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Why Are the Early Gothic Murals in St. Jacob's Church in Ormož, Slovenia, Almost Entirely Black?

Anabelle Kriznar [1,2,*], Katja Kavkler [3] and Sabina Dolenec [4,5]

1 Department of Art History, Faculty of Arts, University of Ljubljana, 1000 Ljubljana, Slovenia
2 Department of Sculpture and Art History, Faculty of Fine Arts, University of Seville, 41003 Seville, Spain
3 Restoration Centre, Institute for the Protection of Cultural Heritage of Slovenia, 1000 Ljubljana, Slovenia; katja.kavkler@zvkds.si
4 Slovenian National Building and Civil Engineering Institute, 1000 Ljubljana, Slovenia; sabina.dolenec@zag.si
5 Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia
* Correspondence: akriznar@us.es

Abstract: In St. Jacob's parish church in Ormož, Slovenia, mural paintings from around 1350–1370 are partially conserved in the northeastern corner of the main nave. They are almost completely black, indicating a large-scale pigment degradation. They were studied as a part of a larger research project aiming to identify materials applied and their possible degradation. First, they were studied in situ, and next, extracted samples of plaster, pigments, and colour layers were analysed by optical microscopy, Raman spectroscopy, FTIR spectroscopy, SEM-EDS, and XRD. Haematite, green earth, malachite, azurite, and tenorite were identified, showing that azurite and perhaps also malachite degraded to black tenorite, probably due to their fine grinding and their application directly on the fresh plaster. The plaster is made with small and large amounts of aggregate with mostly quartz with some impurities, which makes it fragile. The original appearance of these murals was of bright blue and green colours.

Keywords: mediaeval mural painting; Slovenia; supports; pigments; colour changes; optical microscopy; Raman; FTIR; XRD

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1. Introduction

A nationwide project is being carried out in Slovenia, re-evaluating the already known mediaeval mural paintings studied by the previous generations of art historians [1,2] (with additional bibliography), and the new findings that emerged in the past few decades. The important new addition to such art historical studies is a systematic interdisciplinary approach, enriching stylistic and historical knowledge with information offered by natural sciences. The investigation of painting supports, pigments, techniques, and artistic procedures are carried out with different analytical techniques. Due to extremely rich mural painting heritage in Slovenia, the first part of this national project entitled *Transformations—from Material to Virtual. Digital Corpus of Mural Painting—New Dimensions of Medieval Art Research in Slovenia* is limited to murals from around 1220–1230 (the oldest known paintings) until around 1380. Among these, over 70 localities have been studied. Several mural cycles attract our attention, showing wide areas of darkened colours, which generally indicate degradation of lead, copper, or mercury-based pigments [3,4]. One of them especially stands out, being almost totally black, with some rests of greenish-bluish and red areas (Figure 1). There are no other similar cases found in the entire country.

The mural was discovered under a whitewash layer during restoration works in 1976–1978 [5,6] in the left corner of the main nave in St. Jacob church in Ormož, in northeastern Slovenia. The first church in Romanesque style was probably built around 1200 [6] when this area was taken from Hungarians by Frederic of Ptuj (Pettau) with the help of the German Order of Knighthood. The land around Ormož and Velika Nedelja was added to Styra and therefore, the church, donated to the German Order, fell under the jurisdiction of the Archdiocese in Salzburg. The first documentation regarding the building only dates from 127; between 1270–1280 it must have been enlarged and remodelled in a gothic style, under the German Order's patronage. By then, it was probably elevated to a parish church, while Ormož received its market rights around 1293 and its city rights in 1331, indicating its historical importance. The next larger architectonical adaptation must have happened between 1354 and 1375 when the northern chapel was added. In 1354, a daily early mass was established by Klara, countess of Gorizia, while in 1376, the St. Catherine altar is mentioned. The art historians consider these dates as the possible time span for the church remodelling [6,7]. Perhaps this is the time when the mentioned mural paintings were painted, according to their elegant, predominantly linear style.

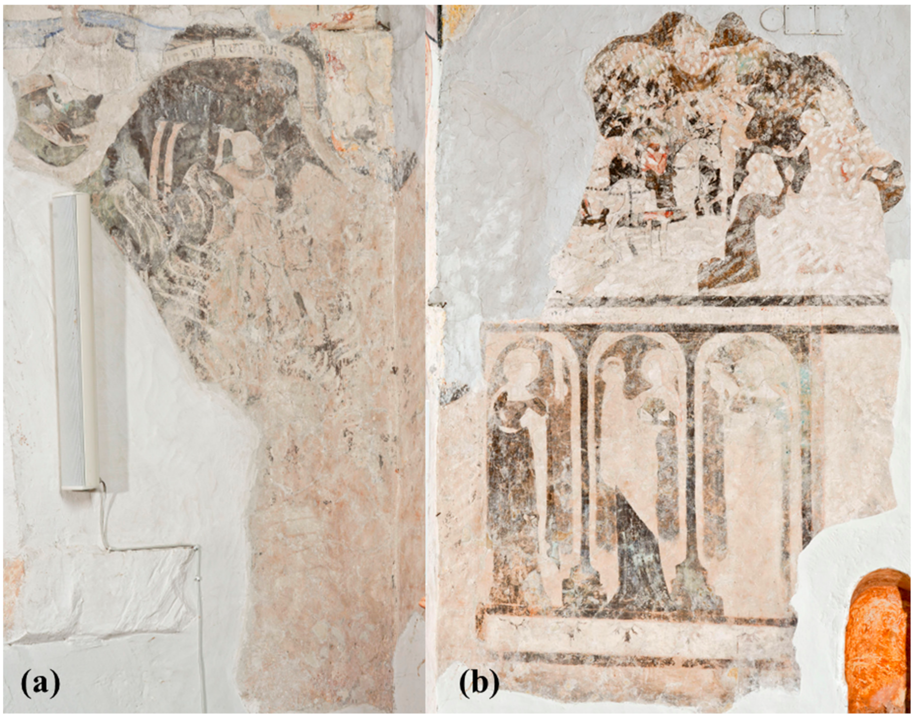

Figure 1. Darkened mural paintings presenting: (**a**) north wall: St. Martin's scene; (**b**) triumphal wall, upper band: Adoration of the Magi; lower band: four female saints. Northeastern corner of the main nave, St. Jacob's church, Ormož, Slovenia. Mid to 3/4 14th century. (Foto: ZRC SAZU).

