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

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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.

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.

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)

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.

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.

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.

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.

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)

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).

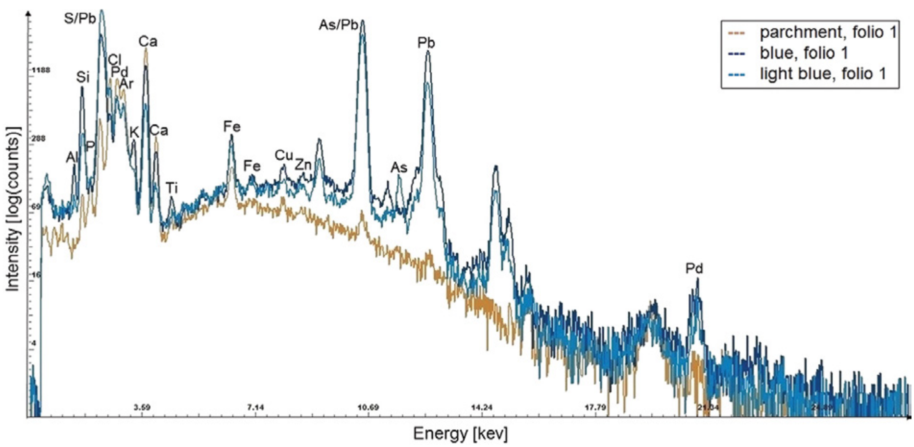

Fig. 1: XRF spectra of a blue (MP1_6) and a light blue (MP1_8) area on folio 1, page 1. A spectrum of the parchment of folio 1 (MP1_3) shows the background signal detected.

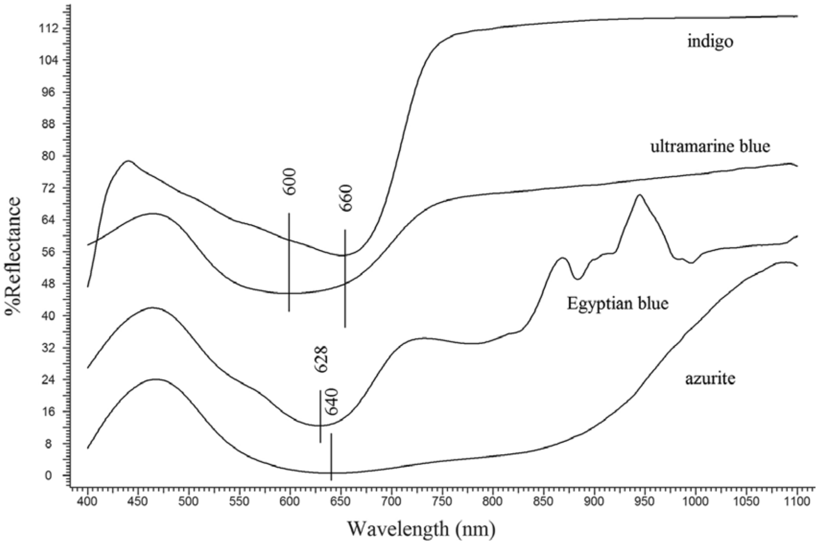

Fig. 2: FORS spectra of blue pigments: indigo, ultramarine blue, Egyptian blue and azurite.

