Laboratory Analysis Report

Title of the object	*Pietà*
Name of the artist	A painting twice bearing a monogram of Michelangelo di Lodovico Buonarroti Simoni (Caprese, Republic of Florence, 1475 - Rome, Papal States, 1564)
Municipality	-
File number	2024.15483
Date	10 September 2024 – updated 13/01/2026

Royal Institute for Cultural Heritage

Applicant	Private
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Date of the report	13 January 2026

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1 Description of the object

KIK-IRPA object number	11079440
Municipality	-
Institution	Private collection
Inventory number	-
Type of object	Painting
Title of the object, author	*Pietá,* a painting twice bearing a monogram of Michelangelo di Lodovico Buonarroti Simoni (Caprese, Republic of Florence, 1475 - Rome, Papal States, 1564)
Material	Oil on linen canvas
Dimensions	137 x 108 cm
Owner	Private collection
Remarks	-

2 Objective

The first aim of the research is to characterise the materials used in the painting, assess its current state of conservation, and determine with scientific evidence whether the painting's materials are consistent with those used in the 16th century. The second aim was assessing the age of the monograms in relation to the painting. Macro-scale and micro-scale elemental mapping and technical photography were selected to gain insight into the material construction of the *Pietà*. In this updated report a dye analysis is added.

3 Methodology

3.1 Non-invasive techniques

3.1.1 UV photography

To properly contextualise the analytical results, the original paint layers and pigments were distinguished from later retouching by examining the painting under UV light. Under UV light, recent retouching usually shows up as dark patches on the surface of the painting, while less recent retouching appears as a lighter, grey-violet colour due to additional layers of varnish. Regions of restoration are excluded when interpreting the painting's original materials.

3.1.2 IR photography and IR reflectography

Infrared (IR) photography and reflectography (IRR) was used to visualise possible underdrawings below the paint layer. Carbon-based black pigments strongly absorb infrared radiation, and if they are used by the artist to sketch on a white base layer, those drawings should be visible in an infrared photograph. There are other pigments that absorb in the infrared, however, which could interfere with the transmission of infrared through the paint layer and limit visibility. The IR light penetrates deeper into the paint layers with IRR than with IR photography.

3.1.3 X-radiography

X-radiography was used as a tool in the examination of the painting to reveal subsurface details that are otherwise invisible to the naked eye. This technique enables the analysis of the underlying structure, including alterations made during the painting process (pentimenti), and the condition of both the support and paint layers. Additionally, X-radiography is instrumental in identifying damages, restorations, and previous repairs, offering valuable information regarding the painting's history and condition.

3.1.4 Macro x-ray fluorescence (MA-XRF)

Macro X-ray fluorescence (MA-XRF) analyses were carried out to identify the pigments used and to evaluate the layers of the composition of the layers. XRF is a technique for the elemental analysis of inorganic pigments. In this technique, a beam of primary X-rays is focused on the surface of the painting, inducing X-ray fluorescence that is characteristic of each chemical element present. The instrument detects the fluorescence and produces XRF spectra at each point measured. MA-XRF combines this technique with scanning, so that each point measured creates a pixel in an image, which in turn can be used to create 'maps' of the distribution of each element across the painting. Information about the pigments used can be deduced from the elements detected. Straightforward identification of a pigment is not always possible, as the elements detected may be from several different pigments, or from organic pigments that cannot be detected by XRF.

Due to the high energy of the incident x-rays, the fluorescence measured comes from all of the paint layers present, not just from the surface layer. Thus, with this technique, all of the pigments from the ground layer to the upper paint layers are analysed simultaneously. However, heavy elements such as lead can block x-rays from reaching the lower layers. Hence, a high concentration of lead in an upper paint layer may prevent the incident x-ray from reaching underlying layers—this is known as the shielding effect.

By scanning the entire surface of the painting, MA-XRF generates detailed elemental distribution maps, revealing the pigments and materials used, underlying compositions, and hidden details.

With the instrument used, qualitative data for elements whose atomic number is equal to or greater than that of aluminium (Z = 13) can be obtained. Measurements were acquired with a Bruker M6 Jetstream XRF instrument (Bruker AXS, Germany) equipped with a rhodium tube as an x-ray source. The following experimental parameters were applied: accelerating voltage of 50 kV, a current of 600 µA, measurement time of 25 ms per pixel (dwell time), x-ray spot size of 500 µm, pixel size 450 µm, normal scanning mode, no filter. The painting was scanned in four parts, the results of which were digitally stitched together to create a map for each element detected. The two monograms cited above were scanned at higher resolution using the following parameters: spot size 50µm, pixel size 45 µm, and dwell time 25 ms.

3.2 Cross-section study

Three samples were taken to help in the interpretation of the MA-XRF results and to better understand the layer structure. A summary is given in Table 1, together with a brief description of the sample spot and the archival number of the sample. The exact locations of the sample sites are shown in figure 1.

Figure 1. Indication of the sampling points.

Table 1. Archival numbers of the samples taken and brief description of sample sites.

N°	Sample P	Cross-section C	Description
1	P253.098	C102.191	Flesh tones, foot Christ
2	P253.102	C102.192	Red coat, Mary
3	P253.103	C102.193	Dark green hill, right edge

Extra material sampled for number 2 – P262.029 on 21/11/2025:

3.2.1 Cross-section preparation

Each sample was prepared into a cross-section by embedding it in a Technovit 2000 LC resin. This methacrylate-based resin cures under blue light via the Technotray CU polymerisation process. The sample is placed on an already-polymerised cube and then covered with a second layer of liquid resin which is polymerised in the next step. The sample is thus completely surrounded by a transparent block of resin, to be polished mechanically with abrasive sheets with grit sizes from 200 to 4000. The final polishing is done by hand with micro-abrasive sheets (Micro-Mesh, grit sizes up to 12000) until the interior of the sample is exposed at the surface. The cross-section is observed with an optical microscope (Zeiss Axio M.1 Imager) using polarised white light and UV-light (excitation bandpass filter from 390 to 420 nm, beamsplitter at 425 nm, and emission lowpass filter from 450 nm). Images from the microscope are recorded and used to describe the layer structure.

3.2.2 Scanning electron microscopy to energy-dispersive x-ray detection (SEM-EDX)

To obtain information on the distribution of pigments within each layer of the painting, the cross-section was analysed by scanning electron microscopy with energy-dispersive x-ray detection (SEM-EDX). In SEM, a stream of primary electrons is focused onto the sample surface, resulting in the emission of a number of different particles or rays (secondary electrons, back-scattered electrons, x-rays, photons, Auger electrons, etc.). The secondary and backscattered electrons are used to generate an image, while the x-rays give characteristic chemical information from the emitting atoms. The depth probed by EDX analysis is around 1-3 µm. Only information on the inorganic elements is obtained from SEM-EDX data. Images were acquired using a Zeiss EVO 15 LS SEM coupled to a back-scattered electron detector and EDX (X-Max80, Oxford Instruments). The instrument was operated under low vacuum mode (50 Pa) at 15kV.

3.3 Dye analysis HPLC-DAD

High Performance Liquid Chromatography with a photo diode array detection system (HPLC-DAD) was used to identify the organic dye composition. This was done using the Acquity Arc UHPLC equipment from Waters (Belgium). The analyses are interpreted using the Empower software system from Waters. The dyes were recovered from the sample using hydrochloric acid (HCl) extraction. (see annexe 6)

4 Analysis results

4.1 Non-invasive techniques - scientific imagery results

Under UV light, the painting shows a light blue fluorescence, with zones of less pronounced fluorescence, zones that have been retouched (Annex 1). In particular, there is a large retouching zone at the level of Mary's robe and a horizontal zone running across the width of the canvas below Christ's knees. From other analyses (see below), these also appear to be areas of heavy intervention. The chest of Christ also shows some retouching, and there are more locally scattered restorations throughout the canvas, both in the background and in the figures, but relatively limited in the faces and hands. More details on these interventions are given in the MA-XRF-section.

An underdrawing cannot be made visible by either IR photography or IRR. This may mean that there is no underdrawing, or that it cannot be made visible because it has not been applied with a carbonaceous material. The thick layer of organic varnish may also be an interfering factor. In the IR and IRR images, a white area can be seen running from Mary's right shoulder to her lips and up to the base of her nose. Its origin is unclear, perhaps a first sketch or part of the background that has not been worked out? However, neither the RX images nor the MA-XRF results show anything that could explain this white zone. Perhaps it is a zone made of a carbon-rich material, visible only in the IR.

There is a difference in brightness between the upper and lower parts of the painting in the IR and IRR images, with the upper part appearing brighter in the IR(R) image. This difference can also be seen in the visible image.

The IR(R) images reveal that a strip has been added to the canvas just below Christ's knees. A rectangular piece of canvas has also been inserted into Mary's robe. Further details as to whether this strip and the insertion are original are given in the section discussing the MA-XRF results.

The XR image also shows losses or damage to the pictorial layer, visible as black spots (due to the local absence of lead). The inserted piece of canvas at the level of Mary's robe is clearly visible, as is the added strip under Christ's knees. The RX image also provides information about the original canvas. The canvas appears to be made up of three separate pieces sewn together. A first horizontal running seam can be seen just below the added strip, a second at the level of Christ's fingers. Changes in the composition or a hidden composition cannot be observed. The nail holes in the original canvas (which has now been re-lined) can be seen near the bottom of the painting.

4.2 Non-invasive techniques – MA-XRF results

Lead white [$(PbCO_3)_2 \cdot Pb(OH)_2$] is the main white pigment used in the painting, as can be seen in the **lead** (Pb) distribution map (Annex 2). Lead is used to render the flesh tones, cloth of Christ, dress, sky, and vegetation. Since the fibres and structure of the canvas are visible in the lead map, the lead white must also be present in the ground in close contact with the canvas. This is confirmed by the results of the analysis of the cross-section containing the ground layer (C102.193), as is further discussed (see 4.3).

Because of its abundance in the paint layers, the absence of lead becomes a marker for assessing the condition of the painting. Losses of lead are visible in the map as dark spots. They indicate areas of damage, which correspond well with what can be seen in the RX-image (Annex 1) and to a certain extent in the UV-image. However, there is not always a one-to-one correspondence between the damage visible in the lead map and the restoration zones in the UV image. Some restored zones visible in the UV image cover a larger area than the damage in the lead map suggests. It is likely that in some cases a larger area was painted over than was strictly necessary. This can be clearly seen, for example, in the upper part of Christ's body (figure 2a), where the UV image shows a larger restored area than the lead map would suggest. However, it is possible that the paint may have worn (without obvious loss), necessitating the restoration of a larger area. Conversely, sometimes damage is visible in the lead map that is barely visible or not visible in the UV image. An example of this can be seen in the bright sky, which shows small losses in the lead map, but no deviant UV fluorescence in the UV image (figure 2b). This means that the sky restorations are from a different intervention than most that are visible in the UV image. It is not surprising to find various restoration interventions on a painting which is several centuries old. The painting´s condition seems good, commensurate with its age.

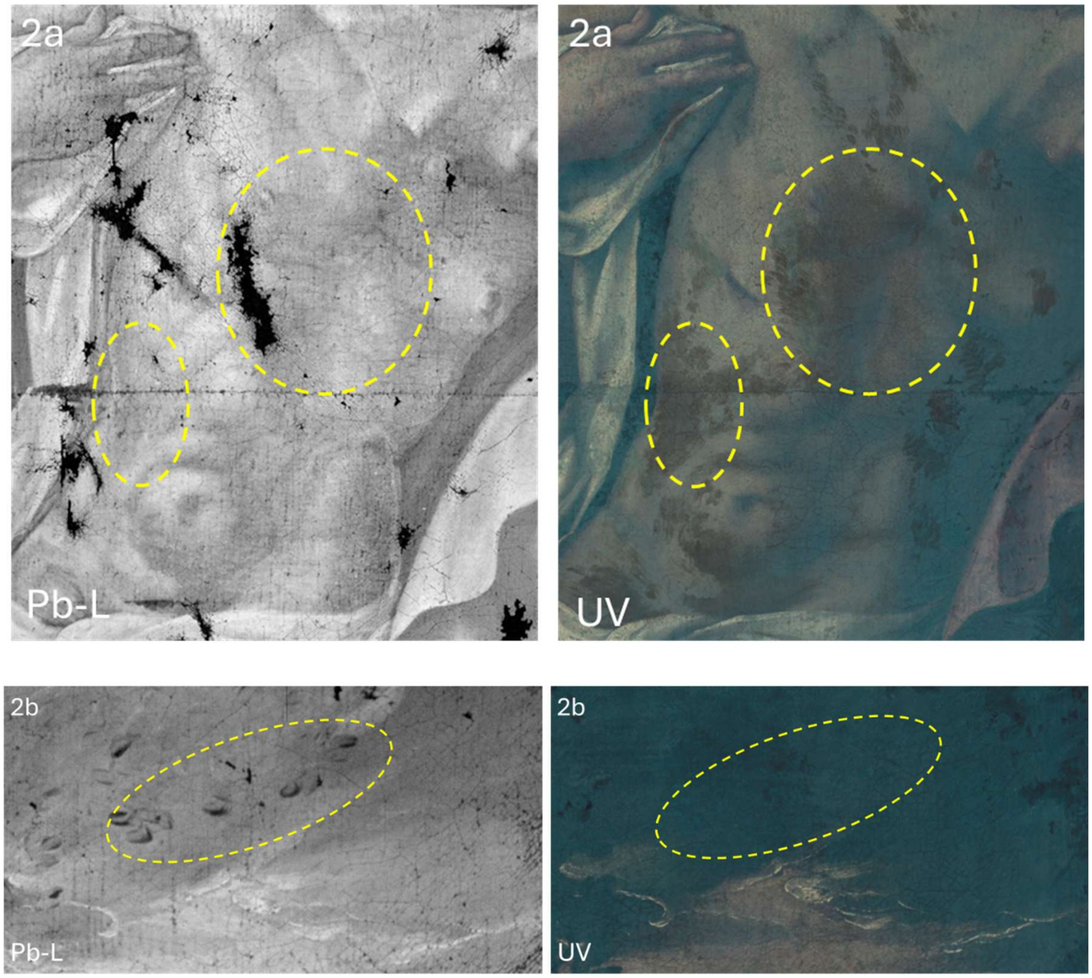

Figure 2. Not all retouched areas visible in the UV image correspond exactly to the damage observed in the lead map. Figure 2a shows some areas (indicated by yellow dashed lines) where the restored area (visible in UV) is larger than would be expected from the damage in the lead map. Figure 2b shows some areas (indicated by yellow dashed lines) where damage is visible in the lead map, but retouching is difficult to see in the UV map.

The inserted strip is also very noticeable, and its composition is very different from the rest of the canvas. This strip was not originally present and was added at a later stage. In the lead map, the figurative elements (Christ's legs, Mary's robe) do not run through the added strip. Instead modern pigments (such as zinc white and titanium white) to paint in these areas (see further) were used. The addition of this strip also affected the folds in Mary's robe (figure 3a) and, to a lesser extent, the folds in the cloth around Christ (figure 3b). When this strip is digitally removed, the lower part of the painting and the upper part match almost perfectly, as can be seen from the maps of the elements lead, cobalt, iron and copper (figure 4). The strip therefore appears to have been added simply to make the painting taller and does not appear to be related to any possible damage to the painting. The encrusted piece of fabric in Mary's dress is also clearly visible, and again the chemical composition of the pigments is different from the rest of the canvas (and from the added strip). The seams between the three joined parts of the original canvas can also be seen. Finally, it is worth noting that in the lead map the vegetation in the darker areas is more visible than in the visual image.

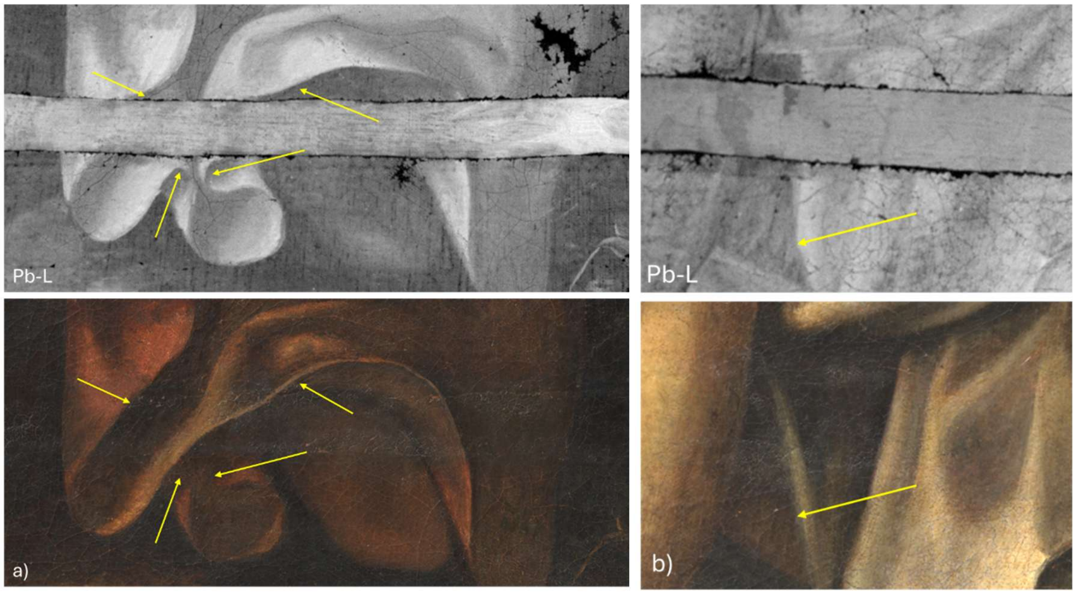

Figure 3. Some changes in the folds of the Virgin's drapery (a) and in the cloth around Christ (b), visible on the lead map (indicated by yellow arrows), resulted from the addition of a strip and the repainting of this new area.

Lead white was the most important white pigment in Western Europe from Roman times until the introduction of zinc white in the late 18th century and titanium white in the 20th century. While the pigment occurs naturally as (hydro)cerussite, it is hardly ever used in paintings in its natural, mineral form. The synthetic form is almost always used, which is prepared by exposing metallic lead to acetic acid, forming lead carbonate or lead white. This process was already described in the Roman period[1].

In terms of intensity, the **calcium** (Ca) map is almost the opposite of the lead map. In areas where lead is high, the calcium signal is weak and vice versa. The calcium signal is also stronger in the craquelure. This implies that the calcium must be at least partly derived from an underlying layer, most likely the ground with lead in top layers suppressing its signal (shielding effect, see 3.1.4). The analysis of a cross-section confirms the presence of a ground containing **chalk** ($CaCO_3$), next to **earth pigments** (which naturally contain calcium as an impurity), **bone white** [$Ca_{10}(PO_4)_6(OH)_2$ and $CaCO_3$], and grains rich in calcium and magnesium, which may indicate the presence of **dolomite**. All these compounds are sources of calcium. In the case of the larger losses, it cannot be ruled out that (some of) the calcium comes from a later restoration, in which the lacunae were first filled with chalk or gypsum, for example, and then retouching was applied.