The church went through several architectonical and painting remodels throughout the next centuries, becoming a large baroque building. It is worth mentioning that the enlargement of the Romanesque choir to a large gothic rib-vaulted presbytery occurred in the beginning of the 15th century, where, according to some headstones, the most important building workshop at the time, from Ptujska Gora, was working on this assignment [6,7]. This is an important fact, showing that the best artists were contracted for the construction and decoration of this church. Through centuries, the city and the church suffered several attacks and fires, and the interior of the church was repainted several times, covering older paintings.

The fragmentary preserved murals, presented in this research, formed part of a side altar, but there is no information about it. In 1376, an altar consecrated to St. Catherine is documented, but its description and location are unknown [6]. Furthermore, rests of a stone-carved gothic canopy altar were found on the triumphal wall [5–7]; one of these two altars was probably linked to these paintings. On the lower band of the triumphal nave wall, four female saints are depicted, each one in an illusionist niche with a semicircular arche, supported by thin columns. Through their attributes, two of them can be identified as Saint Margarete and Saint Agnes, while the other two are not sufficiently conserved for their recognition. On the upper band, a part of the Adoration of the Magi can be recognised. The oldest king is kneeling in front of the Virgin with Child, while in a rocky landscape behind him, two horses and a standing male figure in red (the younger king?) are presented (Figure 1b). On the northern wall, a fragment of a man turned backwards on a horse can still be deciphered (Figure 1a). It probably represents a scene from St. Martin's legend representing the saint sharing his coat with a beggar. Despite the bad conservation and colour changes, it reveals a highly skilled artist [2,8]. His style is fairly elegant, expressed through thin figures. Four female saints are characterised with long wavy hair falling down their shoulders, while their torsos are slightly inclined backwards; the St. Martin's figure shows a certain elegance as well, pointing towards the time around 1350–1370. We can observe a predominantly linear style before the incoming Italian influence in the last quarter of the 14th century. This is also supported by a typical 14th century bordure under the female saints, composed of triangles with acanthus leaves [1,2]. The author is anonymous, as are most of the artists in 14th century Slovenia; however, some stylistic and iconographic similarities can be drawn from several murals in Styria and Carinthia, namely in the churches of Oberzeiring, Deinsberg, and Lind [8].

It is important to mention that these murals were covered several times with newer layers of mural painting, as stated in the conservation report from 1977: "On the northern wall several paintings were observed. Most of them were conserved on the northern part of the triumphal wall, where also parts of the canopy altar were discovered" [5]. According to art historical studies, around 1400, the entire church was repainted. Only some fragments remain, and it is not clear whether the new layer covered the older 14th century murals nor if they were already altered by then. Furthermore, the triumphal wall was overpainted in the first half of the 16th century with figures of several saints, painted on a thin plaster. These were detached during the intervention works and transported to the restoration workshop of the Institute for Protection of Cultural Heritage in Maribor, Slovenia. Other paintings that cover the north, south, and triumphal walls of the nave can be dated from the 17th century, while in 1873 the local painter Jakob Brollo painted the entire interior. His paintings were removed in the 1970s due to their bad conservation state; only three parts of the detached Last Supper are exposed today in the presbytery [5,6].

The principal aim of this research was to find out what happened to the 14th century murals as well as why and when they turned black. For this purpose, besides the stylistic and historic re-evaluation, a material analysis was carried out. Samples of plaster, pigments, and paint layers were extracted in order to: (a) offer scientifically based information on materials (plaster, pigments, binders) and painting techniques (a fresco, a secco, lime, or mixed); (b) to study painting procedures (incisions, pouncing, preparatory drawings, underpaintings, colour modelling) applied by the artist; and (c) to understand the pigment changes.

2. Materials and Methods

The blackened mural paintings from 1350 to 1370 were first studied in situ by the naked eye and with the help of an external light source: a small hand-held lamp. Applied at different inclinations (raking light), it is possible to discern more clearly incisions and pouncing, surface imperfections, colour layer detachments, joints between giornatas, and the possible use of limewash. By this first visual exam, preparatory drawings, basic colour layers, and modelling were also studied. Next, from the areas of specific interest and where the state of the painting allowed it, tiny samples of plaster and colour layers were carefully extracted and documented (Figure 2). Altogether, 14 samples were taken. Among them, there are eight samples as follows: a very dark brownish colour layer (sample numbers ORM 2–6, 8, 10, and 12), three turquoise layers (ORM 1, 7, and 13), samples which are difficult to distinguish whether they are blue or green, one green (ORM 11), and one light pink (ORM 9). The last one (ORM 14) turned out to be just a sample of a brick in the wall; therefore, it was not analysed. Most of the colour layer samples were prepared as cross sections, embedded in epoxy resin, and studied under an optical microscope. Next, selected cross sections were analysed by Raman spectroscopy, while raw samples were analysed by Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). A plaster from the sample ORM 9 (the one that contained the most plaster among all the samples) was separated from the colour layers, ground, and studied with X-ray diffraction (XRD).

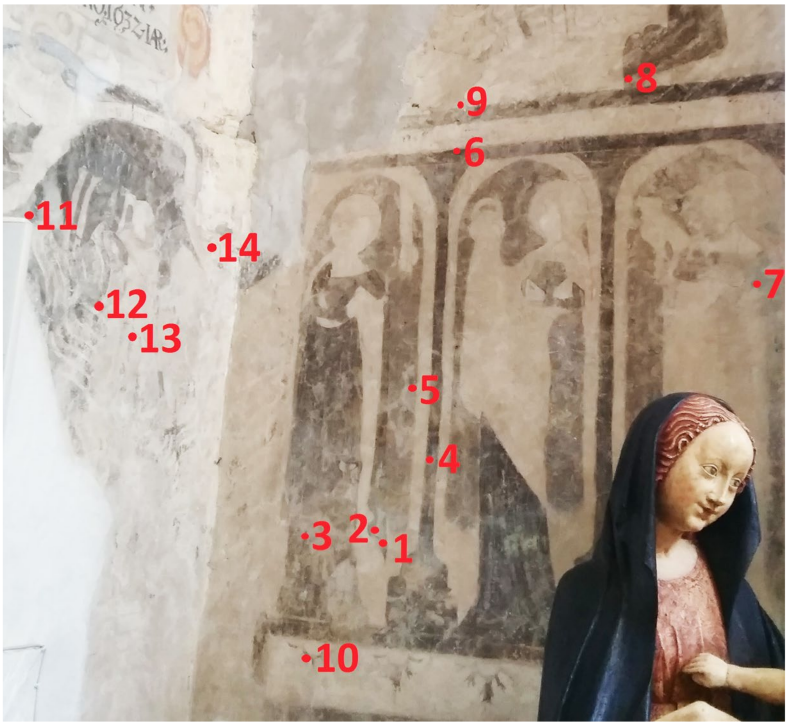

Figure 2. Sampling locations (consecutive numbers in red) on the mural painting, northeastern corner of the main nave, St. Jacob's church, Ormož, Slovenia. In the right lower corner, a part of a gothic sculpture Virgin with Child (1420–1430) by the recognised Workshop from Ptuj, normally situated in front of the murals.