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

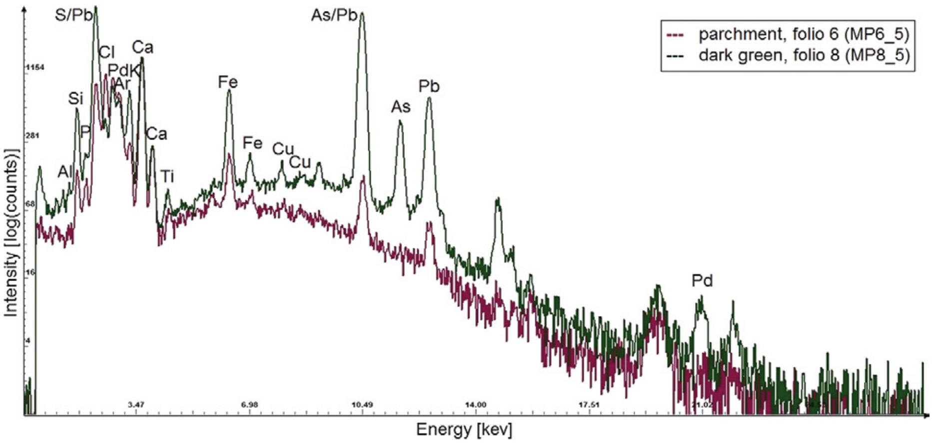

Fig. 4: XRF spectrum of a green area (MP8_5) on folio 8, page 15. For comparison a spectrum of blank parchment of folio 6 (MP6_5) shows the background signal detected.

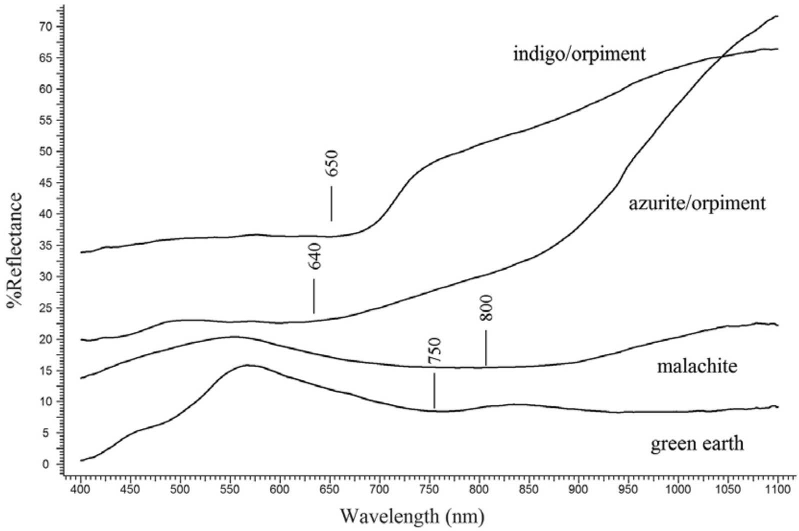

Fig. 5: FORS spectra of green pigments and mixtures: indigo/orpiment, azurite/orpiment, malachite and green earth.

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

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

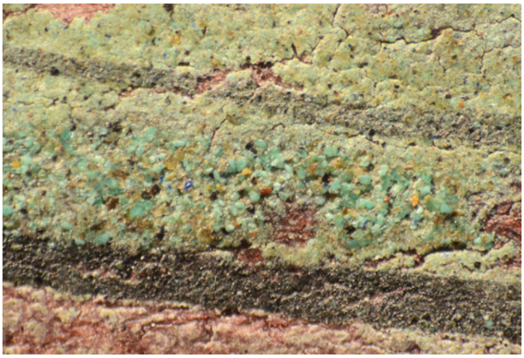

Fig. 7: Microscopic image, 16x magnification, of green on folio 8, page 16.