[1] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium*, Butterworth-Heinemann: Oxford, 2008, p. 200-201, 239-241, 381.

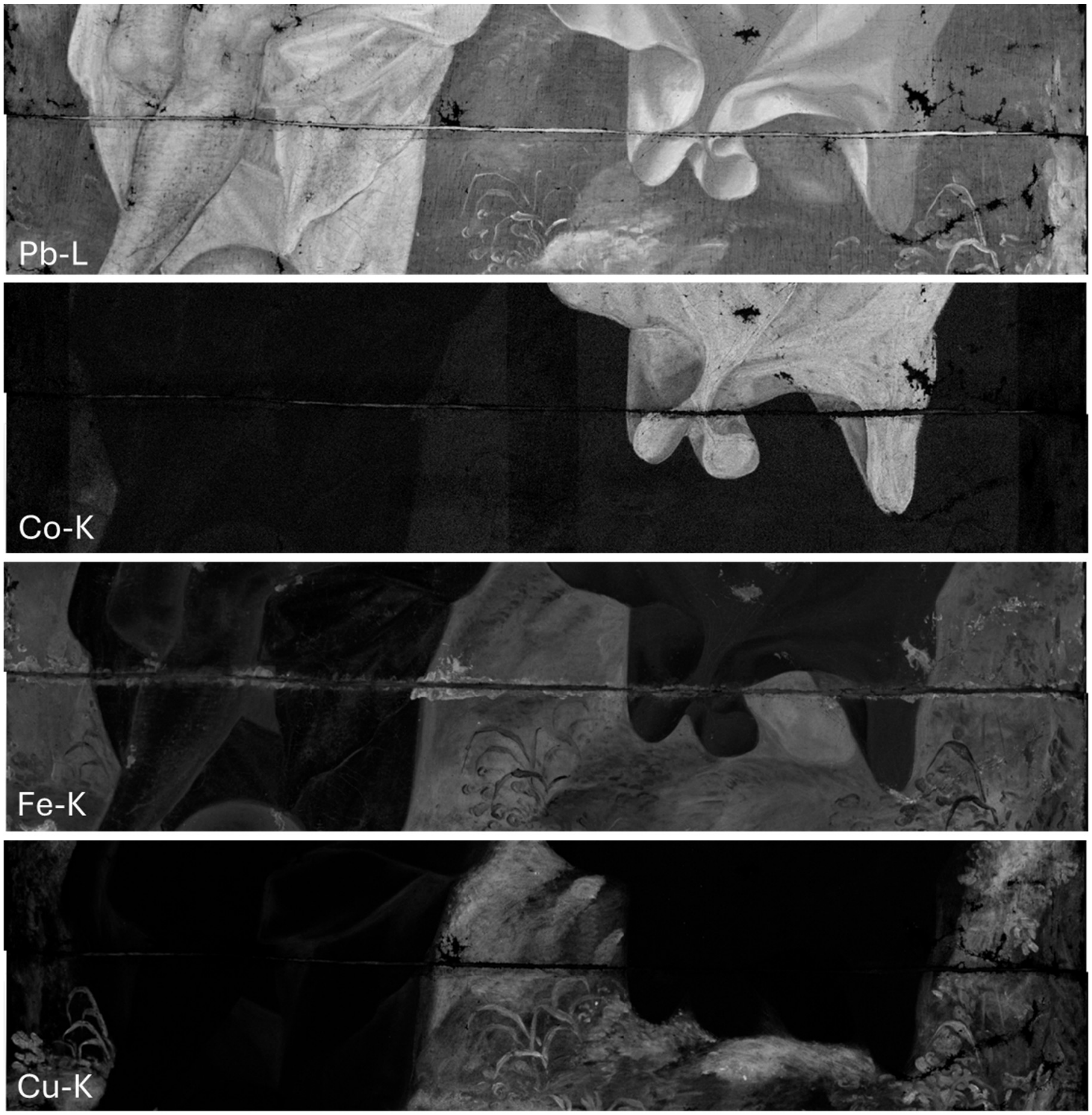

Figure 4. Digital reconstruction of the MA-XRF maps of lead (Pb-L), cobalt (Co-K), iron (Fe-K) and copper (Cu-K) of a detail of the painting without the strip. Considering that there is always some loss when cutting a painting in two, the upper and lower parts match very well.

The **iron** (Fe) and **manganese** (Mn) maps are almost identical. The simultaneous presence of iron and manganese suggests the use of **dark earth pigments such as sienna or umber**. These were used mainly in the dark brown background and the skull at Christ's feet. To a lesser extent, these pigments were also used in the shaded parts of Christ's body, as well as in Mary's pupils, the shadow between her lips, the shadow under the fingers of her left hand and the dark parts of her right hand. A small amount of earth pigment can also be seen in the darkest parts of Mary's robe, but no or less manganese is detected. This is also the case for a part of Christ's hair. In these cases it is likely that **common earth pigments** were used (e.g. brown or red ochres). Finally, it should be noted that earth pigments were also used in the restoration, particularly in the underlayers. The nail holes at the bottom of the original canvas were clearly filled with an iron-rich pigment. Earth pigments have been used since prehistoric times and can be found in hues ranging between dark brown, light yellow, red, and dull green. They are still used today.

There is little iron in the red tones of Mary's sleeve and dress, so the red colour cannot be explained by the use of a red earth. Nor was the commonly used **vermilion** (HgS) used in the reds of Mary's garment, as the **mercury** (Hg) map suggests. However, vermilion was used for Mary's lips, in the red areas around her eyes and in her skin tone, in the shade of red that outlines Christ's right arm and in his hair. There is also some vermilion in Christ's flesh tone, but clearly much less than in Mary's flesh tone. The addition of some vermilion is also likely in the background. Vermilion occurs naturally as the mineral cinnabar, though it has been produced synthetically in China for centuries, a practice which reached Europe in the 8th century[2]. The red colour of parts of Mary's garment cannot be explained on the basis of the MA-XRF results, making the use of an organic **red lake** pigment likely, as confirmed by the study of a cross section of the red garment (C102.192, see further).

Cobalt (Co) is found in Mary's clothing and to a lesser extent in the background and in the lips of Christ, along with **arsenic** (As), **nickel** (Ni), **bismuth** (Bi) and **potassium** (K), indicating the use of **smalt**. Smalt is a blue pigment made from ground cobalt glass, which was widely used in European art from the end of the 15th to the 18th centuries[3]. Smalt was produced by melting a mixture of silica (sand), potassium carbonate (potash), and cobalt-containing ores in a furnace. Nickel, bismuth and arsenic are impurities in the ore from which cobalt is extracted. The resulting blue glass was then ground into a fine powder to be used as a pigment. Smalt was widely used in oil paints in the second half of the 16th century and can be found in later works by artists such as Titian[4]. Smalt was already used in the Sistine Chapel frescoes painted by Michelangelo between 1508 and 1512[5]. While this pigment initially produces a blue colour similar to ultramarine, though less vivid, it is notoriously unstable. Over time, smalt often loses its original hue, especially if it is not mixed with lead white, leading to significant discolouration as the paint ages. Paints with minimal lead content may shift to a dull grey or a deep translucent brown. This instability, combined with the development of synthetic blue pigments in the 18th and 19th centuries (such as Prussian blue), led to a decline in its use. By the 19th century, smalt was largely replaced by more stable and vibrant blue pigments.

Smalt was sometimes used in glazes or mixed with other pigments to create specific hues, as is the case here, as smalt can be found both in the bluish and red parts of the garment of Mary. In the lightest areas of the robe, where lead white is predominant, a faint blue tint remains, suggesting that the blue dress might originally have been bluer. Smalt is also found in the red parts of the robe and cloak. If the smalt in these areas has also discoloured, which is likely, these parts of the garment were originally more purple. Smalt is also identified in the darker parts of the sky and in the dark green hill, but either mixed with a copper-rich pigment, or rather present as an underlayer as shown by the study of the cross-section (C102.193), so any discolouration of the pigment will have had little effect on the dramatic hue of the sky or the dark hill.

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2 R. Gettens, R. Feller, W. Chase, *Vermilion and Cinnabar* in A. Roy (ed.), *Artists Pigments*, *Volume 2*, Oxford University Press: Oxford, 1993, p. 159-182

3 Bruno Mühlethaler en Jean Thissen, *Smalt*, in A*rtists' Pigments: A Handbook of Their History and Characteristics, Vol. 2*, Roy Ashok (Ed.), Archetype Publications, 1993, p113-130

4 Jill Dunkerton and Marika Spring, *Titian after 1540:Technique and Style in his Later Works*, National Gallery Technical Bulletin, volume 36, 2015, p.6-39

5 Gianluigi Colalucci, *Michelangelo Buonarroti: Restorations of the frescoes of the vaulted ceiling and the last judgment in the Sistine Chapel*, Conservation Science in Cultural Heritage 16(1), 2016, p89-108.

Copper (Cu) is present in large areas of the painting, particularly in the sky, the dark green hill, the soil, the vegetation and the leaves of the tree in the upper left corner, which are difficult to see under normal lighting conditions. The source of the copper is difficult to determine using MA-XRF alone, as this is a technique that allows the detection of chemical elements, but does not provide information on the molecular form in which these elements occur. Most commonly, copper is found as azurite [$2CuCO_3Cu(OH)_2$] or verdigris [a basic copper acetate $Cu(C_2H_3O_2)_2 2Cu(OH)_2$], the latter sometimes as a drier in black paints rather than as a pigment. To gain a better understanding of which pigment was used, a sample was taken from the green hill on the right side of the painting and made into a cross section (C102.193). At this point, the source of the copper was identified as azurite, which naturally has a green-blue colour. More information on the composition and structure of this zone is given in the section describing the cross-sections. Blue grains can also be seen in the sky under binoculars (figure 5), and together with the MA-XRF results indicating the presence of copper, it is likely that azurite was also used in the sky. This does not mean that azurite is the source of all the copper found in the painting.

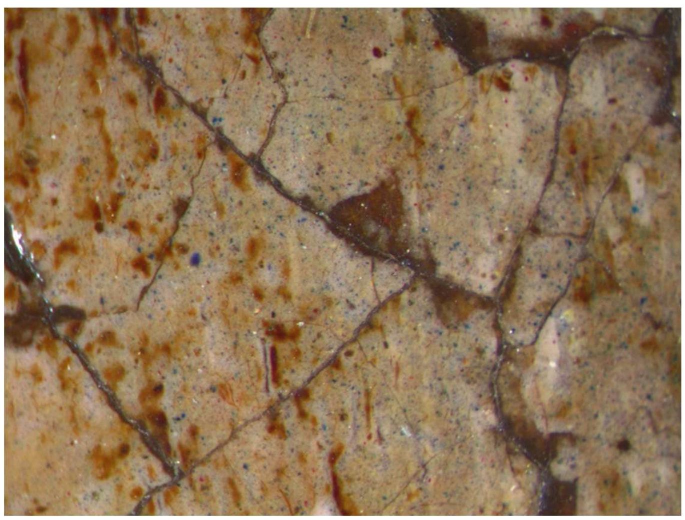

Figure 5. Blue particles are visible in the sky, likely azurite.

Many of the dark green leaves behind Mary contain both copper and **tin** (Sn). Copper and tin are also combined in the vegetation at the level of the soil, and tin can also be seen in the more yellowish leaves of the trees in front of the dark green hill in the background. This suggests the use of **lead-tin yellow** [usually Pb_2SnO_4, or less common $Pb(Sn,Si)O_3$], probably in combination with azurite to give the plants a greener hue, or rather without azurite in the yellowish leaves of the trees in front of the green hill. Lead-tin yellow was a popular pigment from ca. 1300 both in Northern and Southern Europe until it fell into obscurity in the middle of the 18th century, only to be rediscovered in 1941[6].

In addition to these classical pigments available in the 16th century, there are a number of elements detected by MA-XRF that are derived from modern pigments that only date from the late 18th century or later. These pigments, however, are associated with restored areas and therefore do not belong to the original palette. They do give an idea of the extent to which the painting has been restored. The presence of **zinc** (Zn) indicates the use of **zinc white** (ZnO) which was

[6] H. Kühn, *Lead-tin yellow*, in *Artists' Pigments. A handbook of their History and Characteristics*, Volume 2, Ashok Roy (ed.), Oxford University Press, **1993**, p.83.

particularly popular in oil painting from around 1845[7]. An overview of where this pigment is found and where retouching with zinc white has been done, is shown in figure 6a. **Titanium** (Ti) indicates the use of **titanium white** (TiO_2), which was used in painting from the early 1920s[8, 9]. The places where titanium white has been found are shown in figure 6b. There are several **chromium** (Cr) containing pigments, all of which have been in use since the early 19th century[10]. No further analysis was carried out to identify these modern pigments more precisely, but the Cr-map thus also indicates recent retouching (figure 6c). Finally, **barium** (Ba) was also detected (figure 6d). Although it occurs in nature as barite, only the synthetic variant **barium sulphate** ($BaSO_4$) has been used in painting since the late 18th century[11]. It should be noted that a high copper signal intensity results in an apparent zinc signal (partial overlap of energy peaks). Thus, in places where the copper intensity is high, zinc may not be present, although it appears to be in the figure (e.g. in the copper-rich leaves in the background or in the dark areas in the soil).

4.3 Study of the cross sections

As mentioned above, three samples were taken to better understand the layer structure and to refine the MA-XRF results. Due to the thickness of the varnish and possibly the composition of the ground or paint layers, it was not possible to take a complete sample at the centre of the painting, where at least the ground was missing in each case. Only one sample could be taken at the edge of the painting where all the layers were present (including some retouching). This sample came from the dark green hill in the background (see figure 1) and will be discussed first (see also Annex 3, C102.193). The lower layer (layer 1) is beige in colour and consists of a mixture of chalk, earth pigments, including sienna or umber, silicates, probably some dolomite (evidence of calcium and magnesium), which may indicate the use of a clay-like material. Some bone white and black grains rich in manganese (and iron) are also detected. In addition, the presence of **lead soaps**[12], are suspected. Lead soaps are formed in paintings as a result of a chemical reaction between the lead-based pigments (such as lead white or minium) and fatty acids present in the oil medium (like linseed oil) used in the paint. Over time, the metal ions from the lead pigments react with the free fatty acids to form lead carboxylates, commonly known as lead soaps. Minium or red lead is sometimes observed, believed to be a secondary product, resulting from the mineralisation of lead soaps in oil paint, or present from the start as pigment or drier. This process can cause issues in paintings, such as the formation of protrusions on the paint surface, increased transparency, or even paint loss. Binocular observation reveals bright orange grains in several places (figure 7) breaking through the surface. Orange grains can also be seen in the cross section, but it is not clear

[7] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium*, Butterworth-Heinemann: Oxford, 2008, p. 412.

[8] M. de Keijzer, *The history of modern synthetic inorganic and organic artists' pigments*, in *Contributions to conservation: research in conservation at the Netherlands Institute for Cultural Heritage (ICN Instituut Collectie Nederland)*, James & James, London, 2002, p. 42-54.

[9] M. Laver. *Titanium white*, in West FitzHugh E. (editor), *Artists' pigments: a handbook of their history and characteristics, vol. 3*. London: National gallery of Art, Archetype Publications, 1997, p. 295-355.

[10] N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall, *Pigment Compendium*, Butterworth-Heinemann, 2008, p. 107-108.

[11] N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall, *Pigment Compendium*, Butterworth-Heinemann, 2008, p.44-45.

[12] For a nice summary of the research on lead soaps see: Marine Cotte, Emilie Checroun, Wout De Nolf, Yoko Taniguchi, Laurence De Viguerie, Manfred Burghammer, Philippe Walter, Camille Rivard, Murielle Salomé, Koen Janssens, Jean Susini, *Lead soaps in paintings: Friends or foes?*, Studies in Conservation, 62(1), 2016, pp. 2–23 / Francesca Caterina Izzo, Matilde Kratter, Austin Nevin and Elisabetta Zendri, *A Critical Review on the Analysis of Metal Soaps in Oil Paintings,* ChemistryOpen **2021**, *10*, 904

if they were originally present or have formed over time. This does imply that the ground is bound with oil rather than with glue.

Figure 6. Areas with retouching with modern pigments: a) with zinc white, b) with titanium white, c) with chromium containing pigments, and d) with barium sulphate.

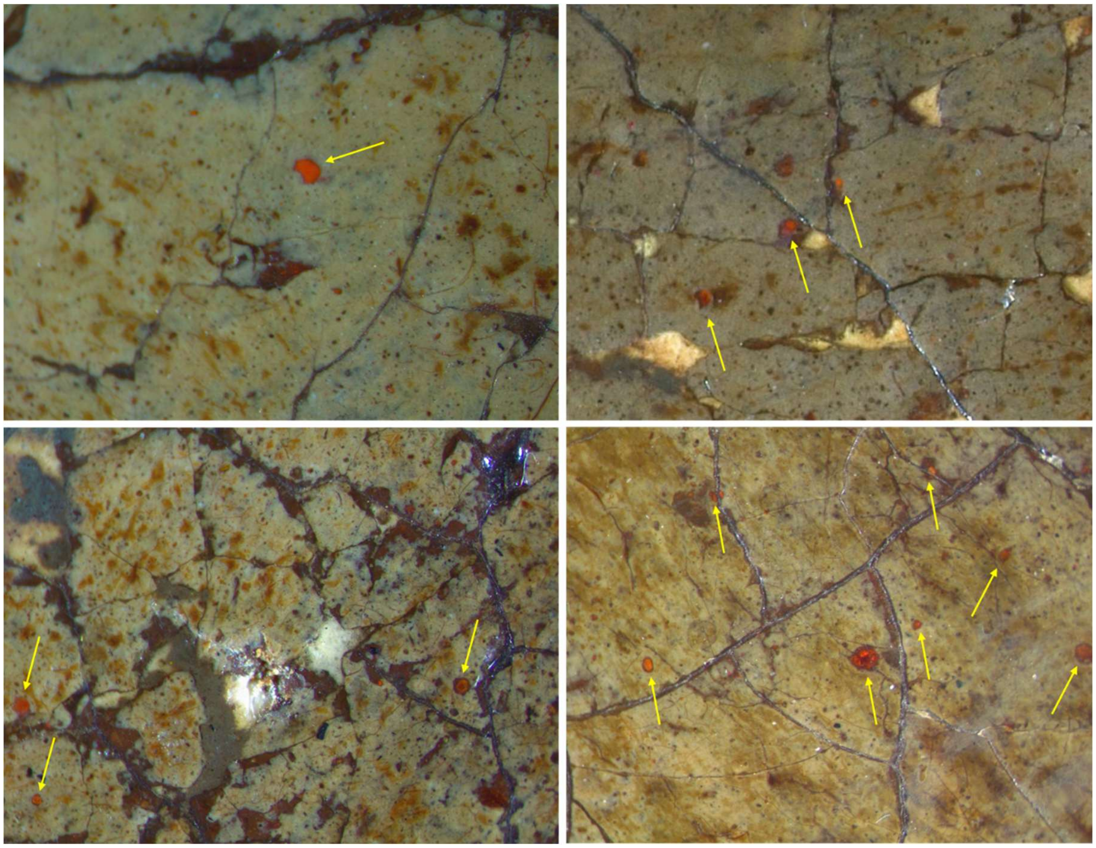

Figure 7. Some examples of orange protrusions penetrating the paint surface (indicated by yellow arrows). These orange areas are most likely minium (or red lead) formed by the mineralisation of lead soaps, resulting from the reaction of lead with free fatty acids derived from an oil-rich binder in the ground.