Cross sections were analysed by an Olympus BX-60 microscope coupled to an Olympus SC50 digital camera, at 50× to 200× magnifications in reflected mode. Visible (VIS) and ultraviolet (UV) light were used on all samples. Plaster composition, colour layers and their sequence, and basic pigment characteristics and their chemical changes were explored with this technique; this also allowed us to discover possible limewash between plaster and/or colour layers.

For Raman analysis carried out on cross sections, a LabRAM HR800 spectrometer (Horiba Jobin-Yvon, Longjumeau, France) was applied, connected to an Olympus BXFM microscope (Tokyo, Japan). A laser with a 785 nm wavelength and a CCD detector were used. Spectra were scanned in the range between 80 cm^{-1} and 1800 cm^{-1} at a spectral resolution of 1 cm^{-1}, while time and filter were adapted to each sample point for better results. Calibration was performed using a Si crystal. Non-processed Raman spectra were interpreted by using NGSLabSpec 5.25.15 software (Horiba). Chemical composition of pigments, and in some cases their chemical changes, were identified.

When Raman results were not conclusive, FTIR spectroscopy and SEM-EDS were added to the analytical procedure. For FTIR, raw samples were used. Sample layers were previously separated by scalpel in order to divide paint layers from the mortar and to minimise cross-contamination between different layers. This is important to enhance paint layer signal compared to the mortar one. Samples were compressed in a diamond anvil cell and scanned in transmission mode with the 50 × 50 µm aperture. A FTIR Spectrum 100 spectrometer connected to a Spectrum Spotlight 200 microscope (PerkinElmer, Waltham, MA, USA) was selected. Spectra were scanned using a MCT detector in the range between 4000 cm^{-1} and 600 cm^{-1} with a spectral resolution of 4 cm^{-1}; 32 scans were averaged for each spectrum. Spectra were processed by using Spectrum 10.7.2.1630 software (PerkinElmer) and were baseline corrected and normalised before interpretation.

Due to different obstacles, only one raw sample could be analysed by SEM-EDS. The employed equipment is composed of an EVO 25 scanning electron microscope (Zeiss, Barcelona, Spain) with a 65 Ultim Max energy dispersive X-ray spectroscope (Oxford Instruments, Barcelona, Spain). The analysis was carried out at 25 kV of EHT energy and 20 μA current at 8.5 mm working distance. The sample was covered by carbon.

For plaster characterization and the identification of aggregate and binder, X-ray diffraction was applied. Raw plaster sample was ground and sieved through a sieve of 0.063 mm diameter, obtaining a particle size of less than 63 μm. The sample was then placed in a zero diffraction plate. A PANalytical Empyrean X-ray diffractometer (Malvern Panalytical, Malvern, UK) equipped with CuKα radiation and a PIXcel ID detector Malvern Panalytical, Malvern, UK) was used. The samples were measured at 45 kV at a current of 40 mA, in the range of 4° to 70° 2θ and step size of 0.013° 2θ with a scan step time of 68 s. X-ray diffraction patterns were analysed with X'Pert High Score Plus diffraction software v. 4.9 from PANalytical, supported by PAN IICSD v. 3.4 powder diffraction files.

3. Results

Material analysis identified plaster composition and several pigments, as well as offered a possible explanation for their darkening. The results obtained by the combination of different techniques are gathered in the Table 1. Despite combining several techniques, some questions remain unanswered and are open for discussion.

3.1. Plaster Characterization

When these murals were discovered in 1977, the conservation report stated that "In this area the construction is very rough, covered with thin, but also rough plaster. . .The oldest painting was made on a thin, polished wavy plaster, known as "gothic" [5]. We can truly observe an uneven surface and confirm the application of only about 3 mm thick plaster, best observed on several cracks that cross the plaster. Due to the fragmentary state of the paintings and many cracks in the plaster, it is difficult to discern joins between possible giornatas, which are daily plaster portions. Nevertheless, a thin joint between the lower and the upper plaster can be observed on the east triumphal wall of the nave, revealing that the upper scene with the Adoration of the Magi was painted before the lower one with four female saints; the lower plaster overlaps the upper one, indicating that the artist was working downwards. Keeping in mind the early gothic origin of these murals, it is indeed more likely that the older system of pontatas was applied. These are larger horizontal plaster portions that generally include the entire pictorial band of the wall [9,10].

All sample cross sections show a support rich in aggregate, but with less binder (Figure 3), which could cause the cracking of the surface and the relatively bad plaster consistence. This could also be due to its thinness. The sand grains are multicolour, and their granulation varies; large transparent and angular grains prevail, indicating that crushed sand with a lot of quartz was used. Raman analysis identified the presence of quartz, together with calcite and haematite. The plaster was applied on a wall containing bricks, as revealed by the brick sample ORM 14.

X-ray diffraction analysis of the ORM 9 sample reveals its mineral composition as observed on the XRD pattern (Figure 4). High quartz peaks compared to much lower calcite and dolomite peaks confirm a high amount of aggregate and less of the binder. There are also some impurities present, such as feldpars, illite/muscovite, and kaolinite. No limewash was found between the plaster and colour layers, as observed under an optical microscope.

