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Painting the Past in the 19th Century: Materials, Methods, and Perspectives in Watercolour Replicas

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Abstract: This study focuses on the material characterisation of a collection of 19th-century watercolour replicas that reproduce ancient Egyptian mural paintings and illuminated decorations from medieval manuscripts. Non-contact analyses, including macro-X-ray fluorescence (MA-XRF), X-ray diffraction (XRD), and fibre-optic reflectance spectroscopy (FORS), were employed to examine the composition of the painting materials, particularly the pigments. The findings are contextualised through archival research into 19th-century technical sources on historical painting and illuminating practices, as well as contemporaneous pigment catalogues that reported commercial prices. Ultimately, this research aimed to explore whether 19th-century artists engaged with historical material practices beyond mere visual representation in their depictions of historical subjects. The results obtained from the replicas of medieval illuminations are groundbreaking, as they challenge prevailing scholarly assumptions. Notably, the use of pigments such as minium and ultramarine blue, which were held in high regard during the Middle Ages, along with the use of chalk in the preparation of the support, suggest that, in an industrialised world where engagement with material culture was increasingly driven by commercial profit, some academic circles still sought to explore and preserve selected historical material practices in the art of painting.

Keywords: pigment analysis; replicas; 19th century; watercolour; illuminated manuscripts; material culture; MA-XRF; XRD; FORS

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1. Introduction

The 19th-century European cultural environment was largely defined by a dual and contrasting fascination: a fervent enthusiasm for the progress spurred by the Industrial Revolution—which significantly impacted the colour manufacturing industry [1–4]—and a deep, pervasive interest in the past, manifesting through cultural movements such as Romanticism and Neogothicism.

This contrasting fascination had a profound impact on major artistic movements across Europe, such as the Pre-Raphaelites in England and the proponents of the 19th-century "tempera revival" in Italy. Extensive technical studies over the past few decades have shown that, while these artists were visually and conceptually inspired by the past, they showed little to no interest in resorting to historical painting materials and methods. Instead, they embraced the new industrial products as innovative means of expression [5–13]. Further research into the painting materials used in various European artistic contexts during this period highlights the rapid and widespread adoption of new synthetic pigments. This trend was particularly evident in leading colour manufacturing countries such as England, France, and Germany, reflecting a fervour for progress [14–19].

These technical studies have significantly shaped modern scholarly perceptions of 19th-century artists' practices. Notably, they have contributed to generating the idea that, overwhelmed by an ever-growing array of new materials whose formulation rapidly became the prerogative of chemical industries [20,21], artists generally became disinterested in understanding the nature and properties of different painting materials and simply used whatever was commercially available. This attitude was exacerbated by the 19th-century lack of formal training regarding technical and material knowledge, with academies emphasising theory and ideas over teaching the practice of painting [22] (pp. 434–5); [23] (p. 3); [24]. In turn, these circumstances seemingly precluded artists from engaging with historical material practices.

While this perspective holds partly true, it is crucial to acknowledge a more articulated reality. For instance, the debate over pigment adulteration and durability that emerged in the second half of the 19th century illustrates that some artists, such as William Holman Hunt, fervently advocated for maintaining control over their painting materials [25,26]. Additionally, a few studies of different 19th-century collections from Europe and beyond have demonstrated that, despite the growing influence of large chemical factories on the production and distribution of colours, some artists, such as John Ruskin, continued to make intentional and informed choices about their materials, influenced by factors beyond the mere commercial price [27–29].

Simultaneously, a specific interest in historical material culture developed across 19th-century European academic circles, leading to numerous publications on the practice of painting and other forms of art. In 1821, the Italian art critic Giuseppe Tambroni published the first printed edition of Cennino Cennini's *Libro dell'Arte* [30,31]. Two decades later, art historians Mary Merrifield and Sir Charles Eastlake produced methodical studies and translations of treatises on artistic techniques from Antiquity onwards [32,33]. These works were followed in the late 1850s and 60s by volumes written by the Italian restorers Giovanni Secco Suardo and Ulisse Forni, whose interest in historical painting practices ranged from academic inquiry to practical application [34–37]. In 19th-century Germany, Ernst Berger made a significant contribution to this field [38], while his compatriot Max Doerner and the Italian chemist Icilio Guareschi continued to develop this area of study into the early 20th century [39,40]. This growing body of knowledge likely influenced the most educated artists. Sporadic technical studies on Italian 19th-century maiolica and Victorian painted furniture have suggested that some artists, such as William Burges, might have been partially inspired by past material cultures in approaching their practice [29,41].

This contribution aimed to shed further light on this complex interplay between innovation and tradition in 19th-century artistic practices by investigating whether and to what extent 19th-century artists might have been interested in exploring past material cultures when depicting historical subjects. To this end, material analyses conducted on a collection of 19th-century replicas are presented and discussed. The replicas are preserved at the Ashmolean Museum and proceed from the teaching collection that the Victorian art critic John Ruskin curated when he became Slade Professor of Fine Arts at Oxford.

2. Materials and Methods

2.1. The Replicas

For this investigation, two groups of watercolour replicas produced in different countries—Italy and England—were selected to enable a comparative study through material analyses. The watercolours were all painted on paper, which is now secured to a cardboard frame that provides support and facilitates handling.

The first group consists of four hand-painted engravings from the early 1830s, produced in a publishing context (accession numbers WA.RS.REF.176, 177, 179, and 180). These replicas depict Egyptian mural paintings from the Abu Simbel temple and various tombs in the Valley of the Kings, originally complementing John Ruskin's copy of the atlas *I Monumenti dell'Egitto e della Nubia*, published in 1832 by the Italian Egyptologist Ippolito Rosellini. Produced by the small Pisa-based publisher "Niccolò Capurro e C.", the engravings were based on original watercolours painted by Rosellini's team during their archaeological missions, which are now housed at the University of Pisa.

The second group includes five watercolours dating from the 1860s to the 1870s, replicating capital letters and pages from medieval illuminated manuscripts (accession numbers WA.RS.ED.204, 205, 206, 207, and 208). These were produced in an academic setting during Ruskin's activity as a professor of art at Oxford and made by his students and his assistant, John James Laing. In his catalogue of the teaching collection, Ruskin explained that these replicas are "copied from various manuscripts in the British Museum" (now scattered across different collections) and praised Laing's replicas as "almost inimitable in execution" [42] (pp. 137–138). One of the anonymous replicas by Ruskin's students bears an inscription reading, "norman letter i put colour right", suggesting that Ruskin assigned students to colour the blank profiles of ornate capital letters.

A complete list of the works studied is given in Table A1. After the analyses were completed, no visible alterations to the objects' surface were observed.

2.2. Macro-X-ray Fluorescence (MA-XRF), Bruker CRONO XRF Spectrometer

The Bruker CRONO XRF spectrometer features a rhodium target tube and a 50 mm^2 SDD detector with an energy resolution < 140 eV for Mn Kα and a signal throughput of up to 500,000 cps. It allows for the fast collection of elemental maps on up to 600 $\times$ 450 mm^2 areas for elements in the range of 13 $\leq$ Z $\leq$ 92 (in air). The analytical time in the automatic acquisition mode was ca. 25 min for an area of 100 $\times$ 100 mm^2 with a 0.5 mm collimator. The data presented in this article were obtained with a 0.5 mm collimator by operating the X-ray tube at 50 kV and 200 µA, and they were processed using the Bruker ESPRIT Reveal software (version 2.2.1.4280).

2.3. X-ray Diffraction (XRD), Bruker HYDRA XRF + XRD Spectrometer

This instrument features a 30 W micro-focus X-ray generator with a Cu anode and parallelising polycapillary optics, a 50 mm^2 SDD detector with an energy resolution < 140 eV for Mn Kα for XRF measurements, and a photon-counting 2D-detector for performing XRD measurements at angles between 20° and 40° 2θ in a first run and 40° and 60° 2θ in a second. A 220 µm collimator, a Ni filter, and an acquisition time of 300 s per run were used, resulting in a 10 min measurement time per spot. The crystalline phases were identified by comparison of the diffraction patterns, both against the Powder Diffraction Files from the ICDD database (https://www.icdd.com/, accessed 15 April 2024) and diffraction patterns calculated from structures in the COD (www.crystallography.net, accessed 1 July 2024). Note that the relative peak intensities sometimes differed from their expected values. This was due to a combination of, on occasion, a poor crystallinity, a preferred orientation, a comparatively low number of crystallites in the probed sample volume, and the small section of reciprocal space that was sampled.

2.4. Fibre-Optic Reflectance Spectroscopy (FORS), University of Durham

A custom-built fibre-optic reflectance spectrometer that operates in the range of 400–2500 nm and was designed specifically for the study of fragile works of art was used to record the FORS spectra [19]. This equipment delivered a light beam with a 2.5 mm diameter and a total power of <0.5 mW to the investigated surface, at a working distance of 3 cm. In the range of 400–1000 nm, the bandwidth of the system was 3.5 nm, whilst in the SWIR region, 900–2500 nm, the bandwidth was 8 cm^{-1}, corresponding to 2.5 nm at 1750 nm. The spectra were recorded relative to a Spectralon standard and took 1 s per measurement. The assignment of the pigments via the reflectance spectra was achieved by comparison to published reflectance spectra and online databases by the CNR-IFAC (https://spectradb.ifac.cnr.it/, accessed 20 March 2024).

3. Results

3.1. Hand-Coloured Engravings Replicating Egyptian Frescoes

3.1.1. Black and Red Printing Inks

Figure 1 shows the hand-coloured engravings investigated during this study, predominantly painted in red, yellow, and blue. They are replicas of frescoes found in different parts of Egypt, with the following represented in particular: Ramesses II receiving Suppliants (WA.RS.REF.176) and the Chariot of Ramesses II (WA.RS.REF.177), both from the depiction of the Battle of Qadesh in the Great Hall of the Temple at Abu Simbel; Merneptah adoring Re-Harakhti (WA.RS.REF.179); and Ramesses III adoring Isis and Ptah-Sokar (WA.RS.REF.180), from the tombs in the Valley of the Kings. The material analyses showed that the outline of all the engravings was printed with black ink that lacked an XRF fingerprint, probably carbon ink. Furthermore, red ink was used in REF.179 and 180 and was found to be rich in lead. XRD further clarified the pigments' composition, showing that the red areas were printed with a mixture of lead-based pigments. Figure 2 shows the XRD diffractogram obtained for REF.179; the measured peaks matched the pattern for minium and hydrocerussite. The broad maximum at about 23° 2θ corresponded to cellulose in the paper/cardboard support (Figure S1) and was visible on most diffractograms, except where the increased X-ray absorption of specific pigments likely prevented its appearance.

Figure 1. Images of the hand-coloured engravings investigated during this study. **Top left**: Ramesses II receiving Suppliants; **top right**: Chariot of Ramesses II; **bottom left**: Merneptah adoring Re-Harakhti; **bottom right**: Ramesses III adoring Isis and Ptah-Sokar.

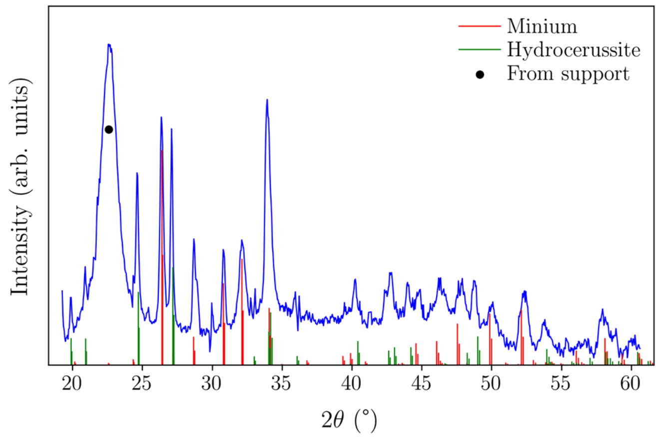

Figure 2. X-ray diffractogram of a red printed ink on WA.RS.REF.179.

