of sub study 1 and 2 as well as two fibre samples of the Vienna Genesis were analysed. While the modern lamb parchment produced by Glaser (NP) had an average thickness of 219 ± 32 µm, the second lamb parchment used for sub study 1, which was prepared according to Late Antique methods (LP), had an average thickness of approximately 104 ± 13 µm. The lamb parchment used for sub study 2 (MP) showed an average thickness of 190 ± 29 µm. Compared with the thicknesses of the parchments for the ageing study, the 24 remaining folios of the Vienna Genesis showed average thicknesses of approximately 100–160 µm. In order to obtain a more detailed documentation of the decrease of the shrinkage temperatures over time, samples of the reference parchments NP, LP and MP were taken prior to and after the artificial ageing as well as in between, i. e. after one half of the ageing time had passed. Due to the different conditions of the samples after the artificial ageing, only determinations of the shrinkage temperatures of the unmodified aged samples (B) and the aged samples that had been treated with acidic parchment glue (D) could be carried out[62]. Samples which had been moistened with a 3.5 wt% solution of sodium chloride (NaCl) in water (C) had curled and stiffened as a result of the artificial ageing, so that neither sampling nor any measurements could be performed.

In the course of the analysis the shrinkage temperatures (T_S) as well as the temperatures at which the first (T_{first}) and the last (T_{last}) shrinkage activity were observed were documented and used to calculate the main shrinkage interval (ΔT) as well as the complete shrinkage interval ($T_{complete}$). Small samples of the eigth reference samples of the first series (ST1–9) and of the five reference samples of the second series (ST10–14) were analysed

62 Here only samples of the second part of the ageing study are discussed, since the parchment glue was not applied extensively enough on the reference samples of the first part of the ageing study.

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by three-fold measurements, respectively[63] and averaged. By averaging these mean values, the average values shown in tables 3–5 were received. As can be seen in Table 3, the most significant decrease of the shrinkage temperatures for all three types of reference parchments takes place within the first five/six days. In the case of the parchment type NP the shrinkage temperature drops from 51.8 ± 0.8 °C down to 39.9 ± 0.5 °C. Compared to that, the main shrinkage temperatures T_S of the reference parchments LP and MP decrease to 44.1 ± 0.8 °C and 46.4 ± 0.4 °C, respectively, originating from higher values of 61.8 ± 1.2 °C (LP) and 62.5 ± 1.4 °C (MP) for the unaged samples. A lower decrease of T_S within the second half of the artificial ageing could be observed for all types of reference parchments: After 13 days T_S of reference parchment NP was 33.3 ± 0.6 °C, while reference parchment LP showed a T_S of 34.9 ± 0.7 °C and reference parchment MP had a T_S of 40.7 ± 1.1 °C. With regard to the samples of the parchment type MP, which were treated with acidic parchment glue, T_S decreased to 46.3 ± 1.6 °C after six days and 41.4 ± 1.1 °C after 13 days originating from T_S of 64.3 ±2.6 °C.

Table 3: Mean values for the temperatures of the first observed shrinkage activity (T_{first}), the shrinkage temperatures (T_S), the temperature at the end of the main shrinkage interval ($T_{S,\ end}$), the length of the main shrinkage interval (ΔT), the temperature of the last observed shrinkage activity (T_{last}) and the length of the entire shrinkage interval ($\Delta T_{complete}$) of the reference samples prior to, after five days and after 13 days of artificially ageing.

sample	T_{first} [°C]	T_S [°C]	$T_{S,\ end}$ [°C]	ΔT [°C]	T_{last} [°C]	$\Delta T_{complete}$ [°C]
NP_p_0d	48,7 ± 2,3	51,8 ± 0,8	54,9 ± 0,5	3,1	56,4 ± 0,8	7,7
NP_p_5d	36,5 ± 1,2	39,9 ± 0,5	42,8 ± 0,5	2,9	47,0 ± 1,3	10,5
NP_p_13d	30,2 ± 0,6	33,3 ± 0,6	36,3 ± 0,7	3,0	41,3 ± 1,6	11,1
LP_p_0d	58,7 ± 1,9	61,8 ± 1,2	65,1 ± 0,5	3,3	67,7 ± 0,6	9,0
LP_p_5d	41,0 ± 1,5	44,1 ± 0,8	47,4 ± 0,5	3,3	52,1 ± 2,2	11,1
LP_p_13d	31,4 ± 0,9	34,9 ± 0,7	39,8 ± 0,9	4,9	44,2 ± 0,9	12,8
MPB_p_0d	57,7 ± 2,2	62,5 ± 1,4	67,4 ± 1,8	4,9	71,0 ± 1,0	13,3
MPB_p_6d	43,9 ± 1,5	46,6 ± 0,4	49,6 ± 0,6	3,0	57,4 ± 2,7	13,5
MPB_p_13d	37,6 ± 1,0	40,7 ± 1,1	43,6 ± 0,8	2,9	52,0 ± 1,1	14,4
MPD_p_0d	60,2 ± 2,8	64,3 ± 2,6	67,4 ± 2,6	3,1	69,8 ± 2,0	9,6
MPD_p_6d	43,5 ± 2,0	46,3 ± 1,6	50,2 ± 1,1	3,9	55,1 ± 2,5	11,6
MPD_p_13d	36,2 ± 0,7	41,4 ± 1,1	45,6 ± 0,7	4,2	50,3 ± 0,9	14,1

63 More detailed results of each reference samples are given in the appendix in table 4 and Malissa, 2017, pp. 89–96.

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Table 4: Mean values for the temperatures of the first observed shrinkage activity (T_{first}), the shrinkage temperatures (T_S), the temperature at the end of the main shrinkage interval ($T_{S, end}$), the length of the main shrinkage interval (ΔT), the temperature of the last observed shrinkage activity (T_{last}) and the length of the entire shrinkage interval ($ΔT_{complete}$) of polished and unpolished reference samples of the first part of the ageing study after five days of artificial ageing.

Sample	T_{first} [°C]	T_S [°C]	$T_{S, end}$ [°C]	ΔT [°C]	T_{last} [°C]	$ΔT_{complete}$ [°C]
ST1B/NP/up/5d	37,8 ± 0,3	40,2 ± 0,8	43,4 ± 0,0	3,2	47,0 ± 0,9	9,2
ST1B/NP/p/5d	37,7 ± 0,6	39,2 ± 0,9	42,8 ± 1,2	3,6	47,1 ± 1,0	9,4
ST2B/NP/up/5d	37,9 ± 0,7	41,1 ± 0,5	43,7 ± 0,6	2,6	46,8 ± 0,4	8,9
ST2B/NP/p/5d	35,8 ± 0,7	40,5 ± 0,7	43,5 ± 3,0	3,0	46,6 ± 0,6	10,8
ST3B/NP/up/5d	37,2 ± 1,7	40,0 ± 0,9	42,5 ± 1,3	2,5	49,1 ± 2,0	11,9
ST3B/NP/p/5d	35,3 ± 0,7	40,0 ± 0,1	42,7 ± 0,5	2,7	53,7 ± 2,5	18,4
ST4B/NP/up/5d	35,6 ± 0,6	38,5 ± 1,1	42,9 ± 3,6	4,4	47,2 ± 2,1	11,6
ST4B/NP/p/5d	34,4 ± 1,6	39,2 ± 1,6	42,4 ± 0,5	3,2	49,8 ± 1,7	15,4
ST1B/LP/up/5d	41,9 ± 0,1	43,9 ± 0,1	47,3 ± 0,4	3,4	50,9 ± 1,8	9,0
ST1B/LP/p/5d	42,0 ± 0,6	44,0 ± 0,1	46,7 ± 0,2	2,7	49,0 ± 1,2	7,0
ST2B/LP/up/5d	43,1 ± 0,7	44,4 ± 0,4	46,9 ± 0,4	2,5	51,3 ± 1,8	8,2
ST2B/LP/p/5d	39,0 ± 0,3	42,5 ± 0,4	46,9 ± 0,6	4,4	51,2 ± 1,6	12,2
ST3B/LP/up/5d	42,8 ± 0,5	44,7 ± 0,2	47,9 ± 0,8	3,2	55,3 ± 3,6	12,5
ST3B/LP/p/5d	41,8 ± 0,4	44,2 ± 0,5	47,5 ± 0,3	3,3	56,1 ± 3,4	14,3
ST4B/LP/up/5d	43,7 ± 2,0	45,4 ± 1,4	47,2 ± 0,8	1,8	53,0 ± 1,3	9,7
ST4B/LP/p/5d	43,0 ± 1,7	44,9 ± 0,3	47,2 ± 0,6	2,3	52,0 ± 1,2	9,0

Along with the discussed decrease of the shrinkage temperatures of the artificially aged samples, a reduction of the possible five shrinkage intervals – A1, B1, C, B2 and A2 – could be observed. The reference samples, which were made of the parchment types NP and LP and aged during the first series of the ageing study, only showed three shrinkage intervals – A1, C and A2 – after 13 days of artificial ageing. In contrast, the reference samples, which were made of the parchment type MP and aged during the second part of the ageing study, still showed all five shrinkage intervals.

As it was described above, one half of each reference sample was burnished with an agate polishing stone prior to the application of the silver inks in the course of sub study 1 with the purpose of checking if this mechanical preparation step had an impact on the condition of the parchment after ageing. As it can be seen in Table 4, the shrinkage temperatures of unburnished and burnished samples only vary between 38.5 °C and 41.1 °C for samples of the reference parchments NP and between 42.5 °C and 44.9 °C for samples of the reference parchments LP. Since these minor variations are in accordance with the

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results discussed so far, the preparation step of polishing does not seem to contribute to a further degradation of the collagen structure.

When comparing the shrinkage temperatures of the two fibre samples of the Vienna Genesis (Table 5) a distinctive difference between the measured values is evident. The first sample (Vienna Genesis_S1), which was taken from folio 2, has a shrinkage temperature of 30.5 °C. A shrinkage temperature of 48.0 °C was measured for the second sample (Vienna Genesis_S2), which originated from folio 9. In accordance with the low shrinkage temperature of Vienna Genesis_S1 very little shrinkage activity could be observed, whereas in the case of Vienna Genesis_S2 three of the five shrinkage intervals – A1, C and A2 – could be documented. Further comparison of the shrinkage temperatures T_S of the fibre samples of the Vienna Genesis and the reference samples after the artificial ageing, given in table 5, shows that the values are approximately at the same level and well comparable.

Table 5: Mean values for the temperatures of the first observed shrinkage activity (T_{first}), the shrinkage temperatures (T_S), the temperature at the end of the main shrinkage interval ($T_{S, end}$), the length of the main shrinkage interval (ΔT), the temperature of the last observed shrinkage activity (T_{last}) and the length of the entire shrinkage interval ($\Delta T_{complete}$) of the reference samples after 13 days of artificial ageing and the fibre samples of the Vienna Genesis.

Sample	T_{first} [°C]	T_S [°C]	$T_{S, end}$ [°C]	ΔT [°C]	T_{last} [°C]	$\Delta T_{complete}$ [°C]
Vienna Genesis_S1	26,4	30,5	31,1	0,6	31,1	4,7
Vienna Genesis_S2	30,3	48,0	48,8	0,8	51,1	20,8
NP_p_13d	30,2 ± 0,6	33,3 ± 0,6	36,3 ± 0,7	3,0	41,3 ± 1,6	11,1
LP_p_13d	31,4 ± 0,9	34,9 ± 0,7	39,8 ± 0,9	4,9	44,2 ± 0,9	12,8
MP_p_13d	37,6 ± 1,0	40,7 ± 1,1	43,6 ± 0,8	2,9	52,0 ± 1,1	14,4

Fibre Morphology

In addition to determining the shrinkage temperatures, the fibre morphologies were analysed. The information gained should contribute to a more detailed characterisation of the condition of the different samples. The description of the fibre morphologies was carried out according to the IDAP guidelines[64]. The analysis was done directly before the analysis of the shrinkage temperatures at room temperature. Therefore, approximately ten well-sep-

64 Larsen, 2007.

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arated fibres out of three different areas of the glass slide, respectively, were analysed and documented photographically.

An exemplary comparison of the fibre morphologies which could be observed for the reference parchment NP most frequently after 13 days of accelerated ageing is given in figure 37. The majority of fibres which were present in all fibre samples of this type of parchment appeared to be damaged, mostly in form of "flat fibres" (Fig. 37 d), "pearls on a string" and "bundles" (Fig. 37 b and c) as well as in a transition state from "pearls on a string" to "bundles" (Fig. 37 a). Due to the fact that the fibre morphologies observed are the direct initial stages to partly and completely gelatinised fibres, they indicate an advanced degradation of the collagen structure[65].

In contrary to the samples of the reference parchment NP, much thinner fibres were present in the samples of the reference parchment LP, which was produced according to Late Antique methods. Due to that, the observation of the fibre morphologies was more complicated. Furthermore, the samples of the parchment type LP showed a smaller amount of damaged fibres. The fibre morphology that could be observed most frequently was "pearls on a string" (Fig. 38).

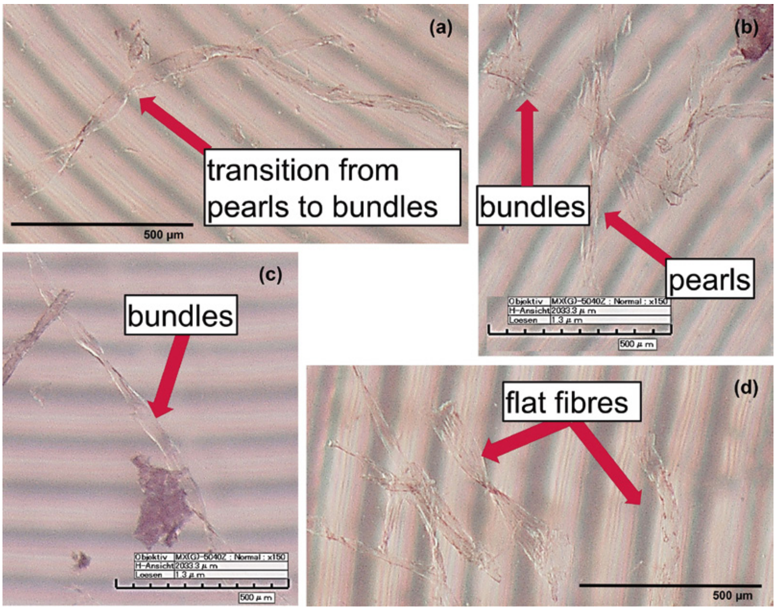

Fig. 37: HIROX images (taken at 150x magnification, scale bar 500 µm) of the most frequently observed fibre morphologies of reference parchment NP after 13 days of artificial ageing.

65 Axelsson et al., 2016, pp. 46–57.

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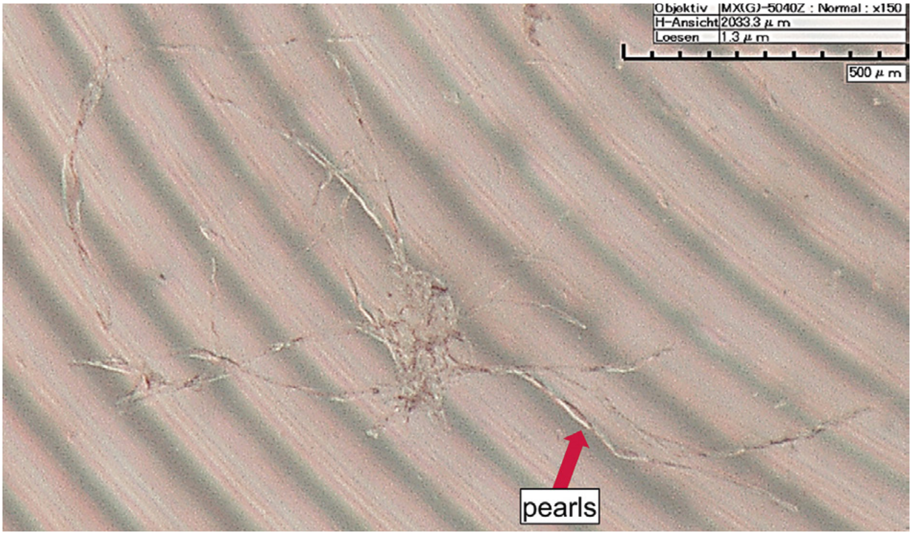

Fig. 38: HIROX images (taken at 150x magnification, scale bar 500 μm) of the most frequently observed fibre morphology of reference parchment LP after 13 days of artificially ageing.

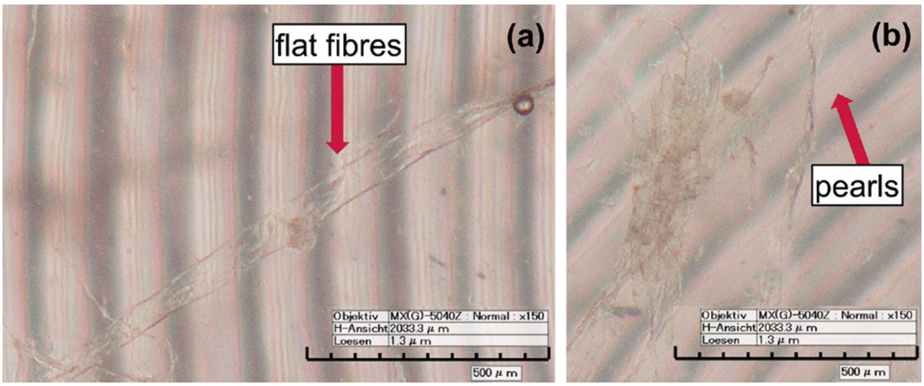

Fig. 39: HIROX images (taken at 150x magnification, scale bar 500 μm) of the most frequently observed fibre morphologies of folio 9 of the Vienna Genesis (Vienna Genesis_S2).

Like the samples of the parchment type LP, samples of the parchment type MP showed a large amount of undamaged fibres. Those fibres which indicated a damage of the collagen structure were present in form of "pearls on a string" and "bundles". In particular the small amount of undamaged fibres that could be observed in the case of parchment LP and MP suggested a less progressed degradation of the collagen structure

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and therefore a better condition of the samples compared to the samples of the reference parchment NP.

In contrast to the fibre samples of the artificially aged reference samples, the fibre samples of the Vienna Genesis contained a smaller amount of fibres. With regard to the fibre morphologies, sample Vienna Genesis_S1, which was taken from folio 2, mainly showed "bundles" and partly gelatinised fibres, whereas in the fibre sample Vienna Genesis_S2 from folio 9 mainly "flat fibres" (Fig. 39 a) and "pearls on a string" (Fig. 39 b) were present. When comparing the information gained by the analysis of the fibre morphologies of the reference samples as well as the fibre samples from the Vienna Genesis with the determined values of the shrinkage temperatures (Table 4), they confirm one another.

Summary and conclusions

A number of 14 reference inks was prepared for the artificial ageing study. The inks ST1–ST9 were artificially aged during the sub study 1 and ST10–ST14 were part of the sub study 2. The observations which were made during the preparation of the reference inks as well as the results of the analyses performed on the reference samples showed that it requires a lot of knowledge and practice to properly prepare silver inks and to write with them. Since the instructions in the original treatises are often not very precise, the interpretation of a single recipe can vary greatly. Even the question of the silver source constitutes a factor with many unknowns. Craftsmen preparing silver inks could have used pure silver with traces of other elements depending on the mine, silver alloys or recycled silverware. Certain preparations were modified in order to be able to write with the inks on the parchment. Nevertheless, for some inks it was not possible to apply them smoothly, as the silver powder either did not disperse in the binder or the inks were too thick or clotted. Additionally, the majority of the reference inks tended to smear or flake off during the burnishing process. Only three reference inks (ST5, ST7 and ST10) could be burnished without problems[66]. The unburnished inks mostly had a greyish colour without a silvery shine, while the burnished ones had shiny silver surfaces.

The colours of the reference inks ranged between yellowish, greenish or brownish grey and a very light grey on purple parchment. Most of them were at least a bit glittery when being observed under magnification. The tests showed that the refining method of the silver powder influences the usability of the inks. The reference inks which were prepared with silver powder gained by grinding silver leaves by hand with gum arabic were easier to

66 These observations were not congruent with the observations of Trost.

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apply to the parchment and appeared finer under the microscope than the inks based on silver powder prepared in a mortar or by amalgamation. The only exception was ST1.

In sub study 1 mainly inks without additional copper were prepared. Instead, the impact of a variety of other components, like sodium hydrogen carbonate ($NaHCO_3$, soda) or potassium nitrate (KNO_3, saltpetre) was tested. Since pure silver inks, like ST7 and ST9, barely showed signs of deterioration, whereas other inks showed severe signs of damage, it is assumed that particularly ink components, like the ones mentioned before, enhance the deterioration of ink and parchment, even in small amounts. In addition environmental factors like humidity or sodium chloride (NaCl, salt) play a significant role in the stability of inks. Sodium chloride can be a component of the ink and an external influence in the form of e. g. seawater. In sub study 2 copper containing recipes were selected, as the analyses of the silver ink of the Vienna Genesis with XRF showed that copper is present in the ink. The investigation of the visual appearances of the aged reference inks ST10, ST11 and ST12, containing copper(II)acetate, as well as reference ink ST1, containing copper(I)oxide, showed that the presence of this element clearly contributes to the degradation of silver ink and parchment. Although varying degrees of corrosion and degradation of different reference inks could be achieved, it was not possible to reproduce the blackening and discoloration of the silver ink of the Vienna Genesis. Sub study 2 showed that the treatment of spraying parchment with parchment glue containing acetic acid can potentially lead to damage, as it was observed on the inks ST10, ST11 and ST12. Rust-like halos formed around the ink lines.

Very intense ageing conditions were chosen to achieve a degree of deterioration of the parchment comparable to the original within a short period of time. It was possible to artificially age the orchil dyed parchment samples until the shrinkage temperature as well as the fibre morphologies resembled those of two micro-samples from the Vienna Genesis. The micro-samples were taken from two folios and are therefore limited in representing the whole manuscript. The analyses of the shrinkage temperature of the two fibre samples of the Vienna Genesis differed a lot, showing that the condition of the folios is not homogeneous. As the shrinkage temperature of the sample Vienna Genesis_S1 is very low, it can be assumed that the parchment of the whole manuscript is very climate sensitive. The results of the analysis of the new parchment show a less advanced degradation of the collagen structure and therefore a better condition of the samples of MP (medieval parchment) and LP (Late Antique parchment) compared to the samples of NP (new parchment). In the case of the described parchment types, the ones produced according to historical methods seem to be more stable than the one produced with modern methods.

The silver ink of the Codex Purpureus Petropolitanus, originating from the same region and time, is very similar to the ink of the Vienna Genesis regarding the ratio of silver and

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copper, but is in a much better condition, see chapter on the silver ink. Organic components were not analysed on the micro-samples of original inks, as sampling of the original inks was kept to a minimum. The original composition of the ink of the Vienna Genesis could not be identified. Therefore, it was not possible to replicate the aged condition of the silver ink. The results of the alteration study show that even minor inorganic components of the ink, like potassium nitrate (saltpetre) or sodium hydrogen carbonate (soda), can cause severe degradation of medium and parchment carrier. Copper ions formed by oxidation of silver–copper alloys, present as trace elements or introduced by copper containing additives seem to play a significant role in the ageing of the inks and the degradation of collagen fibres. The comparison with the inks on the Codex Purpureus Petropolitanus, which also contain copper, shows that copper alone is not responsible for the substantial losses in the Vienna Genesis. Sodium chloride as a component of the ink or as an external factor is probably responsible for the formation of silver chloride, which is the main corrosion product of the Vienna Genesis silver ink. High humidity or even liquid water have contributed to the fragile condition of the Vienna Genesis. Tidelines and the transfer of pigments testify of the exposure to high humidity or water at some point. The unknown history of the manuscript before 1664 could include water damage. A possible transport on sea or eventual storage in a costal town in Italy like Venice could have involved exposure to salty sea water as vapour or liquid.

The consequences for conservation and storage of the Vienna Genesis have been discussed with all project partners and additional experts. There was agreement that adhesives should be applied with a minimum amount of moisture on the ink during stabilisation of fragile areas of the text. As explained in the chapter on conservation, a hydroxypropylcellulose-ether (Klucel G) in water was chosen in the form of a remoistenable tissue. The dry adhesive film on Japanese tissue paper was reactivated with a mixture of ethanol and a small amount of water before application. Remains of adhesives from prior treatments were not removed because the treatment would involve the application of moisture.

The housing materials have to be free of corrosive components and the level of volatile organic compounds in the storage area has to be low. The depository for rare manuscripts has a controlled climate, 20 °C and 45 % RH. The folios of the Vienna Genesis will remain in storage to provide a stable environment and to limit the risks of further alterations.

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Materials

Advent Research Materials Ltd, Oakfield Industrial Estate, Eynsham, Oxford, England, OX29 4JA; www.advent-rm.com (accessed 6 February 2020)
Rolled silver

Australco, Bahnstraße 16, 2104 Spillern, Austria; www.australco.at (accessed 6 February 2020)
Ethanol 96 %

Deffner & Johann GmbH, Mühläcker Straße 13, 97520 Röthlein, Germany; www.deffner-johann.de (accessed 6 February 2020)
Wheat starch

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Europapier, Autokaderstrasse 86–96, 1210 Vienna, Austria; www.europapier.com (accessed 6 February 2020)
Museum matboard, Canson, 1.8 mm

Fetter Baumarkt GmbH, Laaer Straße 252, 2100 Korneuburg, Austria; www.fetter.at (accessed 6 February 2020)
Bamboo

Glaser A., Inh. Martin Rustige, Theodor-Heuss-Straße 34a, 70174 Stuttgart, Germany; www.anton-glaser.de (accessed 6 February 2020)
Lamb parchment

Hofer Kommanditgesellschaft, Hofer Straße 1, A-4642 Sattledt, Austria; www.hofer.at (accessed 6 February 2020)
Wine vinegar, Lomee

Kremer Pigmente GmbH & Co. KG, Hauptstr. 41–47, 88317 Aichstetten, Germany; www.kremer-pigmente.com (accessed 6 February 2020)
Gum Arabic, ox gall, copper(I)acetate, copper(II)acetate

Paper Nao; 4-37-28 Hakusan Bunkyo-ku, Tokyo 112–0001 Japan
Japanese tissue K-37

Neuber's Enkel Dr Brunner & Kolb GmbH, Linke Wienzeile 152, 1060 Vienna, Austria; www.neubers-enkel.at (accessed 6 February 2020)
Ammonia 25 %

Sigma-Aldrich, Marchettigasse 7/2, 1160 Vienna, Austria; www.sigmaaldrich.com/austria (accessed 6 Feburary 2020)
Potassium nitrate (KNO_3, salpetre), Sodium hydrogen carbonate ($NaHCO_3$, soda), Sodium chloride (NaCl), Hydrated magnesium sulfate ($MgSO_4$ x H_2O), Calcium chloride ($CaCl_{2)}$, Urea

Störleim-Manufaktur, Eva Przybylo, In der Helle 21, 59929 Brilon, Germany; www.stoerleim-manufaktur.de (accessed 6 February 2020)
Isinglass

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Wamprechtsamer A. GmbH, Blattgoldschlägerei, Kendlerstraße 14, 1140 Vienna, Austria
Silver leaf

Weinkellerei Lenz Moser AG, Lenz-Moser-Straße 1, A-3495 Rohrendorf bei Krems, Austria: www.lenzmoser.at (accessed 6 February 2020)
Red wine "Alter Knabe"

Cherry gum
provided by the Conservation Science Department of Kunsthistorisches Museum Vienna

Mercury (Hg)
provided by the Atomic Institute, Technical University Vienna

Parchment
Jiří Vnouček
David Frank

Parchment glue
Film of parchment glue from the Conservation Institute at the Austrian National Library

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The miniatures of the Vienna Genesis: colour identification and painters' palettes

Christa Hofmann, Sophie Rabitsch, Antonia Malissa, Maurizio Aceto, Katharina Uhlir, Martina Griesser, Elisa Calà, Angelo Agostino, Gaia Fenoglio

Introduction

The Vienna Genesis is famous for the 48 miniatures, which illustrate the text of the book of Genesis. The paintings are considered the richest cycle of book illuminations from Late Antiquity. Various aspects of these miniatures have been the research focus of numerous scholars over centuries. One question that has been ardently debated for over 100 years is how many painters worked on the illustrations. It is obvious that not only one artist designed and painted the miniatures. So far, the painters have been differentiated by their style and their iconography. The colours used by the artists have not been investigated, therefore the aim of this project was to identify pigments and dyes as well as to differentiate palettes of individual painters. A combination of methods was employed to gain better understanding of the art technology. Based on the latest research and theory on painters by Barbara Zimmermann[1] and visual observation of the paintings, seven painters were identified (painters A, B, C, D, E, F, and G). Representative measurement points in the main colours were selected for each painter. The measurement points were analysed by micro-X-ray fluorescence spectroscopy (µ-XRF) and by UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS). Spectrofluorimetry and optical microscopy were used to obtain additional information. Loose paint particles that could no longer be assigned to definite locations were used as micro-samples for further studies with Raman spectroscopy, surface enhanced Raman spectroscopy (SERS) and scanning electron microscopy with energy dispersive X-ray detection (SEM/EDX). The analytical results were compared with microscopic examination of the measuring points using 6.3x–32x magnification. Observations of the miniatures under visible light and ultraviolet light (UV) as well as on infrared reflectography (IRR) images completed the interpretation of the painting techniques. In discussion with all partners, a suggestion for the colours used by seven different painters was formulated. Not all pigments and dyes could be clearly identified. Despite open questions it is possible to distinguish differences between painters namely in the use of blue, green and black colours.