During the 16th century, the techniques used for canvas grounds underwent a rapid evolution as coloured grounds and imprimaturas spread throughout Europe[13]. Their introduction was linked to a gradual change in painting technique, using a more dramatic setting with greater emphasis on 'chiaroscuro', which was easier to achieve on coloured grounds. As oil painting on canvas spread from Venice to other parts of Europe, artists experimented with different techniques and materials. 16th century Italian sources mention the use of either a first layer of gypsum in animal glue or a layer of flour, nut oil and lead white applied after a glue sizing. Such a layer cannot be seen in the cross-section studied. It is either not present or has not been sampled. It is possible that the artist was experimenting and applied the coloured ground directly to the canvas. This practice became common in painters of the generation after Titian[13].

The ground layer is followed by a first blueish layer (layer 2), composed of smalt, lead (white) and a few grains of azurite. This is followed by a second blue layer (layer 3), a mixture of azurite, lead (white), probably some dolomite (presence of calcium and magnesium) and some trace pigments such as vermilion. This is followed by a transparent layer (layer 4) rich in calcium and lead (white). The calcium could act as a substrate for a **yellow lake**, in combination with the blue underlayer resulting in a green colour, but the presence of a yellow lake cannot be confirmed without sampling this layer followed by destructive analysis, which has not been carried out. No green copper

[13] Maartje Stols-Witlox, *Grounds 1400-1900*, in *Conservation of Easel Paintings*, Joy Hill Stoner and Rebecca Rushfield (Eds), Routledge, 2012, pp. 166-169.

pigment could be identified (such as e.g. verdigris). Some patina[14] may be present on this layer, indicating the end of the original layer built-up. Layer 5 is a partially thin transparent layer followed by a varnish (layer 6). Layer 7 is an overpaint containing some of the modern pigments discussed in the MA-XRF section, such as barium sulphate, titanium white and the chromium-containing pigments.

Looking at the painting through the binoculars, a red layer under the light areas, such as the flesh colour of the characters or the cloth around Christ, can be seen (figure 8). A sample was taken in Christ's foot (C102.191) to get a better understanding of the layer structure. Unfortunately, the lower layers are missing in the cross section (the ground certainly, possibly other layers as well), the first layer present (layer 1) is the red layer observed with the binoculars. It is composed of chalk, red earth including some sienna or umber, smalt, some vermillion and perhaps some dolomite. This is followed by a layer (layer 2) rich in lead white with vermilion, some chalk, sienna and umber and silicates and some dark grains rich in calcium and phosphorus (possibly bone black). Finally a varnish follows. These results are consistent with the MA-XRF results, but also allow a more detailed description of the composition of the red underlayer.

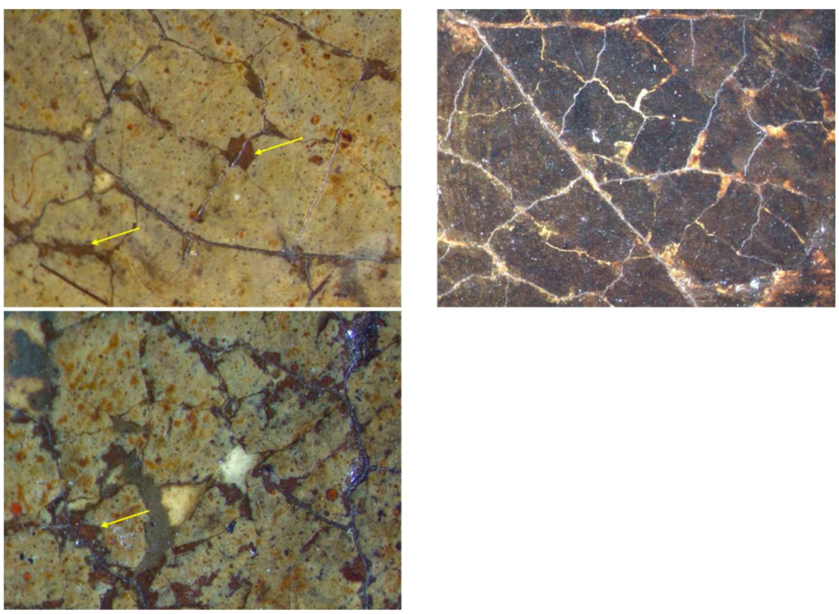

Figure 8. Under the light colours, such as skin colour, a reddish underlayer (on a beige ground) can be seen, as indicated by the yellow arrows in the figures on the left. Under the dark colours, e.g. an area of the background as shown in the right image, this underlayer is not visible, only the beige ground is seen.

A final sample was taken in the red shade of Mary's cloak (C102.192) to get a more detailed insight into its composition. Again, the lower layer(s) are missing. Layer 1 is the red layer of the cloak of Mary, and as expected from the MA-XRF results, it consists of a mixture of smalt and lead white, and the cross section also allows to conclude that a **red lake** was indeed used, as predicted. This layer is followed by a patina, partially a very thin layer and finally a varnish.

[14] A patina is a surface appearance or texture that develops on the artwork over time due to natural ageing and environmental factors. This includes changes in colour, gloss, and texture that can result from the accumulation of dirt, dust, varnish yellowing, the oxidation of pigments, and the formation of craquelure or other surface alterations.

The composition of the original paint layers in the cross-sections is consistent with what is expected of a 16th century painting.

4.4 Dye analysis

Additional analysis of the red lake of Mary's cloak using high-pressure liquid chromatography with photodiode array detection (HPLC-DAD) demonstrated that the red organic colourant was derived from **cochineal insects** (see Annex 6).

4.5 Study of the monograms

The two monograms cited above can be seen at the bottom of the painting. These monograms have been extensively documented with scientific imaging (Annex 4), observed with binoculars, and scanned at high resolution with MA-XRF (Annex 5 and figure 9). Craquelures formed in the paint layer run through both monograms, so they were definitely not applied after the craquelure in the paint had formed (figures 9 and 10).

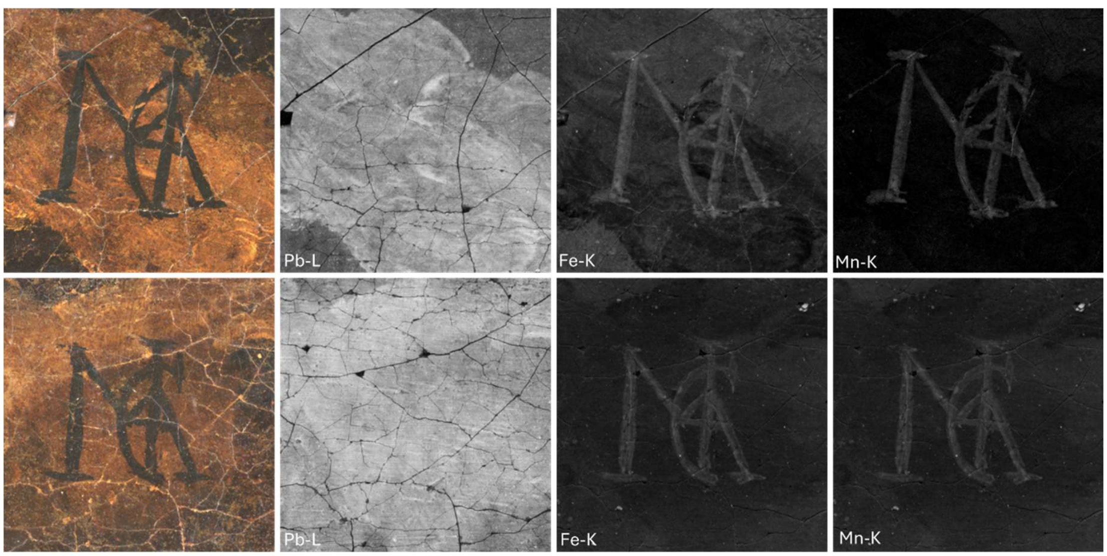

Figure 9. Details of the monograms under normal lighting and some high-resolution MA-XRF results (of lead Pb, iron Fe and manganese Mn). Craquelure in the paint, clearly visible in the lead map, continues in the monograms. The figures in the upper row correspond to the monogram placed in the centre at the bottom, and those in the lower row correspond to the monogram on the skull.

The MA-XRF results show primarily the presence of iron and manganese in the monograms, indicating the use of umber or sienna. An organic black pigment, not detectable by MA-XRF, could also have been added. No elements derived from modern pigments were detected in the monograms or in the paint below the monograms.

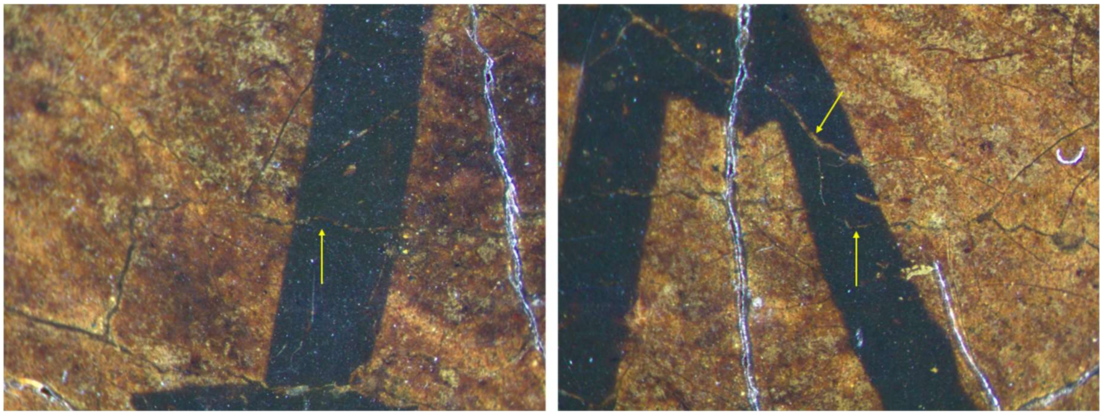

Figure 10. Some detail photos of the central monogram. Craquelures in the paint, indicated by yellow arrows, run through the monogram.

5 Conclusion

The extensive scientific imaging, the MA-XRF study and the study of some cross-sections provide a better insight into the material composition of the painting and its condition. Based on the radiography, the IR and UV image, the IRR recording and the MA-XRF data, it was possible to estimate the extent to which the painting had been retouched. There is a fair amount of localised minor retouching, but the faces and hands are relatively free of retouching. In some cases the retouching is more extensive than is strictly necessary. Of note is the later addition of a narrow strip of canvas just below Christ's knees to make the painting taller. A piece of canvas has also been inserted in Mary's robe. The original canvas, composed of three parts sewn together, was re-lined. The painting is in good condition commensurate with its age.

The MA-XRF analysis and the study of the cross sections reveal a classical palette, consistent with what can be expected of a 16th century painting. The main pigments identified are lead white, chalk, azurite, smalt, lead tin yellow, earth pigments including sienna or umber, a red lake and possibly a yellow lake. The ground has a beige colour and is bound with oil in which lead soaps have formed. The use of a coloured ground is not unusual in the 16th century, especially when a 'chiaroscuro' effect was desired.

The identification of carminic acid gives proof of the use of **cochineal scale insects** in the red lake of Mary's cloak**.** As carminic acid was the only detected compound, no further species recognition can be done to distinguish between cochineal insects from the Old or the New world. In the given 16th century context of the lake however, the **Mexican cochineal** species (*Dactylopius coccus* Costa) is the most likely source used.

As for the two monograms, these were applied on the original and dry painted surface, as was customary, and before craquelure developed. No modern pigments can be identified in the composition of the paint (or in the paint underlying the monograms). Craquelures in the paint run through the monograms.

Stylistic research should reveal whether this painting is by Michelangelo. The results of the material-technical research are consistent with those of a 16th century painting.

Dr. Louise Decq
On behalf of
Dr. Steven Saverwyns
Head Painting Lab

Stéphane Bazzo: photography
Sophie De Potter: IRR
Catherine Fondaire: RX
Alexia Coudray: preparation and analyses of the cross-sections
Alexia Coudray and Steven Saverwyns: MA-XRF analysis
Steven Saverwyns, Louise Decq: discussion of results, writing of the report
Ina Vandenberghe and Alexia Coudray: dye analysis

6 Annexes

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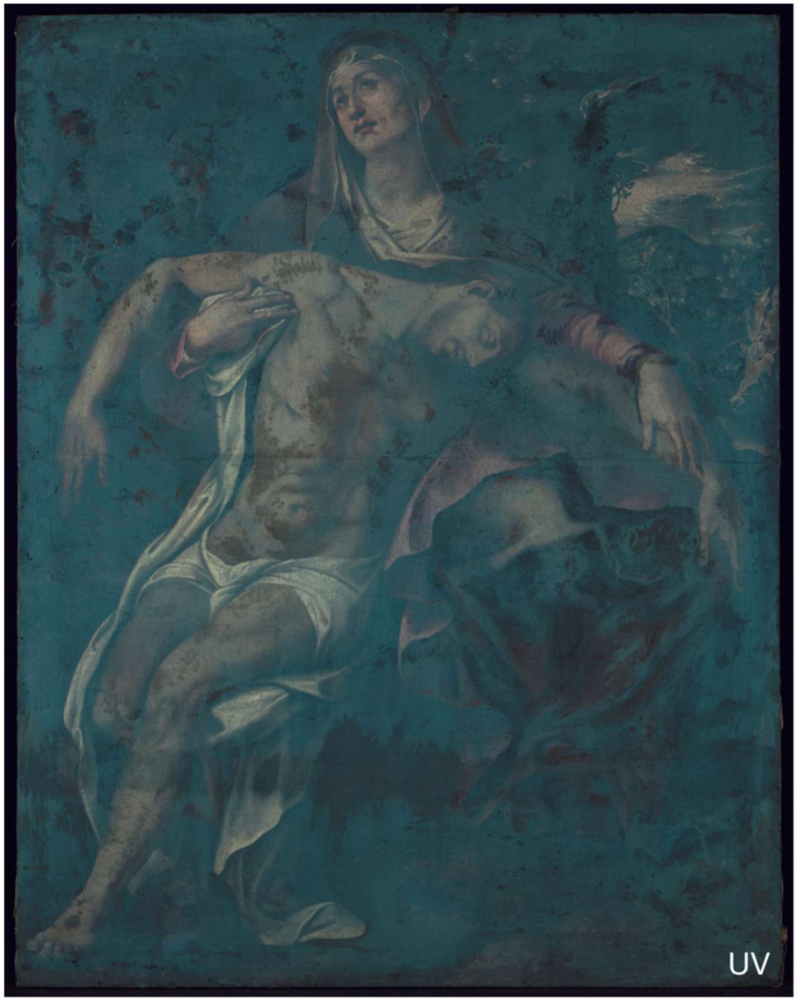
Annex 1 – High resolution and technical photography

The painting under visible (VIS), raking and UV-light, the x-radiograph (RX), the painting under IR-light, the infrared reflectograph (IRR) and the back under visible light.


UV

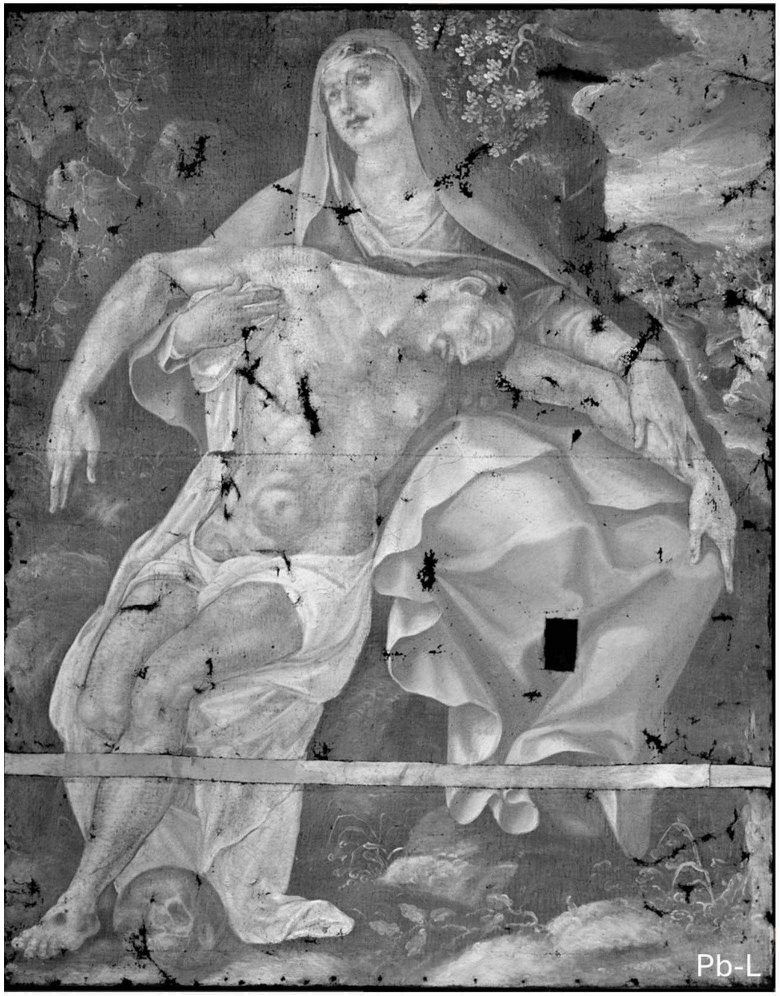

RX

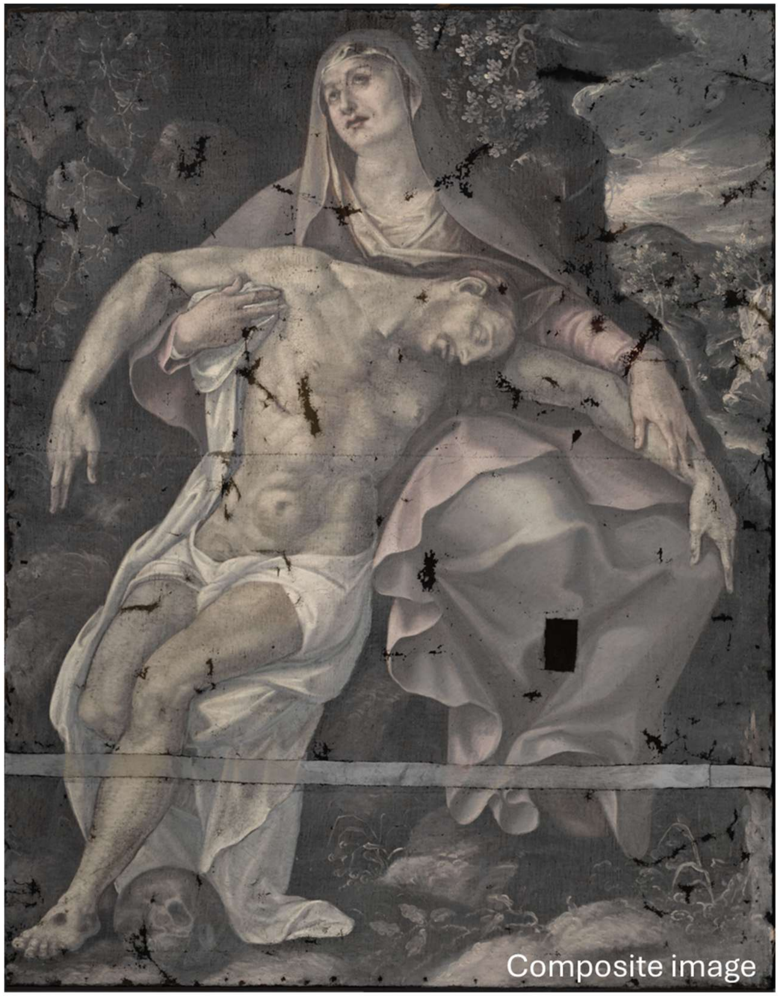

IR


IRR

Annex 2 – MA-XRF element maps and composite images

MA-XRF element distribution maps of the main elements detected. The whiter the tone, the higher the intensity for the specific element. A composite image is shown to clarify the distribution of the element in the painting. All images © KIK-IRPA.