3.1.2. Whites

The material analyses of the hand-painted areas revealed a very similar coloured palette across the four prints, with lead white mixed with most pigments on all of the works analysed, as suggested by the MA-XRF spatial distribution of lead and confirmed by XRD. Figure 3 (top) shows the spatial distribution of lead in REF.176—the units on the colour scales of these and all following XRF maps designate the intensities of X-ray emissions relative to the maximum and minimum intensities observed for these transitions, and the scale is often contracted to highlight patterns in the distributions. The X-ray diffractogram obtained on a blue area matched the patterns for hydrocerussite and cerussite. In addition to lead white, barium white was found to be used in two prints and restricted regions, both as a standalone white pigment and in a mixture with other colours. Figure 3 (bottom) shows the MA-XRF elemental maps of barium in REF.177 and REF.180, indicating that barium white was used for Ramesses' dress in REF.180 and in a mixture with a green pigment in the horse's garment in REF.177.

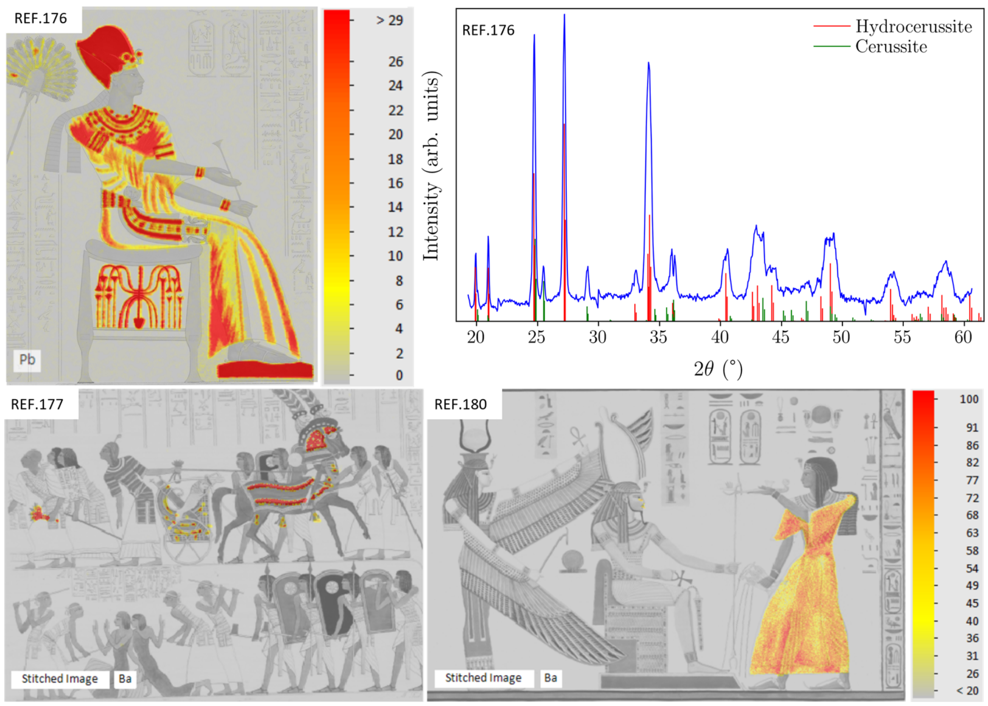

Figure 3. Top: macro-XRF map of lead for WA.RS.REF.176 and X-ray diffractogram of a blue area. **Bottom**: macro-XRF maps of barium for WA.RS.REF.177 (**left**) and 180 (**right**).

3.1.3. Reds

The red hand-painted areas were found to be rich in mercury on all engravings, as revealed by MA-XRF elemental maps. XRD and FORS confirmed the presence of vermilion on all of the prints. Figure 4 shows the elemental map of mercury obtained on REF.179, together with the FORS spectra obtained on the red areas of REF.176, 177, and 180. Their sigmoid shape and the inflection point around 600 nm were consistent with vermilion [43,44]. Finally, the XRD diffractogram in Figure 4, measured on a red area in REF.177, matches the pattern of cinnabar.

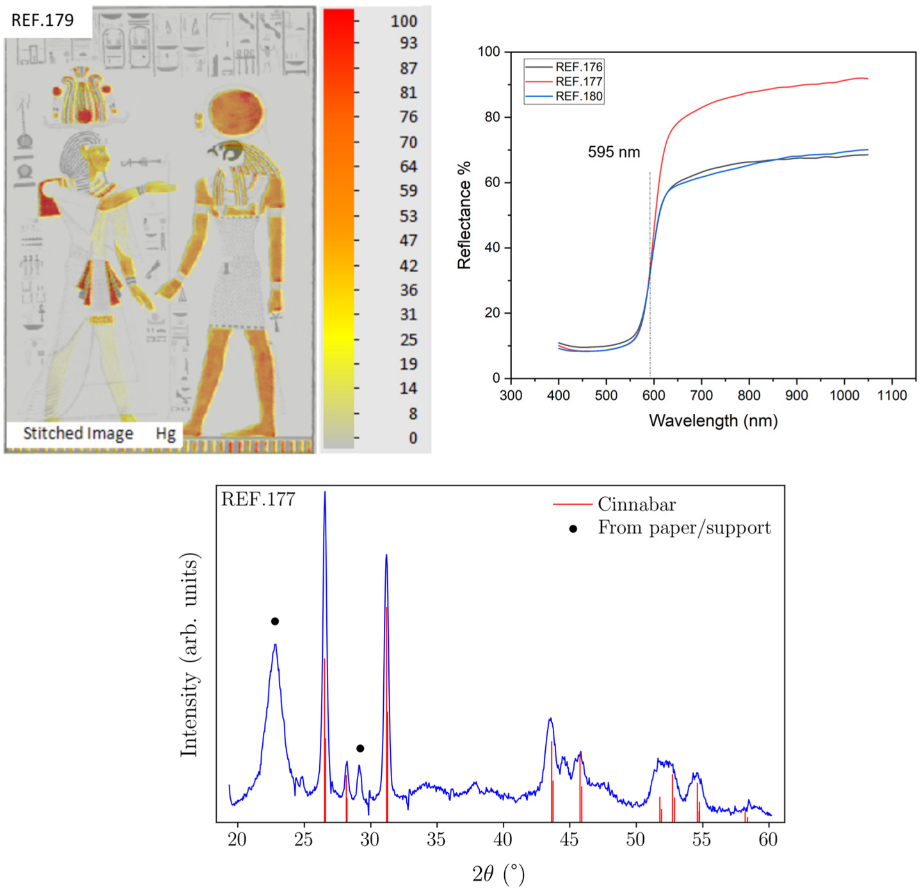

Figure 4. Top: macro-XRF map of mercury obtained for WA.RS.REF.179 (**left**) and reflectance spectra obtained in red areas of WA.RS.REF.176, 177, and 180 (**right**). **Bottom**: X-ray diffractogram of a red area on WA.RS.REF.177.

3.1.4. Yellows

The absence of an XRF fingerprint in most yellow areas revealed that they were painted with an organic colourant, which could not be further characterised by the analytical protocol employed during this investigation. However, in a few restricted regions, MA-XRF and XRD detected the use of cadmium yellow, chrome yellow, and lemon yellow (strontium chromate). Figure 5 shows MA-XRF elemental maps for cadmium in REF.179 and REF.180. In both cases, the comparison of these maps with the images of the prints in Figure 1 showed that cadmium correlated with yellow and red areas, such as Merneptah's yellow skirt in REF.179 and the red hieroglyph on the top right in REF.180, as well as blue areas, such as the blue hieroglyphs in REF.179 and the base of the throne in REF.180, suggesting pigment mixtures.

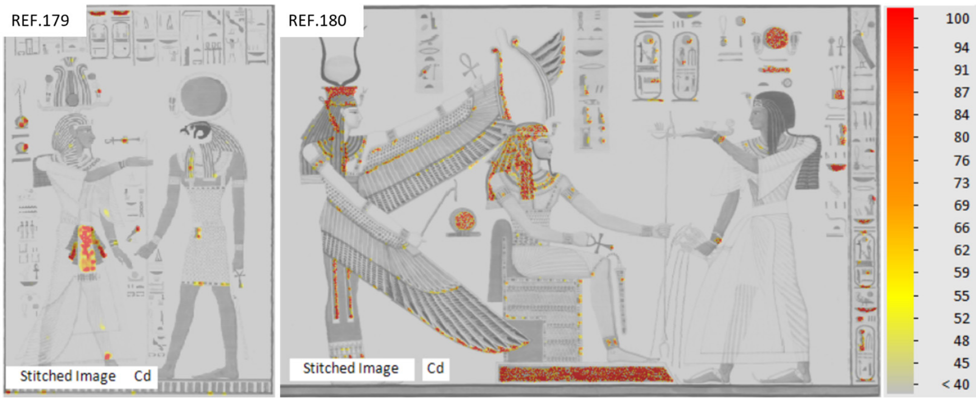

Figure 5. Macro-XRF maps of cadmium obtained for WA.RS.REF.179 (**left**) and WA.RS.REF.180 (**right**).

Furthermore, chromium-based pigments were found in the red, orange, and yellow areas in REF.176 and REF.179. Figure 6 (top) shows the map for chromium and lead in REF.176. Their correlation in the yellow pigment used for the fan and part of Ramesses' headdress indicates that lead chromate was used to paint these areas. In contrast, Figure 6 (bottom) shows the spatial distribution of lead (blue), chromium (green), and mercury (red) in REF.179. In this case, the map shows that both mercury and chromium (but no lead) are present in Re-Harakthi's body, which appears yellow on the map. This suggests that vermilion was mixed with a chromium-based pigment. The map of strontium in Figure 6 shows that this element is present across the entire surface. However, its intensity of emission slightly increases in correlation with Re-Harakthi's body, suggesting that vermilion was mixed with lemon yellow (strontium chromate) in this area.

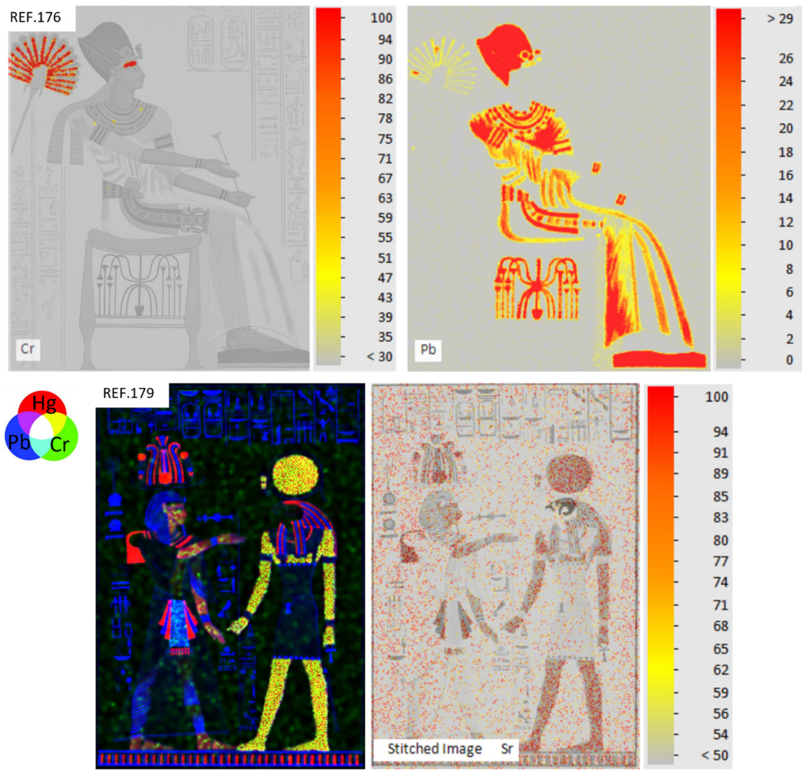

Figure 6. **Top**: macro-XRF maps of chromium and lead obtained for WA.RS.REF.176. **Bottom**: macro-XRF map of lead (blue), chromium (green), and mercury (red) obtained for WA.RS.REF.179 (**left**) and macro-XRF map of strontium obtained for the same print (**right**).