1 Zimmermann, 2003.

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Previous theories on painters' palettes

Franz Wickhoff first emphasized the participation of several painters in the commentary to the facsimile edition from 1895[2] (Table 1). His theories did not consider the system of bifolios and was not shared by his followers. Charles R. Morey recognised the similarities of the miniatures of the Vienna Genesis with the Codex Rossanensis and the Codex Sinopensis. He assumed that six painters worked on the miniatures[3]. Morey, Buberl[4], Mazal[5] and Zimmermann[6] agreed that folios 15 and 16 (pages 29–32), folios 17 and 18 (pages 33–36), folios 19–22 (pages 37–44) and folios 23 and 24 (pages 45–48) were painted by different artists (Table 1). Buberl and Mazal had the opportunity to study the original manuscript and considered the scheme of quires. They assumed that one artist painted the miniatures on both sides of one biofolio. They differed in their attributions of folios 1–8 (pages 1–16). Mazal thought that a different artist painted each of these bifolios. Mazal saw stylistic variations and proposed 11 artists for all miniatures. Zimmermann doubted the differences and assumed that one artist painted folios 1–8 (pages 1–16) as well as folios 10–14 (pages 20–28). In accordance with Morey, Zimmermann proposed six painters based on art historical research. The pigments of the Vienna Genesis have never been investigated. Differences between the painters in the way they used and applied colours have not been studied so far.

Table 1: Theories of painters from 1895 to 2017

Author, Date	Painters	Folios (f) and pages (p)
Wickhoff, 1895	A	f 1–2 (p 1–4), f 3v (p 6), f 5 (p 9–10), f 7–10 (p 13–20)
	B	f 4 (p 7–8), f 6 (p 11–12)
	C	f 11–12 (p. 21–24), f 14–16 (p 27–32)
	D	f 13 (p 25–26)
	E	f 17–18 (p 33–36)
	F	f 3r (p 5), f 19–22 (p 37–44)
	G	f 23–24 (p 45–48)
Morey, 1929	A	f 1–8 (p 1–16), f 11–14 (p 21–28)
	B	f 9–10 (p 17–20)
	C	f 15–16 (p 29–32)

2 Hartel and Wickhoff, 1895, pp. 88, 162–66.
3 Morey, 1929, pp. 5–112.
4 Buberl, 1936, pp. 9–58.
5 Mazal, 1980, pp. 161–166.
6 Zimmermann, 2003, pp. 220–223.

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Author, Date	Painters	Folios (f) and pages (p)
	D	f 17–18 (p 33–36)
	E	f 19–22 (p 37–44)
	F	f 23–24 (p 45–48)
Gerstinger, 1931	A	f 1–3 (p 1–6), f 5 (p 9–10), f 8 (p 15–16), f 11 (p 21–22), f 14 (p 27–28)
	B	f 4 (p 7–8), f 6–7 (p 11–14)
	C	f 9–10 (p 17–20)
	D	f 12–13 (p 23–26)
	E	f 17–18 (p 33–36)
	F	f 19–22 (p 37– 44)
	G	f 23–24 (p 45–48)
Buberl, 1936	A	f 1–5 (p 1–10)
	B	f 6–8 (p 11–16)
	C	f 9–10 (p 17–20)
	D	f 11–14 (p 21–28)
	E	f 15–16 (p 29–32)
	F	f 17–18 (p 33–36)
	G	f 19–22 (p 37–44)
	H	f 23–24 (p 45–48)
Mazal, 1980	A	f 1 (p 1–2)
	B	f 2–3 (p 3–6)
	C	f 4–5 (p 7–10)
	D	f 6–7 (p 11–14)
	E	f 8 (p 15–16)
	F	f 9–10 (p 17–20)
	G	f 11–14 (p 21–28)
	H	f 15–16 (p 29–32)
	I	f 17–18 (p 33–36)
	J	f 19–22 (p 37–44)
	K	f 23–24 (p 45–48)
Zimmermann, 2003	A	f 1–8 (p 1–16), possibly f 10–14 (p. 20–28)
	B	f 9–10 (p 17–20)
	C	f 15–16 (p 29–32)
	D	f 17–18 (p 33–36)
	E	f 19–22 (p 37–44)

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Author, Date	Painters	Folios (f) and pages (p)
	F	f 23–24 (p 45–48)
Genesis-project, 2017	A	f 1–8 (p 1–16)
	B	f 9–10 (p 17–20)
	C	f 11–14 (p 21–28)
	D	f 15–16 (p 29–32)
	E	f 17–18 (p 33–36)
	F	f 19–22 (p 37–44)
	G	f 23–24 (p 45–48)

Methods for colour identification

For the present study, Zimmermann's theory on six painters served as benchmark for the selection of representative measurement points to define the palettes of painters. It is assumed that the miniatures of one bifolio were done by one painter, see scheme of bifolios in the chapter on parchment. Technological observations indicate that the folios 11–14 (pages 21–28) could have been executed by a seventh artist. Folios 11 and 14 formed a bifolio as well as folios 12 and 13. These two bifolios were part of one quire. The initial measurements by Maurizio Aceto in 2014 called for the necessity of opening the polyacrylate mounting sheets to obtain reliable results. As a pre-condition for further analysis the mounting was opened, see the chapter on conservation. First conservation treatments were done to make the investigations possible. In general, the condition of the paint layers was stable. Losses have occurred due to abrasion of colours, deformation of the parchment, possible high humidity and use. Most losses can be seen on areas painted in lead white or with mixtures of lead white. The points for the investigations with µ-XRF, FORS and visual observation were marked on printouts and digital images of each miniature. The aim was to identify the pigments and dyes of the main palette for each painter. The different investigations were compared with one another. First, a survey was performed with FORS and µ-XRF on a large number of measurement points. Then a selection of points was chosen for spectrofluorimetric analysis, in order to gain complementary information on the organic dyes. All measurement points were investigated under a stereo microscope and compared with the other paint layers on the same miniatures. All techniques applied were performed non-invasively, without touching the surface of the manuscript. Finally, Raman spectroscopy, SERS and SEM/EDX analyses were carried out on loose micro-particles that could not be relocated.

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The analysis of the miniature paintings with energy dispersive µ-X-ray fluorescence spectroscopy (µ-XRF) was performed together with the analysis of the silver inks, see chapter on silver inks. Therefore, the same portable instrument[7], which was provided by the International Atomic Energy Agency (IAEA), Seibersdorf Laboratories, Nuclear Science and Instrumentation Laboratory, and identical measuring conditions were used. In order to minimize absorption losses of excitation and X-ray fluorescence radiation by air and thus provide an elemental range from sodium (Na) onwards, a vacuum chamber that can be pumped down to 0.1 mbar forms the centrepiece of the spectrometer. Additionally, the spectrometer is equipped with a low-power Pd tube, which was run with an acceleration voltage of 50 kV, a current of 1 mA and a measuring time of 100 s. The spot analysed has a diameter of 160 µm when focused using the polycapillary of the instrument, which is placed inside the compact vacuum chamber. The chamber is sealed with a Kapton window that allows positioning of the measurement head in front of the spot analysed using two laser pointers, which cross at about 1–2 mm distance in front of the spectrometer, at the focal spot of the polycapillary. For this procedure an internal camera is used. The fluorescence radiation emitted by the investigated sample is collected by a Si drift detector (SDD) with an active area of 10 mm^2. Since an upright positioning of the folios was required by the arrangement of the spectrometer, each folio was mounted on a polyester foam with paper corners and fixed vertically on a perforated plate using a special setup. The qualitative interpretation of the XRF spectra was supported by the comparison with reference spectra of natural and synthetic pigments[8] provided by the Conservation Science Department of Kunsthistorisches Museum Vienna (KHM)[9]. Due to the thinness of the folios of Vienna Genesis, signals originating from the miniature paintings on the respective backsides were likely detected in a huge number of generated spectra. Therefore, the interpretation of the spectra was severely hampered and some inorganic trace components detected are not going to be discussed during further evaluation.

UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS) analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source. Detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5x100 probe. In this configuration, light is sent and retrieved with a single fibre bundle positioned at 45° with respect to the surface normal, in order to exclude specular reflectance. The spec-

7 Buzanich et al. 2007, pp. 1252–1256.

8 Malissa 2015, pp. 17–66.

9 The signals of the elements palladium and argon, which were present in all spectra, are attributed to the Pd anode itself and to the composition of air, respectively, and were not considered for further discussion, as it was done for the silver inks.

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tral range of the detector was 200–1160 nm. According to the features of the monochromator (slit width 50 μm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectral resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at least at 98 % within the investigated spectral range. Blank correction was not efficient on both the extremes of the spectral range, therefore the regions 200–350 nm and 1100–1160 nm were not considered in the discussion. The diameter of the investigated area on the sample was 1 mm. In all of the measurements, the distance between the probe and the sample was kept constant at 2 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1 s for each spectrum. The system was managed by means of AvaSoft v.8 dedicated software, running under Windows 7.

An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal light source. An FCR-7UV200-2-1.5x100 probe (same as FORS) is used to drive excitation light on the sample and to recover the emitted light. The spectrophotometer works in the range 191–886 nm. According to the features of the monochromator (200 μm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in diameter. In all of the measurements, the sample-to-probe distance was kept constant to 12 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 4 s integration time, 3 scans for a total acquisition time of 12 s for every spectrum. The system is managed by SpectraSuite software running under Windows 7.

Micro images were taken with a Lumenera (Ottawa, Canada) Infinity Lite model camera with 1.5 MPixel and CMOS sensor. The camera was connected with a Navitar (Rochester, NY, USA) Zoom 6000 optical lens allowing a 10x–80x magnification range[10]. Illumination of the sample was obtained by means of an Opto Engineering (Mantova, Italy) LT RN 23/W model LED ring light, providing cool white light, so having a minimum impact on the sample.

Raman analysis was performed with a high-resolution dispersive Horiba (Villeneuve d'Ascq, France) LabRAM HR model spectrophotometer coupled with a confocal microscope. The instrument is equipped with a 633 nm excitation laser, two (600 and 1800 lines/mm) dispersive gratings, an 800 mm path monochromator and a Peltier cooled CCD

10 The microimages were taken by Valerio Capra, Laboratorio di restauro del libro, Abbazia benedittina dei S. S. Pietro e Andrea, Borgata San Pietro 10050, Novalesa (TO), Italy.

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detector. The optical arrangement gave a spectral resolution of about 2 cm^{-1}. Spectra were taken placing samples on the microscope stage and observing them with long working distance, 20x, 50x and 80x objectives. The sampled area was identified and focused using either a video camera or the microscope binoculars. Laser power at the sample was initially kept low (< 100 μW) by means of a series of neutral density filters in order to prevent any thermal degradation of the molecules, then gradually increased to the optimal signal-to-noise ratio setting. Exposure time was 1–120 s according to individual needs. The system was managed with LabSpec 5 software running under Windows XP[11].

For Surface Enhanced Raman Spectroscopy (SERS) mode analysis, a colloidal paste of silver nanoparticles was prepared following a procedure based on the Lee and Meisel reduction of silver nitrate. The colloidal paste (1 μl) is poured on the sample and allowed to dry. After 10 minutes, the SERS analysis is performed and the spectral response obtained. The sample size was less than 1 mm.

Scanning electron microscope (SEM) images at different magnification were recorded on a Quanta 200 FEI (Hillsboro, Oregon) scanning electron microscope equipped with EDAX (Mahwah, New Jersey) EDS attachment, using a tungsten filament as electron source at 20 keV. The instrument was used in E-SEM mode (90 mbar of water pressure in chamber) in order to avoid samples metallisation.

Each miniature was examined under normal and raking light. Ingrid Oentrich[12] took photographs of each page under Ultraviolet light (UV). Michael Eder[13] made Infrared reflectography images (IRR) of each miniature. He used a Hamamatsu InGaAs camera C 12741-03 with an IR sensitivity of 950 to 1700 nm. The single shots were put together with Microsoft ICE and Photoshop. With a Wild stereo microscope M 400 (Type 126269), the analysed measurement points of the colours were investigated under the microscope at 6.3x–32x magnification. The points were compared with other areas of similar colour. Digital images were taken with a Nikon D7000 camera equipped with a Nikon camera adapter for microscopes (SKU: CA-NIK-SLR). Analytical results were correlated with visual examination and art technological observations. A spreadsheet per miniature contains the number of the investigated points, the results of μ-XRF, of FORS, optical and technological descriptions, observations under UV light and of infrared reflectography images as well as the number of the microscopic images. The results for every painter were summarised in the spreadsheet. In the following, the palettes are described for each of the assumed seven painters (Table 2).

11 Angelo Agostino and Gaia Fenoglio collaborated in the interpretation of FORS, fluorimetry and Raman spectral responses.

12 Ingrid Oentrich, Department of Digital Services, Austrian National Library.

13 Michael Eder, Kunsthistorisches Museum Vienna.

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Table 2: Palettes of the Vienna Genesis

Colour	Pigments	Painters	Folios, pages
Blue	Ultramarine blue, indigo, lead white	A, B	f 1–8 (p 1–16), f 9–10 (p 17–20)
	Azurite, indigo, lead white	C	f 11–14 (p 21–28)
	Ultramarine blue, Egyptian blue, lead white	D, E	f 15–16 (p 29–32), f 17–18 (p 33–36)
	Ultramarine blue, azurite, lead white	F, G	f 19–22 (p 37–44), f 23–24 (p 45–48)
Green	Indigo, orpiment	A, B, D	f 1–8 (p 1–16), f 9–10 (p 17–20), f 15–16 (p 29–32)
	Malachite	A	f 6–8 (p 12–16)
	Azurite, orpiment sometimes with indigo and/or lead white	C	f 11–14 (p 21–28)
	Green earth	E	f 17–18 (p 33–36)
	Green earth, yellow ochre, lead white	F, G	f 19–22 (p 37–44), f 23–24 (p 45–48)
Red	Red lead	A, B, C, D, E, F, G	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28); f 15–16 (p 29–32), f 17–18 (p 33–36), f 19–22 (p 37–44), f 23–24 (p 45–48)
	Cinnabar	A	f 1 (p 2), f 2 (p 4)
Pink	Madder, lead white	A, B, C, D, E, F, G	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28), f 15–16 (p 29–32), f 17–18 (p 33–36), f 19–22 (p 37–44), f 23–24 (p 45–48)
Violet	Ultramarine blue, madder, lead white	A	f 1–8 (p 1–16)
	Azurite, madder, lead white	C	f 11–14 (p 21–28)
	Ultramarine blue, Egyptian blue, madder, lead white	D, E	f 15–16 (p 21–28), f 17–18 (p 33–36)
	Ultramarine blue, azurite, madder, lead white	F, G	f 19–22 (p 37–44), f 23–24 (p 45–48)
Purple	Orchil from purple parchment	F, G	f 19–22 (p 37–44), f 23–24 (p 45–48)
Yellow	Ochre, orpiment	A, B, C, D, E	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28), f 15–16 (p 29–32), f 17–18 (p 33–36)
Brown	Ochres	A, B, C, D, E, F, G	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28), f 15–16 (p 21–28), f 17–18 (p 33–36), f 19–22 (p 37–44), f 23–24 (p 45–48)
Grey	Lead white, carbon black	A, B, C	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28)
Blue-grey	Lead white, ultramarine blue, indigo	A, B	f 1–8 (p 1–16), f 9–10 (p 17–20)
	Lead white, azurite, indigo	C	f 11–14 (p 21–28)

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Colour	Pigments	Painters	Folios, pages
	Lead white, indigo, ultramarine blue, Egyptian blue	D, E	f 15–16 (p 29–32), f 17–18 (p 33–36)
	Lead white, indigo	F	f 19–22 (p 37–44)
	Lead white, indigo, ultramarine blue, azurite	F, G	f 19–22 (p 37–44), f 23–24, (p 45–48)
Black	Carbon black	A, B, C, F	f 1–8 (p 1–16), f 9–10 (p 17–20), f 11–14 (p 21–28), f 19–22 (p 37–44)
	Iron gall ink	D	f 15–16 (p 29–32)
	Carbon black, iron gall ink	A, B, E	f 1–8 (p 1–16), f 9–10 (p 17–20), f 17–18 (p 33–36)
	Carbon black, brown earth pigment	F, G	f 19–22 (p 37–44), f 23–24 (p 45–48)
Gold	Gold	A, D, F, G	f 1–8 (p 1–16), f 15–16 (p 29–32), f 19–22 (p 37–44), f 23–24 (p 45–48)

Palette of Painter A: folios 1–8, pages 1–16

Painter A illustrated the biblical text from the fall of Adam and Eve in paradise to Isaac and Rebecca in the Philistine city of Gerar (Genesis 3, 4–13 to 26, 1–11). Painter A used ultramarine blue, obtained from lapis lazuli, as blue pigment. Ultramarine blue was often mixed with lead white to obtain different shades. The painter usually worked with three shades. Highlights were added in lead white and the black contours in carbon black were applied at the end on top of the blue layers. XRF and FORS confirmed the presence of ultramarine blue on folios 1–8, pages 1–16. The presence of aluminium (Al) and silicon (Si) on the XRF spectrum (Fig. 1) indicates ultramarine blue ($Na_7Al_6Si_6O_{24}S_3$) while high intensities of lead (Pb) point to the use of lead white. The mixture of blue and white pigments is clearly visible under the microscope. The absorption maximum at 600 nm on the FORS spectra (Fig. 2) indicates ultramarine blue. The absorption maximum at 650–660 nm is instead characteristic for the organic pigment indigo. Ultramarine blue and indigo are confirmed by Raman spectroscopy of loose blue particles. At 80x magnification, the typical shape of lapis lazuli grains with conchoidal fracture can be observed. The size of these particles is mostly in the range 5–10 µm, which indicates that the stone was well ground and purified to obtain the pigment. Painter A used indigo for blue shades, for instance on the miniature of the flood on folio 2, page 3. The heavy rain is painted in indigo on top of the other colour layers (Fig. 3).

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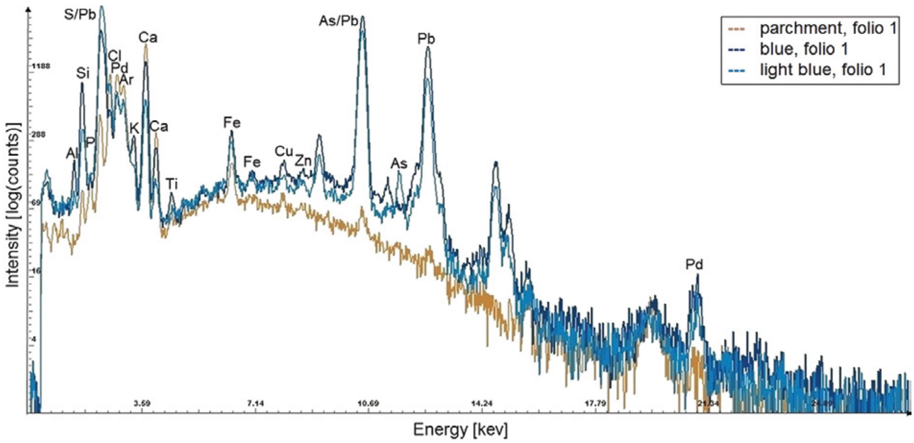

Fig. 1: XRF spectra of a blue (MP1_6) and a light blue (MP1_8) area on folio 1, page 1. A spectrum of the parchment of folio 1 (MP1_3) shows the background signal detected.

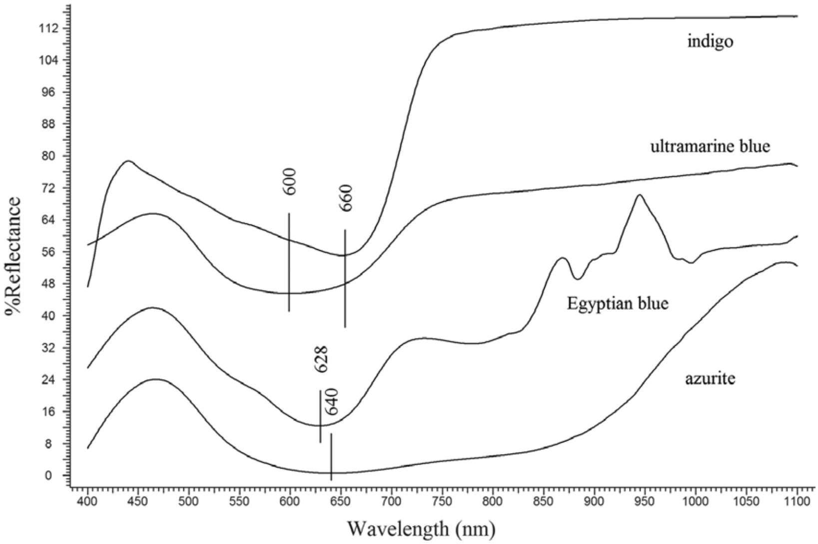

Fig. 2: FORS spectra of blue pigments: indigo, ultramarine blue, Egyptian blue and azurite.

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Fig. 3: Miniature on folio 2, page 3, the flood.

Painter A used a mixture of indigo and orpiment for green areas. Distinct intensities of arsenic (As) on the XRF spectra (Fig. 4) indicate the presence of orpiment (As_2S_3). The yellow particles of orpiment are well visible under the microscope at 6.3x–32x magnification. The FORS spectra of green areas show an absorption maximum for indigo at 650–660 nm (Fig. 5) but orpiment is not verifiable using this method. The yellow pigment is also confirmed by Raman spectroscopy of a loose green particle. The painter applied highlights in orpiment and sometimes added contours or dark areas in carbon black, like on the cushion of Abraham on folio 4, page 8 (Fig. 6). On the folios 6, 7 and 8 malachite, $CuCO_3 \cdot Cu(OH)_2$, could be detected in addition. The XRF spectrum shows high copper intensities (Cu). The identification by means of FORS is given by the absorption maximum at 800 nm (Fig. 5). Particles of malachite can be seen under the microscope (Fig. 7). The green coat of the court official on folio 8, page 4, was painted with malachite (Fig. 8). The tops of the city towers on folios 6 and 7 were accentuated with this green pigment. From painter A only one part (folio 1 and 8) or one bifolio (folios 2–7) from each quire are preserved (see scheme of bifolios in the chapter on parchment). Painter A might have used malachite on the folios that are missing today, as well. The technique with which the colour is applied does not indicate its addition at a later date in the form of a retouching.

Red areas were painted with the pigment red lead or minium (Pb_3O_4), see for example the miniature of Lot and his daughters on folio 5, page 10 (Fig. 9). All painters used red lead as red pigment. High intensities of lead (Pb) in the XRF spectra indicate the presence of red lead (Fig. 10). On the FORS spectra, red lead could be detected by the inflexion point at approx. 560 nm (Fig. 11). Artist A painted highlights in a mixture of red lead and lead white. Contours and shades presumably were applied in madder. Some areas show

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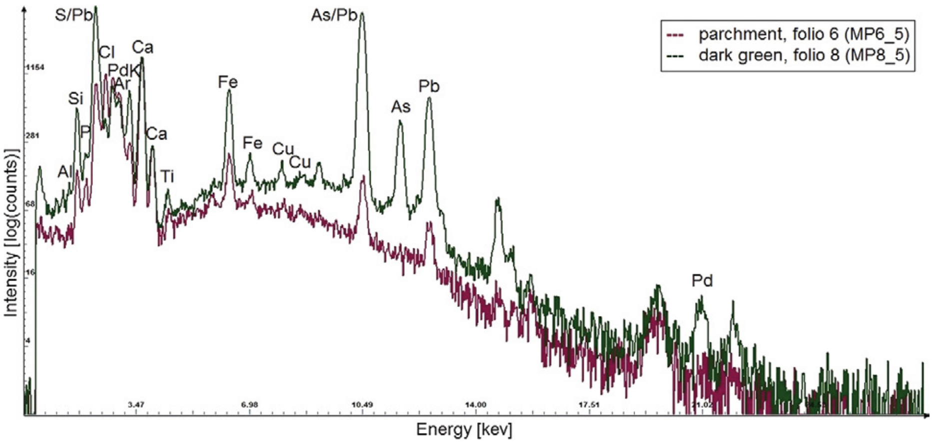

Fig. 4: XRF spectrum of a green area (MP8_5) on folio 8, page 15. For comparison a spectrum of blank parchment of folio 6 (MP6_5) shows the background signal detected.

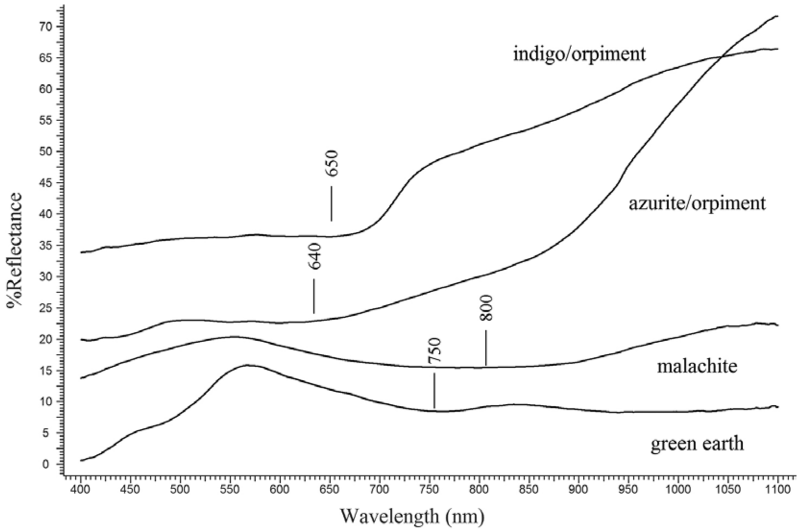

Fig. 5: FORS spectra of green pigments and mixtures: indigo/orpiment, azurite/orpiment, malachite and green earth.

darkening of red lead like on folio 5, page 10 (Fig. 9). The darkening of red lead is an oxidation process, which can be caused by high levels of sulphur in the environment or by the transformation of Pb_3O_4 to black PbO_2. On some occasions painter A used a mixture

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Fig. 6: Miniature on folio 4, page 8, the dream of Abraham.

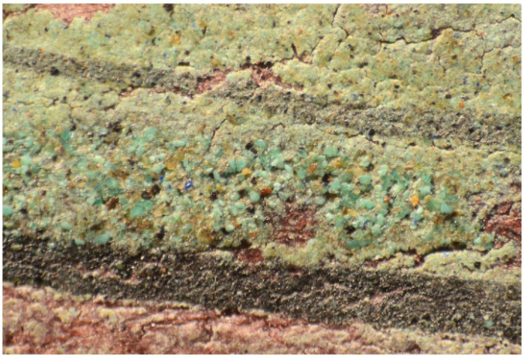

Fig. 7: Microscopic image, 16x magnification, of green on folio 8, page 16.

Fig. 8: Miniature on folio 8, page 16, Isaak and Rahel at the court of Abimelech.

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Fig. 9: Miniature on folio 5, page 10, Lot and his daughters.

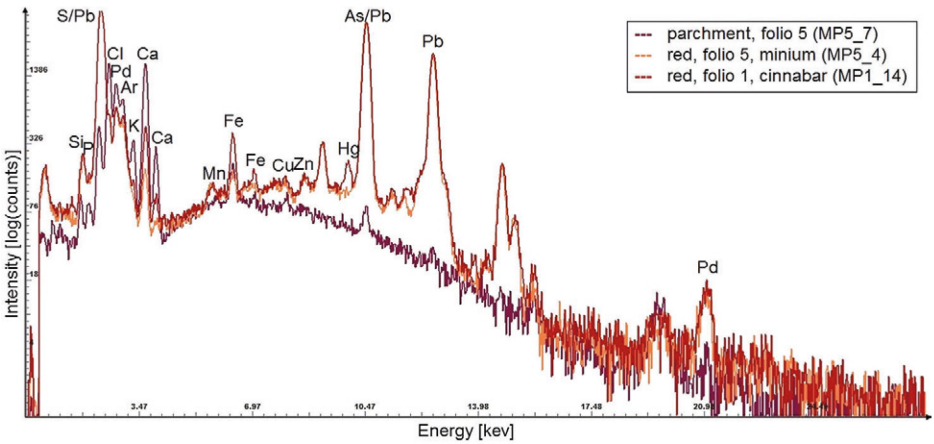

Fig. 10: XRF spectra of red areas on folio 1, page 2 (MP1_14) and folio 5, page 10 (MP5_4). For comparison a spectrum of blank parchment of folio 5 (MP5_7) shows the background signal detected.

of read lead and cinnabar (HgS) like for the flames on folio 1, page 2 and on folio 2, page 4. Cinnabar is indicated by peaks of mercury (Hg) on the XRF spectrum (Fig. 10) and by an inflexion point of approx. 600 nm on FORS spectra (Fig. 11). It is difficult to visually differentiate between red lead, cinnabar and red ochres. Painter A might have added cinnabar to his palette to paint some areas, e. g. the flames, more vividly. He might have used cinnabar more frequently on folios that are now missing.

For pink painter A used madder lake mixed with lead white, a common habit of all

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painters. Highlights were painted with mixtures having a higher proportion of lead white. For shades and contours, pure madder was used. The identification of madder by means of FORS is given by an absorption band structured in two sub-bands occurring at approx. 510–515 and 540 nm (Fig. 11). Madder is an anthraquinonic dye obtained from the root of *Rubia tinctorum* and other plants of the *Rubiaceae* family. To distinguish madder from dyes obtained from scale insects or coccid dyes (like kermes or cochineal) the identification was confirmed by spectrofluorimetry. In this case, a fluorescence peak occurs in the range of 570–600 nm while the peaks of coccid dyes occur at higher wavelengths (Fig. 12). The detection of aluminium (Al) and lead (Pb) in the XRF spectrum points to the use of a lake pigment together with lead white. SERS spectroscopy of loose pink colour particles confirms madder. On folio 8, page 15 a detail shows the use of madder with different shades on the cloth of the servant (Fig. 13).