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

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

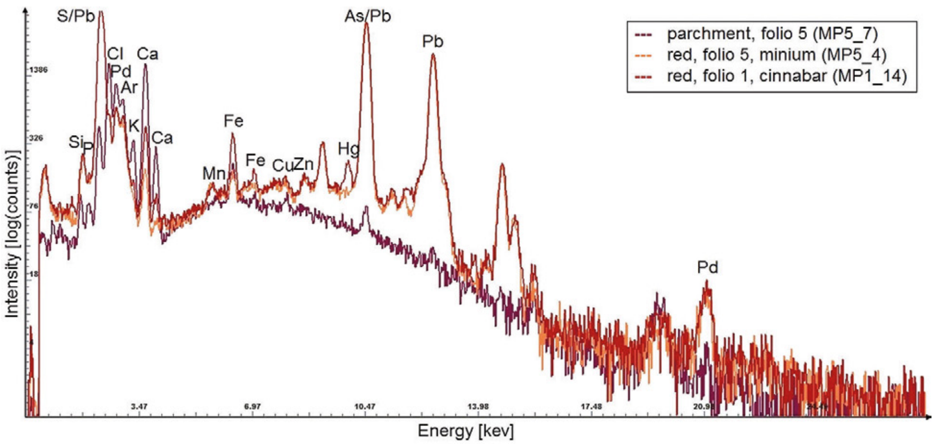

Fig. 10: XRF spectra of red areas on folio 1, page 2 (MP1_14) and folio 5, page 10 (MP5_4). For comparison a spectrum of blank parchment of folio 5 (MP5_7) shows the background signal detected.

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 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 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).

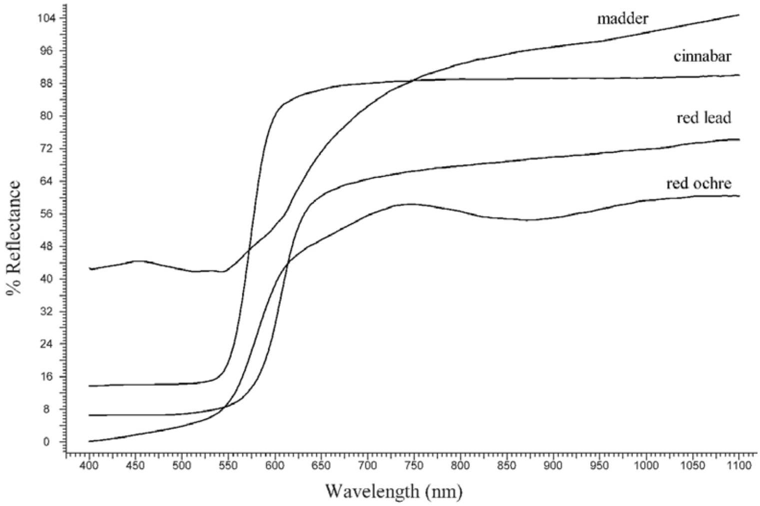

Fig. 11: FORS spectra of red lead, cinnabar, red ochre and madder.

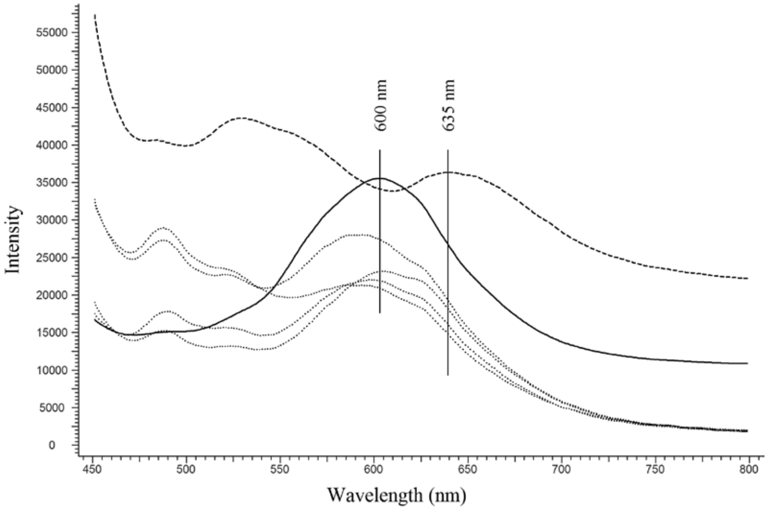

Fig. 12: Fluorescence spectra of madder (solid line), cochineal (dashed line) and pink areas of the Vienna Genesis (dotted lines).