3.1.5. Blues and Greens

In most of the blue areas, Prussian blue was identified using FORS. Figure 7 shows the reflectance spectra acquired for the blue areas of REF.176, 177, 179, and 180. All the reflectance spectra showed the characteristic shape of this pigment, with a maximum in the visible region between 450 and 475 nm, depending on the concentration of the pigment [45]. Further absorption bands in the NIR region between 2360 and 2370 nm, associated with the combination of IR stretching and Raman modes for the nitrile functional group, were visible in the spectra acquired on REF.176, 177, and 180 [46,47]. Furthermore, all the spectra displayed a band at 1450 nm assigned to the first overtone of OH stretching for lead white [48].

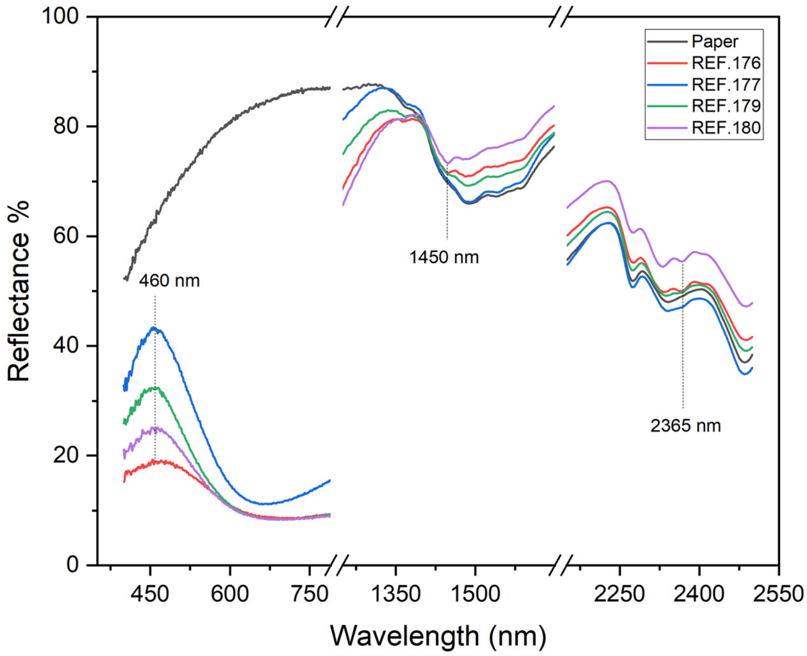

Figure 7. Reflectance spectra of blue areas in WA.RS.REF.176 (red), 177 (blue), 179 (green), and 180 (purple) with reference reflectance spectrum of the paper support (black).

In addition to Prussian blue, the elemental distribution of copper across the blue areas of the horse's mantle in REF.177, shown in Figure 8, suggested the use of azurite (or its synthetic equivalent, blue verditer). The use of other copper-based blue pigments, such as Egyptian blue or blue bice, was, in this case, excluded, since no calcium or silicon appeared to be correlated with copper.

Finally, green was used sparingly, appearing only in very small details in most prints, with the exception of REF.180, where it was abundantly used to paint Isis and Osiris. Figure 8 shows the spatial distribution of arsenic (red) and copper (green) in REF.177 and 180. Both these elements are present in the green stripes on the horse's mantle in REF.177 and in Isis and Osiris's bodies in REF.180, which appear yellow in the maps acquired with macro-XRF. This indicates the use of emerald green.

3.2. Watercolours by Ruskin's Academic Circle

The material analyses on this group of replicas showed that some of them bear similarities in the painting materials used.

3.2.1. WA.RS.ED.204 and 205

Zinc white was used extensively to mix blue and green tones on the watercolours ED.204 and 205, depicting the initials "I" and "N". Its presence was determined thanks to the spatial distribution of zinc observed with macro-XRF and confirmed by XRD in most areas investigated (see, for instance, Figure 9, bottom).

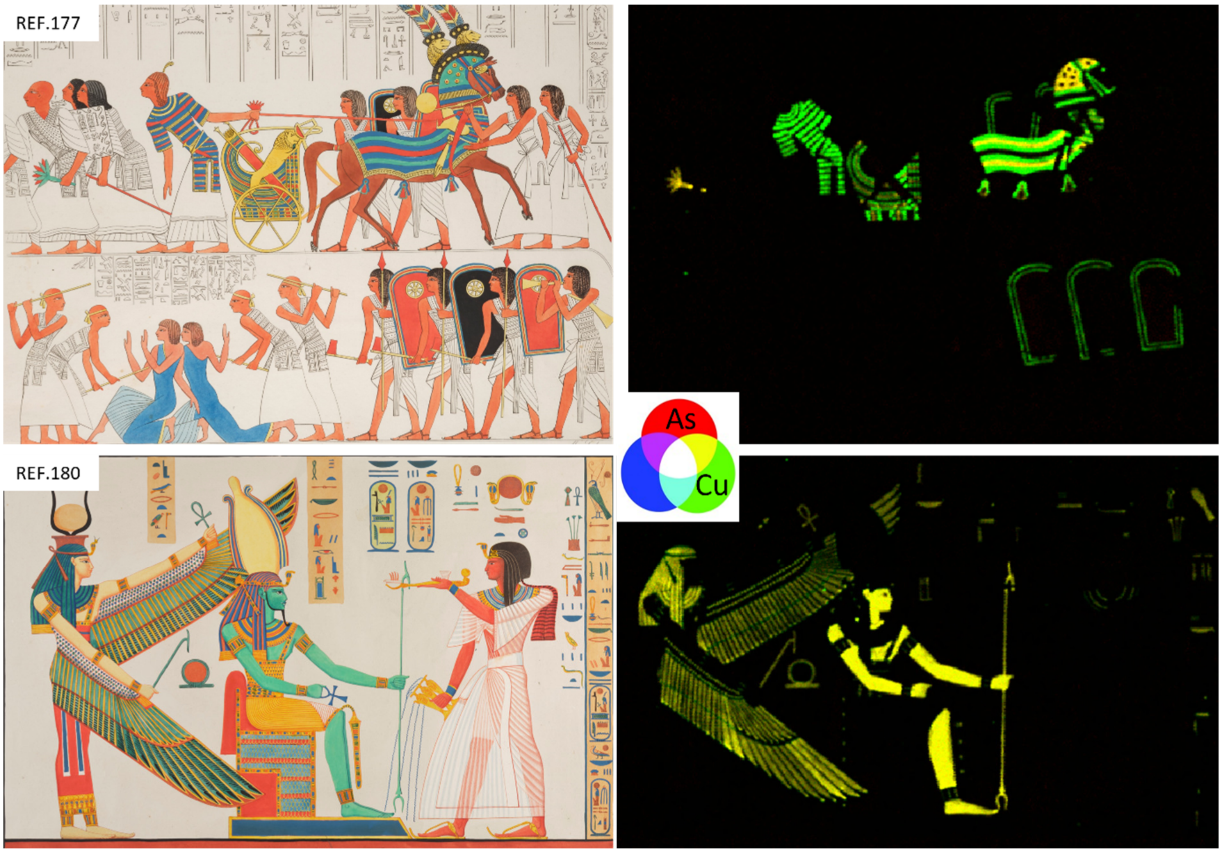

Figure 8. Visible image and macro-XRF map of arsenic (red) and copper (green) obtained for WA.RS.REF.177 (**top**) and 180 (**bottom**).

Figure 9 (top right) shows the elemental maps for chromium, copper, arsenic, cobalt, and mercury on ED.204. The elemental distribution of mercury indicated that the outline of the letter was traced with vermilion, as was the case for ED.205. The use of vermilion was confirmed via XRD on both initials. Furthermore, the elemental maps in Figure 9 show that the green areas in ED.204 contain copper, arsenic, and chromium. The XRD analysis further characterised the composition of this green area and retrieved a pattern that matched emerald green (copper acetoarsenite, Figure 9, bottom), which was likely mixed with a chromium base green pigment. In contrast, chromium-based pigments were not found in the green areas of ED.205, which was painted solely with emerald green. Finally, the distribution of cobalt in the elemental map of ED.204 suggests that cobalt blue (cobalt aluminate) was used for the light blue areas. The presence of aluminium was confirmed via a 1 min XRF spot measurement (Figure 9, top right). The same blue pigment was used for the blue areas in ED.205.

3.2.2. WA.RS.ED.206

In contrast, ED.206, depicting the initials "M" and "E", was painted with a different set of pigments. XRF revealed that the golden areas were laid using a pure gold pigment or foil. Figure 10 (top) shows the spatial distribution of gold and iron across the initial M. The distribution of iron suggests the use of ochres in the red areas, which was confirmed by FORS. Furthermore, the spatial distribution of lead in Figure 10 (middle-left) suggests that minium was used for the thin-shaped outline, while the presence of cobalt (blue), copper (red), and arsenic (green) correlates with the green spiral decoration, which appears white in the elemental map and suggests that a mixture of emerald green and cobalt blue was used. This particular pigment mixture has been reported during previous technical studies of Victorian paintings [27,41]. Furthermore, the distribution of cadmium shown in Figure 10 (middle-right) indicates the use of cadmium yellow in a few restricted areas. Finally, the XRD analysis showed that the blue areas of the background around the letters were painted with ultramarine blue, as shown in the diffractogram in Figure 10 (bottom). The absence of phases such as calcite, wollastonite, diopside, and quartz suggests the use of synthetic ultramarine rather than natural. Furthermore, the diffractogram shows that zinc oxide was mixed with ultramarine. In fact, both XRF and XRD indicated that zinc white was mixed in most pigments.