Violet parts are a mixture of ultramarine blue, madder and lead white. Lighter tones were mixed with a higher proportion of lead white. Contours or folds were painted in black. The presence of ultramarine blue, madder and lead white is confirmed by XRF and FORS in combination, as above. On folios 4 and 5, some violet parts are a mixture of indigo and madder. Indigo is confirmed by FORS. A detail of the cloth of king Abimelech on folio 8, page 16, shows the use of violet (Fig. 14). Particles of ultramarine blue, madder and lead white can be distinguished.

For yellow and brown painter A used earth pigments, ochres. All painters employed ochres for yellow to brown tones. More yellow shades were achieved by mixtures with orpiment. Highlights were painted with a mixture of ochre and lead white. Shades were carried out with darker varieties of ochre. Contours were painted in black. Figure 15 shows a comparison of the XRF spectra of one dark brown and two light brown areas of folio 6 (camels) and folio 3. The spectra reveal the main components iron (Fe) and lead (Pb) as well as arsenic (As) in a minor portion. The intensive iron (Fe) and lead (Pb) signals indicate the use of an earth pigment, presumably containing traces of copper (Cu) and zinc (Zn), which was probably mixed with lead white. The significant arsenic (As) peak suggests the presence of orpiment as well. The main differences between the spectra of the light brown areas and the analysed dark brown hue are the relations of iron, lead and arsenic (Fig. 15). The spectra of both light brown areas show more intense lead (Pb) signals than in the dark brown area. Additionally, the spectrum of the light brown point MP3_5 shows a less intense Fe signal, the most intense Pb peak and a significant As peak. By only detecting chemical elements, without any information on their oxidation state or chemical bonding, XRF does not allow any further classification on the ochres used. The identification of ochres by means of FORS is given by the absorption maximum at approx. 860 nm for Fe_2O_3-containing ochres, red ochres, and at approx. 900 nm for FeO-OH-containing

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ochres, yellow and brown ochres (Fig. 16). Visually, it is difficult to distinguish between different brown earth pigments. In general, painter A applied ochres in thin layers that often show abrasion and losses. The use of yellow and brown pigments can be seen on the miniature of folio 6, page 12 (Fig. 17).

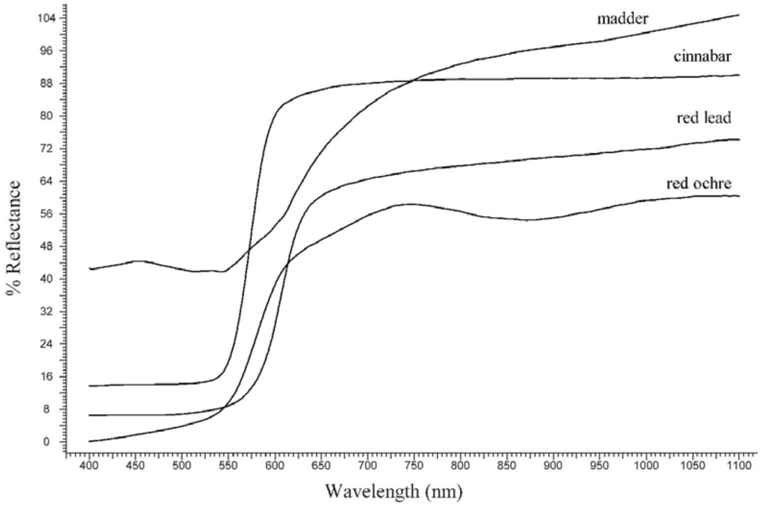

Fig. 11: FORS spectra of red lead, cinnabar, red ochre and madder.

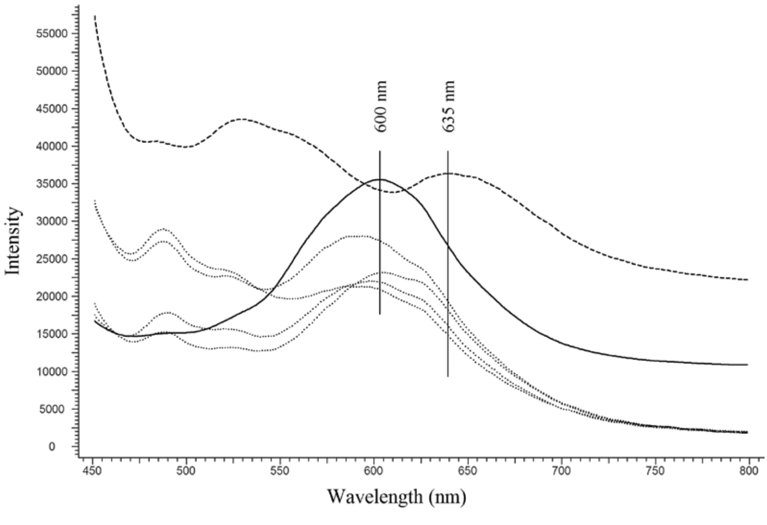

Fig. 12: Fluorescence spectra of madder (solid line), cochineal (dashed line) and pink areas of the Vienna Genesis (dotted lines).

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Fig. 13: Microscopic image, 10x magnification, of pink on the cloth of Esau's servant, folio 8, page 15.

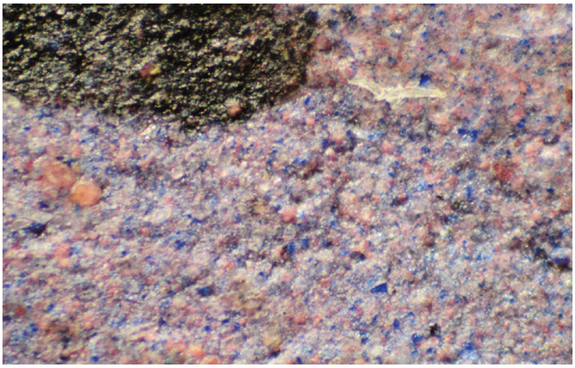

Fig. 14: Microscopic image, 16x magnification, of violet on the cloth of king Abimelech, folio 8, page 16.

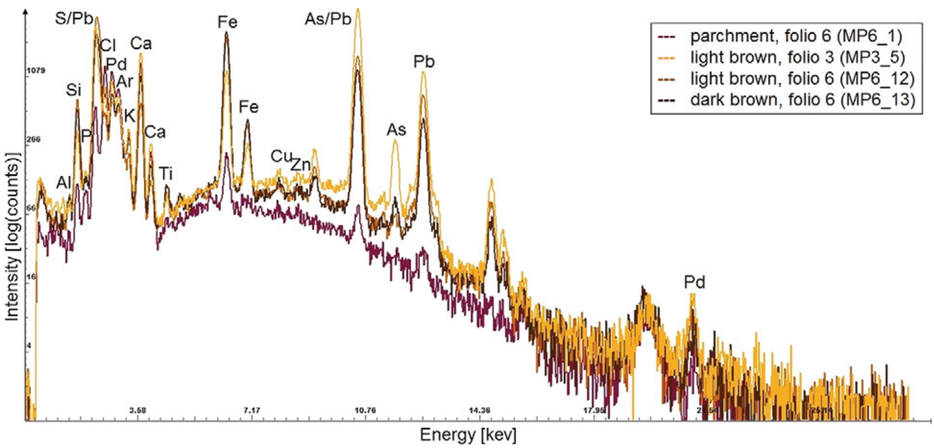

Fig. 15: Comparison of the XRF spectra of light and dark brown areas on folio 3, page 6 (MP3_5, yellow) and folio 6, page 12 (MP6_12 and MP6_13, brown and black). A spectrum of the parchment of folio 6 (MP6_5, purple) shows the background signal detected.

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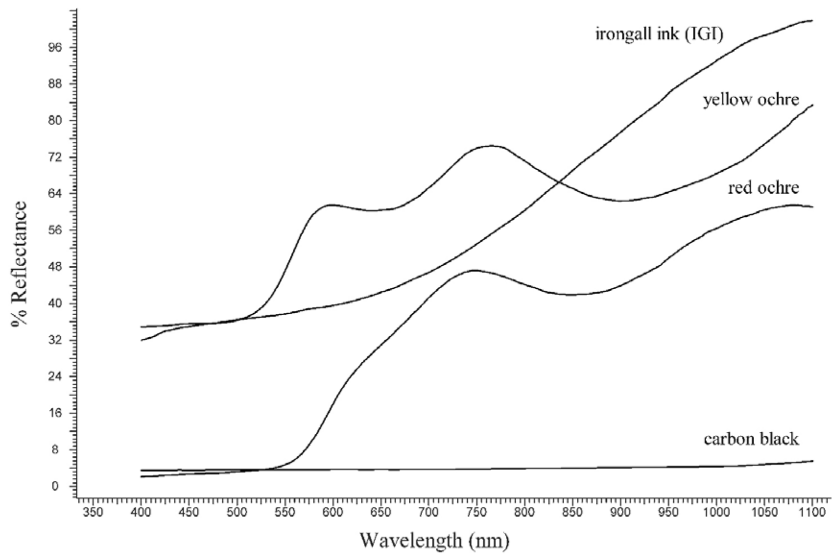

Fig. 16: FORS spectra of yellow and red ochre, iron gall ink and carbon black.

Fig. 17: Miniature on folio 6, page 12, the sending of Eliezer.

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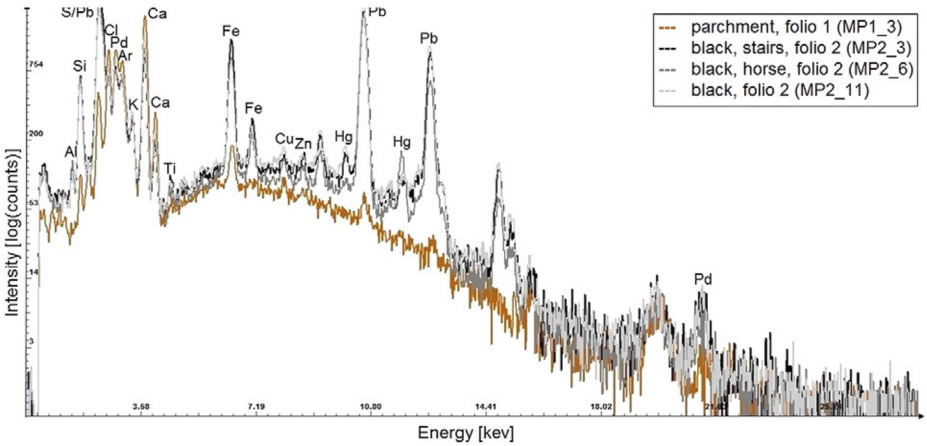

Fig. 18: XRF spectra of black areas on folio 2, page 3 (MP2_3 and MP2_6, black and dark grey) and 4 (MP2_11, light grey). A spectrum of the parchment of folio 1 (MP1_3, brown) shows the background signal detected.

The grey areas are mixtures of lead white with carbon black. Highlights were painted in lead white. Shades are mixtures of indigo and lead white. The contours were painted in black. Painter A used a variety of greys. Frequent blue-grey tones are a mixture of ultramarine blue, indigo and lead white. Indigo is confirmed by FORS, ultramarine blue and lead white by XRF. Raman spectroscopy of a loose grey colour particle indicates orpiment, indigo, ultramarine blue and red lead.

The black is probably mostly carbon black. This can be assumed using FORS, where carbon-based pigments show 0 % reflectance. XRF spectra of black areas on the ark on folio 2 (Fig. 18) indicate high intensities of iron (Fe) and silicon (Si), low intensities of aluminium (Al) and titanium (Ti) with significant traces of copper (Cu), zinc (Zn) and mercury (Hg). Based on the information gained by μ-XRF analysis a clear identification of the used material is not possible. The intensive signals of iron (Fe) can be assigned to an iron gall ink, an earth pigment or possibly to iron oxide black. The Raman spectroscopy of a loose black particle from the ark on folio 2 indicated carbon black mixed with a small amount of iron gall ink and indigo. The use of iron gall ink explains the presence of the trace elements copper and zinc. The origin of mercury stays unclear. A possible explanation is either that it is a component of the ink or that it is present due to blurring from neighbouring regions. Painter A used mixtures of carbon black and iron gall ink to paint different shades in the large black areas of the ark on folio 2 (Fig. 3). In this miniature of the flood, the rain was painted with indigo on top of the other layers. Visually it is difficult to differentiate the various mixtures of carbon black with other pigments like dark ochre,

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indigo or iron gall ink. The black contours and designs are mostly applied on top of the other paint layers. On the IRR images, dark contours and black shades are clearly visible which points towards carbon black.

Painter A used pure gold, probably shell gold, to emphasize the importance of persons like Melchisedek or king Abimelech. Crowns, thrones, parts of the cloth or sacrificial bowls are painted in gold. The presence of gold is confirmed by XRF and FORS. The gold has a reddish shine and lies directly on the purple parchment without any undercoating (Fig. 19).

The incarnate is a complex mixture of colours in different layers. There is a group of light, cool incarnates, and a group of darker and warmer incarnates. Lead white has been used in all incarnates, which have suffered from abrasion and losses. Because of the complexity of mixtures and layers, it was difficult to confirm single pigments by XRF or FORS. The pigments were identified by comparison with areas of similar colour investigated by both methods. The light incarnates of painter A seem to be mixtures of lead white and red lead (Fig. 20). Sometimes madder appears to be added. Highlights were painted in lead white. Shades seem to be added in ochre or indigo. Contours or eyes were painted in carbon black on top of the other layers. On darker incarnates ochre appears to be added (Fig. 21). Lead white was mixed with red lead and ochre. Shades could be a mixture of lead white, ochre, ultramarine blue and carbon black. Dark contours, eyes or hairs are painted in carbon black.

On the IRR images, dark lines and shades of carbon black are visible. Painter A defined contour, the traces of faces or folds in cloth with thin brush lines. He used thick brush strokes to paint animals or landscapes (Fig. 22). No signs of underdrawings or retouching could be detected on the IRR images. The brush lines and strokes appear self-assured.

Characteristic features of painter A are the use of ultramarine in blue, violet and grey colours (Table 2). As second blue pigment, indigo, was applied in blue, green and grey colours. On folios 1, 7 and 8 malachite could be identified as green pigment in addition to the use of a mixture of indigo and orpiment. Red lead is the main red pigment. On two folios, the use of cinnabar was identified by XRF and FORS. The main black pigment appears to be carbon black. In some areas, iron gall ink and indigo were applied together with carbon black, maybe in different shades or paint layers.

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Fig. 19: Microscopic image, 10x magnification, of gold on folio 2, page 4.

Fig. 20: Microscopic image, 10x magnification, face of the nymph on folio 7, page 13.

Fig. 21: Microscopic image, 10x magnification, face of Jacob on folio 8, page 16.

Fig. 22: IRR image of folio 6, page 12, the sending of Eliezer.

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Fig. 23: Miniature on folio 9, page 17.

Fig. 24: Detail of the tree on folio 9, page 17.

Palette of Painter B: folios 9–10, pages 17–20

Painter B illustrated the conflict of Jacob and Laban (Gen. 30, 30 to 31, 34). Buberl, Mazal and Zimmermann judge painter B different in style to painter A. The palette of both artists is similar (Table 2). Painter B mixed ultramarine blue with lead white and in shades with indigo. XRF and FORS results confirm ultramarine blue. The artist used orpiment for decorations on blue layers like on folio 10, page 20 on the blue tunic of Jacob.

Green areas were painted with a mixture of indigo and orpiment. Painter B used mix-

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tures in different proportions to achieve dark, light or yellow greens for his pastoral scenes set in landscapes with painted ground (Fig. 23). A tree on folio 9, page 17, shows the range of greens and the blue shade of the leaves (Fig. 24). Pigment grains of orpiment can be distinguished visually. While orpiment is clearly confirmed by XRF and FORS, respectively, indigo can only be identified definitely by FORS.

Similar to painter A, painter B used red lead as red pigment. Lighter areas are painted with a mixture of madder and lead white, shades and contours with madder. Red lead is confirmed by XRF and FORS. Pink was painted with a mixture of madder and lead white. Shades and contours were accentuated in madder, again confirmed by FORS.

Yellow and light brown are mixtures of ochres with orpiment, similar to painter A. Ochre is confirmed by FORS, the use of an earth pigment and of orpiment also by XRF. Painter B used a wide range of brown tones from yellow to red and dark brown to paint animals and parts of the landscape. The brown tones all contain ochres in different mixtures as confirmed by FORS. Orpiment was employed to add shine to the colours.

Grey areas seem to be mixtures of lead white, indigo, orpiment and ochres. Blue-grey appears to be a mixture of lead white with ultramarine blue and indigo. Outlines in carbon black were painted on top. The black pigment is again carbon black as indicated by FORS. Carbon black can be mixed with indigo and ochres to achieve different hues as for example to paint the goats. Orpiment, again, is clearly confirmed by XRF and FORS, respectively, indigo by FORS only. Similar to the results from painter A the XRF spectrum of the black area shows significant traces of copper, zinc and mercury. The trace elements indicate iron gall ink, as explained for painter A. Therefore, it seems very likely that painter B used iron gall ink in mixtures with carbon black as well.

On the IRR images, carbon black appears as dark lines or shades. Similar to painter A thin brush lines are employed to define figures, faces and outlines. Animals, rocks or the tents are painted with vivid thick brush strokes. The page numbering of Lambeck in brown iron gall ink appears grey. It is not possible to distinguish between areas in diluted carbon black and iron gall ink on the IRR images.

The palette of painter B is similar to painter A (Table 2). Differences are the lack of gold and violet. The rural scenes do not ask for imperial colours. Highlights are set by the frequent use of orpiment in green, yellow, brown and sometimes even grey areas.

Palette of Painter C: folios 11–14, pages 21–28

Painter C continued to depict the story of Jacob and started to illuminate scenes from the life of Joseph (Gen. 31, 6 to 37, 8). The distinctive feature of painter C is the use of azur-

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ite (Table 2). As blue pigment, azurite was mixed with lead white. Shading was applied with indigo. Highlights on top of blue layers were added in lead white. Contours and folds were painted in carbon black. The use of the copper containing pigment azurite, $2Cu_2CO_3{\cdot}Cu(OH)_2$, has resulted in migration of copper ions to the other side of the folio, in brown discoloration and in degradation of the parchment, a phenomenon similar to the effect of free copper ions on paper[14]. The migration is visible as dark shadows. The degradation has caused losses in the miniatures. In the XRF spectrum high copper (Cu) and lead (Pb) signal intensities confirm the use of azurite mixed with lead white (Fig. 25). In the FORS spectra, azurite is identified by the absorption maximum at 640 nm (Fig. 2). Raman spectroscopy of a loose blue particle from folio 13 also confirms azurite. On folio 11, the copper ions from the blue wings of the angels on page 21 have caused dark shadows on page 22 (Fig. 26). The cloth of the servant was painted in azurite. The blue pigment is typically coarser than ultramarine. The size of azurite particles is in the range 20–40 µm. The use of indigo for shades, lead white for highlights and carbon black for folds is visible. Under the microscope at 32x magnification, the azurite particles can be seen (Fig. 27). Azurite shows lighter blue tones than ultramarine, some azurite particles even reveal greenish tones[15].

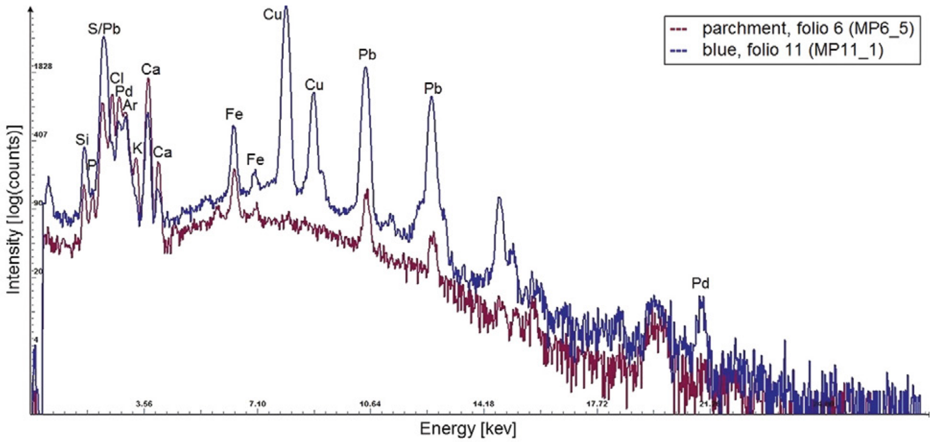

Fig. 25: XRF spectrum of blue pigment (MP11_1) on folio 11, page 23. A spectrum of the parchment of folio 6 (MP6_5) shows the background signal detected.

14 Hofmann et al., 2015.

15 Eastaugh et al., 2004, Optical Microscopy of Historical Pigments, pp. 50–51.

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Fig. 26: Miniature on folio 11, page 22.

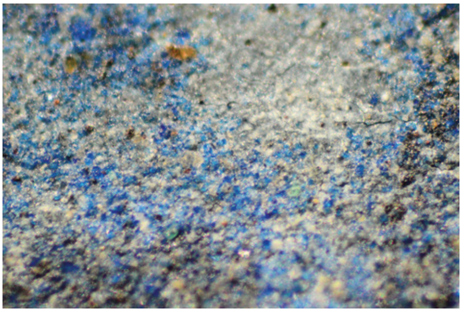

Fig. 27: Microscopic image, 32x magnification, of blue paint layer on folio 11, page 22: grains of azurite in blue and green.

Fig. 28: Miniature on folio 14, page 28, the dream of Joseph.

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Fig. 29: Miniature on folio 12, page 24, Jacob's encounter with the angel.

The green pigment is a mixture of azurite with orpiment. Highlights were applied in orpiment or in a mixture of orpiment and lead white. Copper ions have migrated to the other side of the folio, visible by darkening of the parchment. The copper ions have degraded the parchment, like for example on folio 14, page 28. On this folio, the deterioration has led to large losses on the miniature depicting the dream of Joseph (Fig. 28). The mixture of azurite with orpiment is visible under the microscope at 10x magnification. The presence of azurite and orpiment was confirmed by XRF through the distinct detection of copper and arsenic. Indigo was added for darker green tones in tree leaves and on the wheat. Indigo and azurite are confirmed by FORS. On the trees, shaded leaves were painted in azurite. Pink highlights on top of the trees were added with a mixture of madder and lead white.

As a continuum, painter C also used red lead as red pigment and madder mixed with lead white for pink areas. The way to paint highlights and shades is similar to painters A and B. Pink highlights on trees or stones are specific for artist C. After Jacob's encounter with the angel at night, the shine of the morning sun turns stones and trees pinkish and reddish (Fig. 29). Violet tones are in accordance with the choice of blue pigment a mixture of azurite, madder and lead white.

Similar to painters A and B, painter C also used earth pigments for brown tones. He worked with a broad spectrum of mixtures and shades. As mentioned above it is difficult to differentiate between the earth pigments. For light brown tones, yellow ochre and orpiment seem to have been applied. For red brown, the painter possibly used mixtures of yellow and red ochre with red lead. Dark brown tones were achieved by mixtures with a brown earth pigment.

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The grey tones also show a wide variety of mixtures and shades. The pigments employed range from lead white, azurite, indigo to brown earth pigments and carbon black. Accents are sometimes set with orpiment, lead white and madder. The blue-grey colour of the river Jabbok that Jacob crossed with his family shows severe losses. The copper ions of the pigment azurite have degraded the parchment.

The incarnate parts were painted in a broad spectrum of shades. The mixtures seem to contain red lead, ochres, lead white and sometimes small amounts of madder. In the shades, azurite, indigo and a brown earth pigment appear to be added. The face of the sleeping Joseph on folio 14, page 28, shows in how many hues artist C painted skin. Under the microscope at 10x magnification, different pigment particles can be distinguished.

The black pigment seems to be mostly carbon black. Raman spectroscopy of a loose black colour particle indicates carbon black.

On the IRR images contours, folds of cloth, faces and hair are painted in fine brush lines. Grey shades in the bodies of animals or contours are applied with thicker brush strokes. Buildings and tents are accentuated with dark grey and black forms.

The most distinguishing feature of painter C is the use of azurite as blue pigment (Table 2). Azurite was mixed with other pigments to achieve green, grey, violet and flesh tones. The presence of azurite resulted in migration of copper ions and severe losses in the miniatures. Artist C employed a wide range of pigment mixtures to paint shades of blue, green, pink, violet, and brown.

Palette of Painter D: folios 15–16, pages 29–32

Painter D depicted further scenes of Joseph's life (Gen. 37, 9 to 39, 18). He used a mixture of ultramarine and Egyptian blue as blue pigment. Highlights were painted in lead white. Shaded areas were mixed with indigo. The XRF spectra indicate ultramarine blue and a copper containing pigment mixed with lead white (Fig. 30). Egyptian blue is a synthetic pigment with the formula $CaCuSi_4O_{10}$, which was widely used in Antiquity in Mediterranean areas[16]. It was employed on miniatures in illuminated manuscripts until the Middle Ages and was identified in the Carolingian Godescalc Evangelistary[17]. The identification of Egyptian blue by means of FORS is given by the absorption maxima at 628 and 780 nm as well as by the typical luminescence emission at 950 nm (Fig. 2). The absorption at 600 nm suggests that the main pigment in the blue paint is ultramarine mixed with Egyptian blue. The presence of Egyptian blue could be confirmed by means of infrared (IR) photog-

16 Eastaugh et al., 2004, A Dictionary of Historical Pigments, pp. 147–148.

17 Denoël et al., 2018, pp. 13–14

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raphy, exploiting a physical mechanism known as Visible-induced Infrared Luminescence (VIL)[18]. The typical and extremely selective luminescence of Egyptian blue at 940 nm is induced with a visible LED light and collected with a camera especially modified for being sensitive to IR light. When taking pictures in proper conditions, i. e. inside a dark room, only the areas painted with Egyptian blue will generate a response that can be recorded with the modified camera. The fluorescence of Egyptian blue can be seen on IR images from folios 15 and 16. Figure 31 shows the miniature on folio 16, page 32, figure 32 the same miniature on the VIL image. The fluorescence is lower than expected for pure Egyptian blue, which confirms the use of a mixture with ultramarine. In the areas with fluorescence in VIL, copper was detected by XRF. A detail of blue paint on folio 15, page 30, shows dark blue and light blue particles under the microscope at 32x magnification (Fig. 33). The dark blue particles seem to be ultramarine and the light blue particles Egyptian blue. The size of Egyptian blue particles is in the range of 30–40 µm. A SEM/EDX analysis carried out selectively on a grain of Egyptian blue inside a loose particle showed that the composition was 55.0 % O, 28.4 % Si, 7.4 % Ca, and 6.9 % Cu, which leads to the expected stoichiometry of $CaCuSi_4O_{10}$.

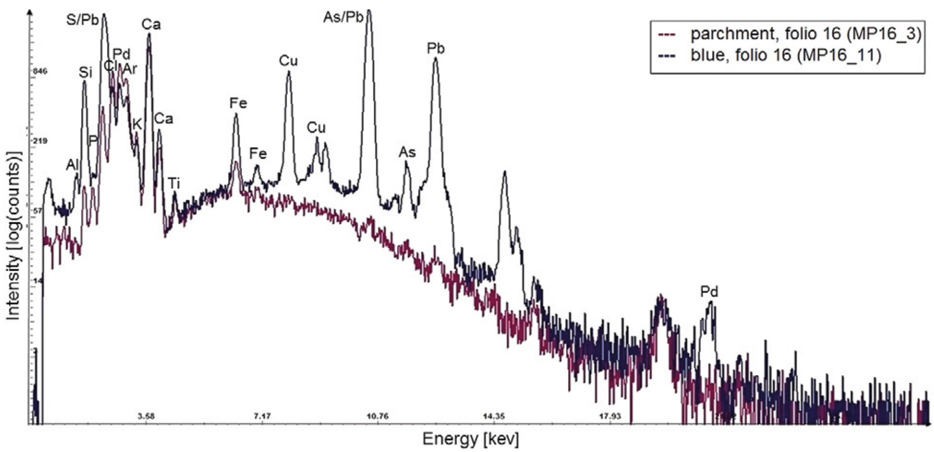

Fig. 30: XRF spectrum of a blue area on folio 16, page 32 (MP 16_11). A spectrum of the parchment of folio 16 (MP16_3) shows the background signal detected.

18 VIL images were obtained with a modified Nikon D70 camera equipped with an Infrarex BLACK filter (cut-off 840 nm); excitation was obtained with a LED ring light set on the camera lens. Exposure parameters were as follows: sensitivity 100 ASA, time 1/30 sec., F-stop f/5, focal length 22 mm.

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Fig. 31: Miniature on folio 16, page 32, the accusation of Potiphar's wife against Joseph.

Fig. 32: VIL image of the miniature on folio 16, page 32.

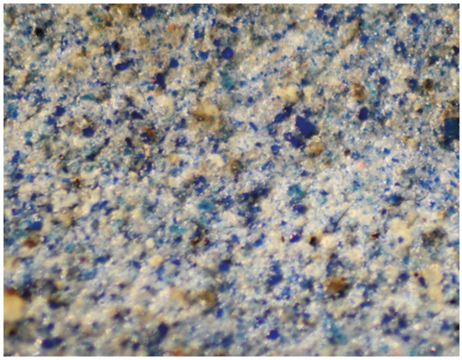

Fig. 33: Microscopic image, 32x magnification, of blue paint on folio 15, page 30: ultramarine and Egyptian blue particles.

Painter D used a mixture of indigo and orpiment to paint green areas. Lead white is added to achieve lighter tones, orpiment is added for more yellow-green tones. Orpiment and lead white are confirmed by XRF, indigo by FORS. The particles of orpiment can be seen under the microscope.

In accordance with the other artists painter D used red lead as red pigment and a mixture of madder and lead white as pink colour. The violet parts are a mixture of ultramarine blue, Egyptian blue, madder and lead white. The painter mixed his choice of blue pigment with madder and lead white. Brown parts are painted with earth pigments. Yellow areas are mostly painted with orpiment eventually with the addition of yellow ochres. Light brown

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paint layers contain yellow ochres. Artist D used red and brown ochres to paint various shades of dark brown sometimes with the addition of red lead.