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

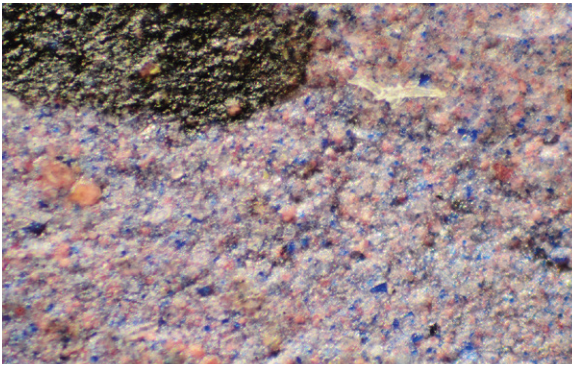

Fig. 14: Microscopic image, 16x magnification, of violet on the cloth of king Abimelech, folio 8, page 16.

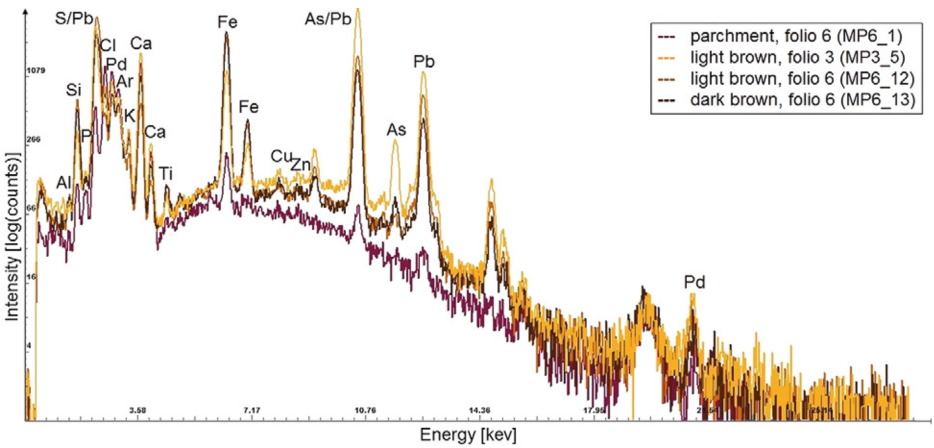

Fig. 15: Comparison of the XRF spectra of light and dark brown areas on folio 3, page 6 (MP3_5, yellow) and folio 6, page 12 (MP6_12 and MP6_13, brown and black). A spectrum of the parchment of folio 6 (MP6_5, purple) shows the background signal detected.

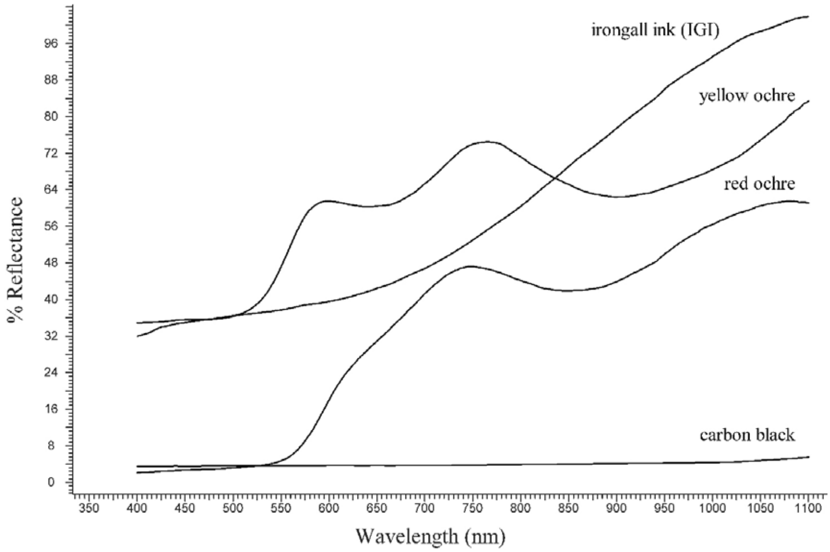

Fig. 16: FORS spectra of yellow and red ochre, iron gall ink and carbon black.