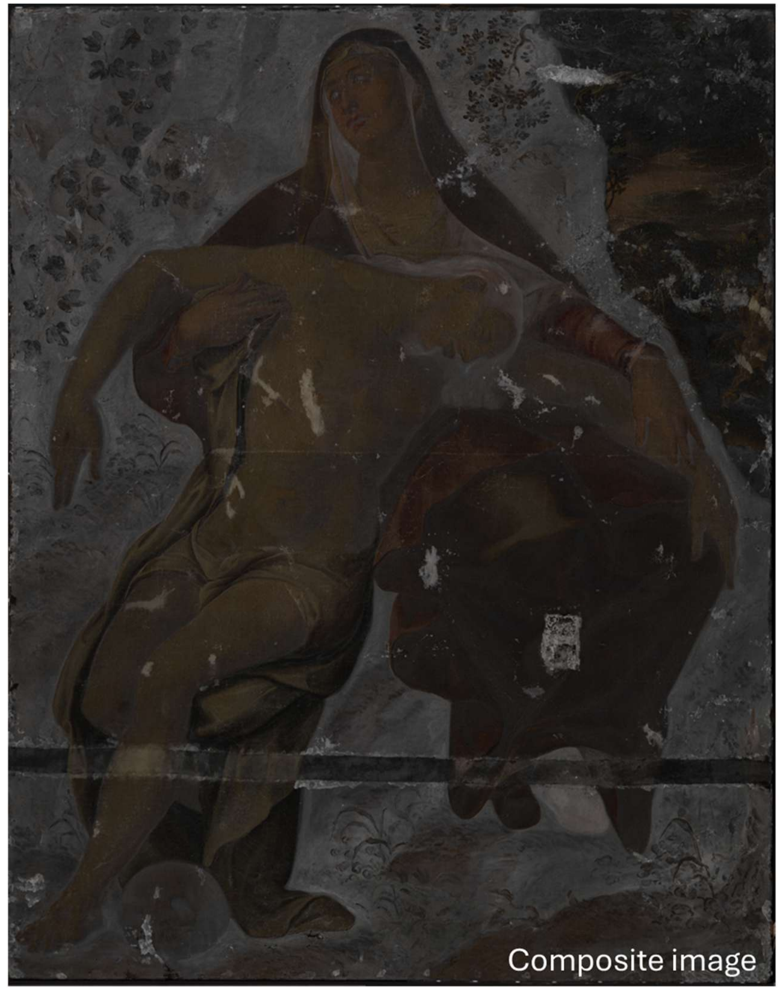


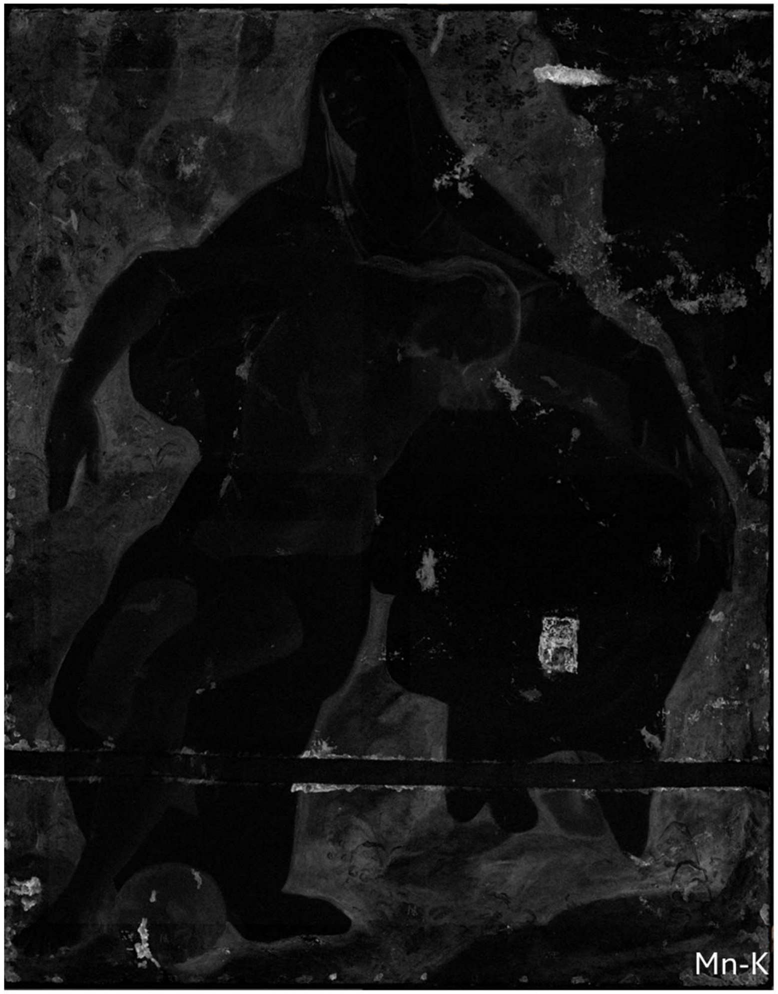


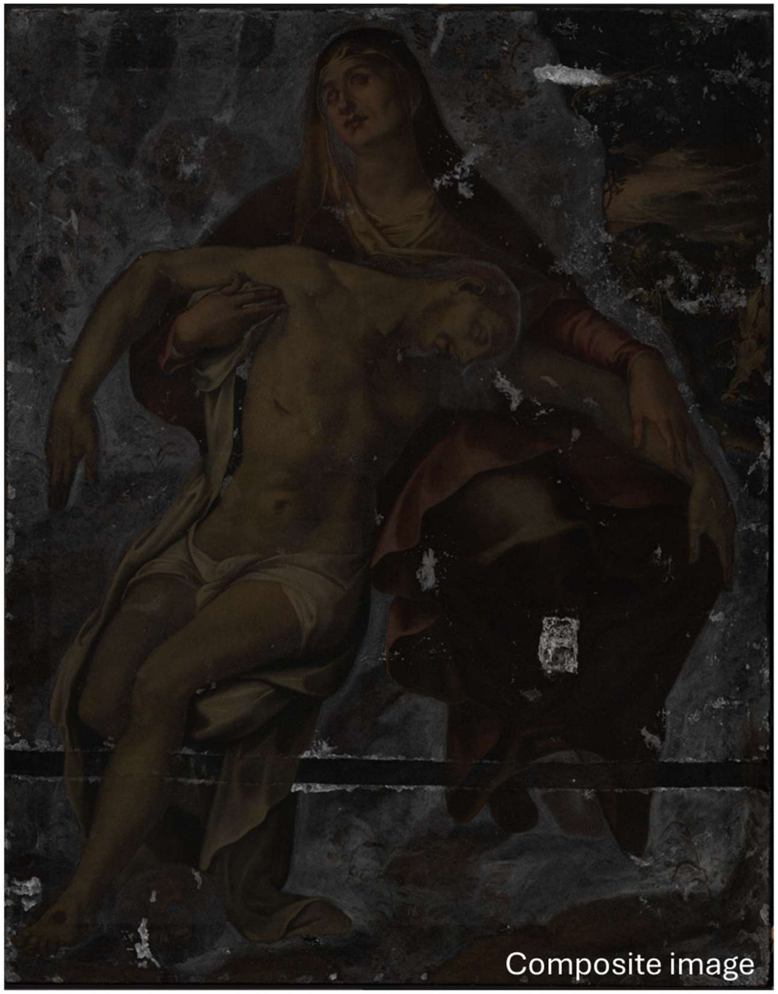

Ca-K


Composite image


Fe-K

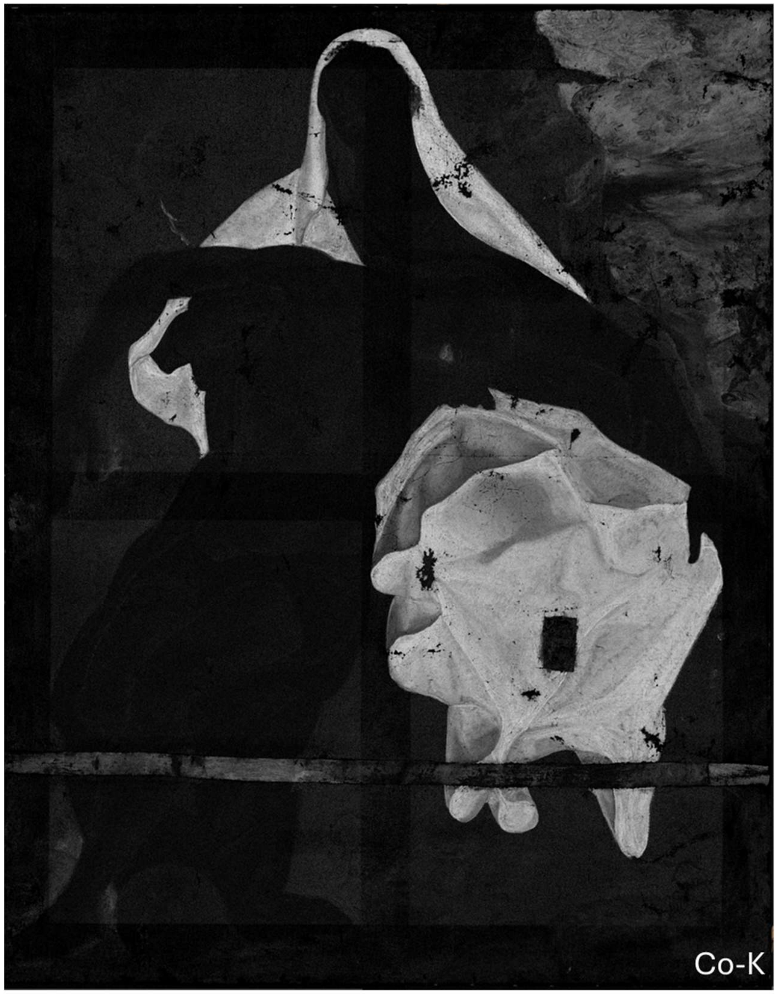

Composite image

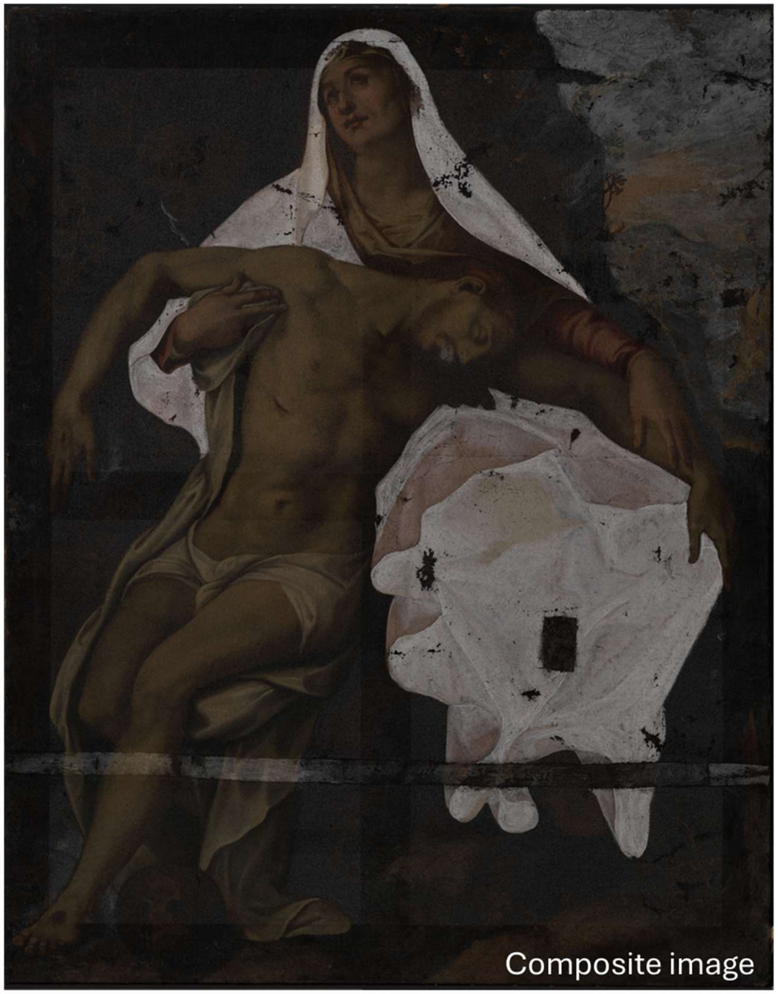

Mn-K

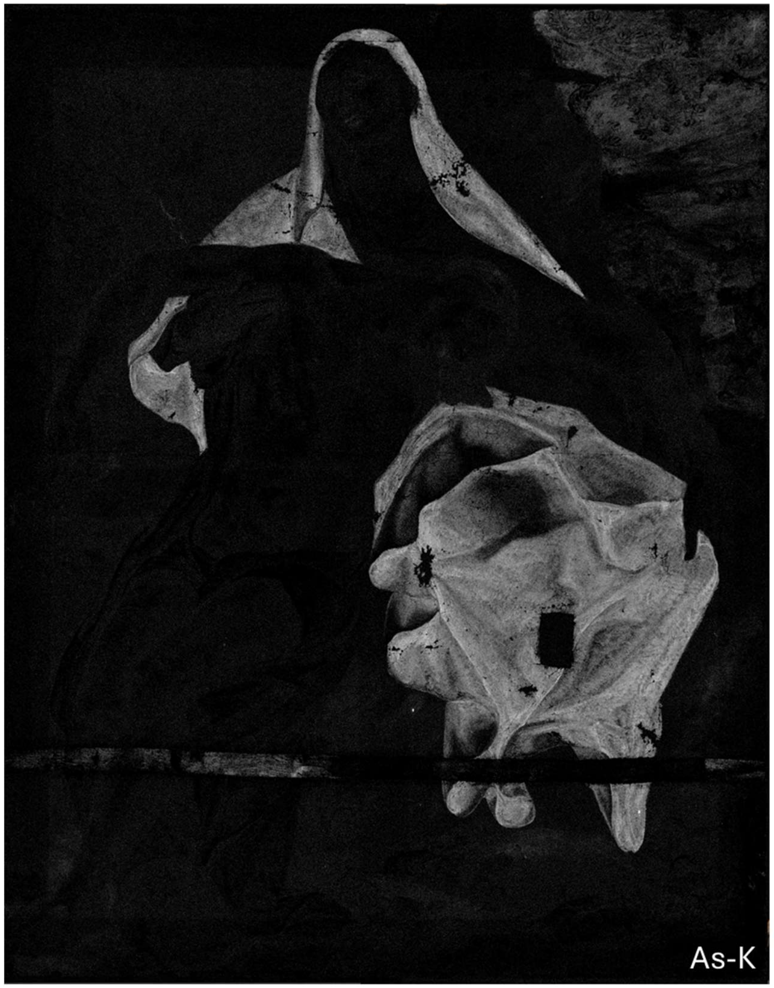

Composite image

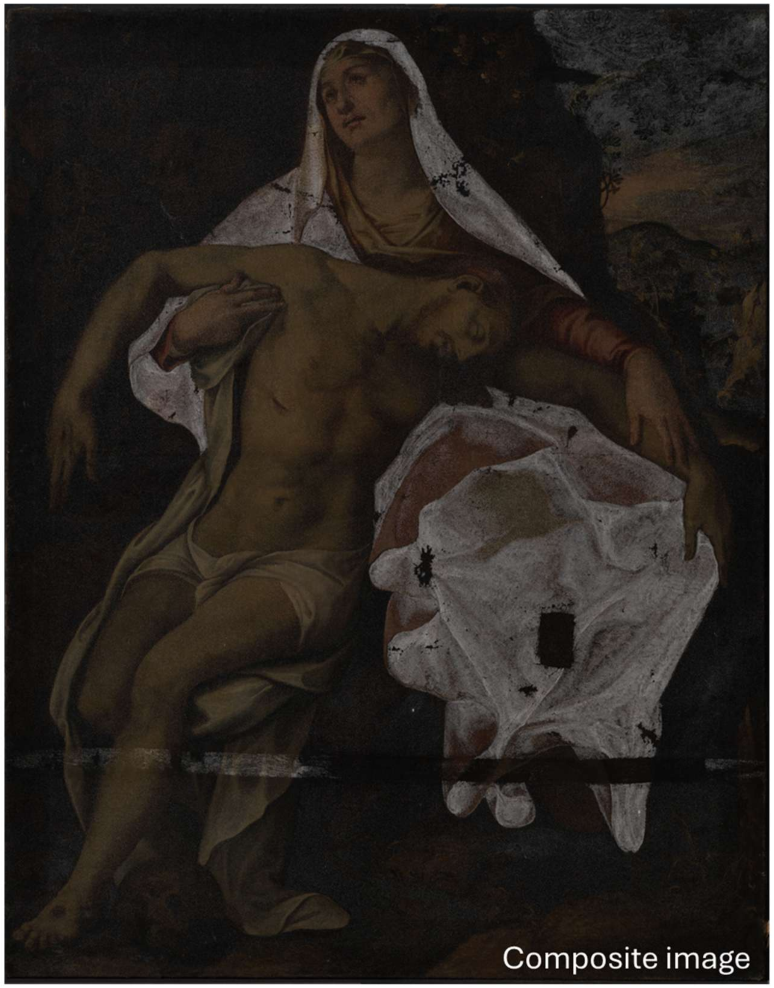

Hg-L


Composite image

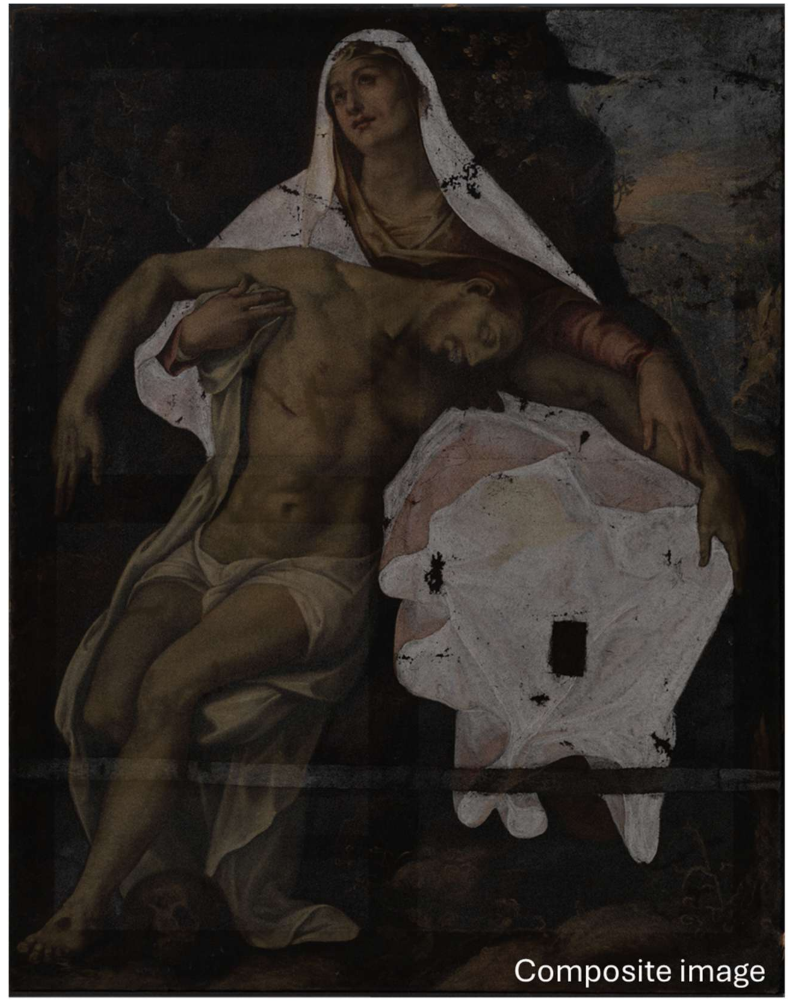

Co-K


Composite image

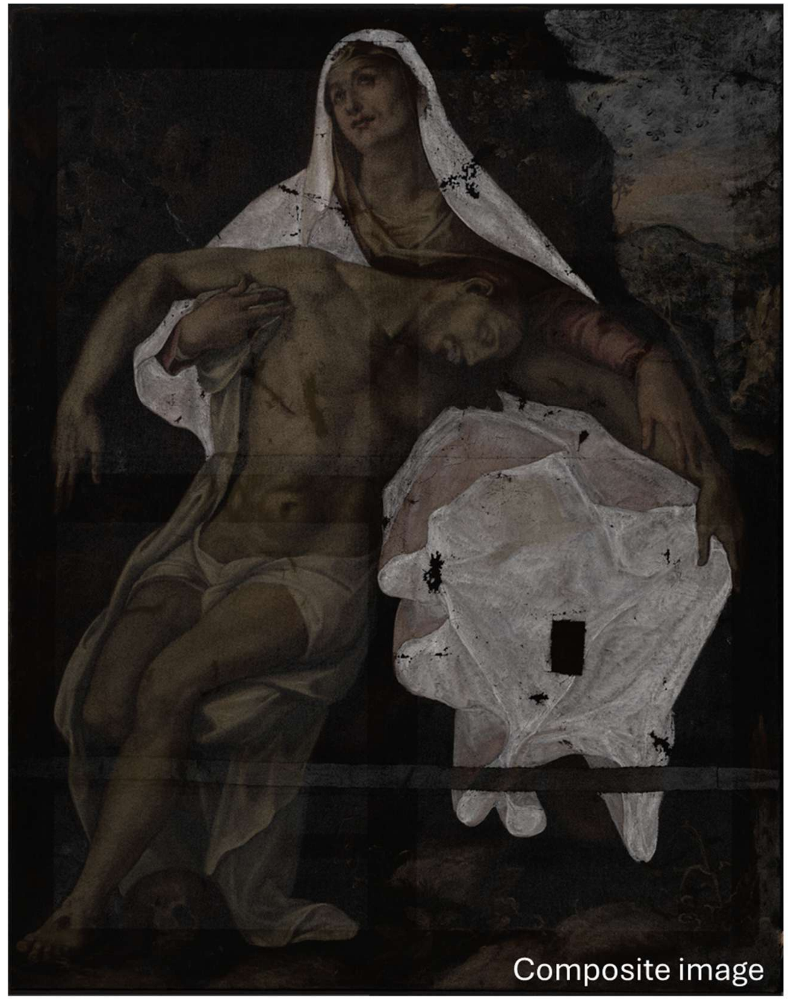

As-K