Grey is a mixture of indigo, ultramarine blue, Egyptian blue and lead white. The feet of the sleeping Joseph were painted with this mixture on folio 15, page 29. In other grey areas, it seems that madder is added.

A distinctive feature of painter D is the use of iron gall ink as black pigment. Cracks and cups disrupt the sometimes brownish paint layers. The iron ions of the ink have degraded the parchment to the point of losses, a phenomenon known as iron gall ink corrosion[19]. In accordance, the XRF spectrum of measuring point MP16_12 on folio 16, page 32, reveals high iron (Fe) intensities (Fig. 34). Additionally, traces of manganese (Mn) as well as intensive signals of copper (Cu), arsenic (As), and lead (Pb) are present. While copper can be assigned to the analysed black area (iron gall ink), the peaks of arsenic and lead probably result from a green hue of the miniature painting on the other side of folio 16, page 31. A further comparison of the XRF spectra of the iron gall inks used by painter D (MP16_12) and painter A (MP2_3) (Fig. 34) shows significant differences regarding the elemental composition of the analysed materials. While the spectrum of the ink used by painter D shows a more intensive copper peak, no signals of the elements zinc or mercury are present. Therefore, the iron gall inks used by the two painters do not appear to be the same. The iron gall ink of painter D, which contains copper, has caused visible degrada-

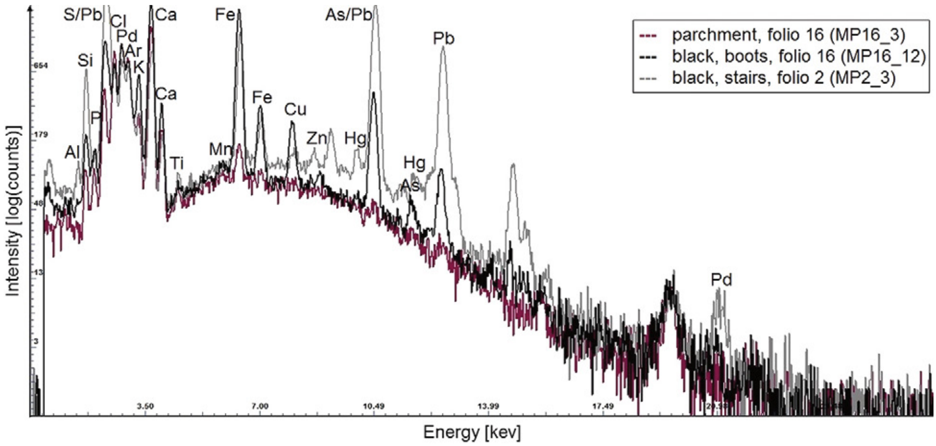

Fig. 34: Comparison of the XRF spectra of the inks used on folio 2, page 3 (MP2_3, grey) and folio 16, page 32 (MP16_12, black). A spectrum of the parchment of folio 16 (MP16_3, purple) shows the background signal detected.

19 Hofmann et al., 2007.

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Fig. 35: Microscopic image, 10x magnification, of black boots on folio 16, page 32.

Fig. 36: IRR image of the miniature on folio 16, page 32, the accusation of Potiphar's wife.

tion of the parchment carrier. On the FORS spectra iron gall ink is identified by a typical rising of the graph in the near infrared region (Fig. 16). A detail of the black boots on folio 16, page 32, shows the characterstic appearance of black paint layers in iron gall ink with a cracked surface and losses in the parchment (Fig. 35). Iron gall ink was mainly used for writing since at least the 4th century A. D. The oldest occurrences were identified in the Vercelli Gospels[20] and in the Codex Sinaiticus[21]. Recently it has been shown that the use of iron gall ink as pigment for painting was more common than previously known[22]. The occurrence of a paint made of iron gall ink in the Vienna Genesis is relevant as it seems to be one of the first evidences recorded so far.

20 Aceto et al., 2008.
21 Moorhead et al., 2015.
22 Aceto et al., 2017.

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Like painter A, painter D used gold, which appears to be shell gold. The bed columns of the bed of the wife of Potiphar were painted in gold with shading in ochre on top. The garment of Potiphar's wife on folio 16, page 32, was decorated with gold as well.

The incarnate parts show mixtures of lead white, red lead and madder. Shades seem to be painted with red ochre and a brown earth pigment. Darker shades were carried out in blue, with indigo and ultramarine blue mixed with Egyptian blue.

On the IRR images, the black lines and paint layers in iron gall ink appear grey, which is a striking difference to the IRR images of folios with carbon black. Only a few definition points in eyes, noses and mouths on faces seem to be painted with the addition of carbon black on folio 15, page 29. The black crosses, a latter addition, were done in carbon black, see for example the IRR image of folio 16, page 32 (Fig. 36).

The use of a mixture of ultramarine with Egyptian blue as blue pigment differentiates painter D from the previous painters (Table 2). In addition, iron gall ink as black pigment constitutes a striking feature of the palette.

Palette of Painter E: folios 17–18, pages 33–36

On folios 17 and 18 painter E depicts Joseph in prison and his meetings with the pharaoh (Gen. 40, 14 to 41, 32). Similar to painter D painter E also used a mixture of ultramarine blue, Egyptian blue and lead white. Highlights have a higher proportion of lead white. Shades seem to be painted with the addition of indigo. Ultramarine blue, the presence of a copper containing pigment and lead white are confirmed by XRF. FORS and VIL images indicate the presence of Egyptian blue, as described above.

A distinctive feature of painter E is the use of green earth as green pigment. Painters A to D all used mixtures of blue and yellow to create green tones. For light greens artist E mixed green earth with orpiment. Shades were applied with ultramarine/Egyptian blue or indigo. Very dark green shades, which are typical for painter E, were achieved with the addition of carbon black. XRF spectra of green paint layers on folio 17, page 33 and 34 show significant iron (Fe) signals (Fig. 37), which indicates green earth. The presence of arsenic (As) confirms the use of orpiment. The identification of green earth by means of FORS is given by the absorption maximum at 750 nm (Fig. 5). The miniature on folio 17, page 33, depicts Joseph in prison (Fig. 38). A detail of the green paint layer shows particles of orpiment and blue pigments added to the green earth (Fig. 39).

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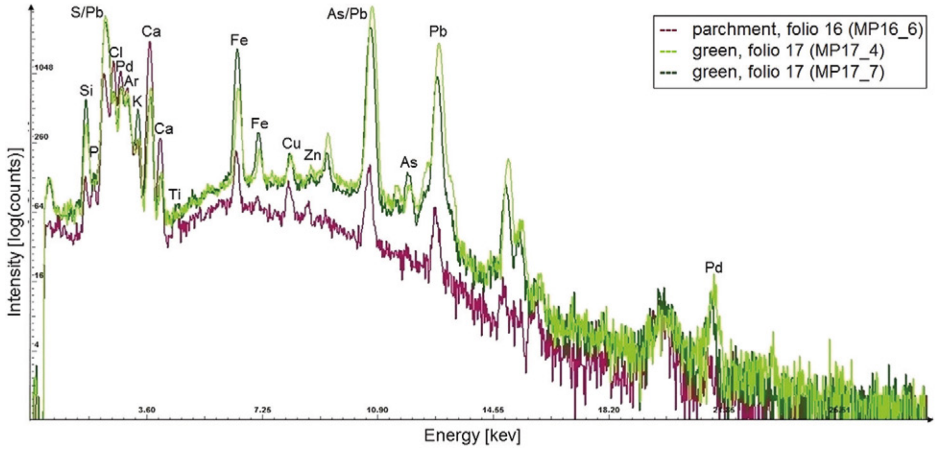

Fig. 37: XRF spectra of green paint layers on folio 17, page 33 (MP17_4, light green) and 34 (MP17_7, dark green). A spectrum of the parchment of folio 16 (MP16_6, purple) shows the background signal detected.

Fig. 38: Miniature on folio 17, page 33, Joseph in prison.

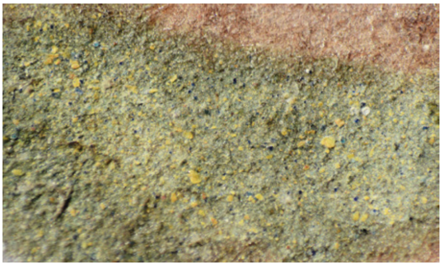

Fig. 39: Microscopic image, 16x magnification of the green paint layer on folio 17, page 33.

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Like on the other palettes red lead was used as red pigment. Pink was painted with a mixture of madder and lead white. The way highlights and shades were applied is similar to previous artists. Violet tones are a mixture of ultramarine blue, Egyptian blue, madder and lead white.

Yellow tones were painted with orpiment or yellow ochre. Painter E used yellow ochre for light browns, e.g. for the throne or for cloth. Highlights were set with mixtures of yellow ochre with lead white. Shades seem to be applied with brown ochre. Dark brown areas were painted with a brown earth pigment. XRF confirms the use of earth pigments and of lead white, FORS additionally the use of yellow ochre.

The prison walls on folio 17, page 33, or the arch on folio 18, page 36, were painted grey with a mixture of lead white, indigo, ultramarine blue and Egyptian blue. Tones that are more violet were achieved by the addition of madder. Shades were painted by adding carbon black.

Artist E vividly painted the shadows of trees black. It seems that carbon black was used on top of green earth as indicated by XRF and FORS. The boots on folio 18 seem to be painted with a brown earth pigment and with carbon black on top. FORS spectra indicate the presence of iron gall ink. No cracks of the paint layer and no degradation of the parchment are visible compared to folios 15 and 16. Nonetheless, also on these folios, carbon black could be mixed with iron gall ink.

The incarnate parts seem to be painted with mixtures of lead white with red lead. Shading was created with the addition of green earth and a brown pigment. Sometimes blue pigment particles are visible. The greenish shades give some figures an unhealthy appearance that has been remarked earlier in art historical literature (Fig. 40). Darker incarnates were painted with a higher proportion of red lead.

On the IRR images, the tree shadows on folio 17 appear as vivid black brush strokes. This indicates the use of carbon black and highlights the way of painting. Contours and folds were painted with thin black brush lines. Some black areas or lines appear grey on the IRR image. This could indicate a mixture of carbon black and iron gall ink.

Fig. 40: Microscopic image, 10x magnification, of the face of the flute player on folio 17, page 34, with green shades.

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Painter E used green earth as green pigment (Table 2). Similar to painter D he painted blue with a mixture of ultramarine blue, Egyptian blue and lead white. His incarnates are marked by green shades in the faces. Some black areas might be a mixture of carbon black with iron gall ink. Painter E avoided the use of gold. The crown and the throne of the pharaoh instead were painted with yellow ochre.

Palette of Painter F: folios 19–22, pages 37–44

Painter F illustrated the journeys of Joseph's brothers to Egypt and their meetings with Joseph (Gen. 42, 21 to 43, 21). Many researchers share the opinion that one painter worked on the folios 19–22 (Table 1). His style is different from the previous painters. All miniatures have a fully painted fore- and background (Fig. 41). For blue colours painter F used a mixture of ultramarine blue, azurite and lead white. Shades were applied in indigo or carbon black. The distinctive black contours or folds were painted in carbon black on top of the blue paint layers. XRF and FORS spectra confirm ultramarine blue. Significant copper intensities (Cu) in the XRF spectra indicate the presence of azurite. High lead signals (Pb) confirm the presence of lead white. Observations under magnification clearly show dark blue and lighter blue pigment particles. The FORS spectra are more compatible to an ultramarine/azurite mixture. As VIL images do not indicate the use of Egyptian blue, the light blue particles are interpreted as azurite.

Similar to that used by painter E, the main green pigment is green earth. Painter F mixed green earth with yellow ochre and lead white. In some areas, he added small amounts of blue. Painter F used a variety of green shades to paint the fore and middle grounds. Green earth is confirmed by XRF and FORS, yellow ochre by FORS, lead white by XRF. Green paint layers show yellow and blue particles under magnification. In some areas, the yellow particles seem to be orpiment.

In accordance with all previous painters, red lead was used as red pigment. Highlights were painted with a mixture of red lead and lead white. Shades or folds were applied in madder and in some areas with carbon black. The presence of red lead is confirmed by XRF and FORS. Pink remains a mixture of madder and lead white. Highlights were painted with a higher proportion of lead white. Shades or folds were applied with madder. The use of madder is confirmed by FORS. The addition of small amounts of blue pigments shifts the hue to old rose like on a detail from the cushion of Jacob on folio 21, page 41 (Fig. 42). Violet is a mixture of ultramarine blue, azurite, madder and lead white confirmed by XRF and FORS. Different pigment particles can be distinguished under the microscope. The light violet in the backgrounds has a higher amount of lead white. Painter

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Fig. 41: Miniature on folio 19, page 37, Joseph meets his brothers.

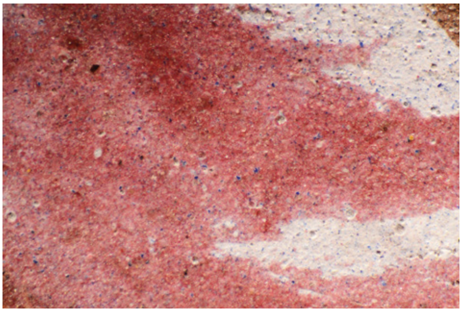

Fig. 42: Microscopic image, 10x magnification, of old rose on the cushion of Jacob on folio 21, page 41.

F painted backgrounds in a variety of violet to blue shades. The artist used yellow ochre for yellow and light brown tones. He mixed yellow ochre with lead white. Sometimes small amounts of ultramarine blue seem to have been added. On light brown areas, highlights were painted with lead white and yellow ochre. Shades were applied with a brown earth pigment. An earth pigment and lead white are confirmed by XRF, yellow ochre by FORS. Dark brown colours were painted with brown ochre and a reddish brown earth pigment. Painter F used carbon black for shades and contours. The hair of Joseph's brothers was painted in this way on folio 19, page 38. The black paint was identified as carbon black by FORS. On some areas like the boots, the first layer is painted with a reddish brown earth pigment. XRF spectra indicate an earth pigment, possibly umber. Carbon black is applied on top.

Blue-grey colours are a mixture of indigo and lead white as confirmed by XRF (lead white) and FORS (both pigments). Painter F also used mixtures of indigo, lead white,

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ultramarine blue and azurite to which small amounts of carbon black or madder can be added. The incarnate parts show a variation of mixtures of lead white with red lead, madder and yellow ochre. Shades were painted with red lead, madder, red and brown ochres and green earth. Different proportions were used for light and dark flesh tones.

Joseph wears a purple pallium with a gold chlamys on folio 19, page 37 (Fig. 41) and on folio 22, page 43. Painter F used the purple tone of the parchment for the pallium, on which he applied contours and folds in carbon black and shell gold. The gold, which was confirmed by XRF and FORS, sits directly on the parchment layer.

On the IRR images contours, folds and shades on hair and cloth appear in strong black brush strokes, which indicate the use of carbon black. Clavi, orbiculi, shoelaces or heads of columns were painted with thin brush lines. Black areas seem to be painted with dark brown and black colours. The dark brown appears grey in IRR.

The characteristics of painter F are the use of a mixture of ultramarine blue and azurite in blue, violet and blue-grey colours (Table 2). He worked with blue-grey, violet and rose colours on all miniatures. He used green earth in a variety of mixtures to paint the foregrounds. Lead white was added to many colours. The purple parchment is only visible as purple colour on the pallium of Joseph or the horses. Black areas were sometimes painted with a reddish brown pigment and with carbon black on top of it.

Palette of Painter G: folios 23–24, pages 45–48

Painter G depicted Jacob's blessings, the calling of his sons and his death (Gen. 48, 16 to 50, 4). There is consensus among art historians and codicologists that folios 23 to 24 were painted by a different painter in another style (Table 1). Similar to those by painter E, the miniatures are fully painted with the fore- and backgrounds covering the parchment (Fig. 43). Painter G also used a mixture of ultramarine blue, azurite and lead white for blue areas. Shading seems to be painted with indigo, darker shades with the addition of carbon black. The contours and folds of cloth were applied with carbon black on top of the blue layers (Fig. 44). Ultramarine blue, azurite and lead white were confirmed by XRF. Similar to folios 12–22 the light blue particles are interpreted as azurite since the presence of copper can be confirmed by XRF.

Green paint layers are mixtures of green earth, yellow ochre and lead white. Light green was painted with a higher amount of lead white, yellow-green with a higher amount of yellow ochre. Small amounts of ultramarine/azurite or carbon black could be added to achieve different shades. Green earth, lead white and yellow ochre are confirmed by XRF and FORS. The dark green of the cloth on folio 23, page 46 and folio 24, page 47 seems to

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Fig. 43: Miniature on folio 24, page 47, Jacob and his sons.

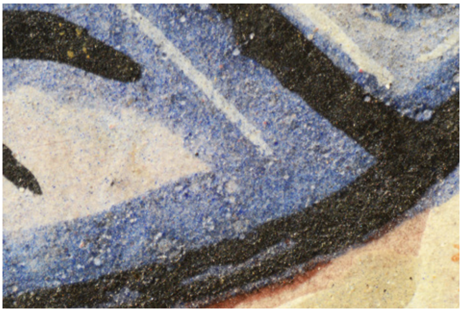

Fig. 44: Microscopic image, 10x magnification, of blue paint on folio 23, page 46.

be a mixture of indigo and orpiment (Fig. 43). Shades and contours were applied in carbon black.

In continuity, painter G used red lead as red pigment. Shades were applied with red ochre sometimes mixed with carbon black. Artist G painted three to four well-defined shades in red areas. Pink is a mixture of madder with lead white. The painter added ultramarine/azurite to achieve old-rose hues in the sky and the background. Violet colours were mixed with ultramarine/azurite, madder and lead white.

Painter G continues to use ochre as brown pigment. He painted light brown areas with yellow ochre. Highlights were set with lead white. Shades seem to be painted with brown ochre and sometimes with a reddish brown earth pigment. Dark brown areas appear to be mixtures of yellow and brown ochre, dark shades mixtures of brown ochre, a reddish brown earth pigment and carbon black. The use of earth pigments and lead white is confirmed by XRF, yellow and red ochres by FORS.

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Fig. 45: Microscopic image, 10x magnification, of the face of Joseph on folio 23, page 45.

Fig. 46: IRR image of folio 24, page 47.

Black areas were painted with carbon black, for instance the grave of Jacob on folio 24, page 48. On some parts, like the boots, a first layer of a reddish brown earth pigment was applied. An earth pigment, which could be umber, is confirmed by XRF for these areas. Contours and shades were painted in carbon black on top as indicated by FORS. The white laces on the boots were applied in lead white.

Painter G used lead white for white and grey colours. He achieved different shades of grey by mixing lead white with ultramarine/azurite, yellow ochre and carbon black. The incarnates seem to be painted with mixtures of lead white and yellow ochre for fair skin and with lead white, madder and red lead for darker skins. Rosy cheeks were added with madder and red lead. The painter used ultramarine/azurite for dark shades and brown earth pigments and carbon black for contours, see for example the face of Joseph on folio 23, page 45 (Fig. 45).

Similar to painter F, the purple tone of the parchment is part of the colour scheme in defining the purple pallium of Joseph (Fig. 43). Folds and shades of the pallium were painted in violet and black. The chlamys and the necklace were applied with gold, probably shell gold. Gold is confirmed by XRF and FORS.

On the IRR images, thick black brush strokes that seem to be carried out with carbon

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black are well visible (Fig. 46). Shades and contours were defined in black. The boots on folio 23, page 46 and on folio 24, page 47 appear grey and the outline black (Fig. 46). This confirms the use of a brown pigment (grey in IRR) in combination with carbon black (black outline in IRR).

Painter G mixed colours more than any of the other painters (Table 2). He usually worked with three to four well-defined shades. The sky and the backgrounds show a range from pink, violet to blue colours. In the faces, the shades are blue. The heads of Joseph's brothers have violet shades in the background. Carbon black seems to be added to blue, green, red, violet, and brown colours. The black contours are painted with strong thick brush strokes.

Discussion of painters' palettes

The pigments that could be identified and observed on folios 1 to 8, pages 1 to 16, (Table 2) confirm the art historical research by Zimmermann, who assumes one painter for these miniatures[23]. The identification of cinnabar on folios 1 and 2 and of malachite on folios 6–8 is not interpreted as specific for a different painter but rather as limited applications for certain parts. Cinnabar and malachite might have been also used on now lost folios. The art historical identification of individual painters for folios 9–10, pages 17–20, and for folios 15–16, pages 29-–32[24], can be confirmed by pigment identification and technological observation. The use of azurite in blue, green, violet and grey parts on folios 11–14, pages 21–28, constitutes a specific feature with impact on the condition of these miniatures. Another individual painter is therefore assumed for these two bifolios based on the palette. There is consensus among art historians on the attribution of folios 17–18, pages 33–36, folios 19–22, pages 37–44, and folios 23–24, pages 45–48 to individual painters[25]. The differences identified in the use of pigments and pigment mixtures confirm this stylistic concurrence.

The painters of Vienna Genesis used similar palettes. The white, red, and brown pigments as well as the pink mixture are generally alike on all folios. They vary in the way highlights and shades are applied. Differences in the choice of pigments can be observed in the use of blue, green, violet, grey and black paint mixtures. Four of seven painters employed gold. Two painters used the purple of the parchment as colour. The choice of colours depended on the themes of the miniatures.

23 Zimmermann, 2003, pp. 220–222.
24 Zimmermann, 2003, p. 223.
25 Zimmermann, 2003, p. 223.

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The blue pigments used in the Vienna Genesis are particularly suitable for identifying the different painters. There were widely divergent market prices for the most important blue pigments used in Antiquity, i. e. ultramarine blue, Egyptian blue, azurite and indigo, with expensive ultramarine blue ranking higher than the other three[26]. The use of ultramarine blue on a painted artwork is generally accepted as an indication for a rich commission. Its identification ranges among the first evidences so far recorded of the use of this pigment in book illumination, together with the 6th century manuscripts the Vienna Dioscorides[27], the Codex Sinopensis[28], the Codex Rossanensis[29] and the Rabbula Gospels[30]. The occurrence of Egyptian blue in mixture with ultramarine blue may indicate that the technology of production was not completely lost or that batches of antique material were available for recycling. The painters of the miniatures made individual choices in the use of blue pigments and pigment mixtures. We do not know if these choices were made for artistic or financial reasons, if they were made deliberately or by chance. The choices indicate different artistic personalities that left their impact on the miniatures. The use of iron gall ink as black pigment, alone and in mixtures, constitutes another specific feature of the miniatures of the Vienna Genesis. It proves the early use of iron gall ink in book illumination and shows the individual choice of a painter.

The Vienna Genesis is a rare example of 6th century book culture. The pigments applied show continuity of palettes in book illumination. Even the pigment Egyptian blue could be identified in Carolingian manuscripts. The technological transfer among painters from Late Antiquity into the Middle Ages seems to be more continuous than in the production of parchment.

Visual examination and IRR images did not reveal traces of underdrawings. No preparatory layers were identified by XRF or FORS. The painters seem to have painted directly on the parchment. No material evidence for later retouching on the miniatures could be found by pigment identification and observation of painting technique. It is assumed that the hole in the parchment on folio 2 was filled with parchment before painting the miniature.

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26 It is difficult to have exact data on the price of pigments and dyes in the early Middle Ages. Just for information, in the Renaissance ultramarine blue was 400 times more expensive than azurite. It must be also considered that ultramarine blue was not used (or was used in very few instances) as pigment for painting until the Late Antique age, while *lapis lazuli*, the rock from which ultramarine blue was obtained, was in use as semi-precious stone at least since 5th millennium B. C.; this seems to suggest an extremely high price for the pigment. On the contrary, azurite, indigo and Egyptian blue were used as pigments since at least the 2nd millennium B. C.

27 Aceto et al., 2012; Austrian National Library, Cod. med. gr. 1.

28 Aceto et al., 2018 unpublished data; Bibliothèque nationale de France, Ms. Supplement grec. 1286.

29 Bicchieri, 2014; Museo Docesano, Rossano.

30 Lanterna et al., 2008; Bibliotheca Medicea Laurenziana, Firenze, ms. Plut. I, 56.

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Comparison with the palettes of the Codex Purpureus Rossanensis and the Codex Sinopensis

The Codex Purpureus Rossanensis and the Codex Sinopensis are regarded as closely related to the Vienna Genesis. All three manuscripts are written in Greek with silver or gold ink on purple parchment. The Codex Rossanensis, preserved at the Museo Diocesano in Rossano, contains the Gospels of Matthew and Mark. 13 miniatures illustrate scenes from the life of Jesus Christ. Four miniatures depict the four evangelists. The Codex Sinopensis is preserved at the French National Library (Cod. Suppl. gr. 1286). Five pages from the Gospel of Matthew are illustrated with miniatures. All three codices are dated to the 6th century. They are estimated to originate from the Near East, probably from a region which is located in today's Turkey. During a recent conservation treatment pigments, inks and purple dye of the Codex Rossanensis were investigated[31]. The manuscript department of the French National Library granted access and study of the Codex Sinopensis for comparison with the Vienna Genesis[32].

Table 3: General palettes of the Codex Rossanensis, the Codex Sinopensis and the Vienna Genesis

Colour	Codex Rossanensis	Codex Sinopensis	Vienna Genesis
Blue	Ultramarine blue	Ultramarine blue, indigo	Ultramarine blue, indigo; azurite; ultramarine with Egyptian blue; ultramarine blue with azurite
Green	Yellow ochre (Goethite) with ultramarine blue or indigo	Yellow ochre with indigo	Indigo with orpiment; malachite; azurite with orpiment; green earth
Red	Red lead	Red lead	Red lead
Orange	Red lead with yellow ochre (Goethite)		
Pink	Red lead with white lead; Elderberry lake	Madder	Madder with lead white

31 Bicchieri, 2014.
32 We thank Charlotte Denoël and Christian Förstel for the permission to study Codex Sinopensis.

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Violet	Red lead with ultramarine blue; Elderberry lake with ultramarine blue		Ultramarine blue, azurite, ultramarine/ Egyptian blue or ultramarine blue/azurite with madder and lead white
Purple	Orchil	Orchil	Orchil
Yellow	Yellow ochre (Goethite); orpiment	Yellow ochre	Yellow ochre, orpiment
Brown	Yellow ochre with ultra-marine blue and carbon black	Yellow ochre	Ochres
Black	Carbon black	Carbon black	Carbon black, iron gall ink
White	Lead white	Lead white	Lead white
Gold	Gold	Gold	Gold

The pigments, dyes and inks on the Codex Rossanensis were analysed by Raman spectroscopy, XRF and Micro-FTIR. The results are summarised in Table 3. The inks were identified as metallic silver inks. The colours were directly painted onto the parchment, no preparatory layers were found. The white pigment was identified as lead white. As in the Vienna Genesis lead white was used in mixtures with other colours. Carbon black was used as black pigment and to obtain darker hues of brown, violet and grey colours. Green colours are a mixture of yellow ochre (goethite) with either ultramarine blue or indigo. On pages 3 and 241, a particular green was identified as a mixture of orpiment and indigo. The presence of gold was confirmed by XRF. Red lead was used as red pigment. On page 241, cinnabar was employed to write the name of the evangelist Mark. Orange tones are a mixture of red lead and yellow ochre (goethite). Pink colours consist of red lead and lead white. Violet parts were painted with red lead, ultramarine blue and sometimes carbon black. A brown-violet tone was obtained by mixing yellow ochre (goethite) with carbon black und ultramarine blue. The Raman spectra of red-mauve areas corresponded well with the spectra of elderberry lake prepared in the laboratory. The investigation showed that the same palette was used throughout the entire codex[33].

The Codex Sinopensis has been preserved at the French National Library since 1901. The sheep parchment is very smooth and thin, similar to that of the Vienna Genesis. The Greek text was written with gold inks on purple parchment. The miniatures seem to be painted directly on the parchment. The five folios with miniatures are stored in window

33 Bicchieri, 2014.

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mats or a folder. The 39 folios without miniatures are preserved in wooden frames between glass plates. The colours have been analysed by FORS and spectrofluorimetry with the same set-up as for the Vienna Genesis (Table 3)[34]. Ultramarine blue and indigo could be identified as blue pigments. The painter mixed indigo with yellow ochre to obtain green colours. For a few details in red, the painter used red lead. Pink architectonic details were painted with madder. Some other features like the tower on folio 30v were rendered with orchil. Yellow ochre was used as yellow and brown pigment. The incarnate parts were painted with yellow ochre. Gold was applied in the miniatures for certain features.

The comparison of the palettes of the Codex Rossanensis, the Codex Sinopensis and the Vienna Genesis confirms the relationship of the three manuscripts. Ultramarine blue, indigo, red lead, ochres, carbon black, lead white and gold were identified in the miniatures of the codices. The early use of ultramarine blue is a common feature of these precious books. The painters worked with lakes to obtain pink colours. They mixed yellow pigments with blue pigments to achieve green hues. The purple dye of the parchment seems to be orcein based in all three cases. The Vienna Genesis is the manuscript with the largest cycle of miniatures. The variations in the palettes in comparison with the other two manuscripts confirm the participation of several artists. The differences in the use of blue, green, violet, and black colours cannot be found in the Codex Rossanensis and the Codex Sinopensis.

Conclusions

The combination of different analytical methods with visual examination revealed seven palettes and painting methods on the Vienna Genesis. Individual choices can be recognised within a common range of pigments. The technological differences correspond well with the stylistic differences established by research in art history. The only distinction to Zimmermann's latest theory is the identification of a seventh artist by the use of azurite. The miniatures of the Vienna Genesis prove to be original art works that have not been altered in later time. They were directly painted on the parchment without any underdrawings. The use of ultramarine blue as blue pigment and of iron gall ink as black colour is an early example of the application of both colours in book art. The similarities between the palettes of the Vienna Genesis, the Codex Rossanensis and the Codex Sinopensis confirm the close relationship of these three Late Antique manuscripts.