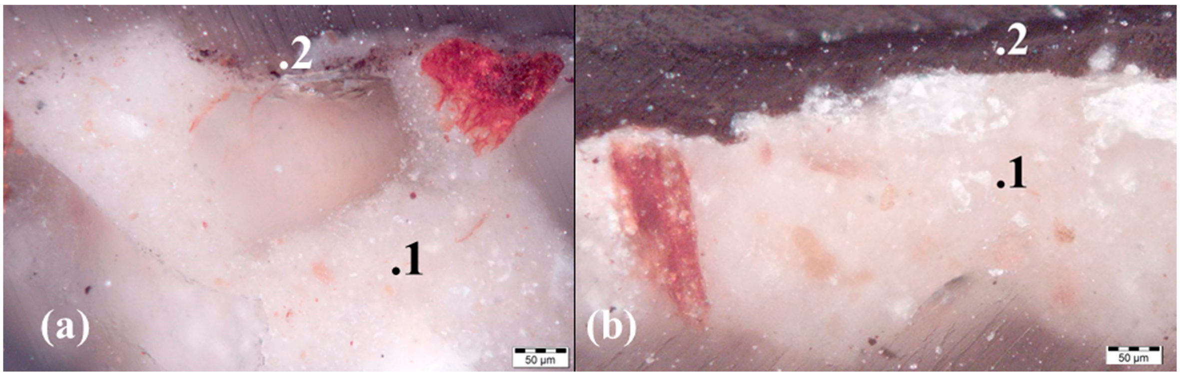

Figure 3. Microphotographs of sample cross sections: (**a**) ORM 9: plaster of lime and aggregate (1), grey-pink colour layer (2), bordure between the upper and lower pictorial band; (**b**) ORM 4: plaster of lime and aggregate (1), thick brown colour layer, copper pigment degradation (2), column between the first two female saints on the lower pictorial band. Triumphal wall of the nave, St. Jacob’s church, Ormož, Slovenia.

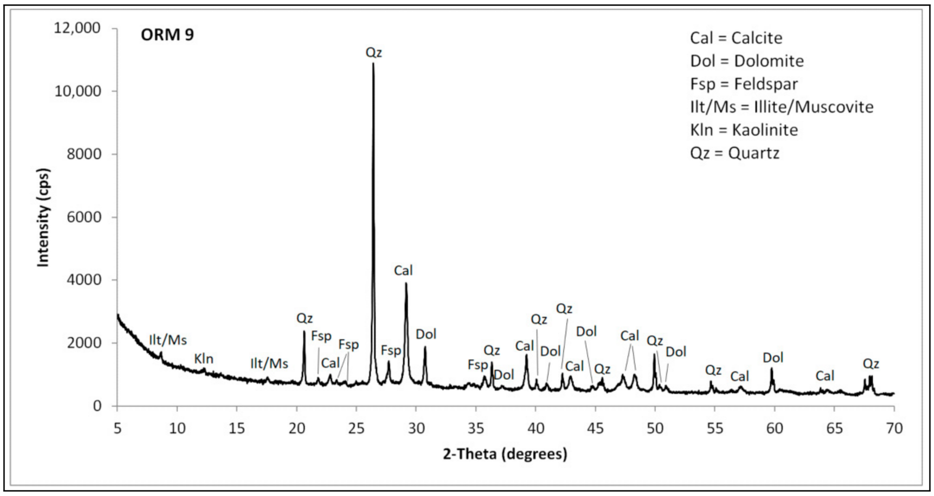

Figure 4. XRD pattern reveals a plaster made with a higher amount of aggregate and less binder, with some impurities. Sample from the pinkish soil, Adoration of the Magi, triumphal wall of the nave, St. Jacob’s church, Ormož, Slovenia.

3.2. Pigments and Their Chemical Degradation

Most of the colours have turned black, and only in some areas, turquoise, green, blue, and red colours remain (Figures 1b and 5). Turquoise colour can be found on a small area of the landscape on the Adoration of the Magi and on some areas on the vestments of the female saints, such as on the coats of the first and the third one, or on the tunic of the second one. Some turquoise rests are also still preserved on the north nave wall, on a fragmentary figure behind St. Martin. Furthermore, the architecture in the scene with the female saints (columns, bases) also reveals some turquoise parts, while the column between the first two saints still shows an intense blue colour. Red colour is still relatively well preserved on the dress of the male figure (younger king?) behind the horse on the upper band, on some areas of the Virgin’s tunic, on the hair of some figures, and under the blackened bordure between the upper and lower pictorial band. Red pigment was also used for underdrawings that can be clearly seen on several areas, especially on the figures of the female saints and on the bordures around them.

Figure 5. Areas of still conserved turquoise and bluish colour are marked with red rectangles. Female saint figures, lower pictorial band, triumphal wall of the nave, St. Jacob's church, Ormož, Slovenia.

Fourteen samples were extracted from several areas of the entire painting (Figure 2). All sample cross sections confirmed the colours observed in situ by the naked eye: very dark brownish colour, turquoise (blue or green?), green, and very light pink. No samples were taken from the red areas, since all areas of interest were too high to reach; we also tried to keep the sample number as low as possible, limiting their extraction to the specific question of pigment darkening. Red earth (iron oxides) was most likely used, which was identified added to other pigments in analysed cross sections. On cross sections of samples extracted from darkened colours, mostly a thick brownish-black colour layer is observed, applied directly on a fresh plaster (Figures 3b and 6). On some samples, some turquoise grains or an entire colour layer are still clearly seen (Figure 6a,c), pointing towards the use of azurite due to its colour and angular grain forms, distinguished under the OM. In one such sample (ORM 3), Raman analysis revealed that these grains are actually quartz particles, which also turn transparent under UV light as additional material proof (Figure 6b). Azurite used in these murals and identified by Raman (as explained further on) is actually finely grained, as can be observed on other cross sections (for example, Figure 6c), also maintaining its blue colour under UV light (Figure 6d).

A sample of green paint (ORM 11) taken from a larger area on the left side of the St. Nicholas scene on the north wall also reveals mostly small granulation of lighter and darker green particles, with some red and orange ones (Figure 7b). By the naked eye, on this part of the painting, we can easily distinguish two different greens (Figure 7a), a darker one from where this sample was extracted, and a lighter, more turquoise one used for the vestments of a figure marked with a red rectangle, which is similar to the one found on the triumphal wall (Figure 5). Two different pigments were clearly used.