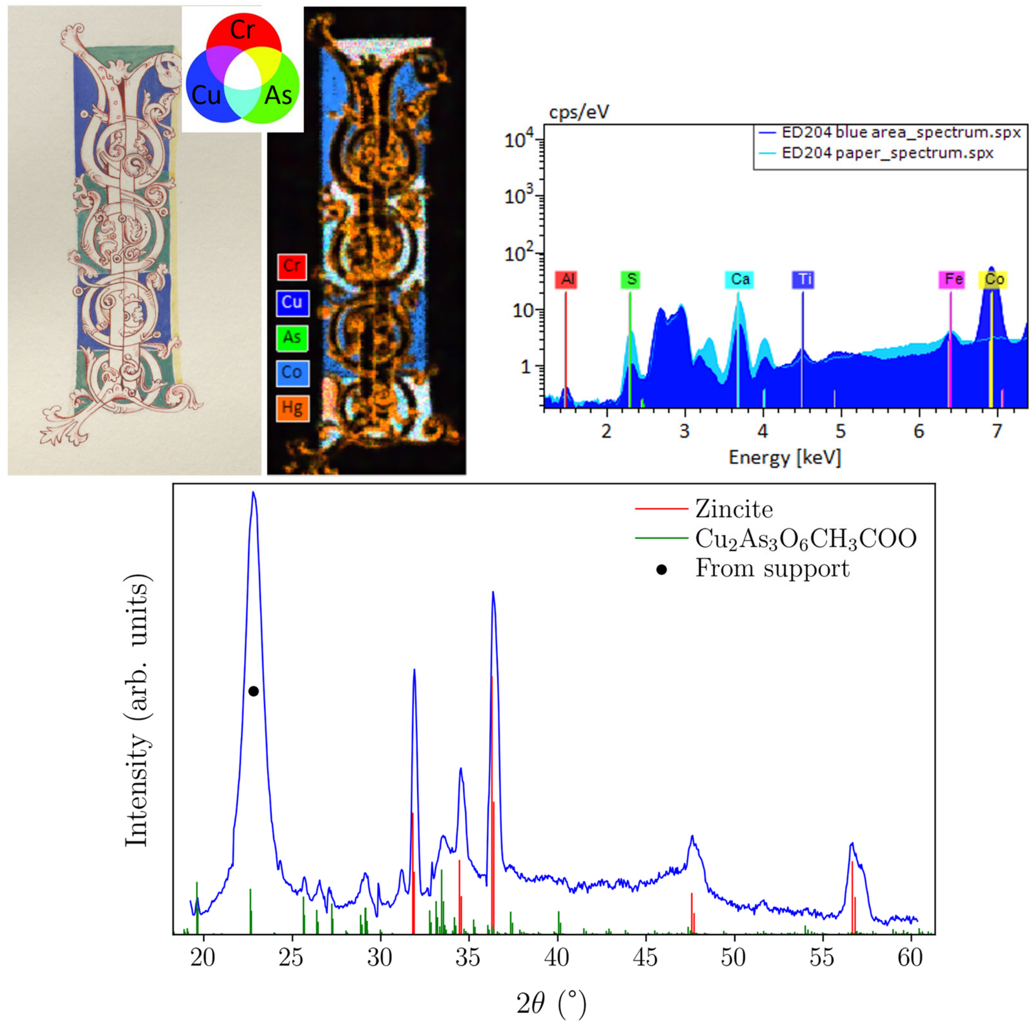

Figure 9. Top left: macro-XRF elemental maps of chromium (red), copper (blue), arsenic (green), cobalt (cerulean), and mercury (orange) obtained for WA.RS.ED.204. **Top right**: XRF spectrum obtained in a blue area. **Bottom**: X-ray diffractogram of a green area.

3.2.3. WA.RS.ED.207 and 208—Replicas by John James Laing

The material analysis revealed that, like Ruskin's students, Laing also made extensive use of zinc white, using it for white areas and mixing it frequently with coloured pigments. In fact, XRD often recovered the pattern of zinc oxide together with other mineral phases.

Although the two replicas by Laing were painted with a similar set of pigments, some discrepancies in the execution were noted. The main difference between the two watercolours was detected in the treatment of the paper support. In fact, the paper support of ED.207 was found to have been prepared before painting, unlike the support of ED.208. Figure 11 shows the spatial distribution of sulphur (red) and calcium (blue) on ED.207. Both elements are evenly spread across the entire paper surface, which appears purple on the map. Furthermore, an XRD analysis on the paper of ED.207 retrieved a pattern matching calcite, gypsum, and magnesite. Calcite also appeared in diffraction patterns collected on just the cardboard frame that supported this watercolour, but with comparatively smaller, less clear peaks (see Figure S2). Thus, calcite is likely present both in the cardboard frame and the paper, whereas gypsum and magnesite appeared only in correlation with the paper.

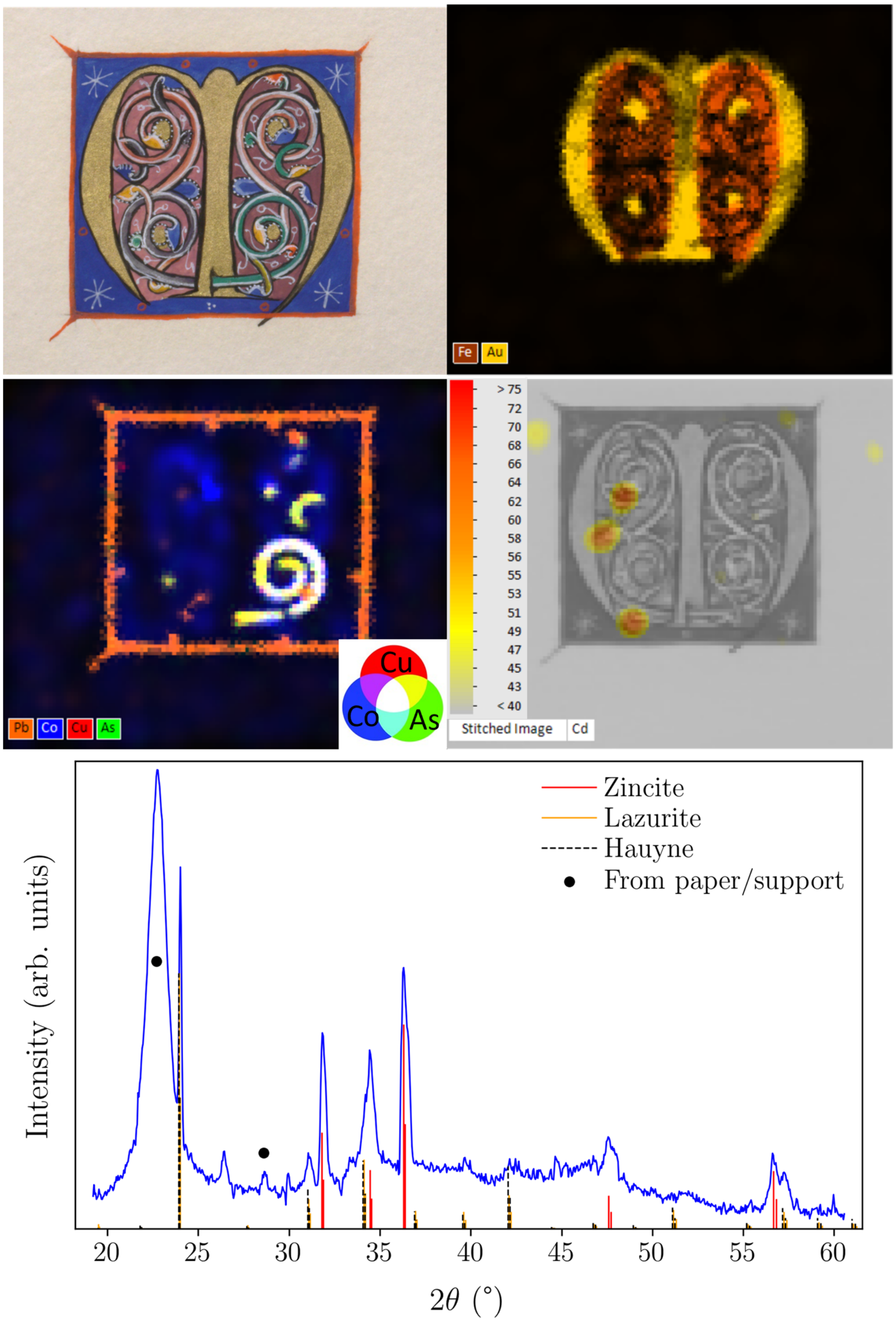

Figure 10. Top: visible image (left) and macro-XRF maps of iron (brown) and gold (yellow) obtained for WA.RS.ED.206. **Middle-left**: macro-XRF elemental maps of lead (orange), cobalt (blue), copper (red), and arsenic (green). **Middle-right**: macro-XRF map of cadmium. **Bottom**: X-ray diffractogram of a blue area from the background. Lazurite and hauyne cannot be distinguished based on these data and may both be present.

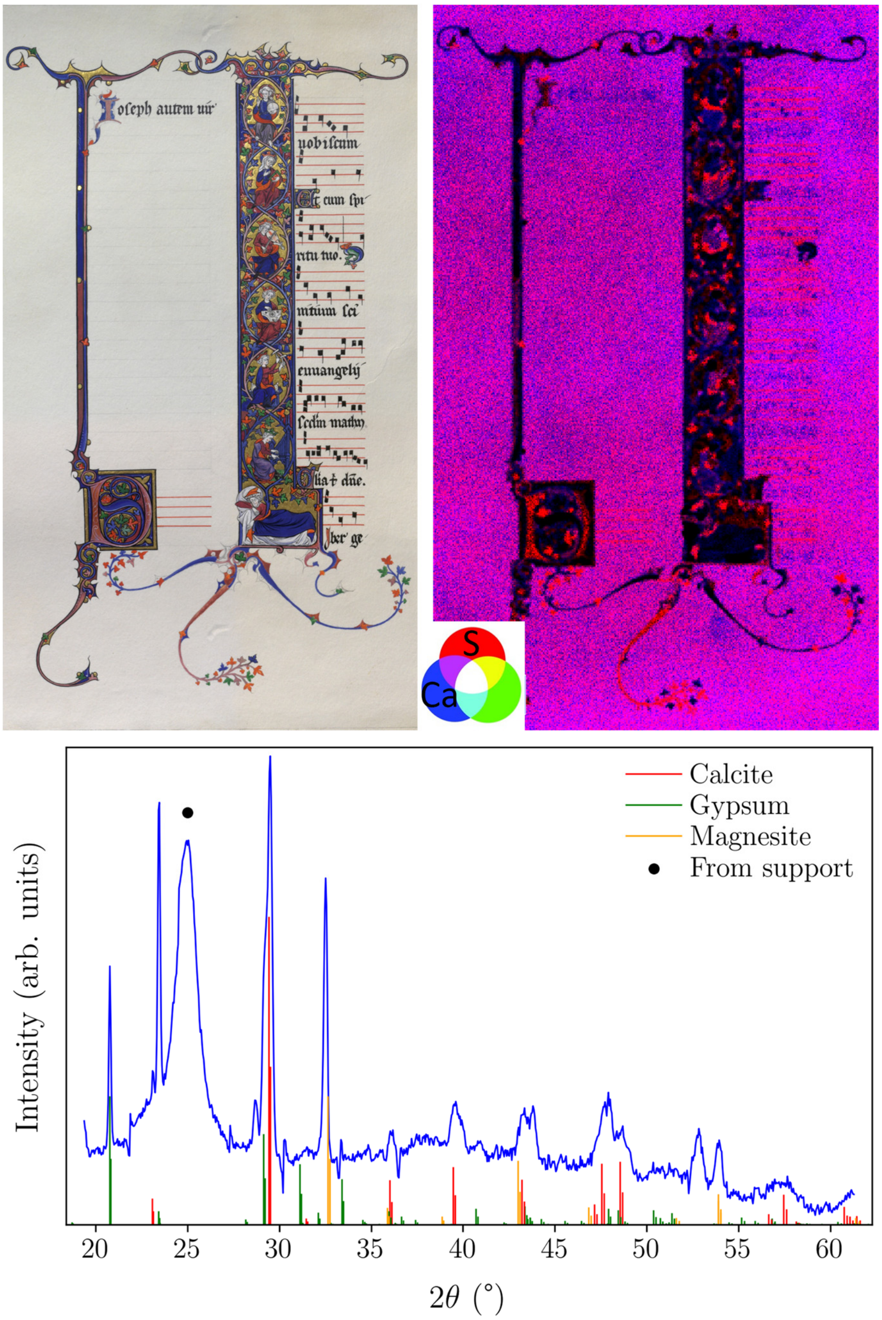

Figure 11. Top: visible image (**left**) and macro-XRF maps (**right**) of sulphur (red) and calcium (blue) obtained for WA.RS.ED.207. **Bottom**: X-ray diffractogram of blank paper on a cardboard frame. Owing to the layer structure of the sample, the peaks from the different phases experienced different shifts, which was especially visible for magnesite.