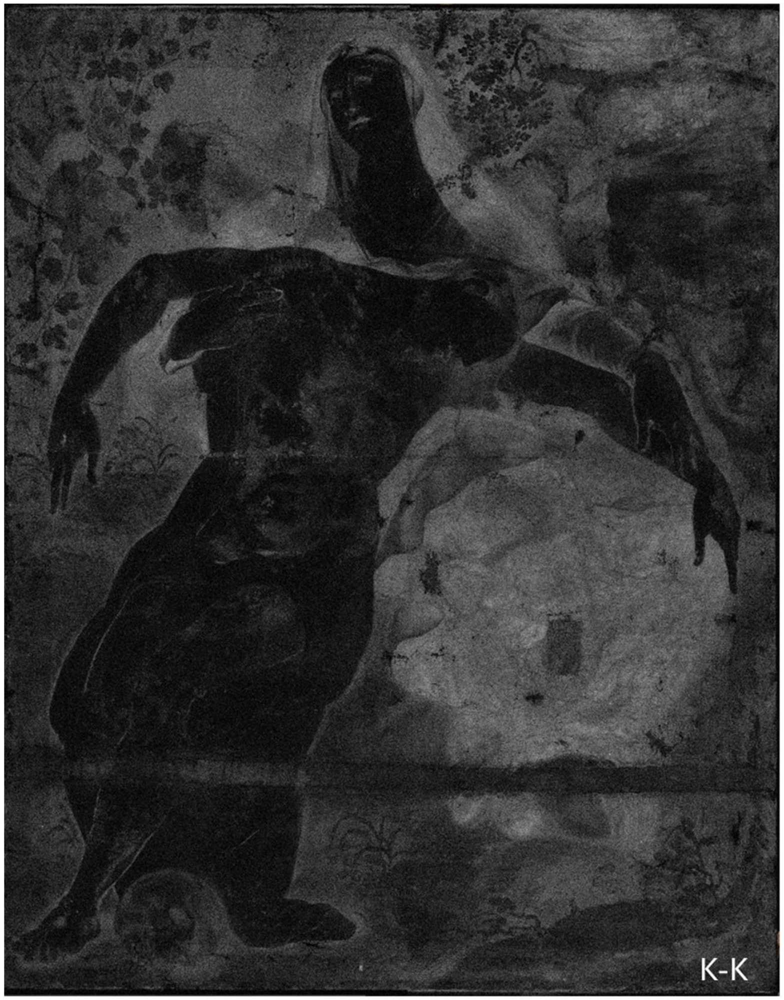

Composite image

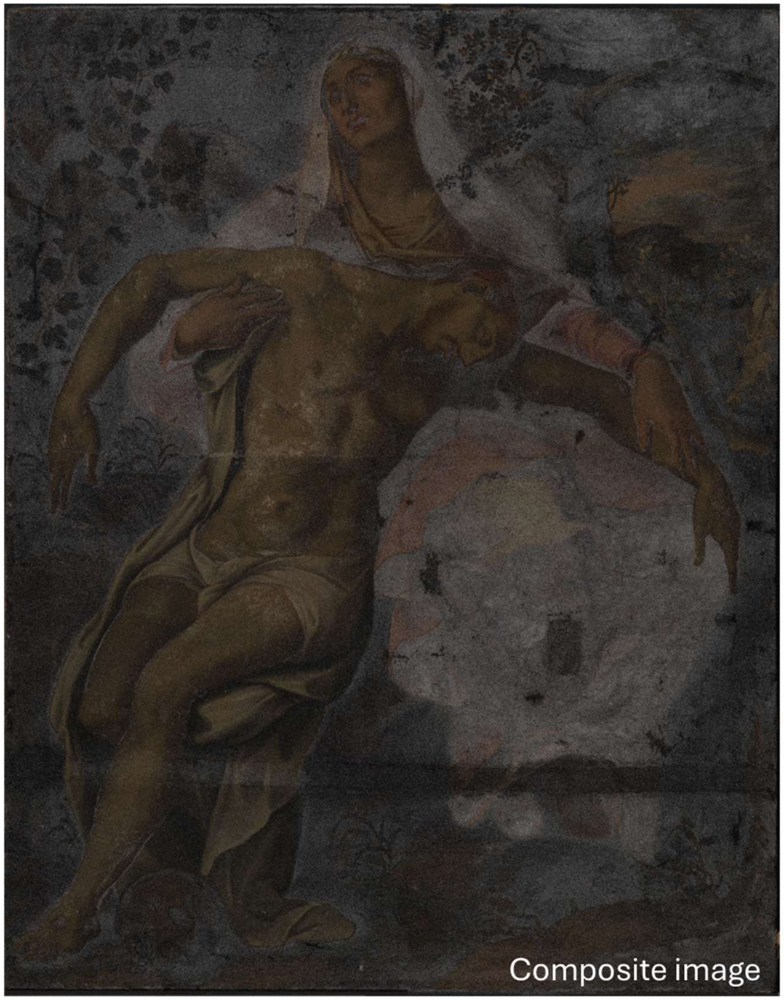

Ni-K


Composite image

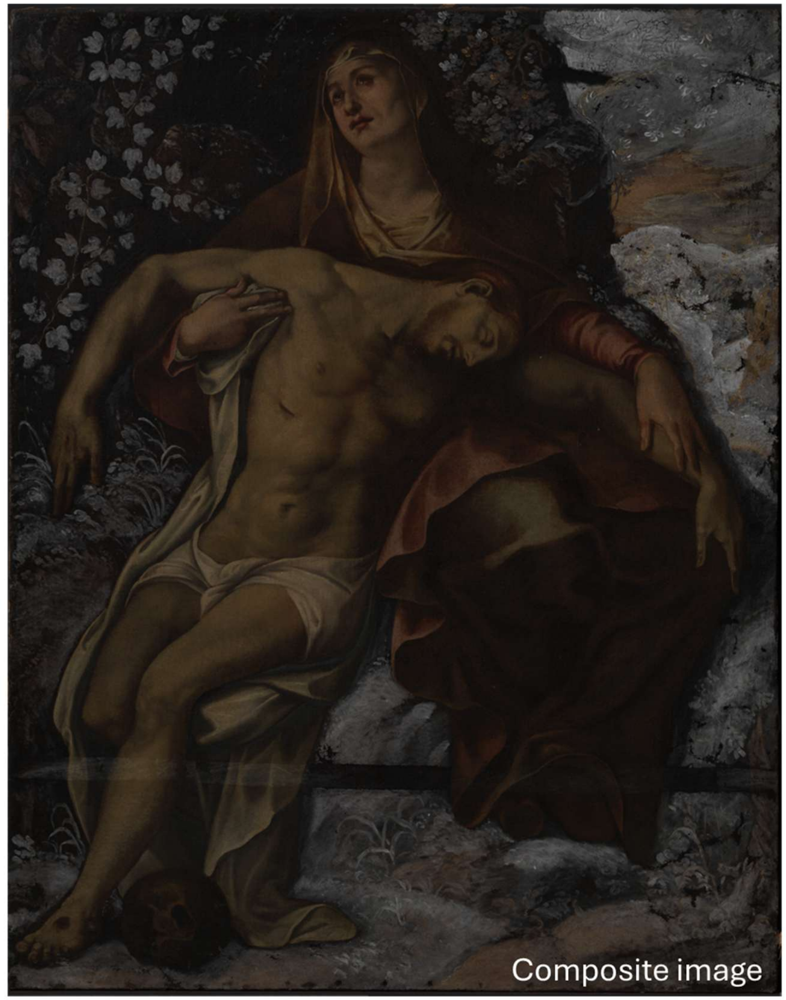

Bi-L

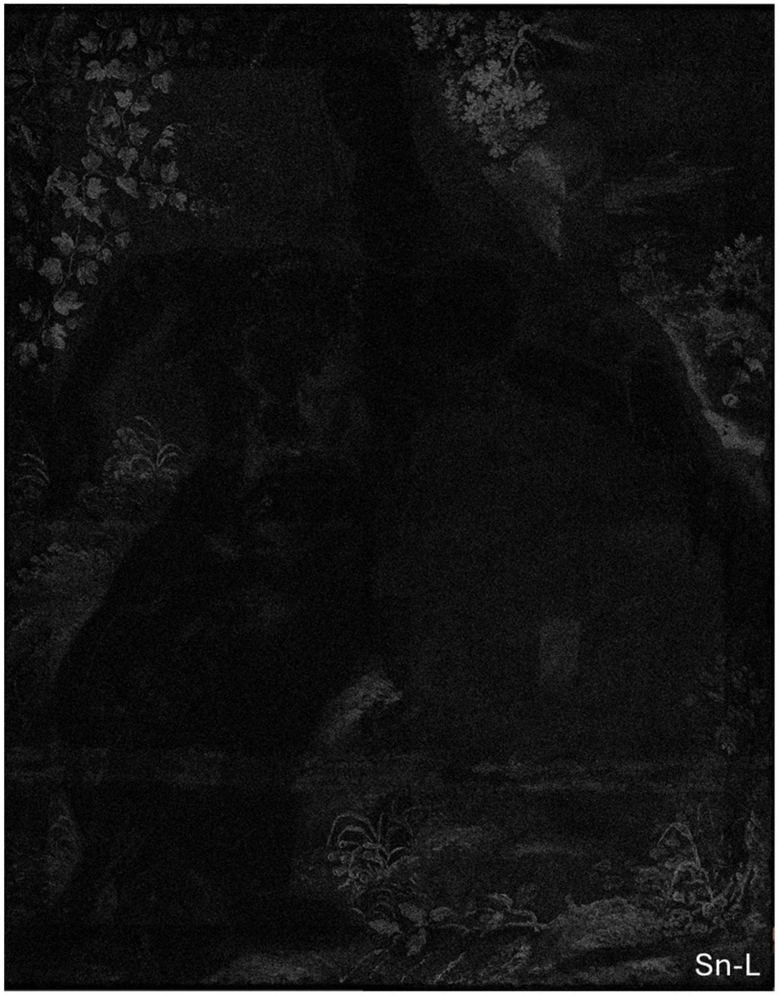

Composite image

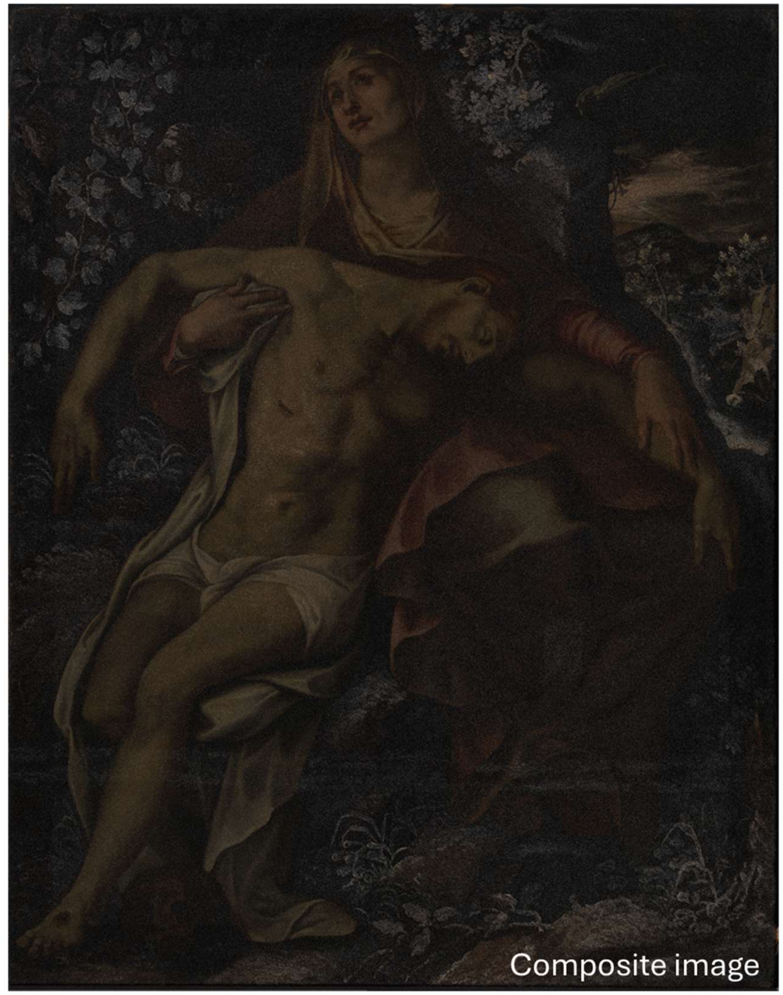

K-K


Composite image

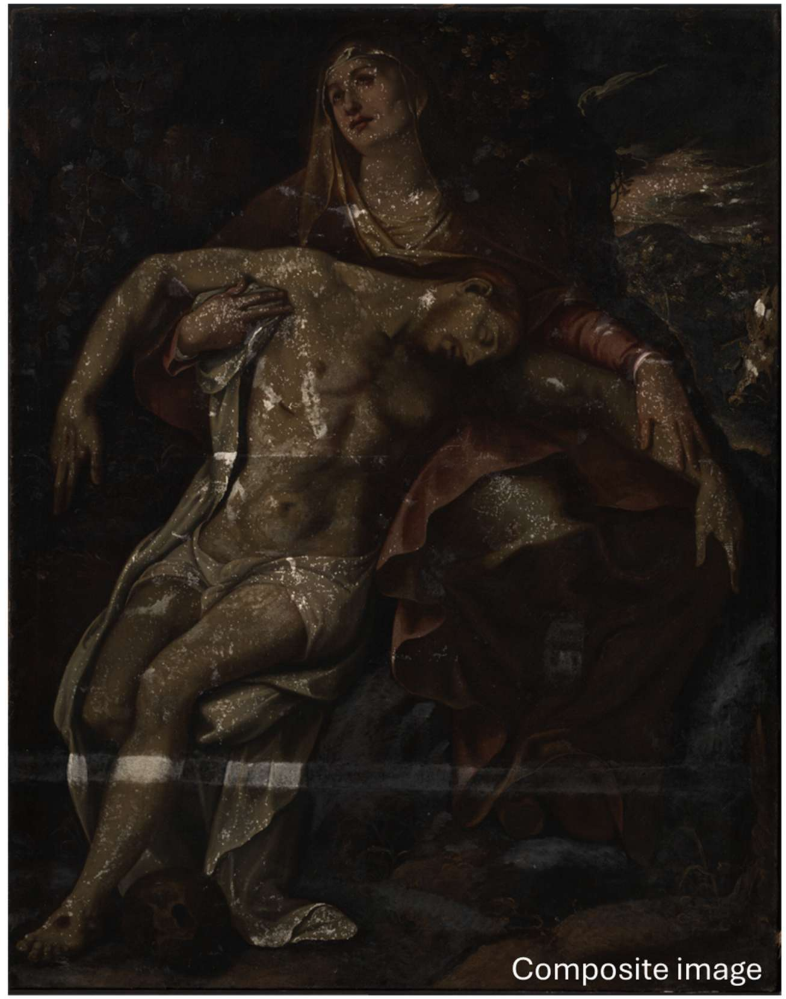

Cu-K

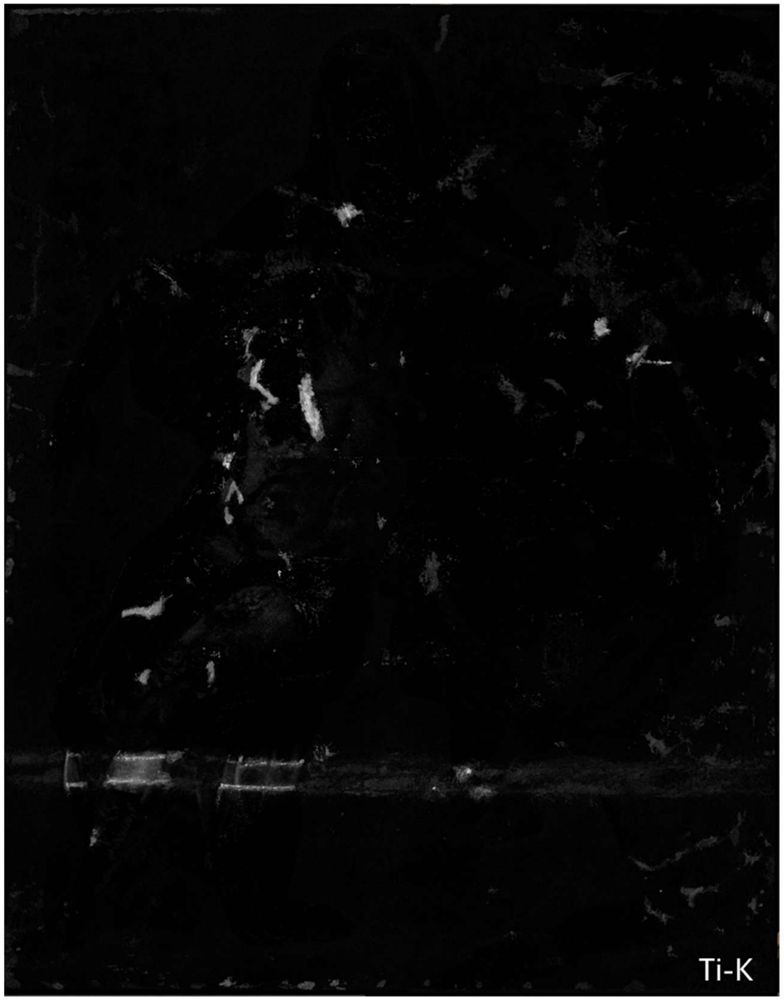

Composite image

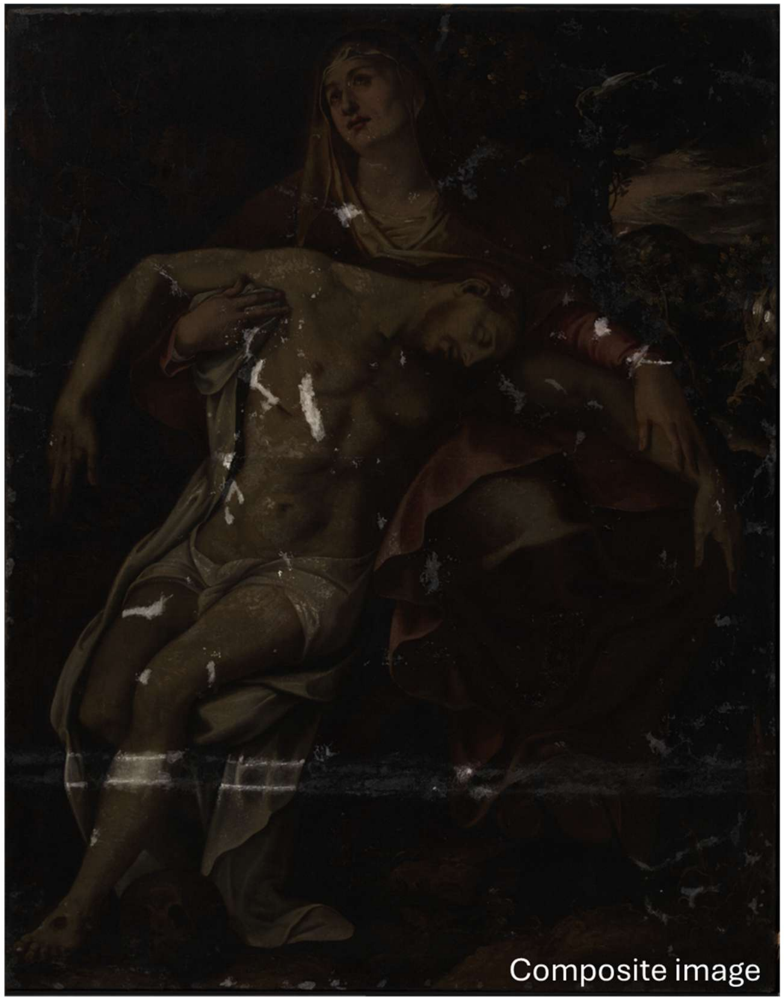

Sn-L


Composite image

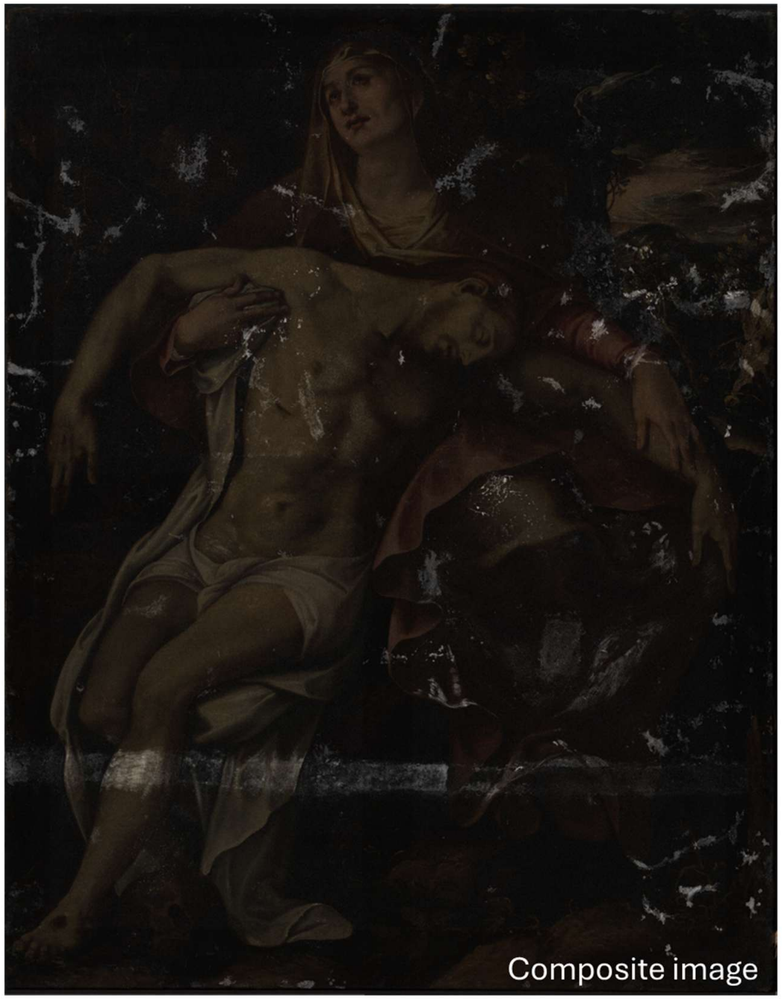

Zn-K