34 Aceto et al., unpublished report.

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Conservation of the Vienna Genesis and the new storage system

Sophie Rabitsch, Christa Hofmann, Junko Sonderegger

Introduction

Since 1895, the folios of the Vienna Genesis have been stored between sheets, first glass and since 1975 polyacrylate sheets. Concerns about this storage initiated the research project. Within the closed mounting high levels of acetic acid, originating from the treatment with parchment glue in 1975, could have developed. Furthermore, the rigid sheets did not allow any movement of the parchment and the electrostatic forces of the polyacrylate might attract loose particles from ink and paint layers. Curators and conservators were concerned whether the conditions of the parchment, the ink and the miniatures were stable. A new conservation treatment and a new storage system should be based on the analysis of the materials and better knowledge of their degradation phenomena. All the studies described so far in this book had the ultimate goal to serve the conservation and preservation of the Vienna Genesis. The conclusions of the different investigations formed the base to decide the treatment and the storage system for the precious folios. Further tests were conducted to evaluate conservation materials like adhesives and papers. During an expert meeting and in consultation with several colleagues the options for conservation and preservation were discussed[1].

Condition of parchment, inks and miniatures

In order to determine if the condition of the Vienna Genesis had changed between the end of the 19th century and today, its current condition was compared with the three existing facsimile editions from 1895, 1931 and 1980, see figures 4, 5 and 7 in the chapter on the history. Today and in the facsimile edition of 1980 the folios of the Vienna Genesis appear a lot flatter and evener than in the reproductions from 1895 and 1930, as they were flattened during the conservation treatment in 1975, see the chapter on the history. No major further losses in the text and in the miniatures could be observed on the original in compari-

1 An expert meeting on the Vienna Genesis project was held from 16 to 17 November 2017 at the Austrian National Library.

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son with the facsimile editions since 1895. The images of all reproductions were edited and possibly retouched, which makes it difficult to judge differences in the size of small losses or tears in the ink. The folios were also compared with scans from colour transparencies (Kodak Ektachrome) from 1975. No visible changes in the condition of the ink and the paint layer could be detected.

Every folio was mounted between two sheets of polyacrylate in the course of the last conservation treatment in 1975[2]. One of those two sheets was adapted with a number of small drilled holes in order to allow some air exchange, see figure 8 in the chapter on the history. Two small pieces of whitish transparent pressure sensitive tape were used to mount the folios on their upper corners on one of the sheets (Fig. 1). The edges of the two polyacrylate sheets are glued together with transparent pressure sensitive tape that has yellowed. First, each folio was examined through the mounting. Visual examination was done under daylight, transmitted light, raking light, UV light and under magnification[3]. To enable further visual and scientific analyses as well as conservation measures, the sheets had to be opened. The sheets without the drilled holes were placed face up and wiped with an antistatic cleaning agent (Burnus GmbH) to reduce the electrostatic charge. The pressure sensitive tapes were cut at the edges and the two sheets were slowly separated. During the opening process, a sheet of smooth Japanese tissue (Bib Tengujo, 12 g/m²; Japico) was slid between the parchment and the acrylic sheet to prevent the folios from adhering to the polyacrylate. The adhesive tapes on the upper corners of the folios were cut with a scalpel. The folios were carefully transferred into temporary storage between sheets of Japanese tissue (Bib Tengujo) and museum matboard (Canson, 1.8 mm).

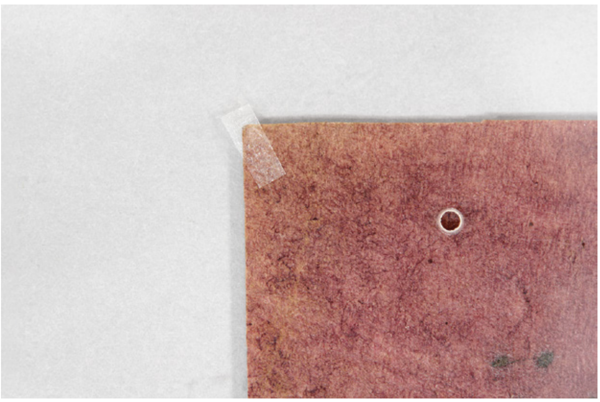

Fig. 1: Small piece of whitish transparent pressure sensitive tape on the upper corner of folio 9.

2 Mazal, 1980, p. 193.
3 Microscope Wild M 400, 6.3x–32x.

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Fig. 2: Three colour groups: folio 10 (dark), folio 2 (medium) and folio 24 (light).

The folios of Vienna Genesis differ in colour, ranging from dark brownish-violet to light brownish-rose. On all folios the flesh side is paler than the hair side, which absorbs the dye better, see chapters on parchment and purple dyeing. In addition, the purple can show darker and paler tones on one page. The folios were grouped in three colour groups (Fig. 2):

- dark purple: folios 6, 7, 8, 9 (page 18), 10 (page 19)
- medium purple: folios 1, 2, 3, 4 (page 8), 5 (page 9), 10 (page 20), 11, 14
- light purple: folios 4 (page 7), 5 (page 10), 12, 13, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24

The purple dye was identified as orchil, a highly light sensitive lichen dye, see chapter on dye identification. The practical experiments described in the chapter on purple dyeing showed that different types of orchil and even different batches of the same type of dye can result in various hues. In addition, the individual skin from which the parchment was made influences the colour. Variations in the dyeing technique can change hues as well. A range of external factors like light and pollutants have affected the aging of the purple dye. The edges of the folios frequently show brownish discolouration (Fig. 3). The changes were probably caused by light exposure; the edges of the folios are more affected by light than the inner parts. The original colour of the purple parchment is unknown, but fading is obvious on the Vienna Genesis. The comparison with parchment samples, dyed with orchil and exposed to light, shows similar hues ranging from reddish purple to brown. Colour changes were observed and documented in the early 20th century[4]. Folios of the Vienna Genesis were presented in at least four exhibitions in the State Hall of the Austrian National Library in 1846, 1901, 1913 and 1916, see chapter on the history.

4 Gerstinger, 1931, p. 29. Dafert, Austrian National Library Archive, record 775/21, 1921.

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Fig. 3: Brownish discolouration on the edge of folio 11, page 21.

The parchment of the folios shows planar distortions (Fig. 4), while mechanical deformation can be observed especially in the text area. On some folios additional small, parallel, horizontal undulations are noticeable. Due to the mounting between acrylic sheets these distortions were not very pronounced and they remained so after opening the mounts. Another phenomenon is the presence of dark, parallel, horizontal stripes on many folios (Fig. 5). They only occur in the areas above, below or within the text area. The parchment does not seem to be thicker in these areas and the stripes are not visible in transmitted light. They can be felt as shallow grooves and might originate from burnishing the parchment before writing.

Fig. 4: Planar distortions on folio 24.

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Table 1: List of damages per folio

Severe damages	Folios
Tide lines	f 4, f 5, f 22, f 24
Stains of unknown origin	f 6, f 10, f 12, f 13, f 21, f 22
Tears	f 1, f 2, f 3, f 9, f 11, f 13, f 14, f 15, f 16, f 18
Insect damage	f 2–5, f 9, f 10, f 23, f 24
Losses due to silver ink corrosion	f 1, f 13, f 17, f 18, f 20, f 21
Losses due to copper corrosion	f 12, f 13, f 14
Losses in the parchment (without the impact of silver ink or copper corrosion	f 6, f 9
Losses in the paint layer	f 1, f 2 (p 3), f 3 (p 6), f 5 (p 10), f 11, f 12 (p 24), f 13 (p 25), f 14 (p 27), f 17 (p 36), f 18 (p 36)

Table 2: List of former treatments per folio

Traces of former conservation treatments and mounting	Folios
Parchment patch	f 2 (p 4)
Pieces of paper or parchment	f 11 (p 21)
Adhesive or wax residues on or next to ink and paint layers	f 1 (p 2), f 2 (p 3), f 3 (p 5), f 7 (p 13), f 8 (p 15), f 9, f 10 (p 20), f 11, f 13 (p 25), f 14, f 15, f 17, 18, f 19, f 20, f 21, f 23, f 24 (p 47)
Strips of silk gauze, type 1	f 1 (p 1), f 2 (p 3), f 3 (p 5), f 4 (p 7), f 7 (p 13), f 8 (p 15), f 9 (p 17), f 11 (p 21), f 12 (p 23), f 13, f 14 (p 27), f 17 (p 34), f 18 (p 35), f 19 (p 37), f 22 (p 43), f 24 (p 48)
Strips of silk gauze, type 2	f 1 (p 1), f 9 (p 17), f 10 (p 19), f 11 (p 21), f 16 (p 32)
Paper fibres next to tears or losses	f 1, f 2 (p 4), f 3, f 9 (p 18), f 15 (p 30), f 16 (p 31), f 17, f 20 (p 39), f 21 (p 41)
Transparent paper	f 20
Transparent pressure sensitive tape (to mend tears)	f 3 (p 6), f 13 (p 26), f 14 (p 28), f 16

On many folios small compression folds can be observed (Fig. 6). We assume that these folds were caused by moistening the folios with parchment glue and by flattening them in 1975. All folios show cuts or tears of different sizes on the edges. Most folios have small tears measuring only a few millimetres. Longer tears measuring up to 25 cm appear on the folios 1, 2, 3, 9, 11, 13, 14, 15, 16, and 18 (Fig. 7). Most of the long tears have been secured during former conservation treatments. Bridges of silk gauze, transparent paper and pressure sensitive tape were used to mend tears, see chapter on history. An overview of severe damages per folio is given in Table 1. In Table 2 the major interventions are listed per folio.

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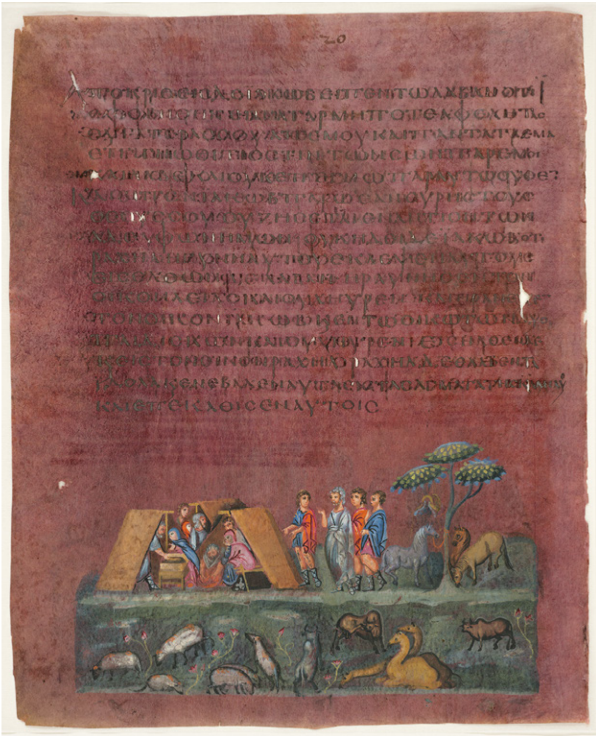

Fig. 5: Dark, parallel, horizontal stripes on folio 10, page 20.

Fig. 6: Small compression folds on folio 22, page 43.

Some folios have been affected by small round holes (0.5–8 mm) caused by insects, usually in the upper or lower part of the folio and not much pronounced in the middle (Fig. 8). On folio 1, page 2, small white insect eggs or cocoons were located in the middle of the text area. They were pressed flat on the surface of the parchment. The insect holes on the folios 2 and 3, on the folios 3, 4, and 5 as well as on the folios 9 and 10 partially correlate. The folios 23 and 24 were especially affected by insects and most of the holes are aligned. This damage possibly occurred when the codex was still bound as those folios are the last ones of the manuscript and therefore nearest to the presumably wooden cover of the binding. The folios 6, 8, 11, 12, 13, 14, 15, 17, 18, and 19 show no signs of insect damage. Holes or losses of different sizes, ranging from about 1 to 72 mm, are common on the edges and the corners (Fig 9). Most folios show very small holes on the spine edge, which could originate from the binding of the pamphlet in the 17th century. It was not possible to reconstruct the different binding campaigns. Larger losses of parchment can be found on the folios 6, 9, 12, 13, and 14, some of which seem to originate from deterioration of the parchment, especially in thinner areas of the material. On folios 11 to 14 the copper ions of the blue pigment azurite degraded the parchment and resulted in severe losses. The most obvious

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Fig. 7: Tears of different sizes, a) folio 1, page 1, b) folio 9, page 17, and c) folios 12, page 23.

deterioration of the parchment was caused by the silver ink, which is described below. The edges of the folios have been trimmed very unevenly. On some folios (e. g. folios 1 and 9) small cut marks can be seen. On folio 1, page 1, parts of a letter on the right and of the miniature on the left are missing. On folio 2, page 4, the miniature has been reduced by trimming on the lower margin and on folio 13, page 25, the miniature has been reduced by trimming on the right margin (Fig. 10). We assume that damaged areas of parchment at the edges have been cut off during rebinding or repairs.

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Fig. 8: Insect holes on folio 23, page 45.

Fig. 9: Holes and losses of different sizes.

Fig. 10: Small cut mark on folio 9 and trimmed miniature on folio 13, page 25.

Most pages show various stains. Water stains especially are visible along the edges of the folios 4–18 and 21–24 (Fig. 11). Tide lines are especially pronounced on the folios 4, 5, 22 and 24. On some folios the stains partially correlate, but it remains unclear if the damage occurred when the codex was still complete or already disassembled. Small black or grey dots that appear in the text area seem to be ink stains such as on folio 20, page 39, folio 22, page 43 and folio 23, page 46. The composition of selected dark stains in the text areas was ana-

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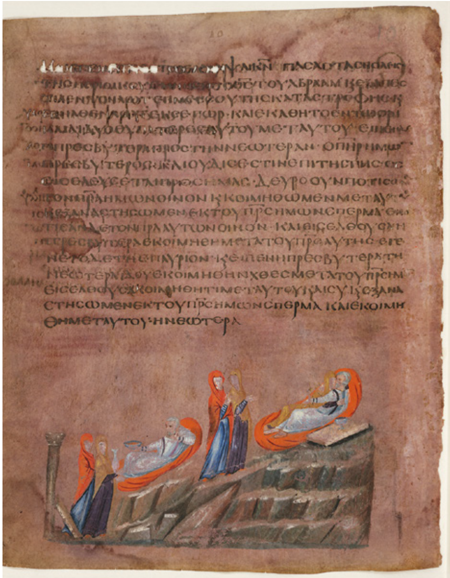

Fig. 11: Tide lines on folio 5.

Fig. 12: Orange stains on folio 12, page 24.

lysed by X-ray fluorescence (XRF), see chapter on inks. Results show that while some of these stains are of unknown origin, some are definitely silver ink. Orange or brown stains on the edges or in the text area are frequently occurring (Fig. 12), which could not be identified. On the folios 20, 21, and 22 large, matching rust-like stains can be found (Fig. 13), but their origin could not be confirmed by XRF. Many folios show glossy brownish stains that seem to have been caused by adhesive residues along the edges and in the text area (Fig. 14). These stains might originate from former repairs or conservation treatments. All folios show brownish or slightly glossy traces of adhesive and discolouration on the inner margins (Fig. 15), which probably stem from former bindings. There were at least three of them: the original binding, the binding with the Latin codex in which the Vienna Genesis was discovered in Vienna, and the pamphlet binding made by Peter Lambeck in 1664. Another phenomenon are wax-like stains (Fig. 16) of indeterminable origin. They could not be identified with XRF nor UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS[5]). Some round waxy stains could originate from the use of candles. Whitish stains that appear in the text area and in the miniatures might have been caused by former treatments with adhesives, for example on the folios 5, page 9, 6, page 11, 9, page 17, 12, page 23, and 17, page 34 (Fig. 17). We assume that numerous efforts were made in

5 Carried out by Aceto et al., 2017.

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Fig. 14: (oben) Glossy brownish stains on folio 12, page 23.

Fig. 13: (links) Matching, rust-like stains on folios a) 20, b) 21, and c) 22.

the past to consolidate the ink and paint layers. It was not possible to identify and to date the different stains.

As described in the chapter on parchment and on the miniatures, a hole on folio 2 was repaired with parchment before painting the miniatures. Many traces of former repairs or conservation measures can be seen, including pieces of parchment, strips of silk gauze, transparent paper, paper fibres and transparent pressure sensitive tapes, see chapter on the history. Pressure sensitive tapes, which look like Filmoplast (Neschen), are applied on the upper corners of every folio and on tears of the folios 3, page 6, 13, page 26, 14, page 28, and 16 on both pages. The ventilation holes in the acrylic sheets did not result in stains or visible surface changes, for instance by the accumulation of surface dirt.

On every folio, silver ink has migrated to the other side of the parchment (Fig. 18). On the thin parchment, the migration strongly interferes with the legibility of the text. On cer-

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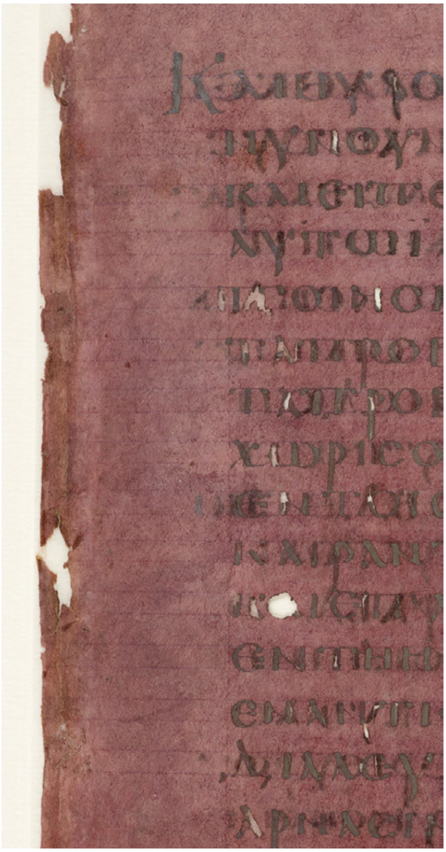

Fig. 15: Traces of adhesive and discolouration on the inner margin of folio 9, page 17.

Fig. 16: Wax-like stains on folio 23, page 45.

Fig. 17: Whitish stain on folio 17, page 34.

tain folios (16, 18, page 36, 20, page 39, 21, page 42, 23, page 45, and 24, page 47), narrow dark halos have formed around letters, which are especially visible under magnification (Fig. 19). Shiny silvery halos appear on some letters on the folios 8, 9, 11, 12, and 22 (Fig. 20). This phenomenon is visible on

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Fig. 18: The dark migration of the silver ink strongly interferes with the readability, folio 12, page 23.

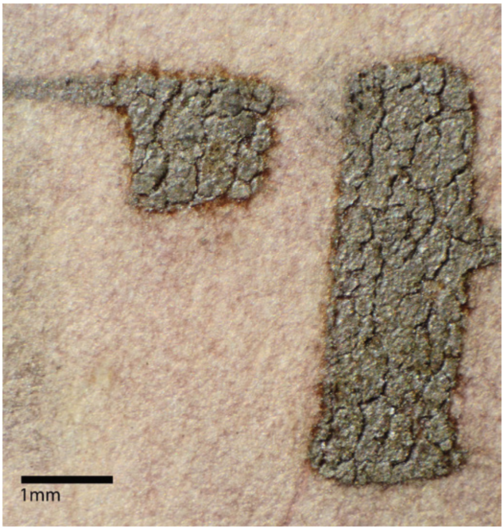

Fig. 19: Microscopic image, 12x magnification (scale bar 1 mm) of narrow dark halo around a letter, folio 12, page 23.

Fig. 20: Shiny silvery halo, folio 9, page 17.

recto and verso. The most striking damages of the Vienna Genesis are the cracking and losses in the text area resulting from ink corrosion and degradation on every folio in varying degrees (Fig. 21). This degradation ranges from 1 mm long cracks but no losses within a single letter up to large losses in entire sections of the text. The parchment appears to be very fragile on the edges of missing areas. Degradation of the parchment due to the silver ink corrosion is especially pronounced on folios 1, 13, 17, 18, 20, and 21. On folios with large losses, small flaps of parchment around an area of loss are folded over, like on the folios 18, 20, and 21 (Fig. 22). The folded flaps of parchment adhere firmly to the surface, which indicates that the thin parchment has been dried under pressure after humidification and flattening.

A number of factors seem to have contributed to the severe degradation of the ink, see chapters on silver inks and on the alteration study. One of them is the significant copper content of the silver ink. The possible addition of compounds containing chlorine during the manufacture of the ink contributed to the formation of the main corrosion product sil-

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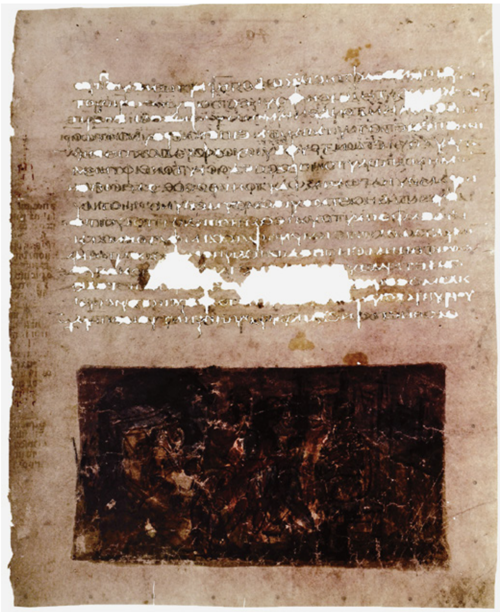

Fig. 21: Cracks and losses on folio 20 in transmitted light.

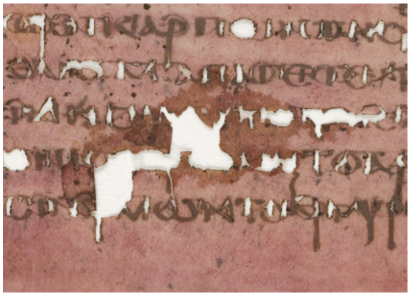

Fig. 22: Folded flaps of parchment, folio 21, page 42.

ver chloride. Environmental factors like the exposure to high humidity or water in addition to external chlorine products enhanced degradation processes of ink and parchment.

Considering the eventful history of the manuscript, the miniatures have survived in surprisingly good condition. Nevertheless, the following changes could be observed. Most miniatures show abrasion, cracks in the paint layers and losses in different degrees (Fig. 23). Larger losses can be found on folios 1 on both pages, folio 2, page 3, folio 3, page 6, folio 5, page 10, folio 11 on both pages, folio 12, page 24, folio 13, page 25, folio 14, page 27, folio 17, page 36, and folio 18, page 36. Paint layers mixed with lead white, such as seen in the incarnate areas, frequently show losses. On folios 11 to 14, the copper blue pigment azurite has caused brown migration to the verso of the parchment (Fig. 24), see chapter on the miniatures. The same phenomenon was caused by the use of the copper green pigment malachite on folio 8. On many folios small patches of colour have been transferred from another page, possibly due to water damage or high humidity: e. g. folio 4, page 8, folio 5, page 9, folio 12 on both pages, folio 13 on both pages, folio 14, page 28, folio 15 on both pages, folio 17, page 35, folio 18 on both pages, folio 22, page 44, folio 23 on both pages, and folio 24, page 48 (Fig. 25). A large round lacuna in the painting layer can be found on folio 23, page 46, and corresponding on folio 24, page 47 (Fig. 26). This loss might be caused by a wax drop and the subsequent adhesion of the two pages. Yellow and white stains on the miniatures could originate from the use of candles or oil lamps next to the codex. Stains with a wax-like appearance show yellow fluorescence under UV-light, e. g. a stain in Joseph's face on

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Fig. 23: Damages in the miniatures, detail from folio 11, page 21.

Fig. 24: Brown migration caused by azurite, folio 12, page 24.

Fig. 25: Transferred patches of colour on Joseph's garment, folio 15, page 29.

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Fig. 26: Corresponding lacunas in the miniature paintings on folios 23, page 46, and 24, page 47.

folio 24, page 47. Some waxy residues might originate from efforts to consolidate the paint layers with beeswax. Regarding the age of the Vienna Genesis, the miniatures appear to be generally quite stable in their current condition. Under magnification, on most folios localized areas of cracking and loose paint layers needing consolidation were detected. Mixtures incorporating lead white, especially incarnate, ochre, and some blue areas seem to be more unstable, presumably due to the drying nature and the weight of lead white.

Conservation strategy

The objectives of the conservation treatment were the stabilisation of the current condition of the manuscript in the full richness of its authenticity[6]. The original materials as well as any traces of its manufacture should not be altered, and the visual appearance had to be preserved. Historical repairs should be respected, as long as they do not pose any danger. Further research or conservation, if necessary, should be possible. The storage conditions should prevent any changes of the integrity of parchment, inks and miniatures. Together with the director of the Department of Manuscripts and Rare books, Andreas Fingernagel,

6 Janis, 2005, pp. 179–189.

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we decided that the Vienna Genesis should continue to be spared from exhibitions and use as practiced since about 1921, especially given that the purple dye identified as orchil is highly light sensitive. A new facsimile[7] and high-resolution digital images on the website of the Austrian National Library[8], provide researchers and the public with new forms of access. The results and the material of this research project are available with open access.

The text areas of the Vienna Genesis are severely damaged by silver ink corrosion in many places. On the edges of these areas and the resulting gaps, the parchment is fragile and vulnerable to further damage. The conservation treatment focused on securing and stabilizing these edges. Only minimal interventions should be applied, so infilling of the gaps was rejected, as this could inflict additional tension with the fragile parchment. The weakened areas should be stabilized with small bridges. All treatments since the late 19th century refrained from filling losses in the parchment. This approach was to be continued. Fragile areas in the paint layers of the miniatures should be consolidated to prevent losses and historic repairs should be respected and left in place, with the exception of the modern pressure sensitive tapes. Additionally, a suitable storage solution should be developed. The folios should be manipulated as little as possible and stored under stable conditions. In rare cases of access, the manuscript will be handled by a conservator.

A method involving as little moisture as possible should be applied in the conservation measures. Parchment tends to react by either shrinking or expanding when exposed to low or high humidity, reactions which cannot be averted[9]. As the shrinkage temperature of the two samples taken from the Vienna Genesis was rather low, it can be assumed that the parchment is at least very deteriorated in parts and therefore even more sensitive to humidity. The ink's components (silver, silver chloride, copper) react with water in its various forms, therefore direct application of moisture must be kept to an absolute minimum. Only materials with proven long term stability should be implemented in the conservation of the Vienna Genesis. Materials that induce corrosion of silver have to be avoided.

For mending the cracks and tears in the parchment and inked areas, pre-coated Japanese tissues, so-called remoistenable tissues, were chosen. The method was based on results and experience gained in a research project on the treatment of copper green pigments at the Austrian National Library's Institute of Conservation[10]. Working with remoistenable tissues reduces the introduction of moisture compared with the direct application of an adhesive. Preliminary tests were executed to evaluate different adhesives and materials for mending; the methods and materials are described below.

7 Gastgeber et al., 2019.
8 www.onb.ac.at (accessed 11 February 2020)
9 Oltrogge and Fuchs, 1989, p. 111.
10 Hofmann et al., 2015.

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Methods and testing of materials for conservation

Remoistenable tissue

Remoistenable tissues have been used for the stabilisation of objects damaged by iron gall ink or copper pigments. The introduction of humidity can be well-controlled and kept at a minimum. In order to prepare a remoistenable tissue, Japanese paper is coated with an adhesive and allowed to dry, and then reactivated with a suitable solvent. Other materials, like reconstituted parchment or goldbeater's skin, can be coated as well[11], but mostly Japanese papers are used. Important criteria are the concentration of the adhesive, the flexibility of the tissue and the adhesive, solvents for reactivation and the swelling capacity of the adhesive layer[12]. The repair should not be stronger than the original material. In literature, different variations of adhesives are mentioned, including mixtures of wheat starch paste and methylcellulose[13], Klucel G, isinglass, gelatine, Kollotex, Aquazol[14] and acrylic dispersion[15]. In practice, remoistenable tissues are prepared by brushing the adhesive on the Japanese paper, or by placing the paper into an adhesive layer[16]. As a support, polyester or siliconized films are often used. Different methods of reactivation are described in literature: spraying on the solvent[17], placing the tissue on a damp ceramic tile[18] or a sponge, reactivating with water vapour from hot water[19], using a GoreTex sandwich[20], applying solvent with a brush[21] or a system of sponge cloth and blotting paper[22]. Depending on the adhesive, different solvents can be used. According to Andrea Pataki, the amount of ethanol should not be more than 50 % v/v when using a mixture of water and ethanol for reactivating isinglass, gelatine, methylcellulose or mixtures of wheat starch paste and methylcellulose[23], while Claire Titus et al. suggest a 3:1 v/v mixture of ethanol and water[24].

11 Pataki-Hundt, 2012.
12 Pataki, 2009, p. 68.
13 Baker, 1990; Brückle, 1996; Wagner 1996; Quandt et al., 2002, Rose, 2006; Pataki, 2009.
14 Pataki, 2009.
15 Anderson and Puglia, 2003.
16 Pataki, 2009, p. 53.
17 Jacobi et al., 2011.
18 Quandt et al., 2002.
19 Jacobi et al., 2011.
20 Pataki, 2009.
21 Pataki, 2009.
22 Van Velzen and Jacobi, 2011.
23 Pataki, 2009.
24 Titus et al., 2009.