Regarding the pigments, the two watercolours are dominated by blue, gold, and red tones. Figure 12 (top left) shows the spatial distribution of gold across ED.207, indicating that gold foil or shell gold was used for the golden details. Furthermore, macro-XRF revealed that the blue areas are characterised by a complex elemental composition. Figure 12 (top right) shows the elemental maps of potassium (red), cobalt (blue), and phosphorous (green) on ED.207. All these elements are contained in the blue colour used for the illumination, which appears white in the elemental map. Furthermore, these blue areas also contain aluminium, as shown by the XRF spectrum in Figure 12 (bottom left). XRD analyses on these areas retrieved a diffractogram partially matching a mixed phosphate containing potassium, aluminium, and cobalt, with the formula $K(Co,Al)_2(PO_4)_2$ and a monoclinic crystal structure. This blue pigment, whose composition is significantly different than the cobalt-containing ground glass used historically, was previously found in John Ruskin's watercolours and was marketed as "smalt" by Winsor and Newton, as revealed by the material characterisation of colour books from the early 20th century conducted at the State Research Institute for Restoration in Moscow [27,49]. Gold and "smalt" also dominate the colour palette in ED.208.

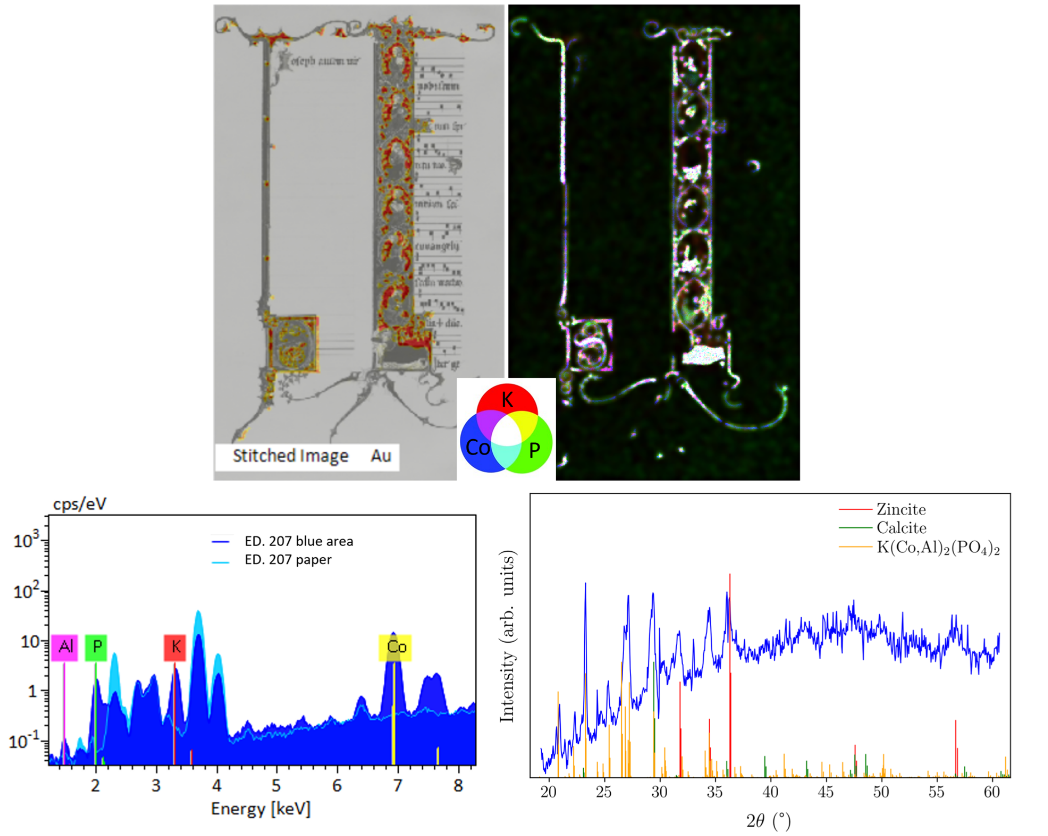

Figure 12. Top: macro-XRF maps of gold (right) and of potassium (red), cobalt (blue), and phosphorous (green) obtained on WA.RS.ED.207 (right). XRF spectrum (middle) and X-ray diffractogram obtained for a blue area.

In both watercolours, dark red areas were often found to be mixtures of vermilion and lead white. Figure 13 shows the X-ray diffractogram obtained on a red area in ED.207, which matches the patterns of cinnabar and hydrocerussite.

Furthermore, bright orange areas rich in mercury were found to contain chromium, suggesting mixtures of red and yellow pigments. Figure 14 shows the spatial distribution of mercury (red), barium (blue), and chromium (green) across ED.208. All these elements correlate to bright orange areas, suggesting that vermilion was mixed with barium chromate (sold as "lemon yellow"). In contrast, barium was not found in the bright orange areas in ED.207, which contain mercury, chromium, and lead. Unfortunately, this pigment mixture could not be characterised further. In fact, XRD did not clarify whether the lead was derived from lead chromate (chrome yellow) or hydrocerussite. If lead was present as hydrocerussite, chromium could be in the mixture as strontium chromate (lemon yellow). However, the elemental maps for strontium acquired on this watercolour show a high emission intensity across the entire paper surface, likely due to strontium sulphate (celestine) contained in the gypsum used to prepare the paper. This prevents a clear association of strontium with the orange areas in the replica from being observed.

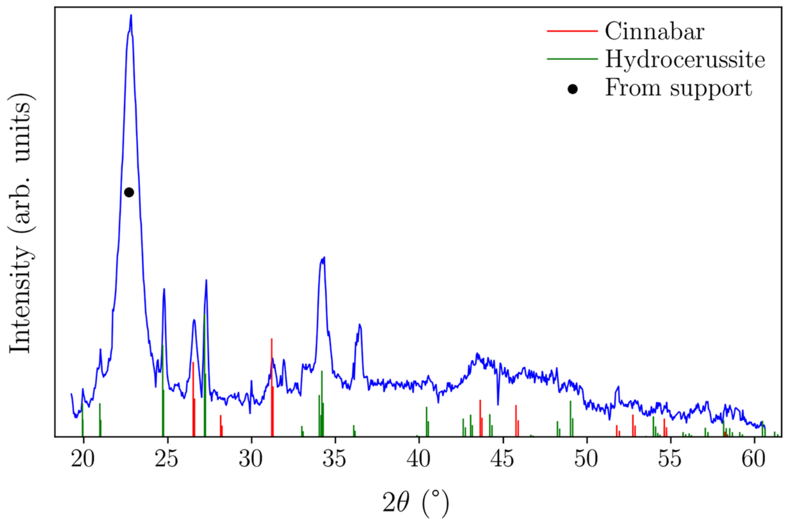

Figure 13. X-ray diffractogram obtained on a red area of WA.RS.ED.207.

Furthermore, FORS revealed the presence of a red lake in two red areas on ED.207. Figure 15 shows the reflectance spectra obtained on the red garments of two figurines. Two absorption maxima were observed at 525 and 563 nm, which were associated with two weak n $\rightarrow \pi^*$ transitions assigned to the combination of the non-bonding p orbitals of the carbonyl oxygens with delocalised σ wave functions. These absorptions resulted in two inflection points observed on the first derivative of the reflectance spectra at 498 and 539 nm and suggest the use of cochineal rather than red madder, whose absorption maxima and resulting inflection points would be slightly more blue-shifted [50–55].

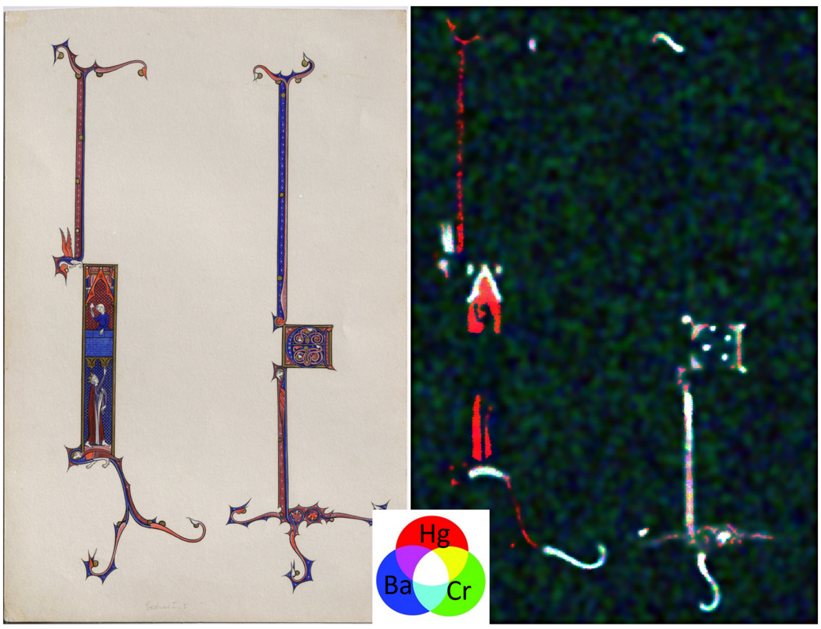

Figure 14. Visible image and macro-XRF map of mercury (red), barium (blue), and chromium (green) obtained on WA.RS.ED.208.

Finally, the green leaves on ED.207 were likely painted with a mixture of emerald green and a chromium-based pigment. Figure 16 shows the spatial distribution of copper, arsenic, and chromium in ED.207, revealing that all these elements were found in the green areas. XRD confirmed the presence of emerald green.

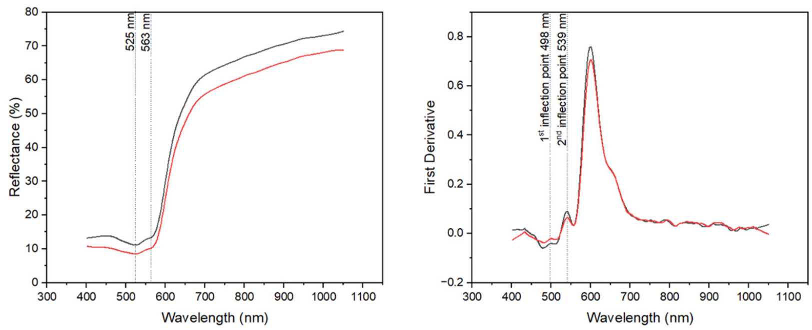

Figure 15. Reflectance spectra (**left**) and first derivative transformation (**right**) of two red areas on WA.RS.ED.207.

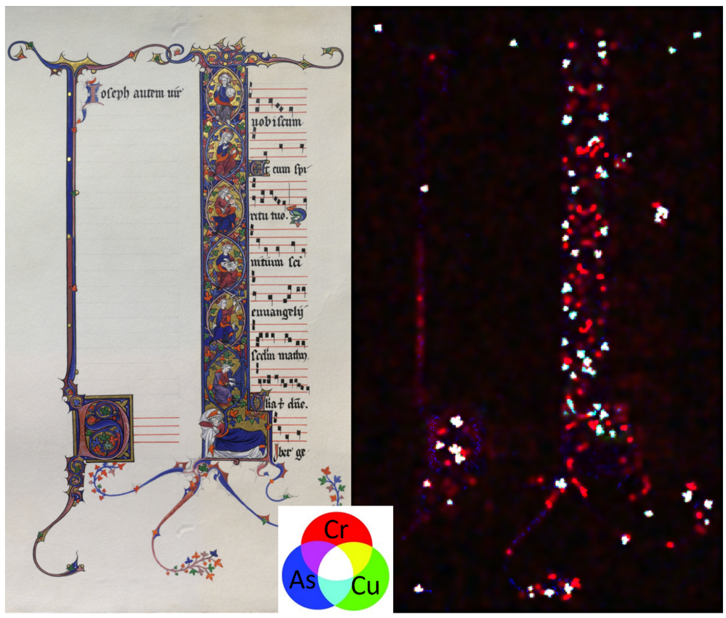

Figure 16. Visible image and macro-XRF map of chromium (red), arsenic (blue), and copper (green) obtained on WA.RS.ED.207.