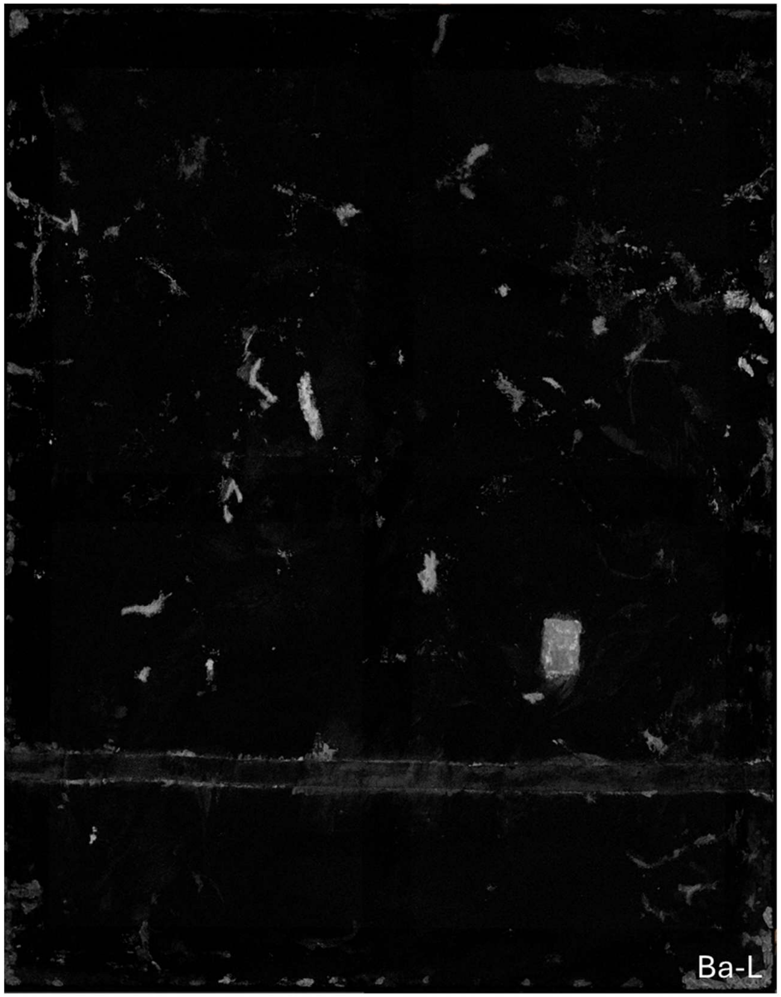

Composite image

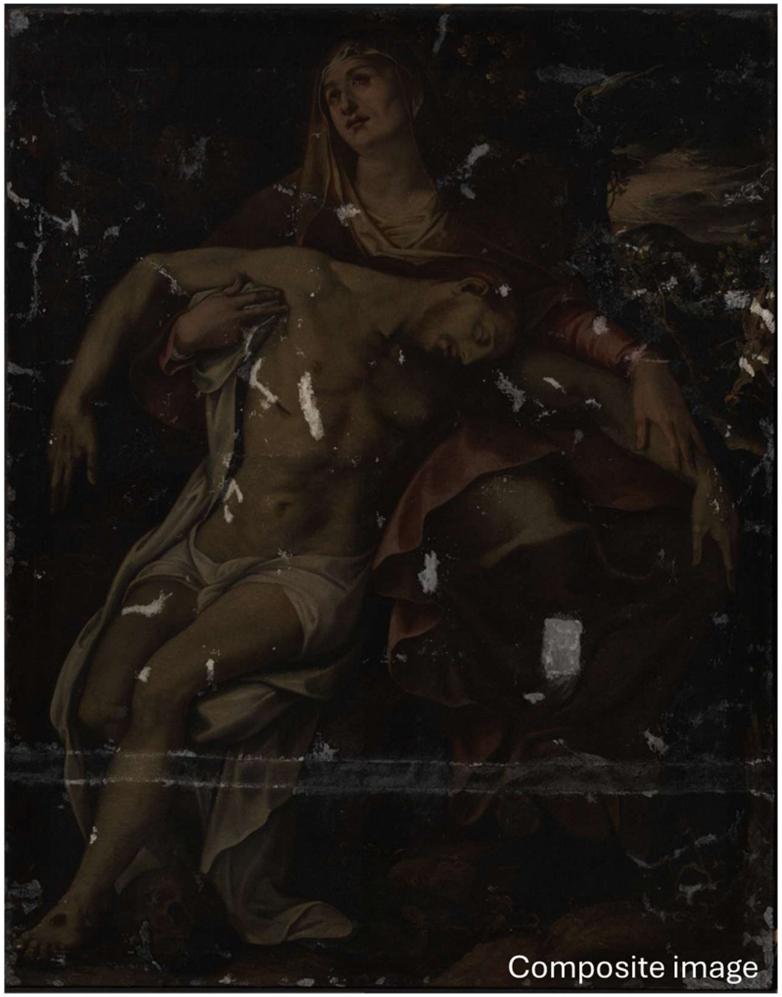

Ti-K


Composite image


Cr-K

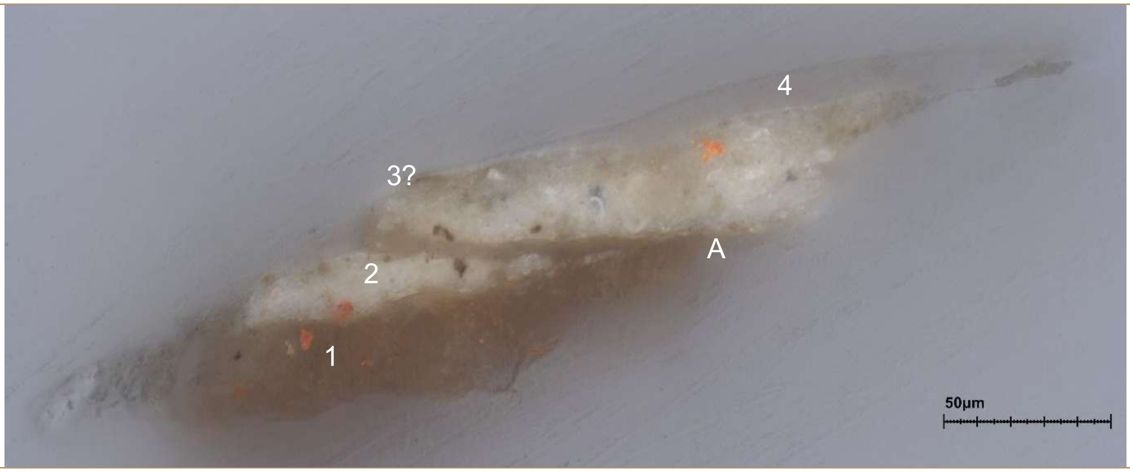
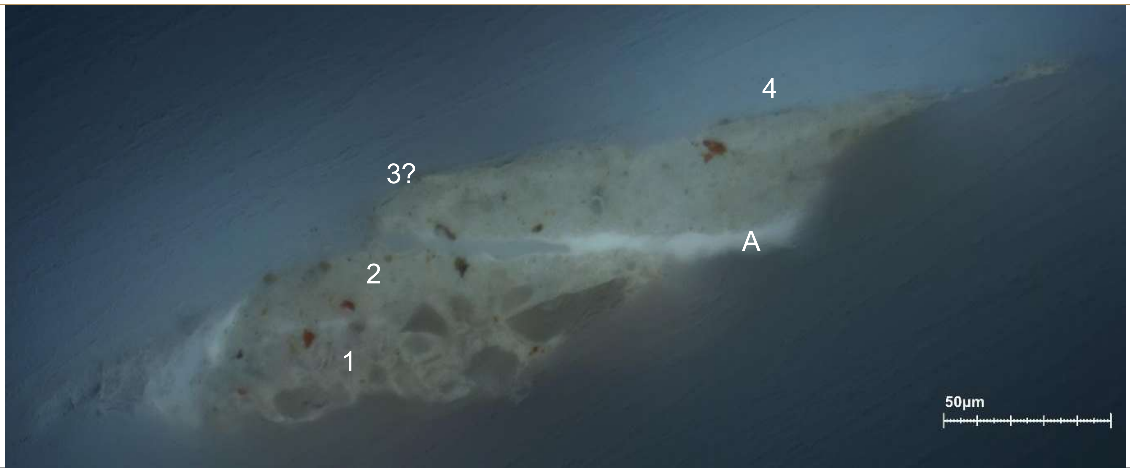

Composite image


Ba-L

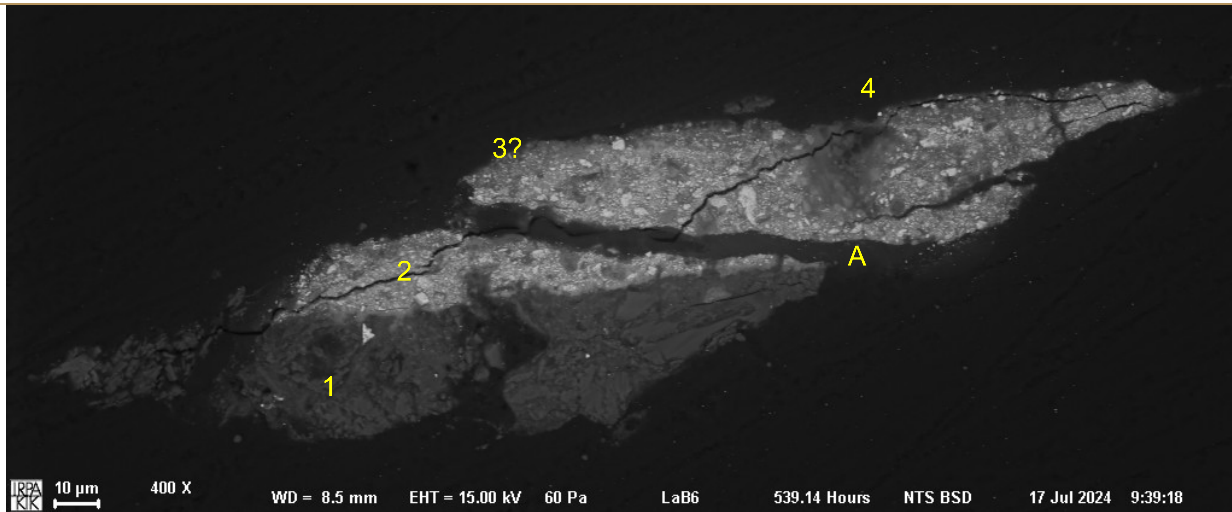

Composite image

Annex 3 – Optical and scanning electron microscopy of the cross-section

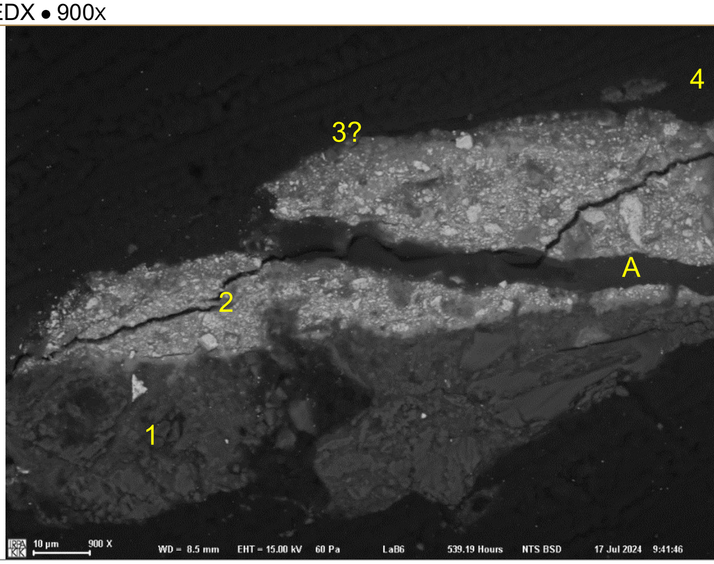
Optical microscopy of the cross-sections, together with the results of the SEM-EDX analyses. All images © KIK-IRPA.