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

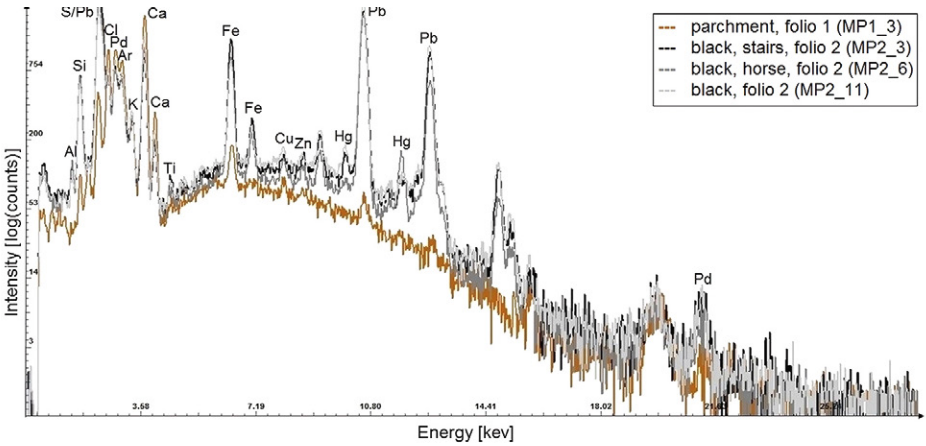

Fig. 18: XRF spectra of black areas on folio 2, page 3 (MP2_3 and MP2_6, black and dark grey) and 4 (MP2_11, light grey). A spectrum of the parchment of folio 1 (MP1_3, brown) shows the background signal detected.

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, 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.

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.

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 mixtures 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 azurite (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].

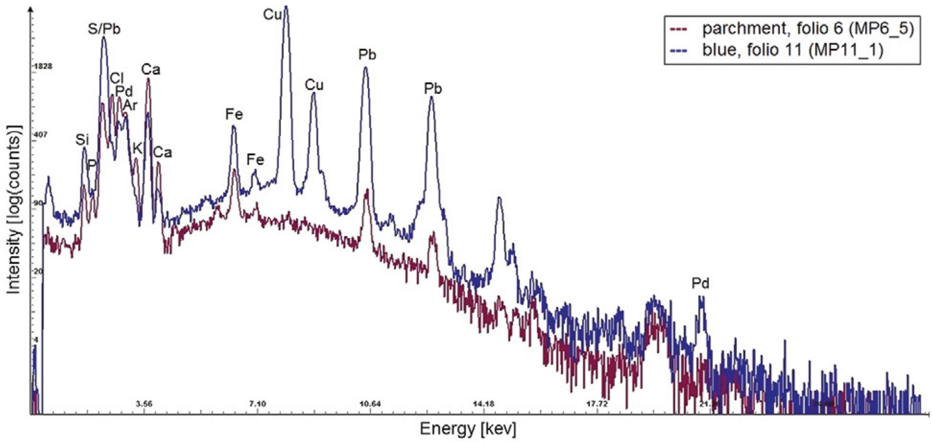

Fig. 25: XRF spectrum of blue pigment (MP11_1) on folio 11, page 23. A spectrum of the parchment of folio 6 (MP6_5) shows the background signal detected.

14 Hofmann et al., 2015.

15 Eastaugh et al., 2004, Optical Microscopy of Historical Pigments, pp. 50–51.

Fig. 26: Miniature on folio 11, page 22.

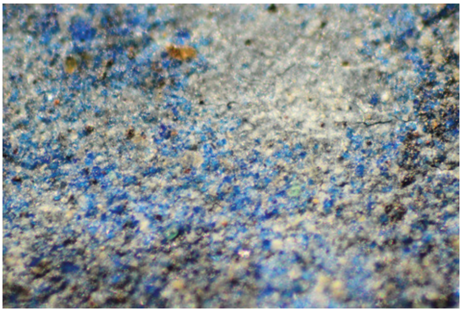

Fig. 27: Microscopic image, 32x magnification, of blue paint layer on folio 11, page 22: grains of azurite in blue and green.