4. Discussion

4.1. Capurro's Workshop: Emphasis on Modernity and Profitability

The original mural paintings in the Abu Simbel temple and the tombs of the Valley of the Kings were created using pigments such as red and yellow ochres, orpiment, Egyptian blue, azurite, and malachite [56]. However, these pigments were largely absent in the replicas under investigation, except for WA.RS.ED.177, where brown ochre and a copper-based blue pigment—likely corresponding to a modern equivalent of azurite—were used in restricted areas. Instead, the replicas were painted with a range of colours that included many new pigments introduced in the early 19th century due to scientific advancements, such as Prussian blue, barium white, emerald green, and cadmium yellow.

This discrepancy could stem from various reasons: the unavailability of specific historical painting materials, a lack of knowledge about the pigments used in Ancient Egypt, or other priorities influencing the choice of materials. In his *Manuale del pittore Restauratore*, published in 1866, Ulisse Forni included a list of pigments by colour and outlined their origin and preparation methods [37]. Ochres, orpiment, Egyptian blue, azurite, and malachite are all mentioned. Since Forni's manual was primarily intended as a practical handbook for restoration, it is likely that the materials listed were available in Italy, at least in the second half of the century. Furthermore, Italy extensively imported painting materials from leading colour manufacturers in England, France, and Germany, as it did not establish large-scale national colour manufacturing until the late 1910s [10,12,13,57–59]. Therefore, examining the broader European landscape could provide an additional perspective. In her extensive survey of 18th- and 19th-century English and French painting manuals and handbooks, Leslie Carlyle reports that ochres of all shades, orpiment, copper-based blue and green pigments, and Egyptian blue were all mentioned in the sources during the late 18th and early 19th century [23] (pp. 465–532).

Regarding the knowledge of historical painting materials circulating in Italy, it is challenging to determine whether Italian artists in the first half of the 19th century were familiar with ancient Egyptian pigments. In the latter half of the century, Forni noted that azurite, orpiment, Naples yellow, and calcium carbonate had been used since Antiquity, while he associated minium and ochres with the Greeks and Romans and Egyptian blue with the Egyptians. In his manual, he frequently referenced recipes on colour manufacture from ancient sources, such as Pliny, Vitruvius, and Theophrastus, which were certainly well-known in academic circles before the second half of the century [37]. However, the lack of accessible, dedicated publications on historical pigments likely prevented this knowledge from reaching beyond academic circles and into the workshops of publishing companies and other artisans before the 1860s.

Most importantly, the material choices involved in producing these replicas were likely driven by the primary goal of mass-producing them as book illustrations while maintaining the profitability of the final product. Therefore, the cost-effectiveness of materials very likely played a crucial role in determining the painting palette used. Table A3 reports the price of pigments across the 19th century, as shown in catalogues published by Winsor and Newton, Rowney, and Barnard between 1860 and 1897 as appendices of painting handbooks [60–72]. While not exhaustive, this table can provide a sense of the relative cost of painting materials in northern Italy, since the country consistently imported pigments from England [12,13,57–59]. It is worth noting that the pigments used in the replicas published in Rosellini's Atlas are among the cheapest, as observed by cross-referencing information in Tables A2 and A3. For instance, lead white, the cheapest white pigment for most of the century, was frequently found in colour mixtures on all the works analysed, while barium white, slightly more expensive, was used only in restricted areas of two prints. Similarly, the only blue found in these hand-painted engravings was Prussian blue, which was cheaper than other blue pigments such as cobalt blue or smalt. Vermilion, extensively used, was also cheaper than organic lakes, which were not detected.

4.2. Ruskin's Academic Circle: Traces of a Historical Approach

If the commercial publishers' approach to producing replicas and disseminating them across a broad public was guided by interests other than historical curiosity, the same does not seem to be true for other personalities associated with academia and the art business. For instance, John Ruskin himself, who deliberately included Capurro's prints in the collection he used to teach art at the University of Oxford, warned his students about the colours of these prints in the catalogue of the teaching collection and remarked: "Observe, respecting these plates of Rosellini, that the colours are in great part conjecturally restored—slight traces of the original pigments, and those changed by time, being interpreted often too arbitrarily [. . .] The student, therefore, can only depend on these plates for the disposition of the colours, not for their qualities". Ruskin's frustrated comment suggests that he believed replicas of Egyptian paintings should have been painted with the same hues of colour used originally and, perhaps, with the same materials as much as possible. Nevertheless, he was aware that this was no easy task to accomplish. In the passage quoted above, he went on to say: "The beauty or vulgarity of any given colour, much more that of its harmony with others, is determined by delicacies of hue which no restorer can be secure of obtaining, and few attempt to obtain" [42] (vol. 21, pp. 44–45).

Ruskin's influence on his academic circle is evident from the materials identified in the replicas of medieval illuminations by his students and his assistant, Laing. Chinese white was used extensively, often mixed with other colours, reflecting Ruskin's technique of mixing this white pigment with others to achieve richer colour layers, as he recommended in his writings [42] (vol. 15, p. 137). Another material trait of these watercolours is the use of more expensive pigments than those found on the replicas from Rosellini's atlas, as can be inferred once again by comparing the information in Tables A2 and A3. This suggests that the commercial price of pigments was not a pivotal factor in the material choices that Ruskin's circle made.

Moreover, these replicas must be contextualised within a much broader framework. In the second half of the 19th century, the art of illumination experienced a revival across Europe, a phenomenon that has so far received little attention [73,74]. Recognising the growing interest in painting replicas of medieval illuminations, English colourmen began collaborating with various authors—many of whom were artists and illuminators themselves—to produce manuals on the art of illuminating [65,67–69,75–79].

A few of these manuals reported lists of pigments used in medieval times, with one in particular going to great lengths to translate and discuss passages from medieval treatises such as those by Heraclius, Theophilus, and the Mappae Clavicula, convinced that this knowledge could be valuable to modern illuminators [75]. However, when discussing the materials suitable for 19th-century illumination, all the consulted handbooks encouraged amateurs to embrace modernity and practice illumination using contemporary materials and media, often on supports that extended beyond the traditional vellum used in the Middle Ages. To this end, they suggested a collection of pigments that included a broad range of recently discovered colours, such as cobalt blue, cadmium yellow, lemon yellow, chrome green, and emerald green. With this context in mind, a few interesting observations can be made, particularly about pieces ED.206 and ED.207.

ED.206 is dominated by bright blue, gold, and red tones, reflecting the common palette of medieval illuminations. Pure gold was used for the initials "M" and "E", a tribute to the Middle Ages and a standard practice in 19th-century illumination, with every modern manual consulted providing extensive instructions on its use. In contrast, the use of ultramarine for the blue area is a less obvious choice. The consulted manuals mentioned three to six different blue pigments. Ultramarine blue (natural or synthetic) and cobalt blue were mentioned in all of them, while smalt appeared frequently, and other blue pigments such as indigo or cerulean blue were noted occasionally. No manual specifically recommended ultramarine over other equally stable blue pigments such as cobalt blue and smalt. Furthermore, the use of minium suggests a historical interest that extends beyond the instructions found in modern manuals. This pigment was never found in Ruskin's watercolours, nor was it recommended in the lists of colours he advised his students to use [42] (vol. 15, p. 142), likely due to its poor durability [27]. Therefore, its presence in a watercolour by one of Ruskin's pupils is surprising. More broadly, minium had a terrible reputation in the 18th and 19th centuries because of its tendency to colour-shift, with several painting handbooks discouraging its use for this reason [23] (p. 510). Its use for modern illumination was mentioned only in one of the ten manuals consulted, which noted its liability to darken [69] (p. 28). Despite its poor stability, minium was probably used to pay homage to the pigments in medieval manuscripts, where it played a significant role in early black and red manuscript illuminations and remained on the illuminator's palette long after [80]. This historical significance was noted in a few of the manuals consulted [68,75,78].

As for ED.207, Laing's replica, blue and gold once again dominate the colour palette. However, rather than using ultramarine blue, Laing used a blue pigment with a modern origin, likely found on the market as "smalt". Instead, the striking finding in this watercolour is the preparation of the paper support with a mixture of calcium sulphate and other compounds. This practice was not reported in the consulted 19th-century manuals on illumination and has never been observed in 19th-century British watercolours, which were typically painted on untreated paper [81–83]. In contrast, the use of a mixture of calcium sulphate, carbonate, and other compounds—generally referred to as "gesso"—was mentioned in medieval recipes for parchment and bookmaking [84] (pp. 134, 147–148).

This pre-treatment was usually carried out by scribes before starting to write, in a stage previous to illumination aimed at reducing the greasiness of the parchment, enhancing the whiteness of the finished sheet, and providing a ground for the coloured decoration. Laing's engagement with this treatment (although performed on paper rather than parchment) shows that his knowledge extended beyond the instruction given in manuals on modern illumination to encompass medieval bookmaking practices at various stages. This indicates a proactive, deeper engagement with the materials and methods originally used in the Middle Ages. Since paper needs no treatment to reduce greasiness, it is possible that Laing experimented with this whitening technique to enhance colour vibrancy, a quality praised in 19th-century handbooks as a remarkable peculiarity of medieval illuminations.

5. Conclusions

This study characterised the pigments used in a collection of 19th-century watercolour replicas to determine whether the artists attempted to explore historically inspired painting materials when painting them. The replicas, reproducing ancient Egyptian mural paintings and medieval illuminated manuscripts, were created in two distinct contexts. The former, printed and hand-coloured by the Pisan publisher Niccolò Capurro, were part of the comprehensive atlas *I Monumenti Dell'Egitto e Della Nubia*, published by the Egyptologist Ippolito Rossellini. The latter were executed by John Ruskin's academic circle while he served as Slade Professor of Art at Oxford.

This research revealed that the replicas produced by Capurro's workshop in the early 1830s featured a range of modern pigments, such as Prussian blue, emerald green, cadmium yellow, and barium white. Archival research on pigment prices and the knowledge available in 19th-century Italy regarding ancient Egyptian pigments suggest that the primary reasons for the material choices behind these replicas were the profitability of the final product and a lack of systematic knowledge about ancient Egyptian materials outside academic circles in the first half of the century.

In contrast, research into 19th-century sources on painting materials and techniques indicated that knowledge of medieval material culture, particularly related to medieval illumination practices, was readily available in the 1860s and 1870s when the replicas of medieval manuscripts were produced. At this time, practical handbooks on the art of illumination circulated widely, encouraging the use of modern materials. Three of the analysed replicas, primarily painted with cobalt blue, smalt, emerald green, and zinc white, reflected this cultural context. However, two replicas showed evidence of a different approach. The use of ultramarine blue and minium on ED.206, and of chalk to prepare the support on ED.207, indicate a deeper engagement with medieval practices beyond mere aesthetics. These replicas seem to reflect Ruskin's own views on the accurate use of colour in reproducing historical subjects, which he briefly introduced in his *Catalogue to the Ruskin Art Collection at Oxford*.

In conclusion, this investigation revealed that, despite artists' dependence on industrial colour manufacture and the prevailing emphasis on progress throughout the century, some academic circles intentionally engaged with historically inspired materials and practices. These findings have likely just scratched the surface of a larger phenomenon, encouraging a more systematic investigation of 19th-century replicas. Further research on artworks by highly educated artists operating within restricted academic circles might uncover additional evidence of 19th-century engagement with historical material cultures.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage7080203/s1, Figure S1: X-ray diffractogram of the paper and cardboard frame, representative of all the watercolours except WA.RS.ED.207; Figure S2: X-ray diffractogram of cardboard frame of WA.RS.ED.207.

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Data Availability Statement: The datasets generated and analysed during the current study are available from the corresponding author upon reasonable request.

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Appendix A

Table A1. Date, accession number, and title of the watercolours analysed in this study.