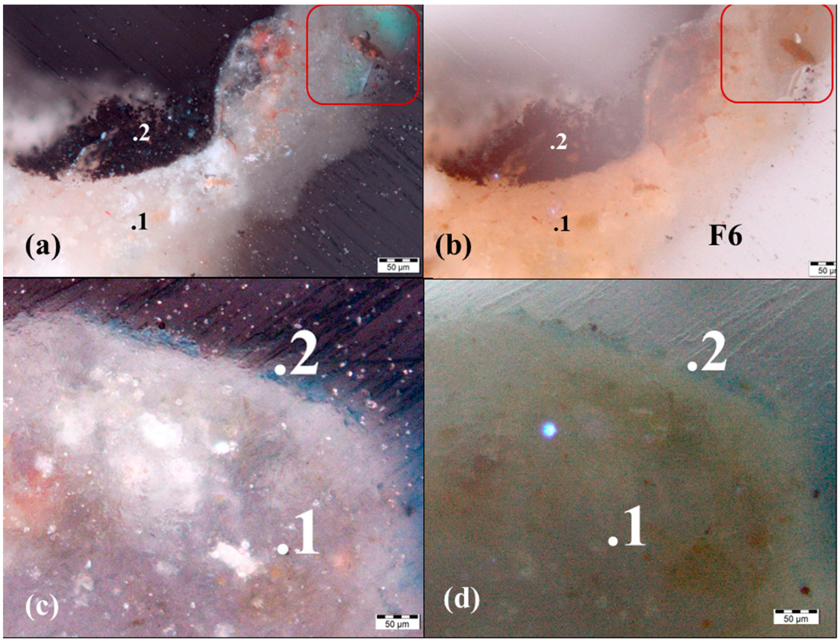

Figure 6. Microphotographs of sample cross sections: ORM 3: (**a**) in visible light and (**b**) in UV light. Lime-aggregate plaster (1) and a dark brownish colour layer of darkened copper-based pigment (2). Some turquoise angular grains (quartz) can be observed in the upper right corner, marked with red rectangle. Under UV light they turn transparent and were recognised as quartz by Raman spectroscopy. ORM 7 (detail): (**c**) in visible light and (**d**) in UV light. Lime-aggregate plaster (1) and a very thin blue colour layer applied directly on the support. Blue grains (azurite) do not turn transparent under UV light. Both samples from the first and third female saints' coats, respectively, lower pictorial band, triumphal wall of the nave, St. Jacob's church, Ormož, Slovenia.

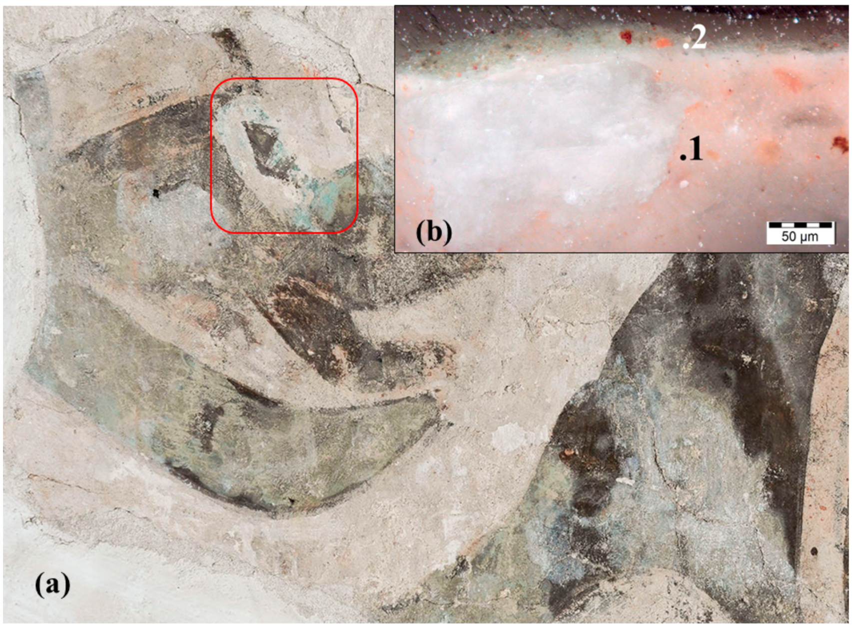

Figure 7. (**a**) Detail of St. Nicholas scene, north wall of the nave with two different green tones. Red rectangle marks a turquoise one. (**b**) Microphotograph of a sample cross section from the darker green area: lime-aggregate plaster (1), green colour layer with some red particles applied a fresco (2).

Raman results for the dark green colour were not conclusive, but SEM-EDS (Figure 8a,b) identified a mixture of green earth (Mg, Al, Si, K, Fe) and probably malachite (Cu), already degraded to atacamite or paratacamite (high Cl presence) [3,4]. We suggest the presence of malachite, since it is the principal (and Cu-based) green pigment used in mediaeval mural painting, besides the green earth [9,10]. A turquoise colour, as analysed on the samples from both walls (ORM 7 and 13), is identified by Raman as azurite with the main vibration at 400 cm^{-1} (Figure 9a) [11,12] and was confirmed by FTIR with the characteristic bands at 3425, 1500 to 1400, and 1100 to 800 cm^{-1} (Figure 9b) [13].

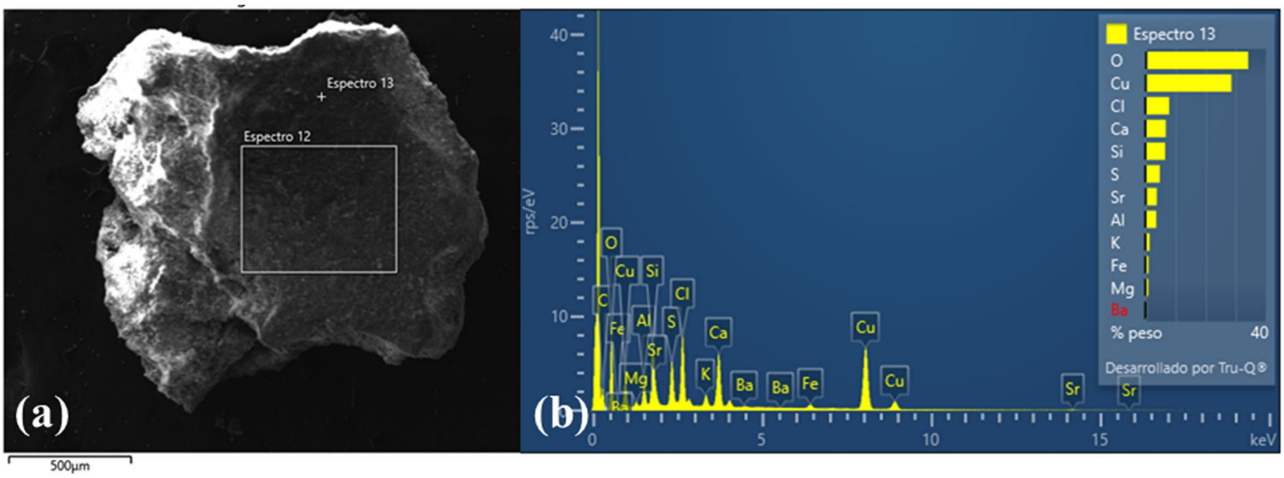

Figure 8. Raw sample ORM 11. (**a**) SEM image with marked point (13) and area (12) of EDS analysis; (**b**) EDS spectrum of the point analysis indicating the presence of green earth (Mg, Al, Si, S, K, Fe) and malachite (Cu) degraded to (para)atacamite (Cu, Cl). Sample from the green background, north wall of the nave, St. Jacob's church, Ormož, Slovenia.