Fig. 28: Miniature on folio 14, page 28, the dream of Joseph.

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.

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

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 $CaCuSi_4O_{10}$.

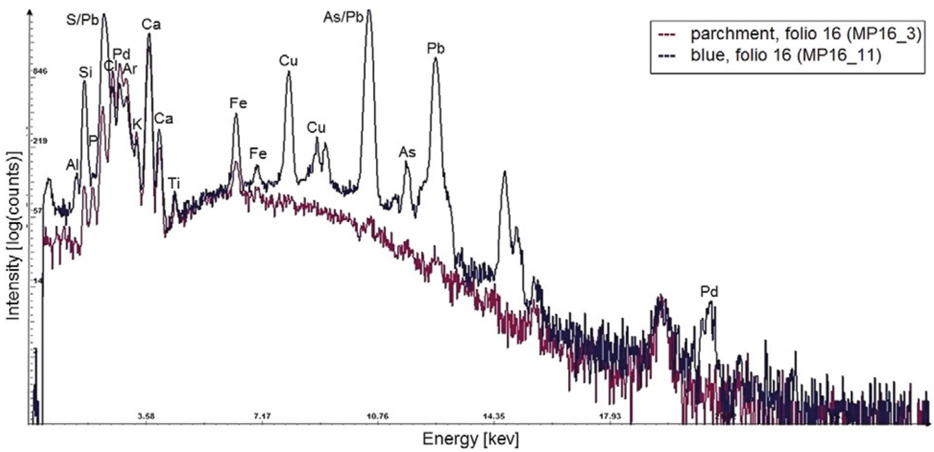

Fig. 30: XRF spectrum of a blue area on folio 16, page 32 (MP 16_11). A spectrum of the parchment of folio 16 (MP16_3) shows the background signal detected.

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.

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.

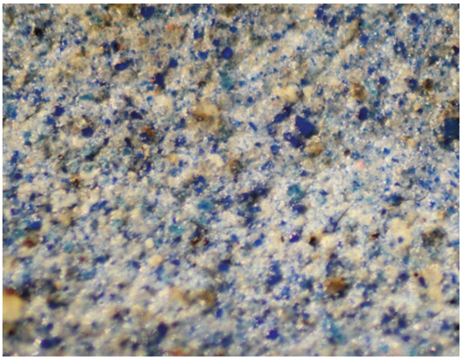

Fig. 33: Microscopic image, 32x magnification, of blue paint on folio 15, page 30: ultramarine and Egyptian blue particles.

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 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-

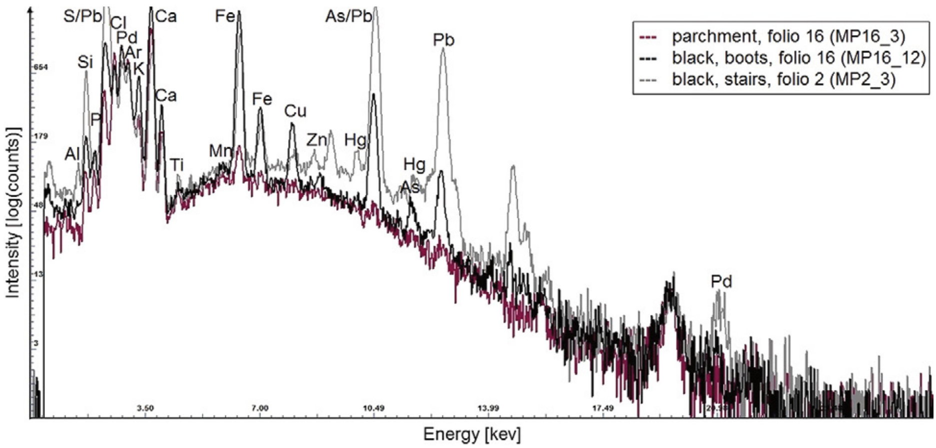

Fig. 34: Comparison of the XRF spectra of the inks used on folio 2, page 3 (MP2_3, grey) and folio 16, page 32 (MP16_12, black). A spectrum of the parchment of folio 16 (MP16_3, purple) shows the background signal detected.