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Materials for mending

Different materials were considered for the stabilisation of fragile areas in the parchment and the corroded ink of the Vienna Genesis. The material should be flexible and as visually neutral as possible. Furthermore, it should meet the required conservation standards and be suitable for coating including activation with no or little moisture. The following materials were considered:

Protein repair materials:

- Thin sanded parchment: it is visually very noticeable on the purple-dyed parchment and the optics of the surface do not match. The new parchment has a tendency to cockle and is stronger than the aged original parchment.
- Reconstituted parchment: the material is more flexible than sanded parchment and can be produced in the required thickness. Nevertheless, it is visually noticeable on the purple parchment due to its opaque and milky appearance.
- Goldbeater's skin: It is translucent and thin, but has a very shiny surface. The material is difficult to apply in small strips, as the skin tends to curl.

Japanese tissue papers:

Japanese tissue papers are thin, flexible and unobtrusive. They are easier to colour than the proteinaceous repair materials and even very small pieces of Japanese paper can be handled without problems. For mending of tears on purple parchment and the stabilisation of corroded silver ink, the visual effect is very important, as the appearance of the folios should not be altered. The viewer should not be distracted by whitish mends that stand out.

Given these considerations, we decided to use Japanese tissue for the stabilisation of the Vienna Genesis. The following papers were evaluated:

- RK0 (5 g/m², machine made, Kozo fibres; Paper Nao)
- RK00 (3.7 g/m², machine made, Kozo fibres; Paper Nao)
- KR4C (4 g/m², machine made, Kozo fibres; Römerturm)
- Berlin Tissue (2 g/m², handmade, Mitsumata and Kozo fibres; Gangolf Ulbricht)

Samples of these papers were laid on purple parchment and ink in order to evaluate their optical suitability. The papers were coated with adhesive and applied to samples of parchment.

RK0 is too thick and too visible on purple parchment and silver ink. Despite its thinness, the fibres of RK00 are also too visible. The paper KR4C is appropriate, as it is thin, but sufficiently strong. Due to its brown hue, it is visually neutral and easy to colour. Berlin Tissue meets the requirements as well. With 2 g/m² it is the thinnest paper but strong enough for mending. Berlin Tissue is handmade from Japanese Mitsumata and Kozo fibres, cooked with potash (potassium carbonate). With its even structure the tissue

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integrates well with purple parchment and dark ink. However, because of its thinness, Berlin tissue is difficult to colour and tears easily when wetted. After further investigating the production process and the ingredients, we decided to choose a modified form of Berlin Tissue. KR4C is produced by different companies, is already dyed and can potentially contain residues of a wide range of chemicals. Berlin Tissue is produced with Acryperse[25] as a lubricant. As we wanted to eliminate the risks of residues of Acryperse in the tissue, we asked Gangolf Ulbricht to produce a Berlin Tissue using Aloe Vera instead of Acryperse especially for this project. RK0 and KR4C were used for the tests because of their lower cost and availability in larger quantities at the Institute of Conservation.

Adhesives

Different adhesives, which are suitable for the use as a remoistenable tissue and can be reactivated with non-aqueous solvents, or a mixture of water and a non-aqueous solvent, were considered and selected for advance testing. The adhesives should have good ageing and bonding properties. They should be flexible and have a matte surface. Furthermore, it should be possible to remove the mends and to retreat the folios, if necessary.

The following adhesives were selected for testing:

- Gelatine (Photogelatine Gelita, Restoration 1 GMW, Type B 264g/Bloom)[26]
- Isinglass (Störleimmanufaktur)[27]
- Parchment glue (Kremer)[28]
- Hydroxypropylcellulose-ether Klucel G (Kremer)[29]
- Methylcellulose Methocel A4M (Kremer)[30]
- Wheat starch paste (Nebel)[31]

25 Acryperse is a polyacrylamide, used to improve dispersion of the fibres in the papermaking process.

26 The gelatine powder was mixed with deionized water (2.5 and 5 %), warmed in a double boiler and stirred from time to time, until it was fully dissolved.

27 Pieces of adhesive film (2.5 and 5 % w/v) were mixed with deionized water, warmed in a double boiler and stirred from time to time, until the film dissolved.

28 Pieces of adhesive film (2.5 % w/v) were mixed with deionized water, warmed in a double boiler and stirred from time to time, until the film dissolved.

29 The powder was mixed with deionized water or ethanol (2.5 and 5 % w/v), stirred and left to stand in the refrigerator for approx. 12 hours, after which the powder was fully dissolved.

30 The powder was mixed with deionized water (2.5 % w/v), stirred and left to stand in the refrigerator for approx. 12 hours. The next day the powder was fully dissolved.

31 The mixture of 24 % wheat starch paste in water w/v was heated while being stirred, until it had a glassy appearance. It was left to cool and pressed through a sieve. Afterwards, it was mixed 1:2 v/v with water.

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- Rice starch paste (GMW)[32]

The adhesives were tested alone and in the following mixtures (Table 3):

- Gelatine-Klucel G 1:1 v/v
- Isinglass-Klucel G 1:1 v/v
- Wheat starch paste-Methocel A4M 1:1 v/v
- Wheat starch paste-Klucel G 1:1 v/v
- Rice starch paste-Methocel A4M 1:1 v/v
- Rice starch paste-Klucel G 1:1 v/v

Table 3: List of the adhesives and their reactivation, which were tested.

Adhesive	Concentration	Reactivation
Klucel G (in ethanol)	2.5 % w/v	Ethanol
	5 % w/v	Ethanol
Klucel G (in water)	5 % w/v	Ethanol-water 1:1 v/v
Gelatine Photogelatine Gelita	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Gelatine-Klucel G (in water), 1:1 v/v	2.5 % w/v	Ethanol-water 1:1 v/v
	5 %; 5 % w/v	Ethanol-water 1:1 v/v
Isinglass	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Isinglass-Klucel G (in water), 1:1 v/v	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Parchment glue	2.5 % w/v	Ethanol-water 1:1 v/v
Wheat starch paste	25 % w/v, 1:2 v/v with water	Ethanol-water 1:1 v/v
Wheat starch paste-Methocel A4M, 1:; 1:2 with water, v/v	20 % w/v, 1:2 v/v with water; 2.5 %	Ethanol-water 1:1 v/v
Wheat starch paste-Klucel G in water, 1:1; 1:2 with water v/v	25 % w/v, 1:2 v/v with water; 5 %	Ethanol-water 1:1 v/v
Rice starch paste	20 % w/v, 1:2 v/v with water	Ethanol-water 1:1 v/v
Rice starch paste-Methocel A4M, 1:1; 1:2 with water v/v	20 % w/v, 1:2 v/v with water; 2.5 %	Ethanol-water 1:1 v/v
Rice starch paste-Klucel G (in water) 1:1; 1:2 with water v/v	20 % w/v, 1:2 v/v with water; 5 %	Ethanol-water 1:1 v/v

32 Rice starch was mixed with tap water (20 % w/v) and warmed in the microwave at 400 watt. The mixture was stirred twice a minute, until it had a glassy appearance. Before use, it was left to cool.

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In order to reduce gloss on the surface of the coating, a 5 mm-thick silicone mould made of the surface of frosted glass was used as support[33]. The adhesives were applied in a single layer with a broad synthetic brush (da Vinci) in a flat angle on the matt silicone surface. Berlin Tissue, which is especially thin and difficult to coat, was placed into an adhesive layer which had been brushed on the silicon support in advance. The coated tissues were left to air dry slowly.

A reactivation system developed by Eliza Jacobi was used[34]: A kitchen sponge cloth (Wettex) was cut to 10 x 10 cm and soaked with 37 ml of water or solvent mixture and placed on a water-resistent support. Two pieces of blotting paper of the same size (Canson, 250 g/m^2) were placed on top and slightly pressed on, until the blotting paper was thoroughly wetted (Fig. 27). The remoistenable tissue was cut to the size needed with a scalpel, placed on the blotting paper with the adhesive layer face down and smoothed on using a finger or a soft brush. After a few seconds it was then picked up with a pair of tweezers, air-dried for a maximum of 10 seconds and placed on the object, where it was dabbed on with a pattern brush (Japanese Surokami-bake); a piece of polyester web can be placed between the brush and surface. A piece of blotting paper and a small weight (lead snake, GMW) were then put on top. Not much pressure should be applied, as this can possibly lead to metal ion migration[35]. Depending on the Japanese tissue, the fibre direction must be taken into account when cutting the pieces. Berlin Tissue was cut following the fibre direction, so it did not tear when wet. For the tests, mixtures of ethanol and water 1:1 or 3:1 v/v and ethanol alone were used.

Different support materials were chosen for the application of samples for the adhesive tests:

Whatman paper No. 1, sheep parchment (Anton Glaser; slightly yellow, thickness of approx. 0.35 mm), and lamb parchment (Anton Glaser; white, thickness of approx. 0.19 mm). RK0 and KR4C were used to produce remoistenable tissues. The application and reactivation of the adhesives were carried out as described above. After the first evaluation, the adhesives that seemed to be the most suitable were tested on the fragmentary purple manuscript Cod. Ser. n. 2804[36] and on the margin of folio 7 of the Vienna Genesis.

RKO and KR4C were coated with the different adhesives and adhesive mixtures described above. For the mixtures with proteinous adhesives, Klucel G was prepared with

33 Hofmann et al., 2015, pp. 166–168; since the publication the mould is made from the surface of frosted glass.

34 Neevel and Reißland, 2005; Jacobi et al., 2011, Van Velzen and Jacobi, 2011, Hofmann et al., 2015.

35 Hofmann et al., 2015, pp. 168 and 171.

36 The fragment is a piece of purple parchment (30 x 10.4 cm) with losses in the place of the former text. The parchment is dated to the 6th century and shows the qualities of Late Antique parchment.

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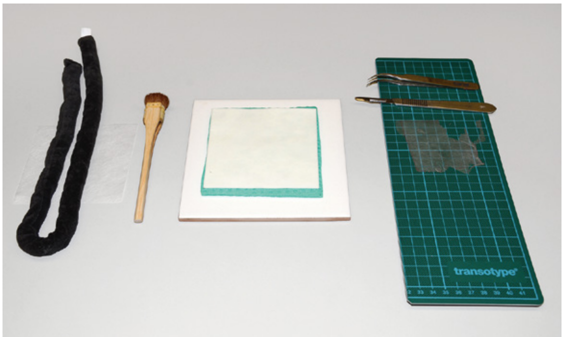

Fig. 27: Reactivation system by Eliza Jacobi and the tools and materials used for mending the fragile areas on the Vienna Genesis.

water, as the adhesives tend to mix better. The adhesives and their activation are listed in Table 3. The tissues were activated and applied on Whatman paper, sheep and lamb parchment. On the lamb parchment, the tissues were applied to both the flesh and hair side. A selection of the listed adhesives was applied on Whatman paper No. 1 and parchment by brushing and in the form of remoistenable tissue (Table 4). These samples were artificially aged for 10 days at 80 °C, 65 % RH in a climate chamber[37] VCC³ 4034 (Vötsch Industrietechnik), which was controlled by the software SIMPAT 4.0. The samples were evaluated visually and mechanically by peeling the tissue off its support. Optical features, handling and solvent mixtures were compared.

Table 4: List of artificially aged adhesives and remoistenable tissues

Adhesive	Concentration	Reactivation
Klucel G (in ethanol)	2.5 % w/v	Ethanol
	5 % w/v	Ethanol
Gelatine Photogelatine Gelita	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Gelatine-Klucel G (in water), 1:1 v/v	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Isinglass	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Isinglass-Klucel G (in water), 1:1 v/v	2.5 % w/v	Ethanol-water 1:1 v/v
	5 % w/v	Ethanol-water 1:1 v/v
Parchment glue	2.5 % w/v	Ethanol-water 1:1 v/v

37 The climate chamber was provided by the Institute of Art and Technology, University of Applied Arts Vienna.

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Gelatine-Klucel G 5 %, isinglass-Klucel G 5 %, rice starch paste, rice starch paste-Klucel G and wheat starch paste-Klucel G showed the best results regarding adhesion and optical features like matt and smooth surfaces. Depending on the surface of the support, Klucel G 5 % (in water) is suitable as well. When isinglass is mixed with Klucel G, it forms better films, as the viscosity is higher. Klucel G prepared with water can be brushed on a Japanese tissue more evenly than when being prepared with ethanol, so it was decided to only use Klucel G prepared with water for further tests. Rice and wheat starch and their mixtures resulted in cockling of the parchment on some samples. As no stress should be introduced to the fragile parchment, these adhesives were excluded from the screening. After the accelerated ageing, all proteinous adhesives and their mixtures yellowed at least a bit, with parchment glue changing the most.

The first tests showed that the Japanese tissues KR4C and Berlin Tissue are more suitable for the mending than RK0. The rougher the surface that has to be mended, the better the bonding of most of the adhesives. The majority of the adhesives showed better adhesion on Whatman paper and on the rougher side of the parchments. The material that has to be stabilised has a great influence on the bonding. Therefore, a smaller choice of adhesives was tested on the fragment of the purple manuscript Cod. Ser. n. 2804 and on folio 7 of the Vienna Genesis.

A selection of adhesives and adhesive mixtures were applied on KR4C. Thin strips of tissues were activated and applied on the fragment of Cod. Ser. n. 2804. The adhesives, their reactivation and the results are listed in Table 5. The small strips of tissue were subsequently mechanically removed.

Table 5: Listing of the adhesives, their reactivation and the results; tested on Cod. Ser. n. 2804

Adhesive	Reactivation	Pros	Cons
Isinglass 5 %	Ethanol-water 1:1 v/v	Sufficient adhesion, but can be removed	Fibrous surface, fibres remain on the surface of the parchment when peeled off.
Gelatine 5 %	Ethanol-water 1:1 v/v		Adhesion is not sufficient
Gelatine 5 %-Klucel G 5 % (in water), 1:1 v/v	Ethanol-water 1:1 v/v		Adhesion is not sufficient
Isinglass 5 %-Klucel G 5 % (in water), 1:1 v/v	Ethanol-water 1:1 v/v	Sufficient adhesion, closed surface, adheres better than Klucel G alone	
Klucel G 5 % (in water)	Ethanol-water 1:1 v/v	Sufficient adhesion, closed surface	

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KR4C coated with isinglass-Klucel G 5 %, 1:1 v/v und Klucel G 5 % (in water) gave the best results. Both show sufficient adhesion on the smooth and thin parchment. The coating with the isinglass-Klucel-mixture adheres better. Both remoistenable tissues have a closed surface after drying, while on the tissues coated with gelatine and isinglass alone, the surface is fibrous.

Klucel is a hydroxypropyl cellulose ether that is soluble in water and ethanol[38]. Klucel G is of medium viscosity and adhesion strength and has been used in conservation for over 25 years. It is the second best film former among cellulose ethers[39]. The studies by Feller rated the adhesive as less stable than methylcellulose given the degree of yellowing observed upon ageing of the dry undissolved powder[40], but the long-term stability is reasonable at low concentrations of dissolved Klucel G[41]. Ageing tests of remoistenable tissues coated with Klucel G showed good colour stability after ageing[42].

Isinglass-glue is made from the swim bladder of the sturgeon. It shows high adhesive strength and low viscosity[43] and is a traditional conservation material for the consolidation of paint layers; the Paintings Conservation Department of the Kunsthistorisches Museum Vienna has long-term experience in its use. Isinglass is an elastic adhesive that is low in tension[44] with a similar refractive index to parchment[45], is soluble in water and according to Pataki, no more than 50 % v/v of ethanol should be used for reactivation of a coated tissue[46]. Sometimes a tendency for yellowing and embrittlement is described, but when the adhesive is of good quality, this should not occur[47]. As it is a natural product, the quality can vary. For this project isinglass was obtained from Störleimmanufaktur[48], a company which uses swim bladders of consistent quality from sturgeons raised in aqua-cultures in Germany.

The adhesives which worked best on Cod. Ser. n. 2804 were tested on the inner margin of folio 7, page 13, using KR4C and different methods of activation (Table 6). The small bridges of tissue were mechanically removed afterwards. Klucel G as well as the mixture of Klucel with isinglass seemed to be suitable for the mending of inked areas in the

38 Reuber, 2010, p. 30.
39 Pataki, 2006, p. 38.
40 Feller and Wilt, 1990, p. 93.
41 Pataki-Hundt, 2012, p. 157.
42 Hofmann et al., 2015, pp. 171–172.
43 Ritter and Masson, 2005, p. 27.
44 Fuchs et al., 2001, pp. 90–91.
45 Fuchs et al., 2001, p. 18.
46 Pataki, 2009, p. 56.
47 Wikarski, 2012, p. 81.
48 http://www.stoerleim-manufaktur.de/ (accessed 19 December 2018).

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parchment of the Vienna Genesis. The reactivation of Klucel G 5 % worked best with a small proportion of water added (ethanol-water 3:1 v/v). 37 ml of the described mixture are enough to work with Klucel G coated tissues for about an hour. When the reactivation did decrease, 10 ml of the ethanol-water mixture were poured onto the kitchen sponge cloth. In discussions, Andrea Pataki expressed concerns towards the mixtures of proteinous adhesives with the cellulose ether Klucel G, as this topic is not sufficiently investigated. Following those concerns, Luise Raab's bachelor thesis[49] for the Stuttgart State Academy of Art and Design dealt with the evaluation of mixtures of Klucel G and isinglass. The results of Raab's thesis revealed that the two adhesives can be mixed, as long as Klucel G is dissolved in water. Alcohols cause denaturation of the protein, which has some effects on the swelling capacity and the adhesion of isinglass containing adhesive layers. A mixture of isinglass and Klucel G does not result in the combination of the qualities of those two components. Adhesive layers consisting of those two adhesives tend to swell more in ethanol than the single components, but do adhere less. It does not seem that a mixture has advantages and it is unclear if the aged mixture of Klucel G and isinglass results in changes of the solubility. It seems more suitable to use each adhesive on its own and not as a mixture.

Table 6: Listing of the adhesives, their reactivation and the results; tested on folio 4, page 7 of the Vienna Genesis.

Adhesive	Reactivation	Pros	Cons
Isinglass 5 %-Klucel G 5 % (in water), 1:1 v/v	Ethanol-water 1:1 v/V	Sufficient adhesion, closed surface, adheres better than Klucel G alone	
Klucel G 5 % (in water)	Ethanol-water 1:1 v/v	Sufficient adhesion, closed surface, barely visible, better adhesion than on modern parchment	
	Ethanol-water 3:1 v/v	See above	
	Ethanol		Adhesion is not sufficient, easy to remove

Due to the tests on the purple manuscripts and the results of Raab's thesis, we decided to use Klucel G 5 % dissolved in water to prepare the remoistenable tissues. When prepared with water, the adhesive is easier to apply. The bonding is strong enough to stabilise tears and fragile areas of ink. The coated paper is visually unobtrusive. It forms an even layer and has a matt and smooth surface. For reactivation, 37 ml of a 3:1 v/v mixture of ethanol

49 Raab, 2017.

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and water should be used, as solely ethanol does not result in sufficient adhesion. Ethanol evaporates quickly and the tissue is harder to handle.

Toning of Japanese tissue papers

White Japanese tissue paper is very visible on the purple parchment and the aged ink. Therefore, it was deemed necessary to tone the Japanese tissue so that the mends integrate visually well with the original. The tissues have to be toned before an adhesive coating is applied. At least two different intensities of colour were needed, due to the varying hue of the folios of the Vienna Genesis. Different types of colour and methods of application were tested, which are listed below. When brushing on the colours, it was easier to work with smaller pieces of Japanese tissue, not larger than 10 x 10 cm. The toned tissues were then coated with Klucel G 5 % in water and reactivated with ethanol-water 3:1 v/v.

Loose pigments (Kremer) dispersed in tap water with a few drops of Methocel 4AM 2.5 % were sprayed on the tissue RK00 and KR4C using an airbrush device (Iwata Eclipse HP-BCS Japan ZD). The tissues were fixed floating between two stands made of matboard and mounted on matboard with pressure sensitive tape. This method of toning Japanese papers was developed by Elisa O'Loughlin at the Walters Art Museum[50] and kindly provided by Abigail Quandt. The single colours were sprayed on separately. The application was difficult, small dots and droplets formed on the surface. It was not possible to achieve an even tone and the tissue stained when being reactivated.

Watercolours (Schmincke Horadam), diluted with tap water, were sprayed on RK00 with an airbrush device, as described above. The same problems arose. Therefore, the mixed colours were brushed on RK00, KR4C and Berlin Tissue on siliconized Mylar, using a broad synthetic brush in a flat angle. Two coats could be applied before the Berlin tissue tore apart. When working with Berlin Tissue it can help to spray the pieces of the Japanese tissue with water on a siliconized Mylar, leave them to air-dry and then brush on the colour. The tissue then sticks to the film, which makes it easier to apply the colour. It works better than spraying, but one has to be careful to avoid tears. Aesthetically pleasing results were achieved, the colour was even and delicate. The tissue can stain slightly during reactivation when left too long on the wet blotting paper.

Cold water dyes for natural fibres (Procion MX Dye) were tested on RK0. These lightfast dyes are not only suitable for textiles, but for paper as well. The dyes have to be applied in a dye bath[51], which makes them unsuitable for very thin Japanese tissues, as those tend

50 O'Loughlin, 2017, internal report from the Walters Art Museum, provided by Quandt.

51 2 l of warm tap water (around 40 °C) were mixed with ¼ tablespoon dye powder and 1 tablespoon

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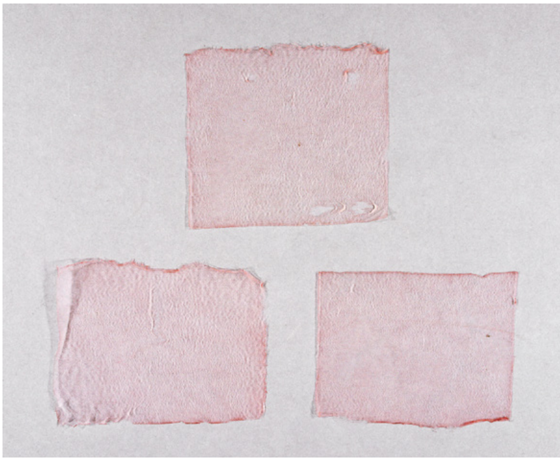

Fig. 28: Berlin tissue toned with watercolours (Schmincke Horadam).

to tear quite easily when wet. RKO was quite difficult to handle and it was not possible to dye the delicate and thin Berlin Tissue. The vivid colour that resulted was very different from that described by the company. A large series of tests with a range of colours would have been necessary to achieve subtle purple hues.

We decided to use watercolours (Schmincke Horadam), as they give good results in colour and the Japanese tissue keeps its delicate character (Fig. 28). The watercolours are easier to mix and to apply than the cold water dyes. Schmincke Horadam watercolours meet the demands of stability and lightfastness[52] and are often used in conservation. When too much colour is applied, the remoistenable tissue can stain a bit when reactivated with a larger amount of water and left on the wet blotting paper too long. Applying the colour only works with smaller pieces of Japanese tissue (max. 10 x 10 cm), otherwise the paper tears apart easily. Before the application of the adhesive, the margins of the pieces of the coloured Berlin Tissue were cut, as the watercolours tend to accumulate in these areas and can stain. The Oddy Test[53] performed on coloured Japanese tissues showed that they are suitable for permanent application.

table salt (NaCl) in a tray and stirred. The Japanese tissue (RK0, approx. 7 g) was immersed flat on a polyester web support and left in for around 40 minutes. Afterwards, it was immersed into a water bath and rinsed with cold water until it was clear. It was then put to dry, still on the polyester web, on a dry support.

52 https://www.deffner-johann.de/schmincke-horadam-aquarell-kompaktkasten.html (accessed 07 November 2018).

53 Sabine Stanek, Conservation Science Department, Kunsthistorisches Museum Wien.

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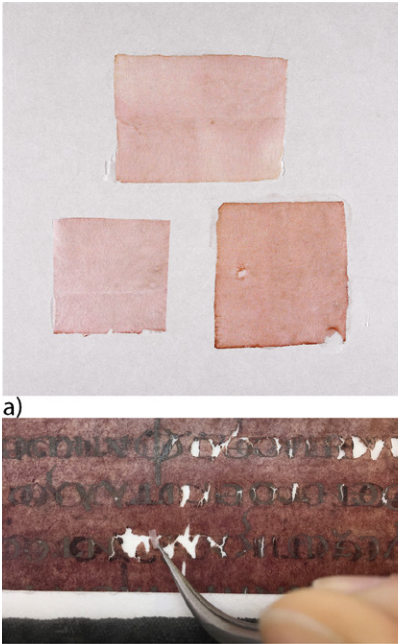
Conservation

Before the scientific analyses of the Vienna Genesis, the acrylic sheets were opened, as described above. An initial mending of the most endangered areas of the parchment had to be carried out in order to prevent further damage during the investigations. The larger gaps, tears and the most fragile areas, where the parchment could curl up or where further losses might occur, were secured with small bridges of remoistenable tissue. Berlin tissue was coloured with watercolours and coated with Klucel G 5 %, dissolved in water. The pieces were cut with a scalpel on a small cutting mat to a size of approx. 5 x 2 mm. For handling the small tissue bridges, a pair of curved tweezers was used (Fig. 29). For reactivation, a system of sponge cloth and blotting paper, soaked with 37 ml of a 3:1 v/v mixture of ethanol and water, was used. The methods of colouring, coating and reactivation are explained above.

After the scientific analyses were concluded, the folios were carefully examined a second time. In addition to the first stabilisation, fur-



a) b)

Fig. 29: a) Toned and coated Berlin tissue approx. 10 x 10 cm, b) application with tweezers, approx. 5 x 2 mm.

a) b)

Fig. 30: Mended areas, a) before and b) after treatment.

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ther cracks and losses in the inked areas were secured. As the interventions should be kept at a minimum, only areas with edges appearing very fragile were mended (Fig 30). Areas with larger losses in the miniatures like on folios 12, 13 and 14 were stabilised with bridges of remoistenable tissue. Considering the minimal handling that the manuscript would receive after treatment, the bridges offered sufficient security. The procedure was the same as described above. The mending measures were carefully mapped. The tissue bridges were applied on the rougher hair side of the folios, except on folio 1, where the flesh side was rougher than the hair side.

In some areas, the paint layer was detaching from the parchment substrate, which resulted in flaking and the loss of paint. In order to locate these areas, the paint layer of each miniature painting was examined carefully under magnification[54] using a fine brush. First tests for consolidation were made with gelatine Restoration Type 1, 2 %, which was considered too weak for this purpose. Isinglass 1.5–2 % was chosen instead, which was kept warm in a bottle warmer. Before applying the adhesive, the paint layer was pre-wetted with ethanol. Thin brushes were used (00, Winsor & Newton, Series 7). If necessary, the lifting paint layer was put down with a fine colour shaper (0, flat chisel, Royal Sovereign Ltd UK, with polyester web placed in between) (Fig. 31). The areas where consolidation was necessary were carefully

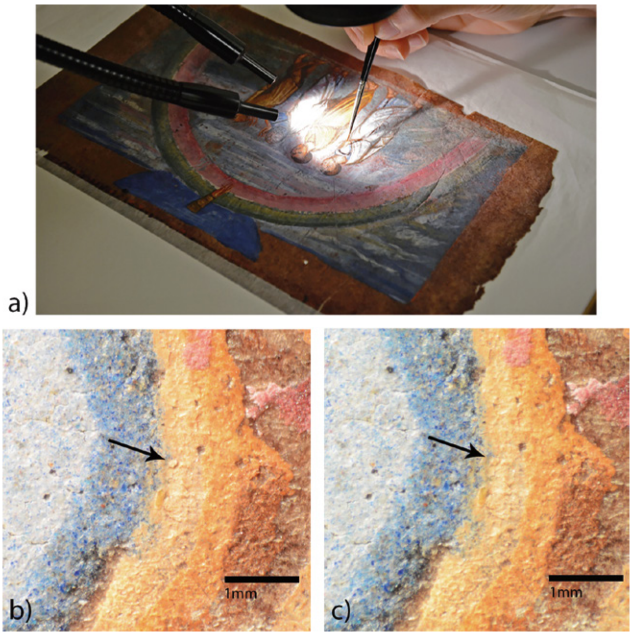

Fig. 31: a) Consolidation of the paint layer under the microscope, b) before and c) after treatment, folio 18, page 35, 10x magnification (scale bar 1 mm).

54 Wild M 400, 6.3x–32x.

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Fig. 32: Removal of pressure sensitive tapes on folio 3, page 6, before and after treatment.

mapped. Most miniatures required at least a few local consolidation measures. The most extensive consolidation was necessary on folio 1, page 1, folio 11, page 21, and folio 14, page 27, while no consolidation was required on folios 7, page 14 and 17, page 33.

It was possible to mechanically remove the pieces of pressure sensitive tape without damaging the surface of the parchment. A blunt scalpel was used for this purpose. On every folio, the tapes adhering to the two upper edges were removed (Fig. 1). On folio 3, page 6, folio 13, page 26, folio 14, page 28, and on folio 16 on both pages, the pressure sensitive tapes could also be mechanically removed (Fig. 32).

After completing the conservation measures, the folios of the Vienna Genesis were digitised with a camera (Microbox) at the Department of Digital Services[55].

Mounting and new storage system

We wanted to change the storage between two polyacrylate sheets, as it prevents close examination and has adverse effects on the folios. There is limited air exchange in the closed package, potentially increasing the concentration of degradation products. The parchment is immobilised as pressure is applied on the folios. Furthermore, the polyacrylate's electrostatic charge can cause damage to the paint layer and the ink. As the sheets have yellowed, they change the visual appearance of the manuscript. The original surface of the folios is not accessible and is visually distorted with this type of mounting.

A simple storage system was sought as the folios would continue not to be exhibited. The folios should be accessible from both sides yet with as minimal manipulation as possible. The use of hinges attached with an adhesive should be avoided or kept at a minimum. No tension should be applied to the edges due to the fragility of the corroded areas.