#	Date	Accession n.	Producer	Title
1	1829-32	WA.RS.REF.176	Niccolò Capurro	Engraving of a relief of Ramesses II receiving suppliants
2	1829-32	WA.RS.REF.177	Niccolò Capurro	Engraving of a relief of the chariot of Ramesses II
3	1829-32	WA.RS.REF.179	Niccolò Capurro	Engraving of a painting of Merneptah adoring Re-Harakhti
4	1829-32	WA.RS.REF.180	Niccolò Capurro	Engraving of a painting of Ramesses III adoring Isis and Ptah-Sokar
5	1870?	WA.RS.ED.204	Anonymous	Drawing of an initial "I" from the Arnstein Bible
6	1860	WA.RS.ED.205	Anonymous	Drawing of an initial "N" from a twelfth-century illuminated manuscript
7	1860	WA.RS.ED.206	Anonymous	Drawing of an illuminated initial "M" and "C" from a manuscript of the late twelfth or early thirteenth century
8	1860	WA.RS.ED.207	John James Laing	Drawing of two illuminated initials from late thirteenth-century English or French manuscripts
9	1860-62	WA.RS.ED.208	John James Laing	Drawing of two illuminated initials from thirteenth-century French manuscripts

Table A2. Summary of pigments identified on the watercolours investigated with indication of the analytical method. A: macro-XRF; B: XRD; C: FORS.

	Red and Orange				Yellow					
#	**Vermilion**	**Ochre**	**Organic**	**Minium**	**Ochre**	**Organic**	**Lead Chromate**	**Barium Chromate**	**Cadmium Yellow**	**Strontium Chromate**	**Gold**
1	A, B						A				
2	A, B, C					A					
3	A, B, C			B		A			A	A	
4	A, B, C			B		A			A		
5	A, B				A						
6	A, B										
7		A		A					A		A, B
8	A, B		A				A?			A?	A
9	A, B							A			A

	Blue				Green		White		
#	**Prussian Blue**	**Cobalt-Based**	**Ultramarine**	**Azurite/Blue Verditer**	**Emerald Green**	**Chromium-Based**	**Zinc White**	**Lead White**	**Barium White**
1	A, C				A			B, C	
2	A, C			A	A, B			B, C	A
3	C							A, B, C	
4	A, C				A, B			B, C	A
5		A (Al, Co)			A, B	A	A, B		
6		A (Al, Co)			A		A, B		
7		A (Co)	A, B		A		A, B		
8		A (Al, P, Ca, Co), B			A	A	A, B	A, B	
9		A (Al, P, Ca, Co), B					A, B	A, B	

Table A3. Price of selected pigments (given in shillings—former English coin—per watercolour cake) as it appears on English colour manufacturers' catalogues found in painting handbooks [59–71]. The pigments are reported with the commercial name that appears in the sources consulted.

Pigment Name *	Composition/Source	Rowney 1846	W&N1852	W&N 1858	W&N 1860	Barnard 1860	Rowney 1861	W&N 1877	W&N 1879	W&N 1880?	W&N 1883	W&N 1897
Vermilion	Mercury sulphide	1	1	1	1	1	1	1	1	1	1	1
Ochre(s)	Iron oxide(s)	1	1	1	1	1	1	1	1	1	1	1
Minium	Lead oxide	1	1	-	1	-	1	-	-	-	-	-
Crimson lake	Cochineal insect	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Madder lake	Madder plant	3	3	3	3	3	3	3	3	3	3	3
Pink madder	Madder plant	3	3	3	3	3	3	3	3	3	3	3
Purple ditto	Madder plant	5	5	5	5	3	5	5	5	5	5	3
Carmine	Cochineal insect	5	5	5	5	5	5	3	3	3	3	3
Gamboge	Gamboge resin	1	1	1	1	1	1	1	1	1	1	1
Chrome yellow	Lead chromate	1	1	1	1	1	1	1	1	1	1	1
Lemon yellow	Barium/strontium chromate	2	3	3	3	-	2	3	3	3	2	2
Cadmium yellow	Cadmium sulphide	-	5	5	5	5	5	3	3	3	3	2
Prussian blue	Iron hexacyanoferrate	1	1	1	1	1	1	1	1	1	1	1
Indigo	Indigo plant	1	1	1	1	1	1	1	1	1	1	1
Blue verditer	Copper carbonate	1	-		-	-	1	-	-	-	-	-
Cobalt blue	Cobalt aluminate	2	2	2	2	2	2	2	2	2	2	2
French blue	Synthetic lazurite	2	3	3	3	3	2	3	3	3	3	2
Smalt	**	5	5	5	5	5	5	5	5	5	5	5
Ultramarine ash	Lazurite	-	5	5	5	-	5	5	5	5	5	5
Ultramarine	Lazurite	21	21	-	21	21	11	21	21	21	21	21
Emerald green	Copper acetoarsenite	1	1	1	1	1	1	1	1	1	1	1
Oxide of chromium	Chromium oxide	-	3	3	3	-	3	3	3	3	3	2
Viridian	Hydrated chromium oxide	-	-	-	-	-	-	3	3	3	2	2
Flake white	Lead carbonate	1	1	-	1	1	1	1	1	1	1	1
Chinese white	Zinc oxide	-	1.6	1.6	1.6	1.6	1.6	1	1	1	1	1
Constant/permanent white	Barium sulphate	1.6	1.6	-	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1

* For correspondence between colour, composition, and commercial name of pigments, we refer the reader to dedicated literature [23]. ** The composition of smalt was believed to be cobalt-tinted potassium glass until very recently. See Section 3.2.3.

References

1. Anonymous. The International Exhibition. *The Illustrated London News*, 5 July 1862; pp. 17–18.
2. Garfield, S. *Mauve: How One Man Invented a Color That Changed the World*; Faber and Faber: London, UK, 2000.
3. Winterbottom, M. 'The Triumph of Colour': The Synthetic Colour Revolution. In *Colour Revolution. Victorian Art, Fashion and Design*; Ashmolean Museum: Oxford, UK, 2023; pp. 86–101.
4. Fox, M.R. *Dye-Makers of Great Britain, 1856–1976: A History of Chemists, Companies, Products and Changes*; Imperial Chemical Industries: London, UK, 1987.
5. Katz, M.R. William Holman Hunt and the "Pre-Raphaelite Technique". In *Proceedings of the Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium*; Wallert, A., Hermens, E., Peek, M., Eds.; Getty Conservation Institute: Los Angeles, CA, USA, 1995; pp. 158–164.
6. Sheldon, L. Methods and Materials of the Pre-Raphaelite Circle in the 1850s. In *Proceedings of the Painting Techniques, History, Materials and Studio Practice*; Taylor & Francis: Dublin, Ireland, 1998; pp. 229–234.
7. Carlyle, L. Contemporary painting materials. In *Pre-Raphaelite Painting Techniques, 1848–1856*; Tate: London, UK, 2004; ISBN 978-1-85437-498-1.
8. Townsend, J.; Poulin, J. Painting: Materials and Methods. In *Holman Hunt and the Pre-Raphaelite Vision*; Lochnan, K.J., Jacobi, C., Eds.; Art Galley of Toronto: Toronto, ON, Canada, 2008; ISBN 978-1-894243-57-5.
9. Rinaldi, S.; Izzo, F.C.; Zanin, C. Ritorno alla tempera: Indagini scientifiche sui materiali dell'atelier di Mariano Fortuny y Madrazo nel contesto italiano del primo Novecento. In Proceedings of the Materiali D'artista. L'atelier del Pittore Nell'otto e Novecento; Edizioni della Normale: Pisa, Italy, 2015.
10. Bensi, P. La pittura italiana della fine dell'Ottocento e dei primi del Novecento tra tecniche innovative e ritorno alla tradizione. In *Dall'olio All'acrilico, Dall'impressionismo All'arte Contemporanea*; Selva Bonino, V.E., Ed.; Il Prato: Saonara (PD), Italy, 2016; pp. 27–31.
11. D'Ayala Valva, M. Documenti dall'archivio Lefranc. Il dossier Muzii. In *Dall'olio All'acrilico, Dall'impressionismo All'arte Contemporanea*; Selva Bonino, V.E., Ed.; Il Prato: Saonara (PD), Italy, 2016; pp. 41–49.
12. Rinaldi, S. Non solo olio: Colori in tubetto e sperimentazioni artistiche in Italia 1860–1935. In *Dall'olio All'acrilico, Dall'impressionismo All'arte Contemporanea*; Selva Bonino, V.E., Ed.; Il Prato: Saonara (PD), Italy, 2016; pp. 22–25.
13. Perusini, T.; Perusini, G.; Izzo, F.C.; Soccol, G. Le tempere di Mario de Maria, Cesare Laurenti, Guido Cadorin, Gennaro Favai e Felice Casorati: Riscontri tra documenti d'archivio, prove di ricostruzione e analisi scientifiche. In *Proceedings of the Tecnica della Pittura in Italia fra Ottocento e Novecento: Atti del Convegno, Venezia, Museo Fortuny, 23 March 2019*; Perusini, T., Ed.; Sargon Editore: Padova, Italy, 2021; pp. 125–166.
14. Richter, E.L.; Härlin, H. The Pigments of the Swiss Nineteenth-Century Painter Arnold Böcklin. *Stud. Conserv.* **1974**, *19*, 83–87. [CrossRef]
15. Peres, C.; Hoyle, M.; van Tilborgh, L. *A Closer Look: Technical and Art-Historical Studies on Works by Van Gogh and Gauguin*; Waanders Publishers: Zwolle, The Netherlands, 1991.
16. Townsend, J.H. Painting techniques and materials of Turner and other British artists 1775–1875. In *Historical Painting Techniques, Materials, and Studio Practice*; Wallert, A., Hermens, E., Peek, M., Eds.; Getty Conservation Institute: Los Angeles, CA, USA, 1995; pp. 176–185.
17. Favaro, M.; Bianchin, S.; Vigato, P.A.; Vervat, M. The palette of the *Macchia* Italian artist Giovanni Fattori in the second half of the 19th century. *J. Cult. Herit.* **2010**, *11*, 265–278. [CrossRef]
18. Callen, A. The Matter of Impressionism. In *The Art of Impressionism: Painting Technique and the Making of Modernity*; Yale University Press: Yale, CT, USA, 2018; ISBN 978-0-300-23813-6.
19. Alfeld, M.; Mösl, K.; Reiche, I. Sunset and moonshine: Variable blue and yellow pigments used by Caspar David Friedrich in different creative periods revealed by in situ XRF imaging. *X-ray Spectrom.* **2021**, *50*, 341–350. [CrossRef]
20. Carlyle, L. Authenticity and adulteration: What materials were 19th century artists really using? *Conservator* **1993**, *17*, 56–60. [CrossRef]
21. Townsend, J.H.; Carlyle, L.; Khandekar, N.; Woodcock, S. Later nineteenth century pigments: Evidence for additions and substitutions. *Conservator* **1995**, *19*, 65–78. [CrossRef]
22. Ayres, J. *Art, Artisans and Apprentices: Apprentice Painters & Sculptors in the Early Modern British Tradition*; Oxbow Books: Oxford, UK, 2014; ISBN 978-1-78297-743-8.
23. Carlyle, L. *The Artist's Assistant Oil Painting Instruction Manuals and Handbooks in Britain, 1800–1900, with Reference to Selected Eighteenth-Century Sources*; Archetype Publications: London, UK, 2001; ISBN 978-1-873132-16-6.
24. Smith, A. Revival and reformation: The aims and ideals of the pre-Raphaelite brotherhood. In *Pre-Raphaelite Painting Techniques*; Tate: London, UK, 2004.
25. Hunt, W.H. The present system of obtaining materials in use by artist painters, as compared with that of the old masters. *J. Soc. Arts* **1880**, *28*, 485–499.
26. Katz, M.R. Holman Hunt on himself: Textual evidence in aid of technical analysis. In *Looking through Paintings*; Hermens, E., Ed.; Uitgeverij de Prom: Baarn, The Netherlands; Archetype: London, UK, 1998; pp. 415–444.
27. Ghigo, T.; Occhipinti, M.; Beeby, A.; Domoney, K.; Bone, D. Concerns over colour durability in the nineteenth-century industrial revolution: Insights from John Ruskin's teaching collection. *Herit. Sci.* **2023**, *11*, 168. [CrossRef]