Results of the blackened pigments by Raman and FTIR are not always conclusive, since not all of them offer vibrational information. Nevertheless, on several samples (ORM 3, 4, 6, 8, and 10; Figures 3b and 6a,b), tenorite was identified by its characteristic Raman vibrations at 300 and 600 cm^{-1} [11,12,14] (Figure 10).

The original pigment (azurite or malachite or both) was not identified, as all particles have already deteriorated. Some black areas do not give conclusive results on the type of black material (e.g., ORM 2). Only strong vibrations of quartz were observed in sample ORM 2, which could have originated from an unidentified pigment, filler, or plaster underneath the analysed paint layer. Typical vibrations of carbon black were not identified in either of the black samples, despite the dense black layer being analysed at a very high magnification; several pigments can be excluded: charcoal, soot, black coal, as well as silicate minerals with inclusions of charcoal [15]. In two samples (ORM 5 and 13), a vibration around 140 cm^{-1} was observed. Several different materials have a peak at this position: kaolinite, anatase, or lead oxides. Kaolinite was identified in the plaster (FTIR, XRD); therefore, this is the most probable interpretation. If the vibration originates from massicot, this is probably the degradation of plattnerite during Raman analysis [16]. However, despite decreasing laser power, no plattnerite (degradation product of lead-based pigments) was detected in the samples. In several samples (ORM 4 and 8), Raman identified haematite, confirmed by FTIR as an earth pigment by the presence of a silicate group (1030 cm^{-1}).

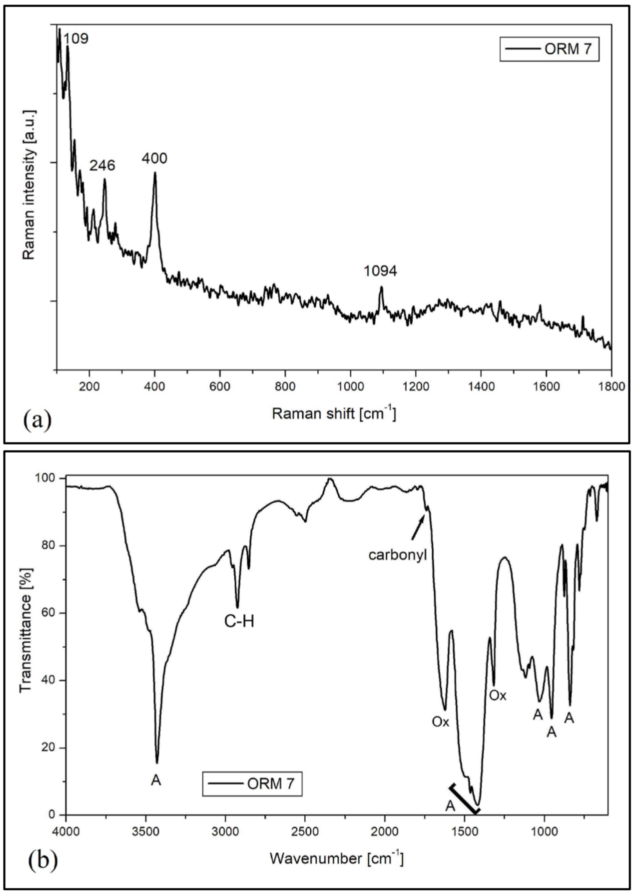

Figure 9. Sample ORM 7: (**a**) Raman spectrum identifies azurite with the main vibration at 400 cm^{-1} and additional bands at 81, 135, 180, 245, and 1094 cm^{-1}. (**b**) FTIR spectrum confirms azurite with bands at 3425, 1500–1400, 1030–1010, 950, and 830–815 cm^{-1} (marked with A) and shows a carbonyl band in the area 1700–1750 cm^{-1} and C–H stretching vibrations in the 2800–3000 cm^{-1} range that could indicate an organic binder or a later added consolidant. Additionally, bands for calcium oxalates were observed at 1600 and 1320 cm^{-1} (Ox). Sample from the pinkish soil, Adoration of the Magi, triumphal wall of the nave, St. Jacob's church, Ormož, Slovenia.

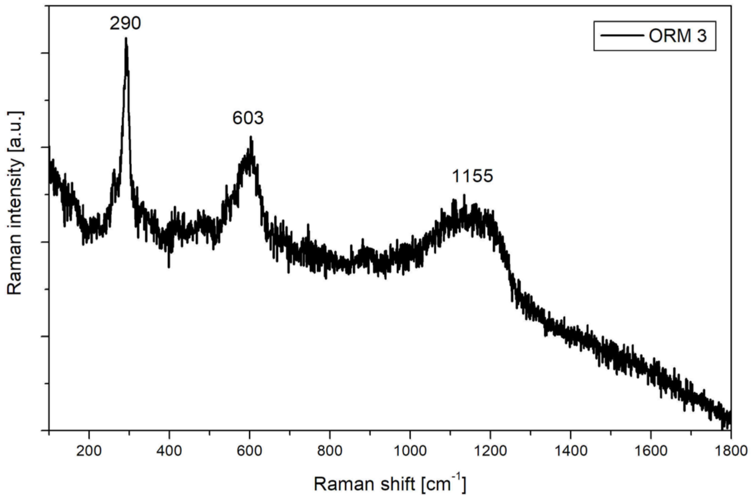

Figure 10. Raman spectrum of the sample ORM 3 identifying tenorite by its characteristic Raman vibrations at 300 and 600 cm^{-1}. Sample from the first female saint's coat, lower pictorial band, triumphal wall of the nave, St. Jacob's church, Ormož, Slovenia.

Table 1. Results obtained for each sample by different techniques, showing the importance of the combination of various procedures for more precise results. Sample 14 was prepared only as a cross section, but no chemical analyses were carried out, since it was just a brick with no colour layers.