55 Veronika Wöber, Department of Digital Services, Austrian National Library.

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The parchment should not be pressed, but larger movements of the material should still be avoided. Furthermore, the surface of the folios should be accessible, without visual distortion. Future scientific research should be possible, therefore the storage solution should be reversible, in case other alternatives or solutions prove to be better in the future. Monitoring of fragile areas should take place once a year.

Different storage models were considered during intensive discussions with several colleagues:

- A common solution for single parchment folios is the mounting in a window mat, using Japanese tissue strips adhered on all the margins. In the case of the folios of the Vienna Genesis, a double sided window mat that can be closed would be necessary. This version was considered too risky, due to the fragility of the parchment, especially the corroded areas. Furthermore, an adhesive would have to be applied to the edges of the folios in order to attach the Japanese tissue strips, which could introduce tension or moisture in the parchment.
- Another possibility for storage is the sink mat, developed by Junko Sonderegger: single folios are placed in a smooth folder made of Japanese tissue paper, which is stored in a museum matboard folder adjusted with small spacers to avoid pressure applied to the parchment. The matboard folder is further protected in a larger sink mat with a cover board. This solution is minimally invasive, without the introduction of an adhesive, and the folios can be accessed on both sides.
- Pockets of Japanese tissue or silk gauze were considered, such as for some folios of the Archimedes Palimpsest[56]. A model involving silk or synthetic gauze in combination with a closable double sided window mat was developed by Abigail Quandt. The single folios would be fixed between two matboard frames adjusted with two layers of gauze in the middle without the introduction of an adhesive. The two matboard frames are fixed together with small magnets. This model is minimally invasive, but even with the very thin gauze, the impression of the folios is changed.
- Another model for storage was developed by Valerio Capra and Diego Rivella[57]. The single folios would be stored floating inside an acrylic box, adjusted with springs. Strips of Japanese paper would have to be applied to the margins of the folios. The tension could be adjusted, depending on the movement of the parchment. Like the first option, this version was considered too risky, due to the fragility of the folios.

The models and different solutions were discussed at the expert meeting in November 2017. Valerio Capra kindly provided a full model of the frame-box. Colleagues at the Institute of Conservation at the Austrian National Library and the Conservation Department of the Al-

56 Quandt, 2011, pp. 156–161.

57 Valerio Capra presented the model at the expert meeting in November 2017.

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bertina Museum were consulted. The pros and cons of the different systems were intensely debated. The requirements for storage were discussed with Andreas Fingernagel, Director of the Department of Manuscripts and Rare Books. Finally, we jointly decided upon the folder-sink mat model of storage. The mat provides access to the surface of both sides and excludes the use of an adhesive and pressure. The system was modified with valuable input from colleagues.

First, two folders of Japanese tissue were prepared for each folio, measuring a few millimetres larger than the parchment. The Association for Successors of Traditional Preservation Techniques in Japan provided custom made papers of the highest quality. The inner folder (Fig. 33), which is in direct contact with the folio and opens along the right side, was made from Mitsumata paper with a very smooth surface (Mitsumata fibres, 6.5 g/m^2, cooked with soda ash, natural Neri tororo-aoi as a mucilage, dried on wood panel). The second folder, which opens at the left side, was made from Mino paper, which adds support to the parchment (Nasu Kozo fibres, 18 g/m^2, cooked with Soda ash, natural Neri tororo-aoi as mucilage, dried on wood panel)[58].

Together with the Japanese tissue folders, the folio was then placed into a folder (Fig. 34) made from museum matboard (Canson, 1.8 mm). For this purpose, two matboards measuring 37.5 x 31 cm were fixed together with a strip of the Mino paper (see above) and a 1:1 v/v mixture of wheat starch paste 25 % and Methocel 4AM 2.5 %. On the inside of each matboard, frames made of thinner matboard (Canson, 1.2 mm) were applied with double-sided adhesive tape (Deffner & Johann, 3M, Type 415, 12 mm). The frames function as spacers and

Fig. 33: Japanese paper folders.

58 Both Japanese tissues were hand and custom made by Eikan Ebuchi in Kochi, a paper maker who is a member of the Association for Successors of Traditional Preservation Techniques in Japan.

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Fig. 34: Matboard folder with frame and click system.

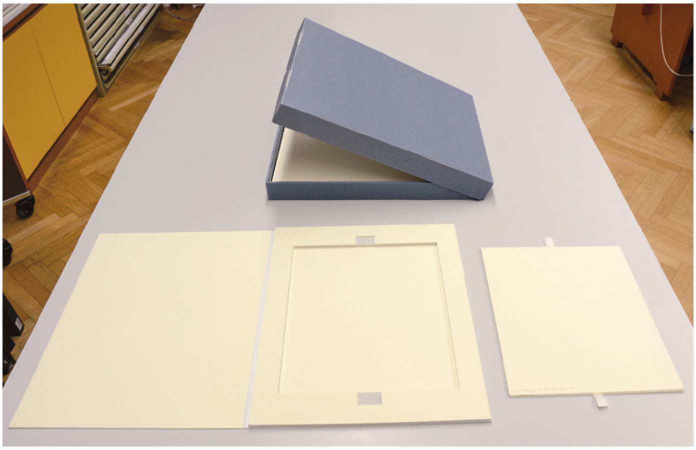

Fig. 35: The passepar-tout with sink mat and cover, the matboard folder and the archival box.

were adjusted to the size and depth of each folio. A small space was left on the lower inner corner of the frames to facilitate the opening of the tissue folders. A click system of matboard was applied to keep the folders closed (Fig. 34). Straps of cotton ribbon (Stoffkeller) were recessed into the back side of the matboard folder, fixed with Japanese tissue and wheat starch paste. The matboard folder is then stored in a larger sink mat with a cover (Fig. 35). For this purpose, a case made of museum matboard (1.8 mm) and corrugated board (Klug, 6.4 mm) measuring 50 x 40 cm was created[59]. A window a bit larger than the small matboard folder was cut inside the corrugated board and the matboard. All open edges of the corru-

59 Helmut Molacek made the sink mat-cases, Institute for Conservation, Austrian National Library.

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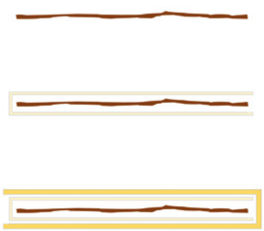

Fig. 36: Diagram of the folio in the first and second Japanese paper folders.

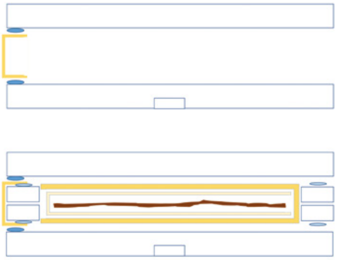

Fig. 37: Diagram of the matboard folder.

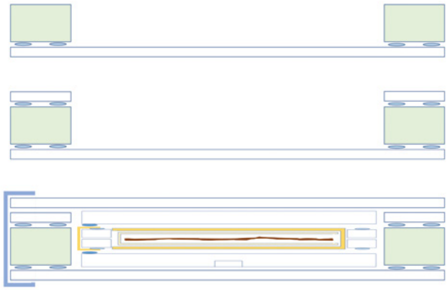

Fig. 38: Diagram of the sink mat.

gated board were coated with the Mitsumata paper (see above) and wheat starch paste. The corrugated board and the matboard were mounted together with double sided adhesive tape. They were then adhered on matboard of the same size with the adhesive tape. A cover made of matboard was attached with textile adhesive tape (Klug) on the left margin of the sink mat. A diagram of the sink mat is provided in figures 36–38.

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We wanted to use only emission free archival materials of long-term stability for the housing of the Vienna Genesis. The Japanese tissues and small packages of matboard, corrugated board and double-sided adhesive tape were Oddy tested at the Conservation Science Department of Kunsthistorisches Museum Vienna. All materials were classified as suitable for permanent use[60].

The sink mats are stored in archival boxes made of corrugated board (Klug). Each box contains three folios. Small coupons of silver, copper and lead were added to each box. They function as a small long-term Oddy test, to monitor for the potential evaporation of volatile organic compounds within the boxes. A powder-coated metal archival cabinet (Schäfer) houses the boxes in the climate-controlled high security storage room of the Department of Manuscripts and Rare books. The climate of the storage unit is 20 °C and 45 % RH. The parameters are adjusted to the range of different objects and material combinations stored in this place.

Conclusions

During the initial testing of conservation materials, Berlin Tissue proved to be the most suitable paper for mending cracks, tears and losses on the folios of the Vienna Genesis. Small pieces of Berlin Tissue were toned with Schmincke Horadam watercolours using a brush to make the mends less visible on the purple parchment and the dark silver ink. Berlin tissue was coated with the hydroxypropylcellulose-ether Klucel G (5 % in water) on a matte silicone support. The Klucel coating was reactivated with a 3:1 v/v mixture of ethanol and water, which allowed enough time for accurate placement of the mends. Experience showed that the adhesive coating was strong enough for the reinforcement of tears, cracks and losses, given future restrictions in handling. These described methods were successfully applied to all folios of the Vienna Genesis. The remoistenable tissue proved to be flexible and visually unobtrusive on different areas of the manuscript. The mends can be mechanically removed with a scalpel if needed. Localized areas of fragility in the paint layers were consolidated with isinglass (1.5–2 % in water, w/v). The conservation treatment tried to balance stability of the folios with minimal changes of aesthetics and authenticity.

All folios were stored in double folders of custom-made Japanese paper and in sink mats, which consist of an inner and outer mat. No adhesive, tension or pressure had to be applied and the folios can be seen from both sides. The imperatives are that the manuscript will not be exhibited and access is strictly limited. The folios will only be handled by con-

60 Sabine Stanek, Kunsthistorisches Museum Vienna, 2018, internal report.

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servators. Three mats were put into one archival box. All boxes are stored in a metal cabinet in a climate-controlled storage area. A monitoring system will be established to evaluate the condition of the Vienna Genesis once a year. Particularly fragile areas of parchment, inks and miniatures will be compared with the digital images and the mapping of damage.

Like our predecessors we have tried to conserve the Vienna Genesis as well as possible with our current knowledge and with the support of our partners and colleagues. Aware of our limitations, we trust that future generations will do their best for the safekeeping of this invaluable manuscript.

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Materials

Association for Successors of Traditional Preservation Techniques in Japan, Kakimotocho 405, Muromachi Higashi-hairu, Aneyakoji Dori, Nakagyō-ku, Kyōto-shi, Kyōto-fu, Japan 604-8173
Mitsumata and Mino-paper

Australco, Bahnstraße 16, 2104 Spillern, Austria; www.australco.at (accessed 6 February 2020)
Ethanol 96 %

Burnus GmbH, Rößlerstraße 94, 64293 Darmstadt, Germany
Antistatic cleaning agent

Deffner & Johann GmbH, Mühläcker Straße 13, 97520 Röthlein, Germany; www.deffner-johann.de (accessed 6 February 2020)
Double side adhesive tape (3M); Watercolours (Schmincke Horadam; crimson, ultramarine, ochre, umber, sepia); Brushes (00, Winsor & Newton, Series 7); Colour shaper (0, flat chisel, Royal Sovereign Ltd UK)

DM-drogerie markt GmbH, Günter-Bauer-Straße 1, 5071 Wals, Austria
Sponge cloth (Wettex)

Europapier, Autokaderstrasse 86–96, 1210 Vienna, Austria; www.europapier.com (accessed 6 February 2020)

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Museum matboard, Canson, 1.8 and 1.2 mm

Farben Wolf, Margaretenstraße 124, 1050 Vienna, Austria; www.farbenwolf.at (accessed 7 February 2020)
Silicone resins, ELASTOSIL® M 4641 A/B, RTV-2

Glaser, Inh. Martin Rustige, Theodor-Heuss-Straße 34a, 70174 Stuttgart, Germany; www.anton-glaser.de (accessed 7 February 2020)
Sheep parchment

Kleindorfer, Aster Str. 9, Kapfing, 84186 Vilsheim, Deutschland; www.gmw-shop.de (accessed 7 February 2020)
Gelatine Type Restoration 1, rice starch, polyester web (Hollytex)

Klug-Conservation, Zollstraße 2, 87509 Immenstadt, Germany; www.klug-conservation.de (accessed 7 February 2020)
Currogated board, textile adhesive tape, archival boxes

Kremer Pigmente GmbH & Co. KG, Hauptstr. 41–47, 88317 Aichstetten, Germany; www.kremer-pigmente.com (accessed 6 February 2020)
Klucel G, Methocel A4M, pigments (ultramarine extra dark, green earth, ochre, crimson)

Nebel GmbH & Co KG, Otto Bauer-Gasse 4–6, 1061 Vienna, Austria; www.nebel.co.at (accessed 6 February 2020)
Wheat starch

Paper Nao; 4-37-28 Hakusan Bunkyo-ku, Tokyo 112–0001 Japan
Japanese tissue RK0, RK00; Japanese Surokami-bake (size 9)

Putrich & Sohn, Vordere Zollamtstraße 11, 1030 Vienna, Austria,
Blotting paper, Canson 250g/m^2

Römerturm Feinstpapier GmbH & Co. KG, Alfred-Nobel-Straße 19, 50226 Frechen, Germany; www.roemerturm.de (accessed 7 February 2020)
Japanese tissue KR4C

Rupert, Gibbon & Spider, Inc., Manufacturers of Jacquard Products, Healdsburg, CA

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95448, USA; www.jaquardproducts.com (accessed 7 February 2020)
Procion MX Dyes, rose-brown

Sigma-Aldrich, Marchettigasse 7/2, 1160 Vienna, Austria; www.sigmaaldrich.com/austria (accessed 7 February 2020)
Whatman Paper

SSI Schäfer Shop GmbH, Etrichstraße 9, 4600 Wels, Austria; www.schaefer-shop.at (accessed 7 February 2020)
Archival cabinet

Stoffkeller, Sabine Machowitsch, Ennsgasse 7–11, 1020 Vienna, Austria; www.stoffkeller.at (accessed 7 February 2020)
Cotton ribbon

Störleim-Manufaktur, Eva Przybylo, In der Helle 21, 59929 Brilon, Germany; www.stoerleim-manufaktur.de (accessed 7 February 2020)
Isinglass

Ulbricht G., Mariannenplatz 2, Kunstquartier Bethanien, 10997 Berlin, Germany; www.papiergangolfulbricht.de (accessed 7 February 2020)
Berlin Tissue

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Summary

Christa Hofmann

During the three-year research project funded by the Austrian Science Fund (FWF), the parchment, the inks, the pigments and dyes of the Vienna Genesis were investigated.

The parchment was made from sheep skin. Parchment in Late Antique style, which is thin and has a very smooth surface on hair and flesh side, was re-created during experiments of manual parchment making. Dyeing experiments showed that parchment can be dyed purple with orchil, folium and shellfish purple. The parchment samples dyed with orchil resemble the parchment of the Vienna Genesis the most. By analysis, orchil, a highly light sensitive lichen dye, was identified as the main purple dye of the parchment.

The composition of the silver inks is consistent on all preserved folios. The presumably two scribes used the same recipe. The ink is a pure silver ink with copper as minor component. The main corrosion product is silver chloride. Chlorine containing substances could have been added during the production of the inks, e. g. in the form of salts as grinding aids for silver. External sources of chlorine like salty sea water could be responsible for the detection of chlorine in inked areas and parchment. We assume that the fragile condition of the inks and losses in the text part are due to a combination of the composition of the inks, external influences and the thin parchment.

The pigments and dyes of the miniatures were defined by analysis and visual investigation. The different painters of the miniatures used palettes with variations especially concerning blue, green and black pigments. We identified seven painters by the use of their palette and their painting style. Specific for the manuscript is the early use of ultramarine blue as blue and iron gall ink as black pigment. The painters created the images directly on the parchment. No signs of underdrawings were found. The comparison of parchment, pigments and dyes confirm the close relationship of the Vienna Genesis with the Codex Rossanensis and the Codex Sinopensis.

The aim of the conservation treatment was to preserve the historic condition and the authenticity of the manuscript as well as to improve the storage situation. The folios were removed from the tight polyacrylate sandwiches and pressure sensitive tapes were taken off. During conservation, fragile areas of the inks were reinforced with small bridges of Japanese tissue paper coated with hydroxypropylcellulose-ether. Berlin Tissue, a 2 g/m^2 handmade paper without synthetic additions, was coated with 5 % Klucel G in water. The adhesive layer was activated with a mixture of ethanol and water 3:1. Loose paint layers were locally consolidated with isinglass. The folios are now stored in folders of custom-made Japanese paper and mounting board with a spacer. Within the folders the fo-

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lios are preserved in sink-mats of corrugated board in an archival box under controlled climate. Due to the fragile condition, the high light sensitivity and the importance of the manuscript, the folios of the Vienna Genesis remain without public access and will not be exhibited. New digital images and a new facsimile edition will provide researchers and the public with improved forms of access.

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Fig. 1: folio 1, page 1, the fall of man.

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Fig. 2: folio 1, page 2, the expulsion from paradise.

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Fig. 3: folio 2, page 3, the flood.

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Fig. 4: folio 2, page 4, departure from the ark and Noah's sacrifice.

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Fig. 5: folio 3, page 5, God’s covenant with Noah.

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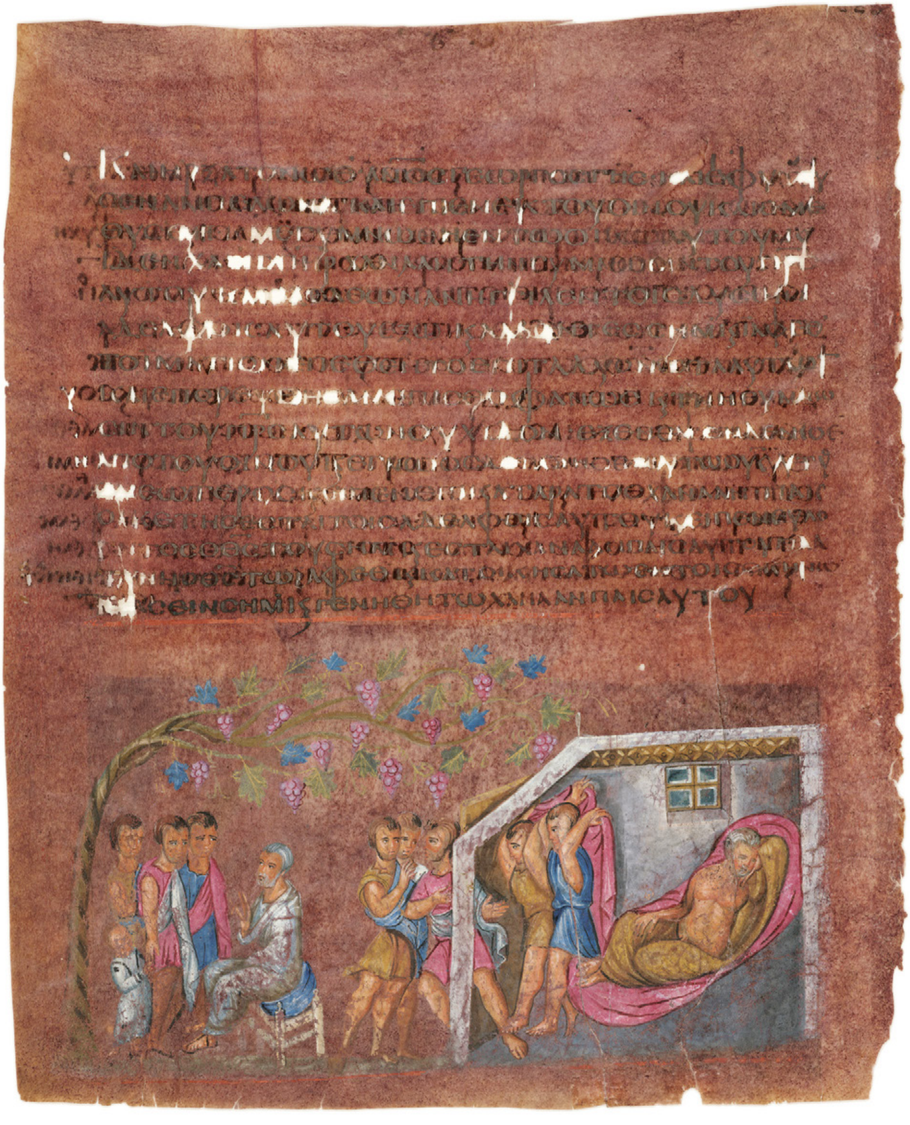

Fig. 6: folio 3, page 6, Noah's drunkenness.

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Fig. 7: folio 4, page 7, Abraham and Bera, Abraham and Melchisedek.

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Fig. 8: folio 4, page 8, God's promise to Abraham.

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Fig. 9: folio 5, page 9, the fall of Sodom and Gomorrha, the salvation of Lot and his family.

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Fig. 10: folio 5, page 10, Lot and his daughters.

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Fig. 11: folio 6, page 11, new promise to Abraham, return to Beersheba.

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Fig. 12: folio 6, page 12, the sending of Eliezer.

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Fig. 13: folio 7, page 13, Rebecca at the fountain.

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Fig. 14: folio 7, page 14, Eliezer’s gifts for Rebecca, Rebecca and her family.

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Fig. 15: folio 8, page 15, Esau sells Jacob his birthright.

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Fig. 16: folio 8, page 16, Isaac and Rebecca in Gerar.

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Fig. 17: folio 9, page 17, Jacob asks Laban for the division of the flocks.

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Fig. 18: folio 9, page 18, Laban gives the selected animals to his sons, Jacob's trick.

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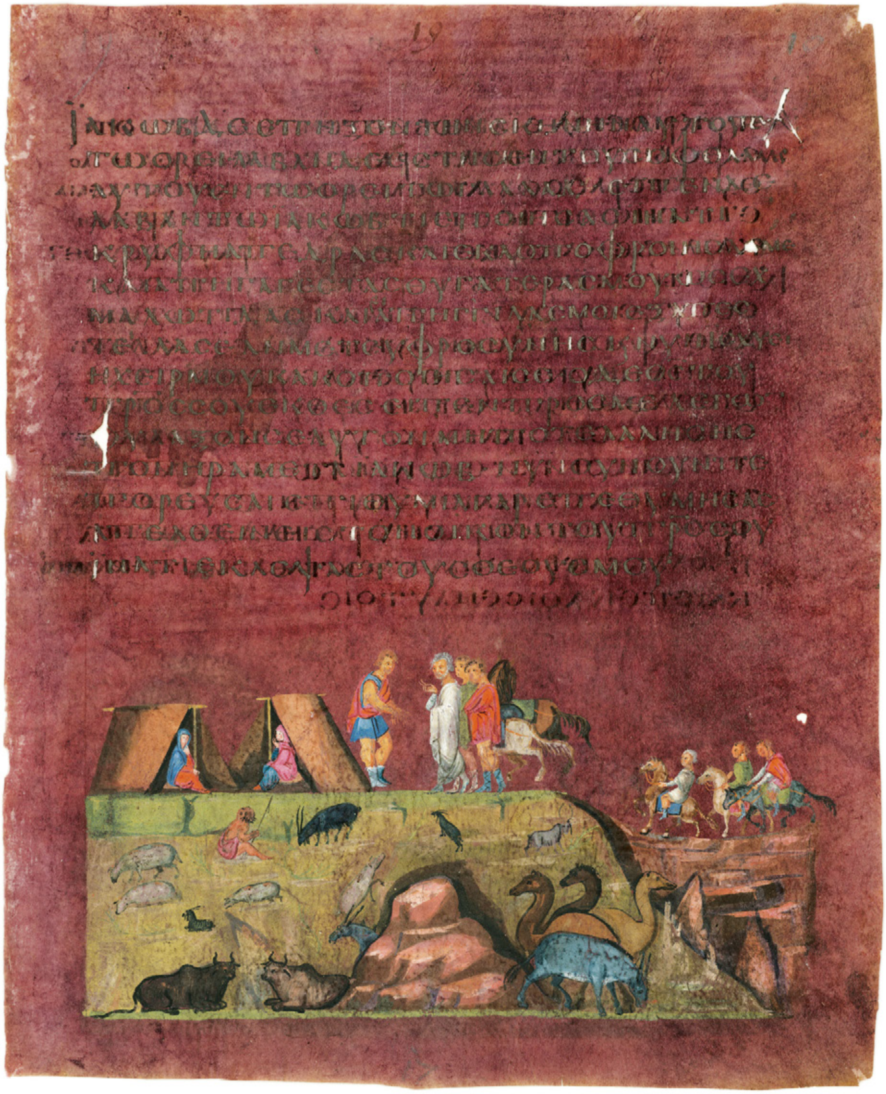

Fig. 19: folio 10, page 19, Laban's negotiations with Jacob.

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Fig. 20: folio 10, page 20, Laban seeks the stolen idols.

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Fig. 21: folio 11, page 21, Jacob and the angelic messengers.

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Fig. 22: folio 11, page 22, Jacob’s gifts for Esau.

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Fig. 23: folio 12, page 23, Jacob's crossing of the river Jabbok.

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Fig. 24: folio 12, page 24, Jacob's encounter with the Man of God, sunrise.

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Fig. 25: folio 13, page 25, the return to Bethel, the construction of an altar, the removal of the idols.

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Fig. 26: folio 13, page 26, Deborah's death, Benjamin's birth, Rachel's death and burial.

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Fig. 27: folio 14, page 27, Isaac's death and burial, Joseph receives a coloured dress.

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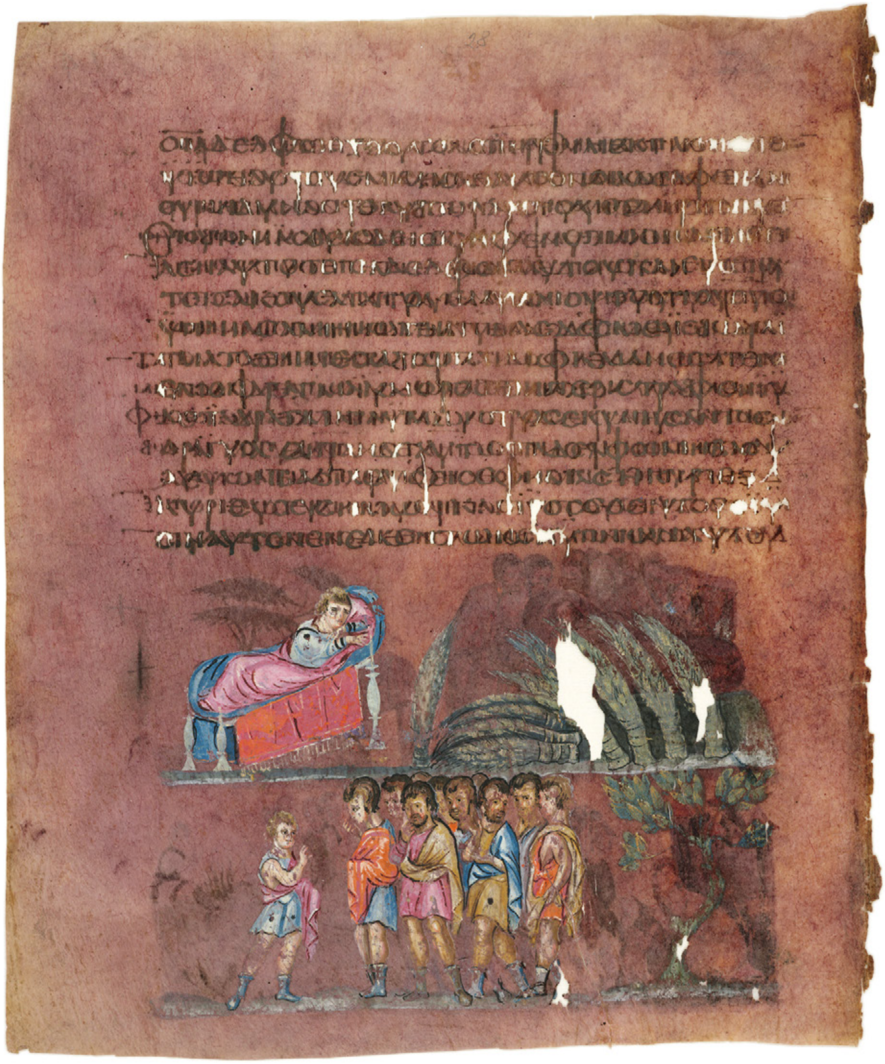

Fig. 28: folio 14, page 28, Joseph's dream of the sheaves.

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Fig. 29: folio 15, page 29, Joseph's dream of the stars; he tells his family his dreams; his brothers in Sichem.

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Fig. 30: folio 15, page 30, Jacob sends Joseph to Sichem, Joseph’s parting from Benjamin, Joseph finding his brothers in Dothaim.

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Fig. 31: folio 16, page 31, Joseph's temptation by Potiphar's wife.

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Fig. 32: folio 16, page 32, the accusation of Potiphar’s wife against Joseph.

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Fig. 33: folio 17, page 33, Joseph in prison.

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Fig. 34: folio 17, page 34, Pharaoh's banquet; the death of the upper baker.