28. Cesaratto, A.; Luo, Y.-B.; Smith, H.D.; Leona, M. A timeline for the introduction of synthetic dyestuffs in Japan during the late Edo and Meiji periods. *Herit. Sci.* **2018**, *6*, 22. [CrossRef]
29. Manca, R. Non-Invasive, Scientific Analysis of 19th-Century Gold Jewellery and Maiolica. A Contribution to Technical Art History and Authenticity Studies. Ph.D. Thesis, Università Degli Studi di Firenze, Florence, Italy, 2021.
30. Mazzaferro, G. Il Libro dell'Arte di Cennino Cennini (1821–1950): Un esempio di diffusione della cultura italiana nel mondo. *Zibaldone. Estud. Ital. Torre Virrey* **2015**, *3*, 342–357.
31. Cennini, C. *Trattato della Pittura. Messo in Luce la Prima Volta con Annotazioni dal Cavaliere Giuseppe Tambroni*; Tambroni, G., Ed.; Paolo Salviucci: Roma, Italy, 1821.
32. Eastlake, C. *Materials for a History of Oil Painting*; Longman, Brown, Green, and Longmans: London, UK, 1847.
33. Merrifield, M.P. *Original Treatises: Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems*; J. Murray: London, UK, 1849.
34. Secco Suardo, G. *Sulla Scoperta ed Introduzione in Italia Dell'odierno Sistema di Dipingere ad Olio: Memoria*; G. Bernardoni: Milano, Italy, 1858.
35. Secco Suardo, G. Pensieri sulla pittura ad encausto, ad olio e a tempera. *L'Arte Ital.* **1870**, *69*, 82–119.
36. Secco Suardo, G. Alcune idee sulla pittura degli antichi. *L'Arte Ital.* **1872**, *65*, 81–100.
37. Forni, U. *Manuale del Pittore Restauratore*; Successori Le Monnier: Firenze, Italy, 1866.
38. Berger, E. *Beiträge zur Entwicklungs-Geschichte der Maltechnik*; G. D. W. Callwey: München, Germany, 1897.
39. Guareschi, I. *Sui Colori Degli Antichi*; Unione Tipografico-Editrice: Torino, Italy, 1905.
40. Doerner, M. *The Materials of the Artist and Their Use in Painting, with Notes on the Techniques of the Old Masters*; Harcourt Brace: New York, NY, USA, 1934; ISBN 978-0-15-657716-8.
41. Ghigo, T.; Bone, D.; Howell, D.; Domoney, K.; Gironda, M.; Beeby, A. Material characterisation of William Burges' Great Bookcase within the disruption of a global pandemic. *Stud. Conserv.* **2022**, *69*, 1–16. [CrossRef]
42. Ruskin, J. *The Complete Works of John Ruskin in 39 Volumes*; Cook, E.T., Wedderburn, A., Eds.; The Library Edition; George Allen and Unwin: Crows Nest, Australia, 1903.
43. Aceto, M.; Agostino, A.; Fenoglio, G.; Idone, A.; Gulmini, M.; Picollo, M.; Ricciardi, P.; Delaney, J.K. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. *Anal. Methods* **2014**, *6*, 1488–1500. [CrossRef]
44. Beeby, A.; Garner, L.; Howell, D.; Nicholson, C.E. There's more to reflectance spectroscopy than lux. *J. Inst. Conserv.* **2018**, *41*, 142–153. [CrossRef]
45. Biron, C.; Mounier, A.; Le Bourdon, G.; Servant, L.; Chapoulie, R.; Daniel, F. A blue can conceal another! Noninvasive multispectroscopic analyses of mixtures of indigo and Prussian blue. *Color. Res. Appl.* **2020**, *45*, 262–274. [CrossRef]
46. Bacci, M. UV-VIS-NIR FORS spectroscopies. In *Modern Analytical Methods in Art and Archaeology*; Ciliberto, E., Spoto, G., Eds.; J. Wiley: Hoboken, NJ, USA, 2000.
47. FitzHugh, E.W. (Ed.) *Artists' Pigments Vol. 3: A Handbook of Their History and Characteristics*; National Gallery of Art: Washington, DC, USA, 1997; ISBN 978-1-904982-76-0.
48. de Viguerie, L.; Pladevall, N.O.; Lotz, H.; Freni, V.; Fauquet, N.; Mestre, M.; Walter, P.; Verdaguer, M. Mapping pigments and binders in 15th century Gothic works of art using a combination of visible and near infrared hyperspectral imaging. *Microchem. J.* **2020**, *155*, 104674. [CrossRef]
49. Krotova, A.; Filatova, D. Investigation of three 20th-century Winsor and Newton colour charts by micro-XRF. In Proceedings of the MA-XRF scanning in Conservation, Art, and Archaeology Conference, Delft, The Netherlands, 26–27 September 2022.
50. Fonseca, B.; Schmidt Patterson, C.; Ganio, M.; MacLennan, D.; Trentelman, K. Seeing red: Towards an improved protocol for the identification of madder-and cochineal-based pigments by fiber optics reflectance spectroscopy (FORS). *Herit. Sci.* **2019**, *7*, 92. [CrossRef]
51. Langdon-Jones, E.E.; Pope, S.J. The coordination chemistry of substituted anthraquinones: Developments and applications. *Coord. Chem. Rev.* **2014**, *269*, 32–53. [CrossRef]
52. Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants: Theoretical Treatment and Empirical Rules*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2013; Volume 12.
53. Bisulca, C.; Picollo, M.; Bacci, M.; Kunzelman, D. UV-Vis-NIR reflectance spectroscopy of red lakes in paintings. In Proceedings of the 9th International Conference on NDT of Art, Jerusalem, Israel, 25–30 April 2008; pp. 25–30.
54. Reta, M.R.; Cartana, R.; Anunziata, J.D.; Silber, J.J. Solvatochromism of anthraquinone and symmetrical dihydroxy derivatives. Local interactions. *Spectrochim. Acta Part A Mol. Spectrosc.* **1993**, *49*, 903–912. [CrossRef]
55. Swenson, J.R.; Hoffmann, R. The Interaction of Nonbonding Orbitals in Carbonyls. *Helv. Chim. Acta* **1970**, *53*, 2331–2338. [CrossRef]
56. Nicholson, P.T.; Shaw, I. (Eds.) *Ancient Egyptian Materials and Technology*; Cambridge University Press: Cambridge, UK, 2000.
57. Bensi, P. Materiali e procedimenti della pittura italiana tra '800 e '900. Il progresso tecnologico nellaconfezione delle materie coloranti: Adozione delle novità o il suo rifiuto in nome della tradizione. *Ric. Stor. Dell'arte* **1984**, *24*, 75–79.
58. Gioli, A. Produttori e venditori di colori a Milano tra metà 800 e primo 900. In *Dall'olio All'acrilico, Dall'impressionismo All'arte Contemporanea*; Selva Bonino, V.E., Ed.; Il Prato: Saonara (PD), Italy, 2016; pp. 32–40.

59. Biadaioli, I. La pittura murale accademica all'inizio dell'Ottocento e la tecnica artistica di Gaspero Martellini (da un raro manoscritto dell'autore). *OPD Restauro* **2011**, 356–369.
60. O'Neill, H. *A Guide to Pictorial Art: How to Use the Black Lead Pencil, Chalks, and Water Colours*; Rowney: London, UK, 1846.
61. O'Neill, H. *A Guide to Pictorial Art: How to Use the Black Lead Pencil, Chalks, and Water Colours*; Rowney: London, UK, 1861.
62. Weigall, C.H. *Figure Drawing: Practical Instructions for a Course of Study in This Branch of Art*; Winsor and Newton: London, UK, 1852.
63. Penley, A. *A System of Water-Colour Painting*, 17th ed.; Winsor and Newton: London, UK, 1858.
64. Penley, A. *A System for Watercolour Painting*, 56th ed.; Winsor and Newton: London, UK, 1897.
65. Bradley, J.W. *A Manual of Illumination on Paper and Vellum; A Companion to Manual of Illumination*; Winsor and Newton: London, UK, 1860.
66. Bradley, J.W. *A Manual of Illumination on Paper and Vellum; A Companion to Manual of Illumination*, 22nd ed.; Winsor and Newton: London, UK, 1880.
67. Laurent de Lara, D. *Elementary Instruction in the Art of Illuminating and Missal Painting on Vellum: A Guide to Modern Illuminators*; Winsor and Newton: London, UK, 1860.
68. Jewitt, E. *Manual of Illuminated and Missal Painting*; J. Barnard: London, UK, 1860.
69. Audsley, W. *Guide to the Art of Illuminating and Missal Painting*; Rowney: London, UK, 1861.
70. Carmicheal, J.W. *The Art of Marine Painting in Watercolours*; Winsor and Newton: London, UK, 1877.
71. Duffield, W. *The Art of Flower Painting*; Winsor and Newton: London, UK, 1879.
72. Robertson, H.R. *The art of etching explained and illustrated*; Winsor and Newton: London, UK, 1883.
73. Hindman, S.; Rowe, N. *Manuscript Illumination in the Modern Age: Recovery and Reconstruction*; Mary and Leigh Block Museum of Art, Northwestern University: Evanston, IL, USA, 2001; ISBN 978-0-941680-21-9.
74. Cooman, T.; de Mayer, J. *The Revival of Medieval Illumination: Nineteenth-Century Belgium Manuscripts and Illuminations from a European Perspective*; Leuven University Press: Leuven, Belgium, 2007.
75. Wyatt, M.D. *The Art of Illuminating as Practised in Europe from the Earliest Times*; Day and Son: London, UK, 1860.
76. Lucien, H.M. *Hints on Illuminating with an Essay on the Art of Ornamenting in Gold or Metal*; Barnard & Son: London, UK, 1860.
77. Harrison, W.R. *Suggestions for Illuminating*; Barnard & Son: London, UK, 1861.
78. Shaw, H. *A Handbook of the Art of Illumination, as Practised during the Middle Ages*; Bell & Daldy: London, UK, 1866.
79. Ward, M. *A Practical Treatise on the Art of Illuminating: With Examples, Chromographed in Fac-Simile and in Outline, of the Styles Prevailing at Different Periods, from the Sixth Century to the Present Time*; Marcus Ward & Co.: London, UK, 1873.
80. Gameson, R.; Beeby, A.; Fiorillo, F.; Nicholson, C.; Ricciardi, P.; Reynolds, S. *The Pigments of British Medieval Illuminators: A Scientific and Cultural Study*; Archetype Publications: London, UK, 2023.
81. Townsend, J.H.; Ormsby, B.A. Blake's Painting Materials, Technical Art History, and the Legacy of G.E. Bentley Jr. In *Blake in Our Time*; Mulhallen, K., Ed.; University of Toronto Press: Toronto, ON, Canada, 2010; ISBN 978-1-4426-8711-0.
82. Mann, F. A "born rebel": Edward Burne-Jones and watercolour painting 1857–1880. *Burlingt. Mag.* **2014**, *156*, 657–664.
83. Mann, F. 'Opaque with a vengeance': Burne-Jones's later watercolours, 1880–1898. *Burlingt. Mag.* **2019**, *161*, 128–139.
84. Reed, R. *Ancient Skins, Parchments and Leathers*; Seminar Press: London, UK, 1972; ISBN 978-0-12-903550-3.

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