19 Hofmann et al., 2007.

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.

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).

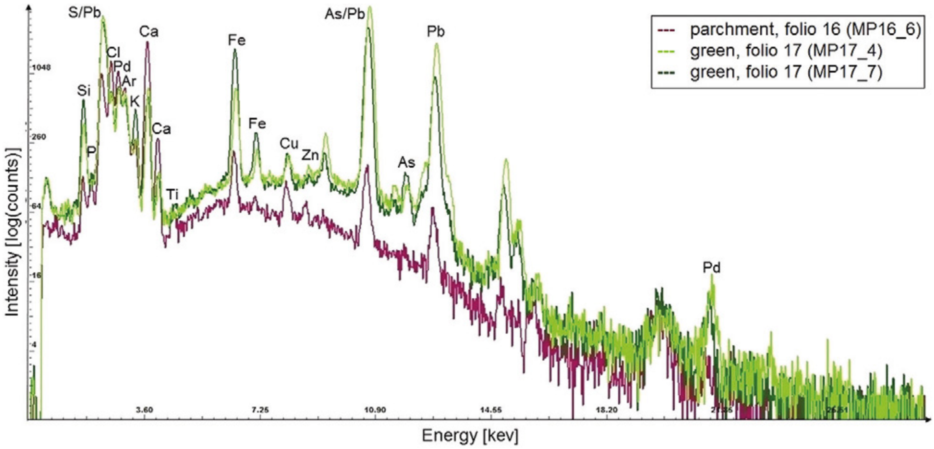

Fig. 37: XRF spectra of green paint layers on folio 17, page 33 (MP17_4, light green) and 34 (MP17_7, dark green). A spectrum of the parchment of folio 16 (MP16_6, purple) shows the background signal detected.

Fig. 38: Miniature on folio 17, page 33, Joseph in prison.

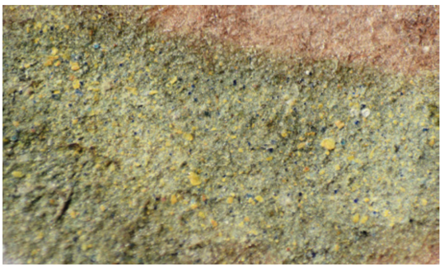

Fig. 39: Microscopic image, 16x magnification of the green paint layer on folio 17, page 33.

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.

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

Fig. 41: Miniature on folio 19, page 37, Joseph meets his brothers.

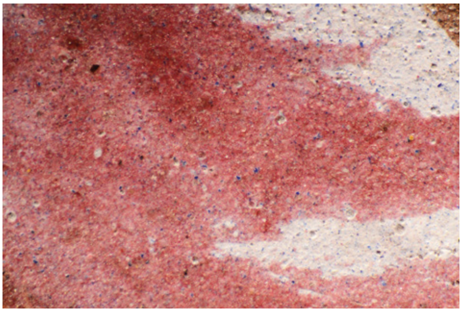

Fig. 42: Microscopic image, 10x magnification, of old rose on the cushion of Jacob on folio 21, page 41.

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, 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

Fig. 43: Miniature on folio 24, page 47, Jacob and his sons.

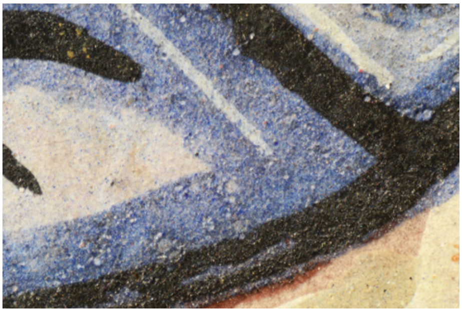

Fig. 44: Microscopic image, 10x magnification, of blue paint on folio 23, page 46.

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.

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 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.

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.

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.

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.

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.

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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