P253.098 ● C102.191 ● Flesh tone, foot Christ
OPTICAL MICROSCOPY ● VIS ● 500X

OPTICAL MICROSCOPY ● UV ● 500X


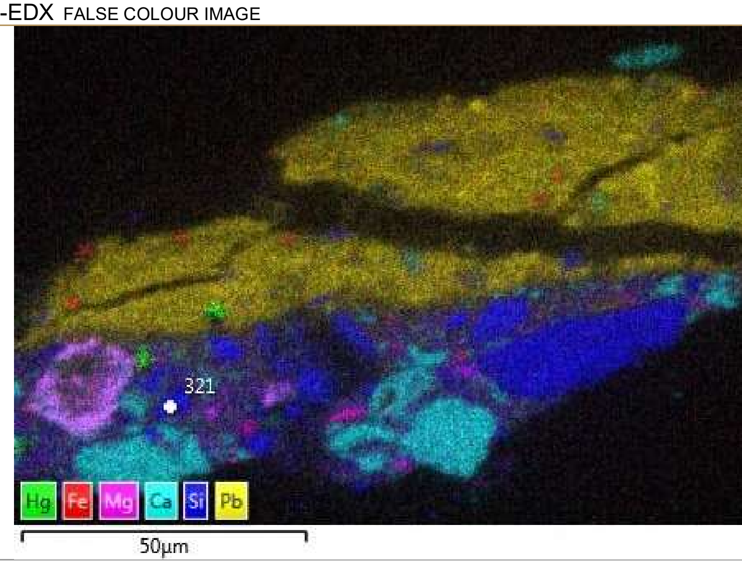
SEM-EDX • 400x



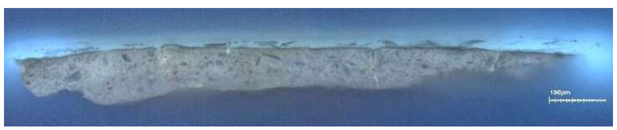
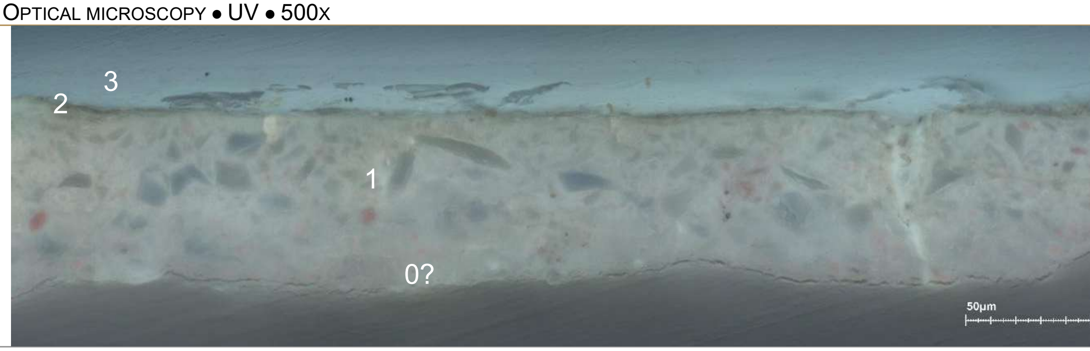
SEM-EDX • 900x



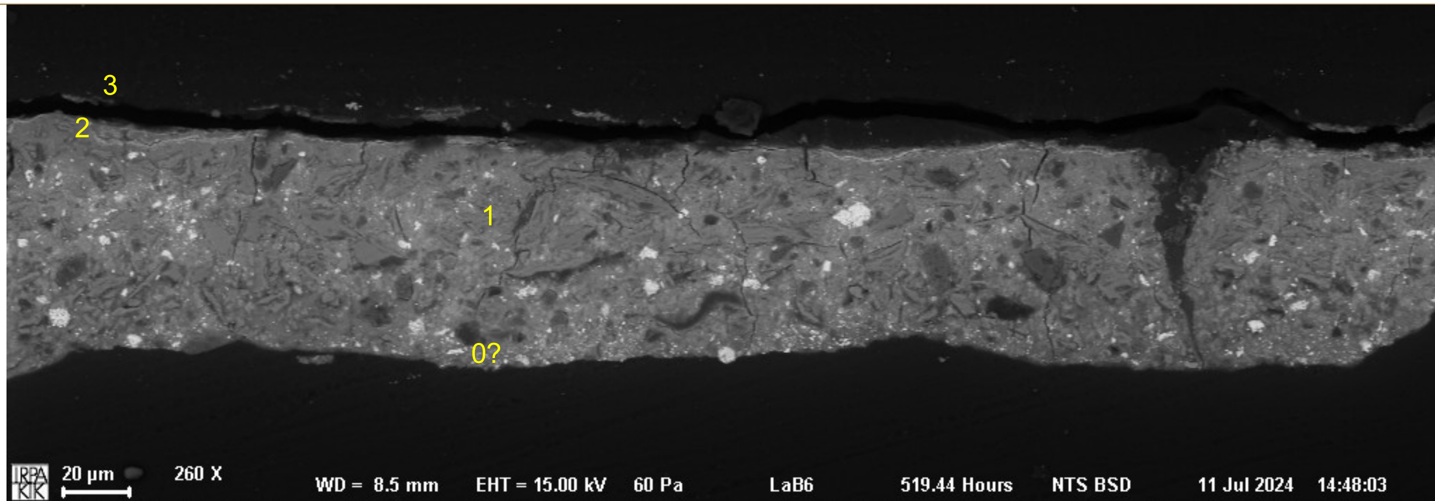
SEM-EDX FALSE COLOUR IMAGE



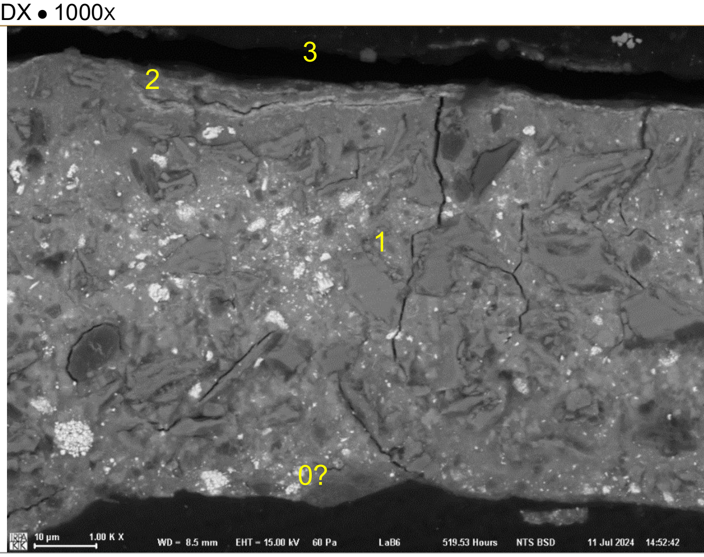
Layer description and summary of the SEM-EDX analysis results	
4. Varnish **3?. Partial fluorescent brown layer:** Possibly brownish spot? **2. White:** Flesh tone: Lead white, vermilion, a little chalk, some grains of Sienna/umber pigment, some silicates, two dark grains P-Ca **1. Reddish:** Chalk, silicates, earth pigments and Sienna/umber pigments, smalt, some grains of vermilion, grains with Ca and Mg (dolomite?) + (Pb), one grain with P	**A. Varnish** – likely infiltration

P253.102 ● C102.192 ● Red coat of the Virgin	
Optical microscopy • VIS • 200x	Optical microscopy • VIS • 500x
	
Optical microscopy • UV • 200x	Optical microscopy • UV • 500x
	

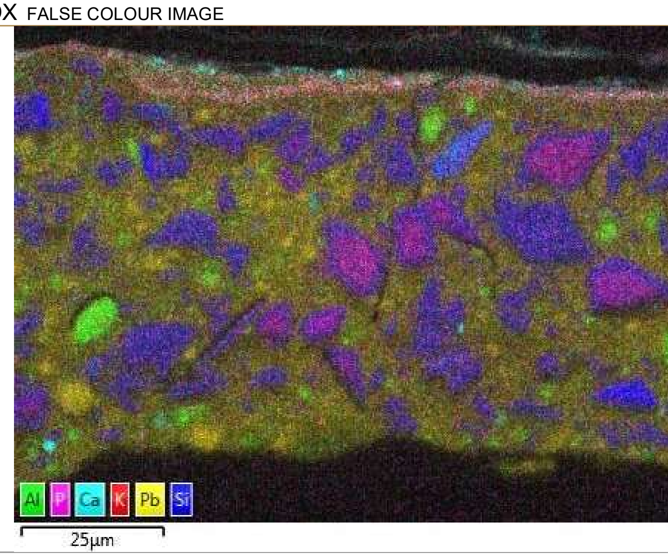
SEM-EDX • 260x



SEM-EDX • 1000x



SEM-EDX FALSE COLOUR IMAGE

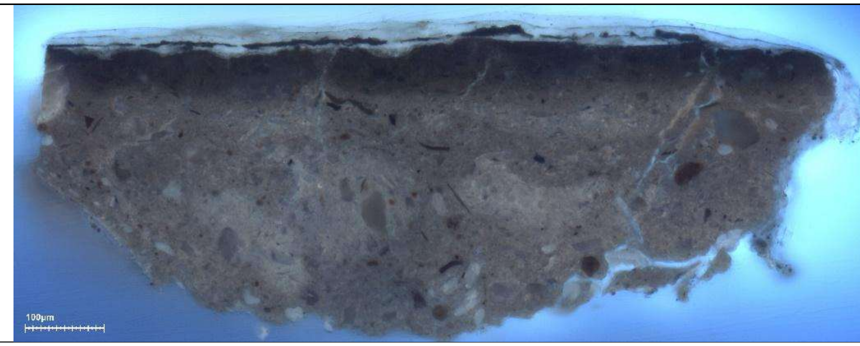


Layer description and summary of the SEM-EDX analysis results
3. Varnish *Thin layer rich in calcium on the surface of layer 3 thin layer or patina? Visible with SEM-EDX* **2. Partial thin layer** Pb/S, K, Ca, Si, (P), (Al) *Presence of patina on the surface of layer 2 – rich in phosphor, visible with SEM-EDX* **1. Red-purplish:** Smalt (As, Ni and Bi impurities), red lake (fixed on aluminium-rich substrate), lead white, some silicates, a little chalk, some grains of earth pigment **0? Possibly pale pink underlayer?:** Lead white, red lake (fixed on aluminium-rich substrate), a little chalk

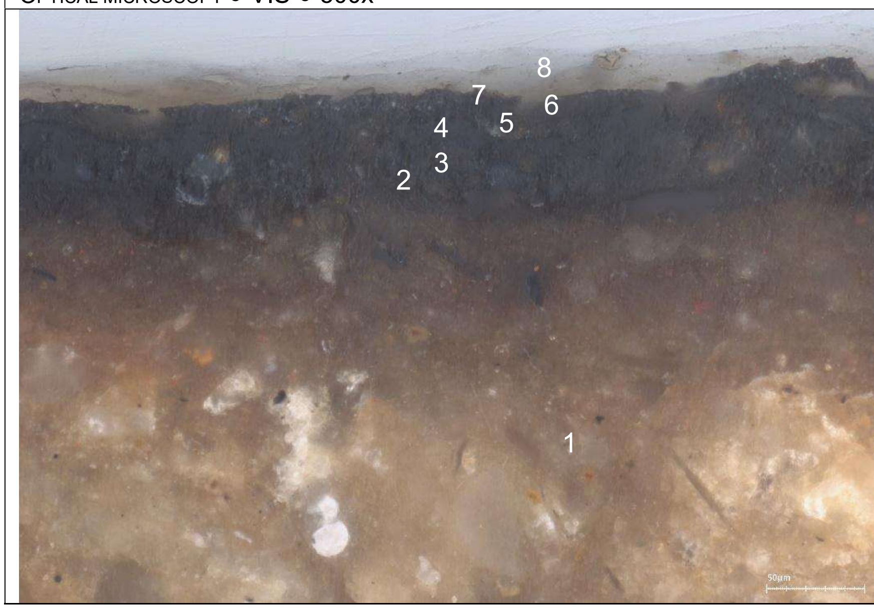
P253.103 ● C102.193 Dark green vegetation ● Right edge

OPTICAL MICROSCOPY ● VIS ● 200x

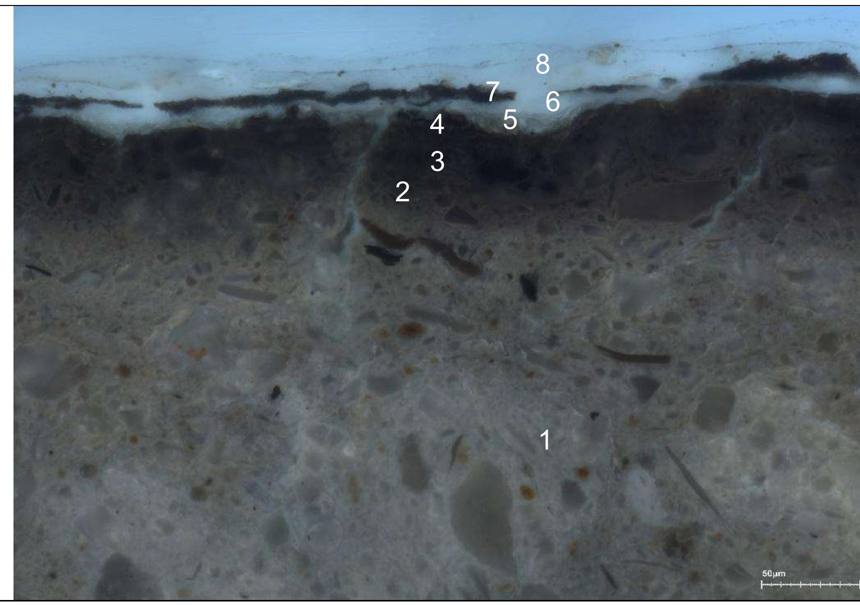
OPTICAL MICROSCOPY ● VIS ● 500x



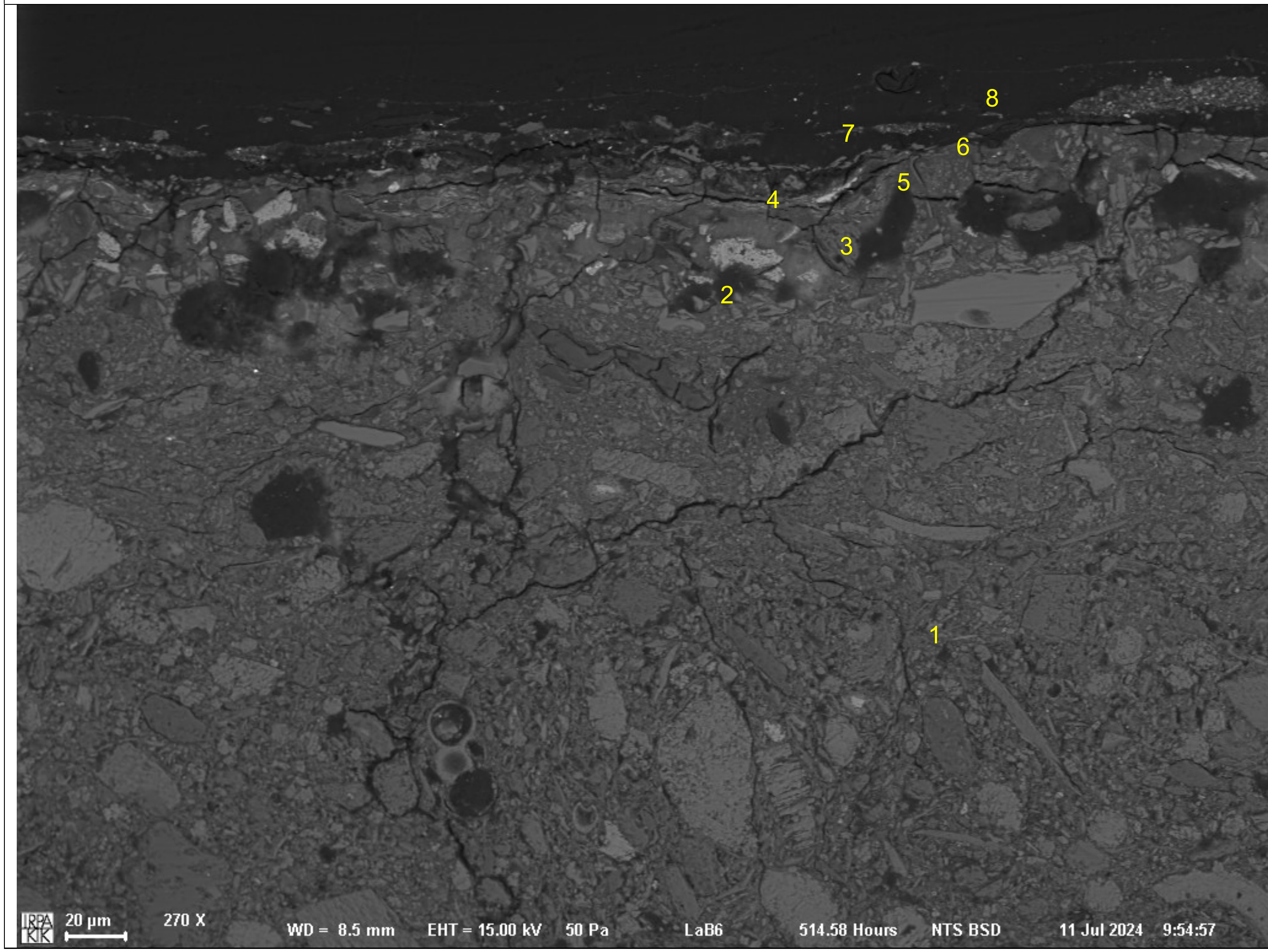
OPTICAL MICROSCOPY ● VIS ● 500x

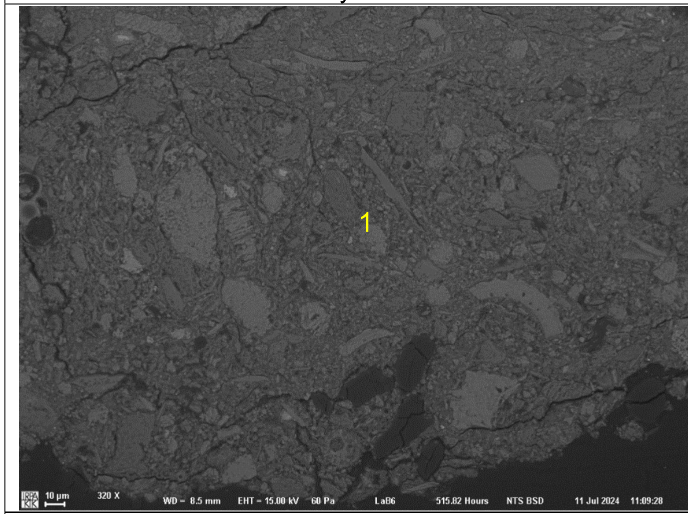
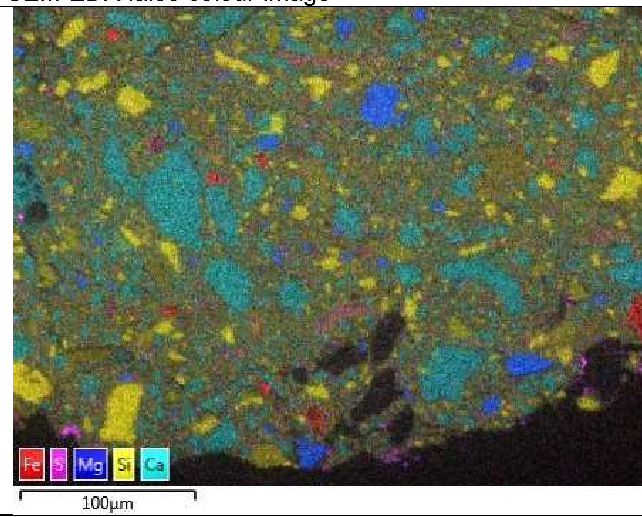