Samples	Colour	Raman	FTIR	SEM-EDX	XRD
ORM 1	turquoise	calcite	calcite, calcium oxalate, silicates, carbonyl vibrations (weak)	-	-
ORM 2	black	quartz, calcite, no visible vibrations for black particles	calcite, kaolinite, calcium oxalate, aluminium oxide	-	-
ORM 3	black	tenorite, quartz, calcite, haematite	-	-	-
ORM 4	black	tenorite, calcite, maybe haematite	greasy tempera, silicates	-	-
ORM 5	grey	calcite, kaolinite	calcite, gypsum, silicates, carbonyl vibrations (weak)	-	-
ORM 6	black	tenorite	-	-	-
ORM 7	turquoise	azurite, calcite, quartz	azurite, calcite, calcium oxalate, carbonyl vibrations	-	-
ORM 8	black	tenorite, calcite, quartz, haematite, maybe moganite (503 cm^{-1})	calcite, gypsum, dolomite, calcium oxalate, probable silicates, calcium hydroxide	-	-
ORM 9	pink	-	-	-	quartz, calcite, dolomite, feldspar, kaolinite, illite/muscovite,
ORM 10	black	tenorite, calcite	calcite, calcium oxalate, silicates, carbonyl vibrations	-	-
ORM 11	green	kaolinite	-	O, Mg, Al, Si, S, Cl, K, Ca, Fe, Cu, Sr	-
ORM 12	black	calcite, kaolinite	calcite, gypsum, quartz, calcium oxalate, carbonyl vibrations	-	
ORM 13	blue	azurite, calcite	-	-	-
ORM 14	brick	-	-	-	-

3.3. Painting Technique

About half of the painted surfaces still conserve colour layers, while the other half lost them completely with only the plaster surface remaining. Colour modelling is also lost. This fact indicates that some areas were painted a fresco, on a fresh plaster layer, while others a secco, on the already dry surface. Cross sections of the extracted samples confirm that most of them were painted a fresco. The line between the plaster and the colour layer is blurred (Figures 3a,b, 6c, 7b and 11a), showing that the lime from the plaster penetrated through the colour layer, binding it through the carbonation process [9,10,17,18]. Nevertheless, some areas were painted on a partially or a completely dry plaster (Figures 6a and 11b), as indicated by quite a clear line between the support and the paint layer. Despite a fresco application, most of the colour layers are thick and dense, which points towards the addition of an organic binder, such as animal glue or casein. In several samples, FTIR discovered the presence of carbonyl vibrations in the area 1700–1750 cm^{-1} and C–H stretching vibrations in the 2800–3000 cm^{-1} range of an unidentified organic material (Figure 9b) that could indicate an organic binder or a later added consolidant. A secco painting with an organic binder must have been extensively used for all the modelling and the colours that are lost today.

3.4. Painting Procedure

Thin incisions were used to trace the haloes and the external head contours of the female saints, as well as their attributes (Figure 12a). It seems that their coats and the architectonical niches were also incised, but the lines are very thin and shallow and hence, not very clear. The painter must have used patterns, applied on fresh plaster that was still fresh. We would also expect incisions for St. Martin's figure on the north wall, being represented as a knight, but none were found. The preparatory drawing is clearly seen on the figures from the Adoration of the Magi and on several areas of the female saints, mostly their hands (Figure 12a); the painter used about a 0.5 cm thick brush and a red colour (red earth). The same red colour was applied for straight vertical and horizontal lines that divide the four arched niches, as observed next to the last (and lost) female saint where the colour layers are almost lost. They were performed by splashing a rope soaked in red colour on a wall, easily recognizable by a typical discontinuous line (Figure 12b). Perhaps these lines were first carried out with a rope and then incised, although this double procedure is not common in Slovene mediaeval mural painting. The colour modelling was carried out on the local basic tones, of which only some red, dark yellow, and blackened areas are conserved. All upper layers fell off; therefore, we cannot distinguish the formulation of the faces or draperies, which could tell us more about the author and would support a more precise stylistic characterization. We can just expose the long, elegant figures with oval heads, high foreheads, long chins, and somehow accentuated profile cheekbones (Figures 1 and 12a).

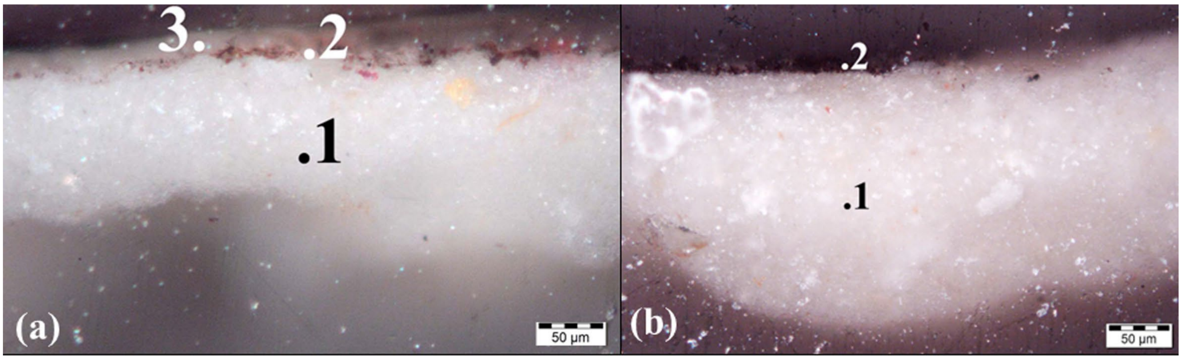

Figure 11. Microphotographs of sample cross sections: (**a**) ORM 12: lime from the plaster (1), red-brownish (probably degraded pigment) colour layer a fresco (2), white colour layer a fresco (3), St. Martin scene, north wall. (**b**) ORM 10: lime from the plaster (1), darkened colour layer (2), decoration bordure under the four female saints. Triumphal wall of the nave, St. Jacob's church, Ormož, Slovenia.