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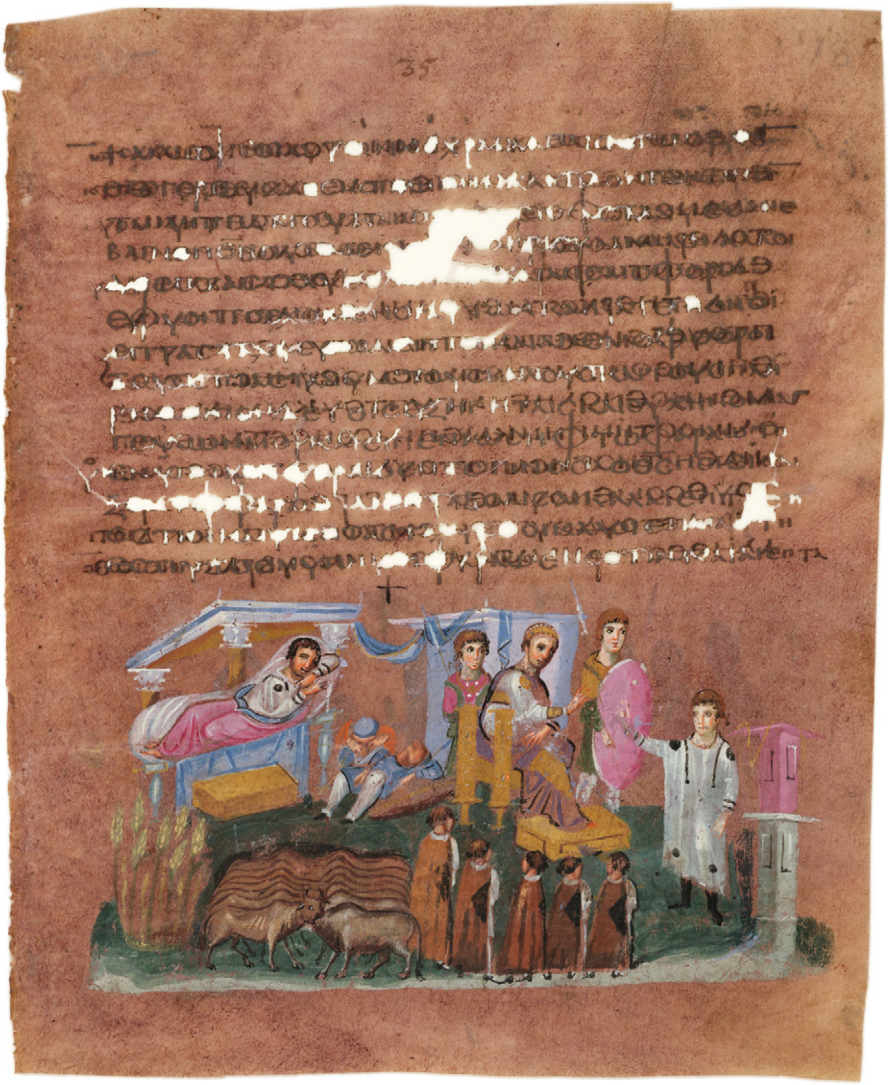

Fig. 35: folio 18, page 35, the pharaoh's dreams; the pharaoh tells Joseph his dreams.

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Fig. 36: folio 18, page 36, Joseph interprets the pharaoh's dreams.

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Fig. 37: folio 19, page 37, Joseph's brothers in Egypt; Joseph weeps; Simon as hostage; hiding the purses in the sacks of grain.

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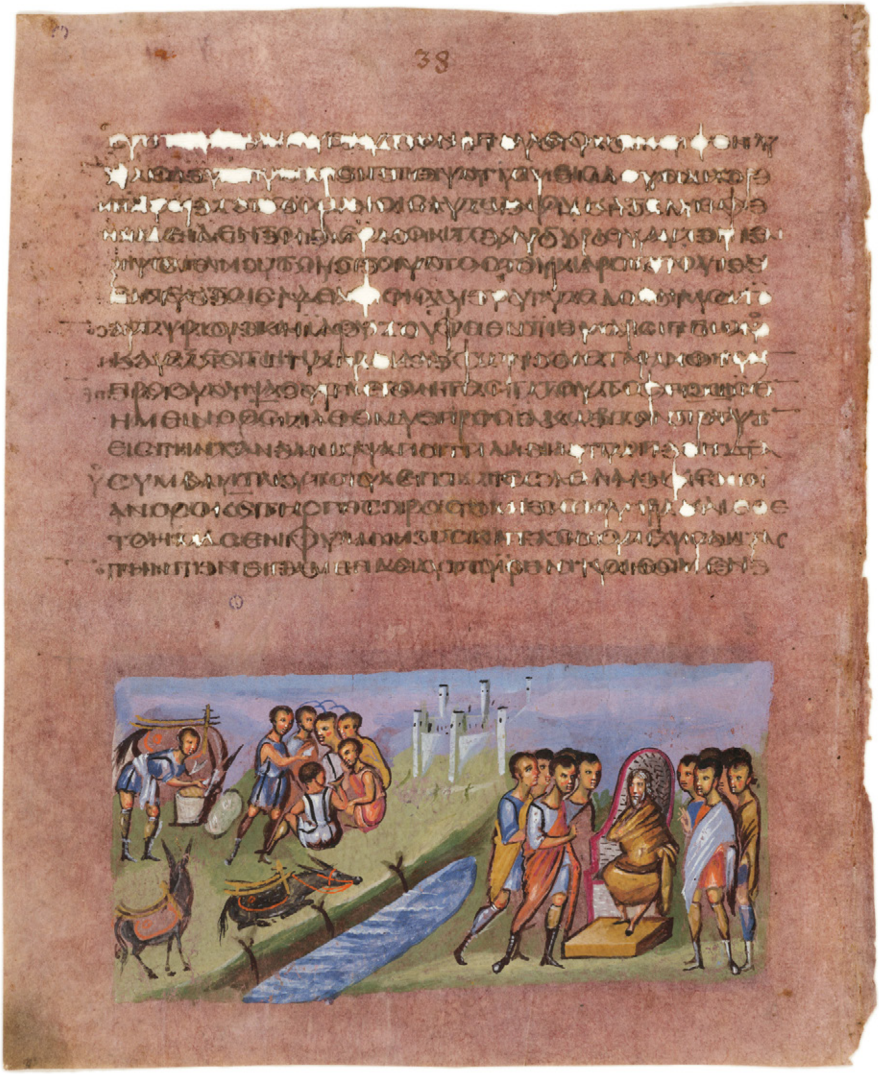

Fig. 38: folio 19, page 38, finding the purses in the sacks of grain; the report of Jacob's sons to their father.

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Fig. 39: folio 20, page 39, Joseph's brothers show their recovered purses to their father.

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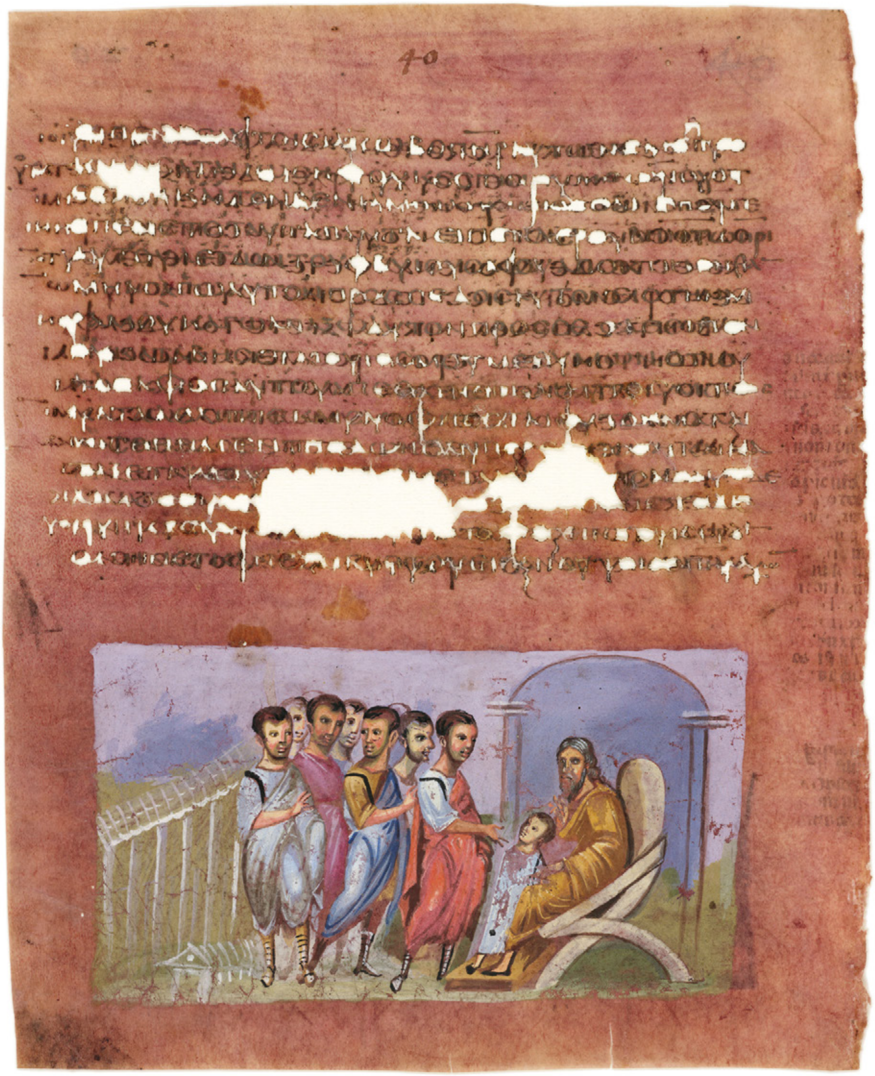

Fig. 40: folio 20, page 40, Ruben asks Joseph for the company of Benjamin.

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Fig. 41: folio 21, page 41, Jacob sends his sons again to Egypt; Juda asks for the company of Benjamin.

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Fig. 42: folio 21, page 42, Jacob entrusts Benjamin to Juda and orders gifts to be taken on the trip.

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Fig. 43: folio 22, page 43, second journey to Egypt; Joseph welcomes his brothers.

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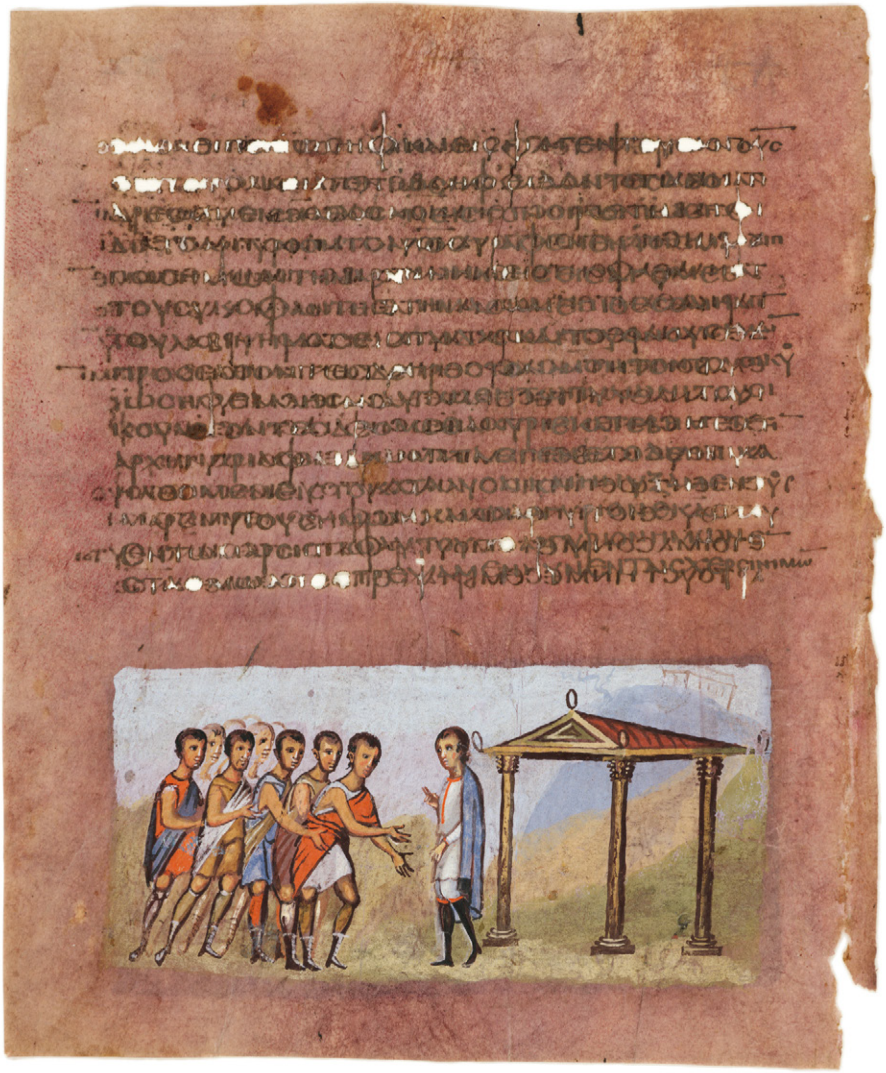

Fig. 44: folio 22, page 44, Joseph's brothers talk with Joseph's caretaker.

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Fig. 45: folio 23, page 45, Jacob blesses Ephraim and Manasseh.

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Fig. 46: folio 23, page 46, Jacob appoints his sons.

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Fig. 47: folio 24, page 47, Jacob asks his sons to bury him in Canaan.

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Fig. 48: folio 24, page 48, Jacob’s death, lamentation and burial.

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Our consultants included specialists from different fields that joined us for the expert meeting in November 2017. Verena Flamm encouraged the idea of a conservation research project and shared her long-term experience with parchment. Abigail Quandt was a mentor of the project and accompanied it with her expertise and her contacts. Zita Breu and Helene Hanzer expanded our view on silver and silver objects. Virginia Costa contributed her profound knowledge of silver corrosion. Cheryl Porter and Mark Clarke advised us on pigments and dyes. Isabella Withworth was an invaluable help in all questions concerning dyeing. Andrea Pataki and Andrea Giovannini supported us with their expertise on parchment manuscripts and important feedback on questions of conservation. Sigrid Eyb-Green added her views on conservation and encouraged us throughout the project. Luise Raab dedicated her bachelor thesis to the investigation of papers coated with isinglass and Klucel G. Regina Hofmann-de Keijzer and Ines Bogensperger were always ready to answer questions on dyes.

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Pitthard did the VOC-measurements in the storage area. Michael Eder from the Photography Department of Kunsthistorisches Museum made and composed the IRR images with great care.

Werner Artner and Erik Lübke from the X-ray Centre of the Vienna University of Technology conducted the XRD measurements, which were evaluated by Erik Lübke as well.

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Authors and co-authors

Maurizio Aceto

Prof. Maurizio Aceto obtained a Degree in Chemistry at the Università degli Studi di Torino (Italy) in 1988 and a PhD in Chemical Sciences at the same University in 1993. From 1997 to 2017 he has been Research Assistant at the Università degli Studi del Piemonte Orientale (UPO) in Alessandria (Italy); in 2017 he was appointed Associate Professor at the same University. In UPO he teaches courses in the field of analytical chemistry. His main research interests deal with characterisation of colorants on painting and textile artworks, using non-invasive and micro-invasive techniques.

Contact, corresponding author Italian team: Prof. Maurizio Aceto, Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, Viale Teresa Michel, 11, 15121 Alessandria, Italy
T: +39 131 360265 E: maurizio.aceto@unipo.it

Angelo Agostino

Dr. Angelo Agostino obtained his PhD in Chemical Sciences at Università degli Studi di Torino, Italy, where he works as assistant professor at the Department of Chemistry. His research interests concern application of X-ray spectroscopic techniques to the characterisation of materials of artistic-archaeological interest, with several experiences at international and national facilities (ESRF, ISIS) and research institutes (Getty Research Institute). His focus is on the application of non-invasive techniques and, in particular, he is developing a quantitative approach based on X-ray fluorescence for the study of light matrices (glass and enamel).

Rita Araújo

Rita Araújo holds a PhD in Conservation Science from the Faculty of Sciences and Technology – New University of Lisbon and is currently a researcher at REQUIMTE and Institute of Medieval Studies (IEM). Her research subjects focus on the study of bookbinding materials and techniques and their importance in the conservation of illuminated manuscripts.

Contact: Rita Araújo, Department Conservation and Restoration, Faculty of Sciences and Technology, New University of Lisbon, Campus Caparica, 2829-516 Caparica, Portugal
T: +351 212 948 300 - 11310 E: a.araujo@campus.fct.unl.pt

Elisa Calà

Dr. Elisa Calà obtained a Master's Degree in Chemical Sciences at Università degli Studi del Piemonte Orientale in 2015, with a thesis on the study of purple natural dyes histori-

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cally used for illuminated manuscripts. In 2019, she obtained a PhD in Chemistry & Biology with a research in the cultural heritage field, focused on the characterisation of natural historical dyes used in painting and textile dyeing. These studies are performed with a non-invasive approach through spectroscopic techniques such as Fibre Optic Reflectance Spectroscopy (FORS) and Fluorescence Spectroscopy, and with micro-invasive analysis such as Raman Spectroscopy and Surface Enhanced Raman Spectroscopy.

Matthew Collins

Professor Matthew Collins holds a Niels Bohr Chair at the Statens Naturhistoriske Museum, Copenhagen and the McDonald Chair in Palaeoproteomics at the University of Cambridge. His research explores the processes by which proteins undergo decay and how we can exploit new palaeoproteomics methods in the service of palaeontology, archaeology and cultural heritage. He set up BioArCh and the interdisciplinary research centre in Biology, Archaeology and Chemistry at the University of York (BioArCh). Two years ago, he joined Tom Gilberts' Evogenomics Group at the Natural History Museum in Copenhagen where, together with Erico Cappellini, he is trying to establish a research group developing the new field of Palaeoproteomics. He has now taken 40 % McDonald Chair in palaeoproteomics at the University of Cambridge, commuting between there and Copenhagen.

Contact: Matthew Collins, Niels Bohr Professor of Palaeoproteomics University of Copenhagen

CSS, Øster Farimagsgade 5, 1353 København K, Denmark, McDonald Professor of Palaeoproteomics University of Cambridge, Downing St, Cambridge CB2 3ER, UK

E: matthew@palaeome.org

Rudolf Erlach

Rudolf Erlach graduated as engineer and physicist. Since 2005, he is Assistant Professor at the University of Applied Arts Vienna. He was educated in electrical engineering and studied physics at TU Wien. In 1986, he joined the University of Applied Arts Vienna, lecturing colour theory and scientific methods for the investigation of objects of art. He is an expert in scanning electron microscopy for the investigation of objects of art and thermoluminescence dating of ceramic objects.

Contact: AProf. Dipl.-Ing. Rudolf Erlach, Institute of Art and Technology, University of Applied Arts Vienna, Salzgries 14/1, 1010 Vienna, Austria

T: +43 1 71133 4823 E: rudolf.erlach@uni-ak.ac.at

Gaia Fenoglio

Dr. Gaia Fenoglio is a conservation scientist specialised in the characterisation of cultural

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heritage inorganic materials, in particular pigments, metals, glasses and enamels. She received her Master's Degree in Science and Technology applied to Cultural Heritage in 2009 from the Università degli Studi di Torino, Italy, and obtained her PhD in Chemical and Materials Science in 2015. Her field of expertise includes the use of X-ray Fluorescence, X-ray Diffraction and SEM/EDX, and she has a key interest in non-invasive techniques, specifically p-XRF and Raman Spectroscopy.

Sarah Fiddyment

Dr Sarah Fiddyment received her BSc in Biochemistry from the University of Zaragoza, having completed three years of medical school and two years specialization in Biochemistry. Her MSc and subsequent PhD were both completed at the same university, working in the field of proteomics in cardiovascular research. She then completed a Marie Curie postdoctoral research fellowship at the University of York, focusing on biomolecular analysis of parchment through history. During this time she developed a non-invasive sampling technique that has allowed her unprecedented access to thousands of parchment documents, helping to establish the emerging field of biocodicology. She continued this work during a subsequent a British Academy Postdoctoral Fellowship. She is currently a Postdoctoral Research Associate on the Beasts 2 Craft ERC project at the McDonald Institute for Archaeological Research, University of Cambridge.

Contact: Dr. Sarah Fiddyment, Universty of Cambridge, The Henry Wellcome Building, Fitzwilliam Street, Cambridge CB2 1QH, United Kingdom
T: +44 1223 764 719, E: sarah.fiddyment@palaeome.org

Martina Griesser

Dr. Martina Griesser gained her degree (Dipl.-Ing.) in chemistry at the Vienna University of Technology in 1993 and finished her PhD at the same university in 1995. In 1996, she was employed by the Kunsthistorisches Museum, Vienna, to set up the Conservation Science Department for assisting the Conservation Departments of the museum with scientific information. Today she is Head of the Conservation Science Department and deals mainly with investigations of the painting techniques and alterations of old master paintings and polychrome sculptures, the identification of corrosion products on metal objects, the development of new conservation treatments, and the preventive conservation measures within the museum's collections. Since 1999, she is a lecturer at the University of Applied Arts, Institute of Conservation and Restoration, Vienna.

Contact: Dr. Martina Griesser, Conservation Science Department, Kunsthistorisches Museum Vienna, Burgring 5, A-1010 Vienna, Austria
T: +43 1 52524-5701 E: martina.griesser@khm.at

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Christa Hofmann

Christa Hofmann graduated from the conservation program of the Academy of Fine Arts in Vienna specialising in paper conservation. She received further training in conservation of photographic materials during internships in the USA and France. She has been working as paper and photo conservator at the Austrian National Library. In 2003 she was appointed head of conservation. Topics of research have included bleaching methods of paper, transparent papers, matt albumen prints, iron gall inks and green copper pigments.

Contact: Christa Hofmann, Institute of Conservation, Austrian National Library, Josefsplatz 1, 1015 Vienna, Austria
T: +43 1 53 410-322. E: christa.hofmann@onb.ac.at

Klaudia Hradil

Dr. Klaudia Hradil received her PhD in crystallography from LMU Universität München, Germany. She then worked at different large-scale neutron facilities (Helmholtz Zentrum Berlin, Heinz Maier-Leibnitz Zentrum Garching) in instrument development to investigate time and space dependent structural properties of materials and, subsequently, served as the head of the central laboratory for investigation of structural properties at the X-ray center of the TU Wien. Her main scientific interests are within the investigation of structural properties of materials.

Contact: Dr. Klaudia Hradil, Head X-ray center, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria
T: +43 1 58801 406620 E: klaudia.hradil@tuwien.ac.at

Inge Boesken Kanold

Inge Boesken Kanold is an artist with a special interest in ancient and forgotten colours. She began research on colours during her 14-year stay in Asia during the seventies. Since 1982, she has lived and worked in Lacoste, Provence. The local fish markets provide her with the sea-snails from the Mediterranean which are necessary for her art-work with purple. In January 2001, together with John Edmonds, she succeeded in reconstructing a fermentation vat using fresh *H. (Murex) trunculus*. She continued with research on a related subject: the purple parchment. In 2005, twenty-six years after the first attempt, she obtained the purple pigment she was looking for. Using oil or egg yolk modifies the purple hue to a greyish blue. As an artist, she always wanted to show what the real purple colour looks like by choosing it as the main theme of her work.

Contact: Inge Boesken Kanold, Chemin du Château, 84480 Lacoste, France
T: +33 652564386, E: ingebkanold@free.fr website:http://pourpre.inge.free.fr

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Antonia Malissa

Dipl.-Ing. Antonia Malissa, BSc, received her BSc in Technical Chemistry from the Technical University of Vienna in 2015. She completed the subsequent Master programme in Technical Chemistry at the same university in 2017. Her diploma thesis was part of the Vienna Genesis project, focusing on the artificial ageing of samples of parchment and silver inks and further analyses of parchment, silver inks and miniature paintings by means of the MHT method, ED µ XRF analysis and Py-GC/MS. She is currently a PhD student in Technical Chemistry in the Research Group for Mass spectrometric Bio- and Polymer Analytics at the Technical University of Vienna, working on the mass spectrometric analysis of the degradation of collagen in parchment.

Contact: Antonia Malissa, Technical University of Vienna, Institute of Chemical Technologies and Analytics, Research Group for Mass spectrometric Bio- and Polymer Analytics, Getreidemarkt 9, A-1060 Vienna, Austria
E: antonia.malissa@tuwien.ac.at

Maria João Melo

Maria João Melo is Full Professor at the Department of Conservation and Restoration of the Faculty of Sciences and Technology-New University of Lisbon. Her research interests center on the study of the photodegradation mechanisms of dyes in paints and plastics, for the development of new conservation methodologies of medieval illuminations and of contemporary art. Other fields of expertise are colour in nature.

Contact: Maria João Melo, Full Professor, Department Conservation and Restoration, Faculty of Sciences and Technology, New University of Lisbon, Campus Caparica, 2829-516 Caparica, Portugal
T: +351 21 2948300 ext. 10945 E: mjm@fct.unl.pt

Paula Nabais

Paula Nabais is a PhD student at the Department of Conservation and Restoration of the NOVA University of Lisbon, on the development of new innovative techniques for the identification of dyes, namely microspectrofluorimetry. This methodology is tested on the study of medieval manuscripts from different ambiances. Recently she has also started working on a project funded by FCT, Polyphenols in Art, regarding the identification of the complexes of iron-gall inks and selection of natural sources for yellow dyes in Portugal.

Contact: Paula Nabais, Department Conservation and Restoration, Faculty of Sciences and Technology, New University of Lisbon, Campus Caparica, 2829-516 Caparica, Portugal
T: +351 21 2948300 ext. 11307 E: p.nabais@campus.fct.unl.pt

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Abigail Quandt

Abigail Quandt received a Master of Science and Diploma in Conservation from the Winterthur/University of Delaware Art Conservation Program in 1982, after a third year internship at the Library of Congress. From 1982–84 she was an advanced intern at Trinity College Library, Dublin. She spent four years as a visiting manuscripts conservator at the Walters Art Museum and joined the staff in 1989. Since 2001, she has been Head of the Department of Book and Paper Conservation at the Walters. She specializes in the conservation of illuminated manuscripts on parchment and has lectured and published extensively on this and related topics. From 1999 to 2012, Ms. Quandt was the lead conservator for the Archimedes Palimpsest Project and, at the same time, supervised the conservation of the Syriac Galen Palimpsest for imaging at the Walters. Since 2014, Ms. Quandt has focused her research on the purple codices from the sixth through the tenth centuries and has collaborated with fellow conservators, scientists and scholars in investigating the materials and techniques of these manuscripts as well as their history of restoration.

Contact: Abigail B. Quandt, The Walters Art Museum, 600 North Charles Street, Baltimore, MD 21201
T: 410-547-9000 ext.626, E: aquandt@thewalters.org

Sophie Rabitsch

Sophie Rabitsch studied paper conservation at the Academy of Fine Arts Vienna and graduated in 2015, specializing in parchment conservation. She completed internships at different institutions, like the Austrian Museum of Applied Arts, the Austrian National Library, the Weltmuseum Wien or the Duchess Anna Amalia Library in Weimar, Germany. From 2010 to 2015, she was a part-time member of the conservation department of the archive of the Natural History Museum Vienna. Since 2015, she works as a freelance conservator, based in Vienna. From 2016 to 2019, she was involved in the Vienna Genesis project at the Austrian National Library as a conservator and researcher.

Contact: Sophie Rabitsch, Restaurierungsatelier, Heiligenstädterstraße 187/2, 1190 Vienna, Austria
E: sophie.rabitsch@gmx.at

Junko Sonderegger

Junko Sonderegger studied oil painting and prints (BA. Tama Art University, Tokyo, 1995) and oil painting conservation (MA. Tokyo University of the Arts, 1997). From 1998 to 2002, she received the Research Fellowship from the Agency for Cultural Affairs and the Foundation for Cultural Heritage and Art Research, Japan, to study European paper conservation (MA. Academy of Fine Arts Vienna, 2004). From 2005 to 2011, she worked as

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paper conservator at the Leopold Museum, Vienna. Since 2012, she is paper conservator at the Institute of Conservation, Austrian National Library.
Contact: Junko Sonderegger, Institute of Conservation, Austrian National Library, Josefsplatz 1, 1015 Vienna, Austria
T: +43 1 53410-347. E: junko.sonderegger@onb.ac.at

Katharina Uhlir

Katharina Uhlir studied chemistry at the University of Vienna. She received her PhD at the Academy of Fine Arts Vienna (Scientific investigations on ancient glasses of Ephesos using μ-XRF and SEM/EDX), where she also was assistant professor. Since 2004, she works as scientific assistant at the Conservation Science Department of the Kunsthistorisches Museum Vienna (KHM), discontinued from 2008–2013 from the activity of a project staff for an Austrian Science Fund (FWF) project (Project no. L430-N19) leading to the implementation of the PART II μ-XRF instrument at the Conservation Science Department of the KHM. Since 2011, she is responsible for the XRF investigations at the KHM.
Contact: Dr. Katharina Uhlir, Conservation Science Department, Kunsthistorisches Museum Wien, Burgring 5, 1010 Vienna, Austria
T: +43 1 52524 5705. E: katharina.uhlir@khm.at

Jiří Vnouček

After completing studies in conservation in Prague, Jiří Vnouček studied as intern with Christopher Clarkson at the West Dean College, England. In 2010, he received a Master degree in Conservation Science from the School of Conservation of the Royal Academy of Fine Arts in Copenhagen, Denmark. Jiří Vnouček was head of the Conservation department at the National Library in Prague for 12 years. Since 2005, he is employed as conservator at the Department of Preservation of The Royal Library, Copenhagen. He specialized in conservation of parchment, participated in the EU project IDAP (Improved Damage Analyses of Parchment) and several other research projects in the field of the conservation of parchment manuscripts. His research includes experimental parchment making and production of manuscripts. The theme of his PhD thesis is interdisciplinary research of the visual assessment of parchment in medieval manuscripts at the University of York (Centre of Medieval Studies and department of Archaeology).
Contact: Dr. Jiří Vnouček, Conservation Department, The Royal Library Copenhagen, PO-box 2149, 1016 Copenhagen, Denmark.
E: jiv@kb.dk

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Abbreviations

eZooMS: electrostatic Zooarchaeology by Mass Spectrometry
FORS: Fibre Optics Reflectance Spectroscopy, UV-visible diffuse reflectance spectrophotometry with optic fibres
IRR: Infrared reflectography
MHT method: Micro Hot Table method
SEM/EDX: Energy dispersive X-ray analysis in the scanning electron microscope
SERS: Surface enhanced Raman spectroscopy
XRD: X-ray diffraction
XRF: X-ray fluorescence spectroscopy
UV: Ultraviolet light

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