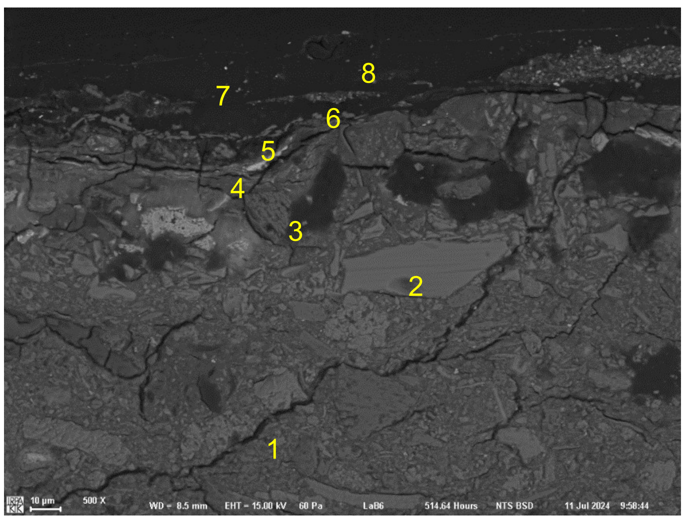
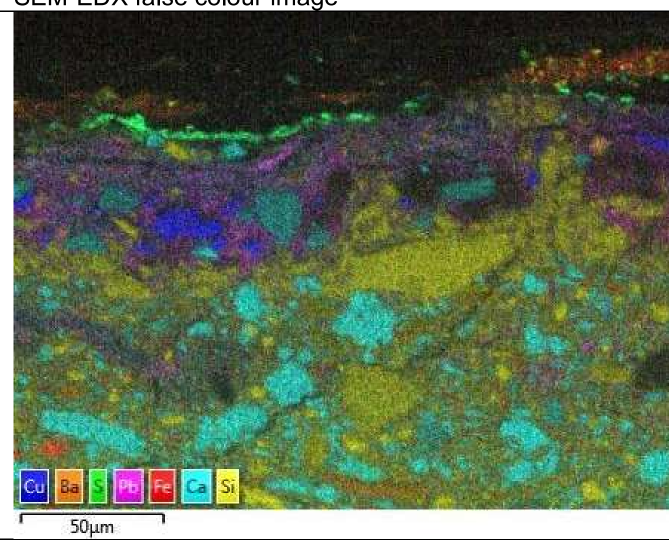
OPTICAL MICROSCOPY ● UV ● 500x



SEM-EDX ● 270x


8
7
6
5
4
3
2
1
20 µm
270 X
WD = 8.5 mm
EHT = 15.00 kV
50 Pa
LaB6
514.58 Hours
NTS BSD
11 Jul 2024
9:54:57

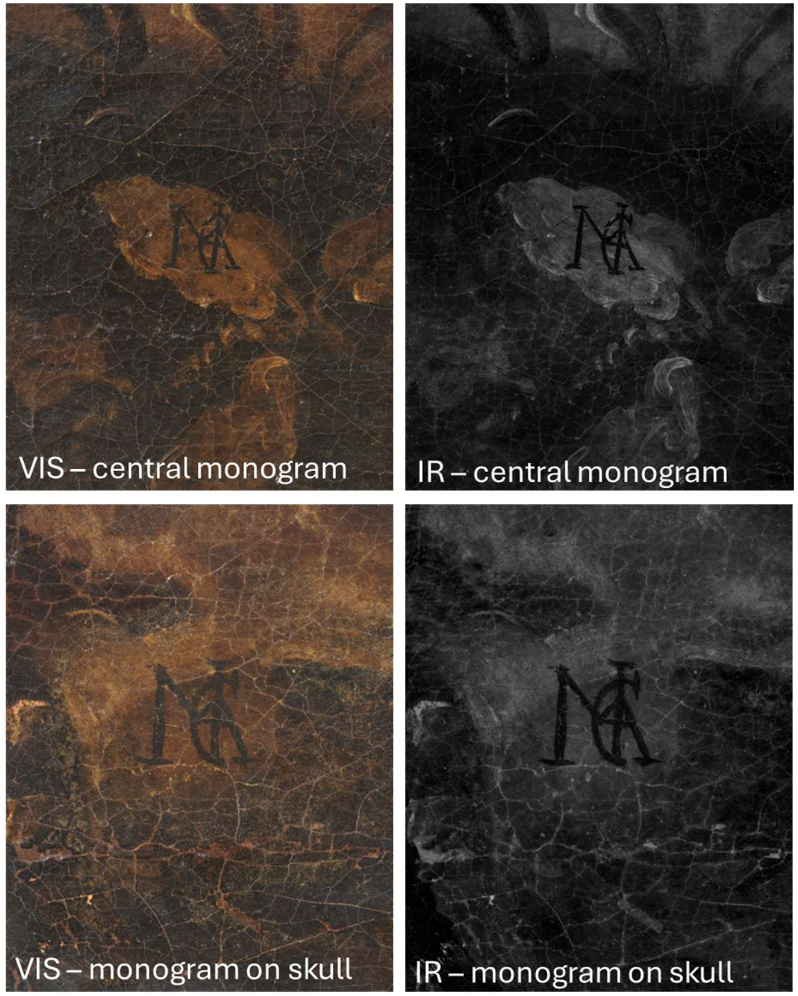
SEM-EDX ● 320x – Lower layer	SEM-EDX false colour image
	

SEM-EDX ● 500x – upper layers	SEM-EDX false colour image
	

Layer description and summary of the SEM-EDX analysis results
8. Varnishes – 2 layers **7. Dark layer:** Sienna earth/umber pigments, barium sulphate, titanium white, chromium pigment, silicates, calcium, little grains with P-Ca, two little grains with Zn **6. Varnish** *Patina on the surface of layer 5 – Rich in sulphur and calcium* **5. Partial thin transparent layer** *Possibly patina on the surface of layer 4* **4. Transparent layer (possibly yellow glaze?):** Richer in calcium, richer in lead, some silicates, two grains of smalt **3. Blue layer:** Azurite, lead, (richer than layer 2), grains with Ca + Mg, calcium, one grain of vermilion, one grain Cu (+Zn) **2. Blue layer:** Smalt, lead, some grains of azurite **1. Beige ground:** Earth pigments, some grains of Sienna/umber pigments, rich in silicates, chalk, grains with Ca+Mg (dolomite?), carbon-based black grains, some grains of bone white, black grains rich in Mn (+ Fe), some grains rich in sulphur (small grains) Presence of lead → soap formation

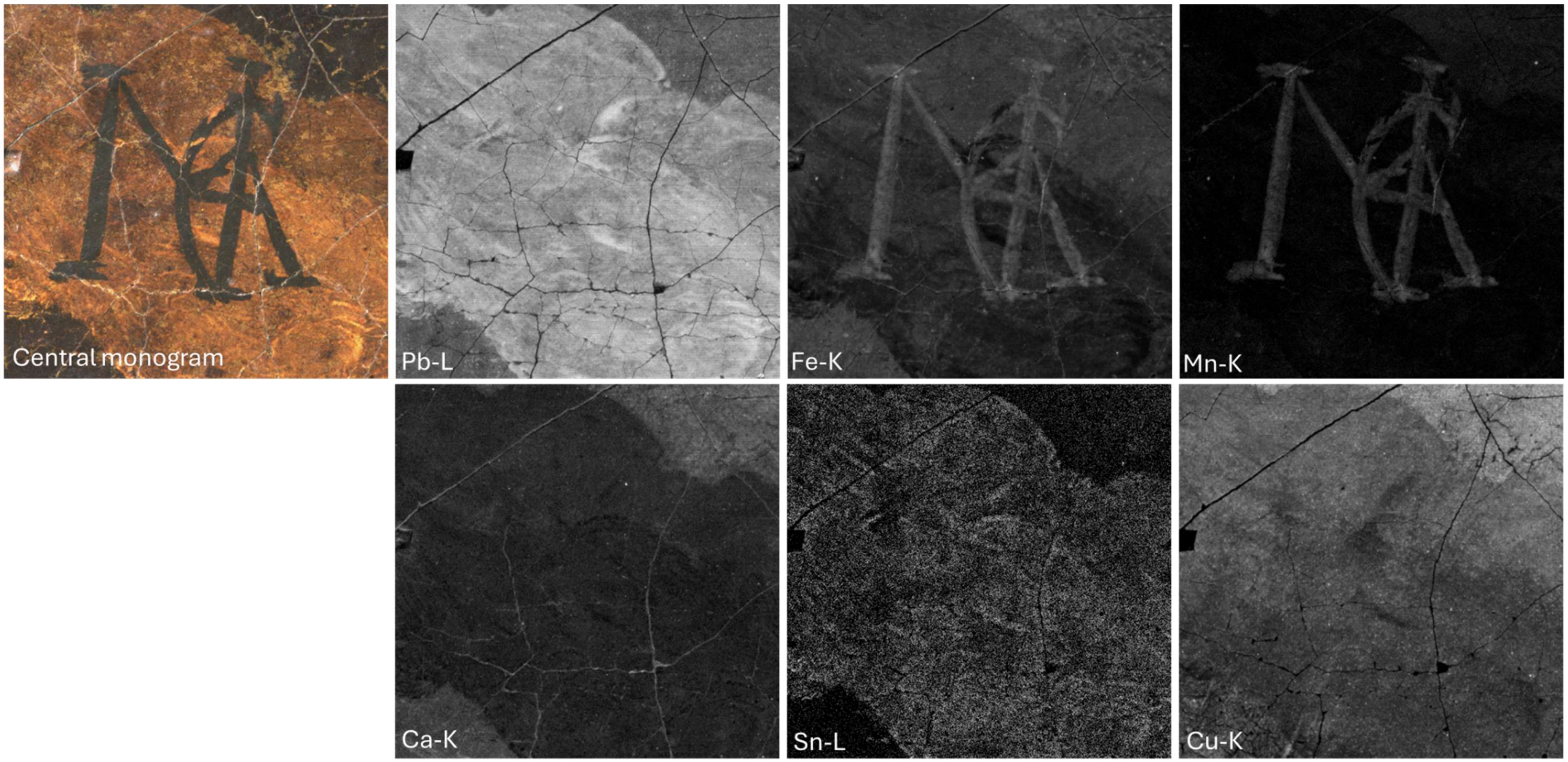
Annex 4 – High resolution and technical photography of the monograms

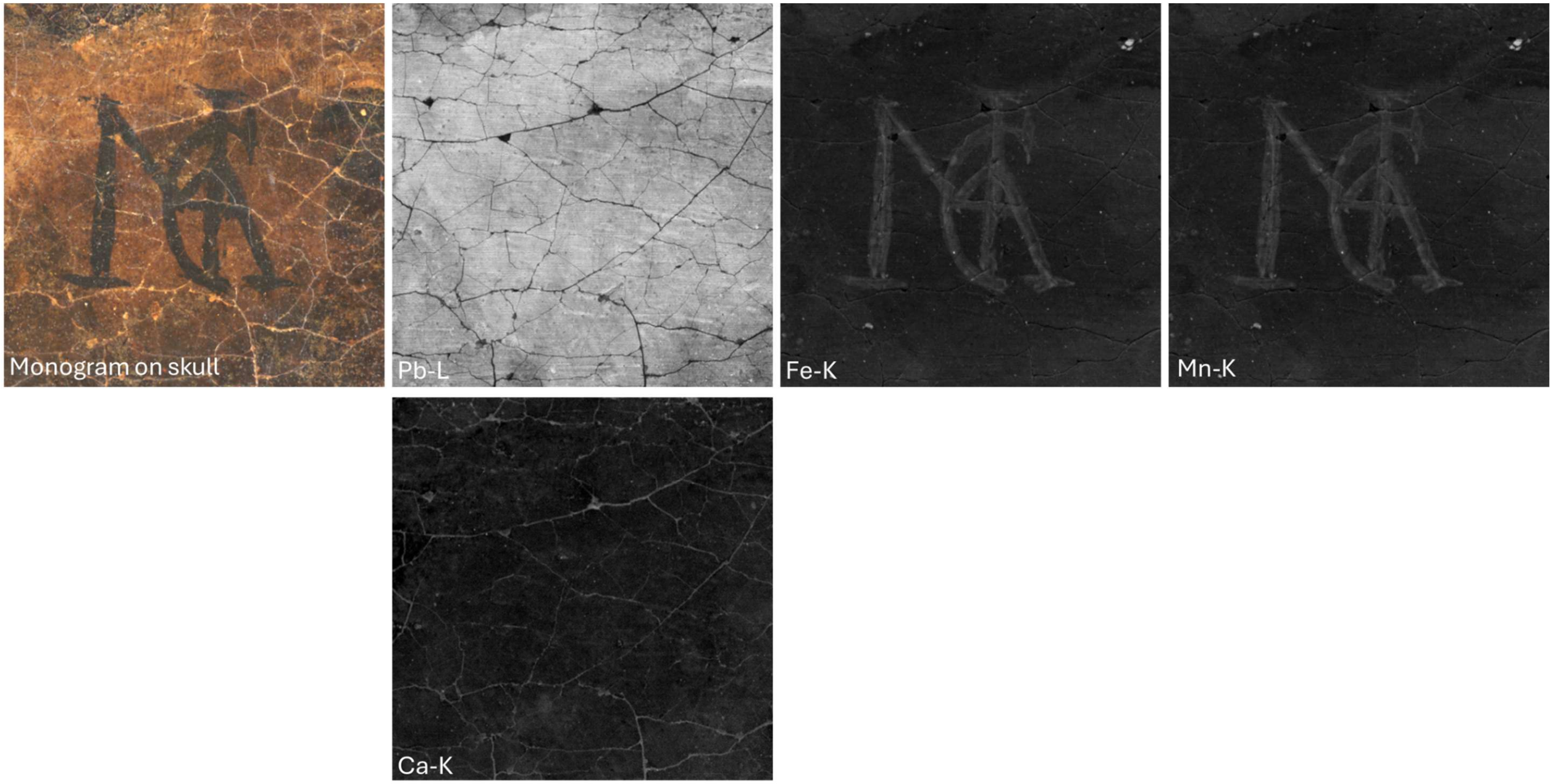
The monograms under visible (VIS) and IR-light. All images © KIK-IRPA



Annex 5 – MA-XRF element maps of the monograms

MA-XRF element distribution maps of the main elements detected. The whiter the tone, the higher the intensity for the specific element. All images © KIK-IRPA




Monogram on skull
Pb-L
Fe-K
Mn-K
Ca-K

Annex 6 –Analysis of the red lake from layer 1 of the cloak of Mary with HPLC-DAD

By Ina Vanden Berghe and Alexia Coudray, KIK-IRPA Textile Research Lab

The sample

A minute sample of the varnish layer was scraped off at the location of Mary's cloak to investigate the origin of the red lake (P262.029).

Analytical technique

High Performance Liquid Chromatography with a photo diode array detection system (HPLC-DAD) was used to identify the organic dye composition. This was done using the Acquity Arc UHPLC equipment from Waters (Belgium). The analyses are interpreted using the Empower software system from Waters. The dyes were recovered from the sample using hydrochloric acid (HCl) extraction (Vanden Berghe et al. 2009)[15].

Result

The detected dye components are indicated in table 2. The first three columns comprise the KIK/IRPA sample code, the sample colour and the type of extract analysed. The analysis number is given in the next column. The detected dye composition is mentioned in column 5, expressed as relative proportions of the dye constituents after calculation of their peak area measured at the wavelength (nm) given in the next column. The results of the HPLC analyses in terms of the attribution to biological sources is listed in the last column.

Table 2. HPLC-analyses, dye composition and related biological dye source(s)

Sample code	Colour	Extract	Analysis n°	Dye composition	λ(nm)	Biological dye source(s)
P262.029	red	HCl	02/251121/0	100 carminic acid	255 R275	cochineal

[15] Vanden Berghe, I., Gleba, M. and Mannering, U. (2009) Towards the identification of dyestuffs in Early Iron Age Scandinavian peat bog textiles. Journal of Archaeological Science 36, 1910-1921.

The identification of carminic acid gives proof of the use of **cochineal scale insects.** As carminic acid was the only detected compound, no further species recognition can be done to distinguish between cochineal insects from the Old or the New world (Vanden Berghe 2016)[16]. In the given 16th century context of the lake however, the **Mexican cochineal** species (*Dactylopius coccus* Costa) is the most likely source used.

[16] Vanden Berghe, I., (2016) The Identification of Cochineal Species in Turkmen Weavings; A Special Challenge in the Field of Dye Analysis. In Turkmen Carpets. A New Perspective, volume I. Eds. Jürg Rageth and 'Freunde des Orientteppiche Basel', Abächerli Media AG, Sarnen (Switzerland), 303-310; 333-348.

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