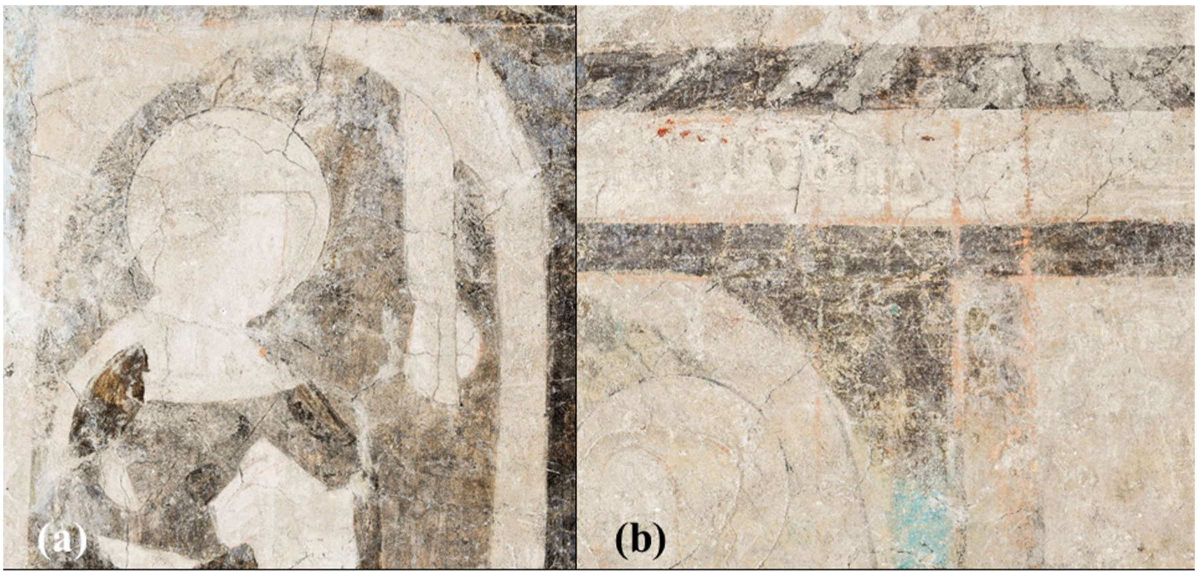

Figure 12. (**a**) Detail from the first female saint; incisions for her halo, head contour, and knife. The red underdrawing for her right hand is clearly seen. (**b**) Detail of the bordure between the last two female saints; signs of a pressed rope soaked in red colour are visible for vertical and horizontal lines. Lower pictorial band, triumphal wall, St. Jacob's church, Ormož, Slovenia.

4. Discussion

There are several pigments that can turn black due to different, mostly atmospheric, agents such as alkaline environment, the presence of sulphur, or heat. These are lead pigments (lead white, massicot or litharge, and minium), cinnabar or vermillion, and copper-based pigments such as azurite and malachite [3,4]. In the studied paintings in Ormož, the analysis of paint layers confirmed the use of haematite, green earth, malachite (Figure 8), as well as azurite (Figure 9). Nevertheless, there are no lead pigments or cinnabar/vermillion; at least, they are not conserved. In several samples of darkened colour, tenorite was identified (Figure 10) [11,12,14]. Black tenorite (CuO) is generally a degradation product of azurite ($2CuCO_3{\cdot}Cu(OH)_2$); however, malachite ($CuCO_3{\cdot}Cu(OH)_2$) can also change to tenorite, but normally this occurs after its degradation to paratacamite [3,19]. Paratacamite can also be a corrosion product of azurite. Although both copper-based mineral pigments are considered stable—especially malachite—they can suffer chemical changes due to various agents. Malachite can discolour when applied on a fresh plaster due to the alkaline pH of the lime binder. Both pigments can degrade to paratacamite or other copper hydroxychlorides ($Cu_2Cl(OH)_3$) such as atacamite, clinoatacamite, or botallackite due to the presence of chloride salts in the wall (Cl^- ions present in the plaster, sand, or in the bricks that can react with the basic carbonate). On the other hand, the darkening of tenorite can occur in an alkaline environment (e.g., a fresco painting) and/or due to the exposure to high temperatures (e.g., fire) [3,4,19]. Azurite and malachite can rarely turn bluish-black when exposed to H_2S vapours, especially in frescoes, forming covellite (CuS) [3]. However, in Ormož, Raman analysis did not find this compound.

The degradation is faster and more common when pigments are ground to fine, small particles, as is the case in this painting, according to cross sections (Figure 6c,d). These semi-precious expensive minerals were often ground to small grains in order to spend less of it; however, this causes colour intensity loss. For this reason, both pigments were generally underlaid with grey (veneda) or reddish (morello) colour layers to raise the colour intensity [9,10], as already suggested by Teophilus in the 12th Century [20] and by Cennino Cennini in the 15th Century [21]. In Ormož, we did not find such underlayers and pigments were applied directly on the plaster, as observed on sample cross sections (Figures 3, 6, 7b and 11). When applied directly on fresh plaster, the pigment particles must be small for the lime from the plaster to act as a binder. Sometimes, a small amount of an organic binder can be added to the pigment, suggested by FTIR analysis of some samples (Figure 9b). An experiment by Mattei et al. [22] researching the different behaviour of small-grained azurite applied a fresco or a secco revealed that the pigment painted on a fresh plaster turned to tenorite within 24 h, while no alteration was observed when painted on a dry surface. There was also no difference observed when azurite was mixed with animal glue as binder. The same experiment also established the transformation to tenorite below the particle size of 25 μm. This degradation does not necessarily occur fast, since it can depend on the progressive alteration of the alkalinity of the plaster, during which the OH^- ions are released. They react with the copper atoms present in the azurite or malachite molecules and first form copper hydroxide, which can transform into water and copper oxide, as pointed out already by Liberti in 1950 [23].

Therefore, the blackening of copper-based pigments in these murals could have occurred due to their direct application on a fresh plaster, very soon after they were finished. However, it is surprising that in such condition they would not be repaired/repainted soon after; cross sections do not reveal any overpaintings, but they could have been removed together with the upper layers of younger paintings during the intervention works in 1977–1978. An interesting fact mentioned in the restoration report is that Brollo's paintings from the 19th century were heavily darkened and that the binder was almost entirely degraded [5,6]. Perhaps this darkening has the same causing agent as the murals subject to this study and these darkened much later. However, since in this case we have no information on the Brollo's painting technique, it could be a result of the degradation of one of the organic materials, such as the binder.

It is worth taking into consideration other possible causes for the transformation of copper-based pigments into tenorite, such as the heat. Some experimental studies confirmed that the thermal decomposition of azurite takes place in six stages: at 205 °C, 321 °C, 332 °C, 345 °C, 362 °C, and 842 °C [24,25]; this establishes the crucial temperature to be above 300 °C [25] or, more specifically, at 384 °C [26]. In order for this to occur on mural paintings, a fire must break out. Historic documents mention several fires in Ormož. The first known fire happened in 1487 when the emperor Frederic III of Habsburg burned down the city during the battle for the land that once belonged to the noble Styria family of Ptuj (Pettau) after the last member, Frederic IX, had died. During this fire, the church was heavily damaged and it is very likely that the mural paintings suffered. Other city fires are documented in 1647, 1704, and 1778, but it is not clear whether the church was also captured by the flames [6]. In any case, the darkening of Brollo's paintings that could have been connected to the darkening of the gothic ones could not be a result of a fire since they were made much later. Therefore, their degradation must also have been the result of the interaction with the support or other biological and/or atmospheric agents.

Another cause of darkening could be the alteration of organic materials, such as the binder [3,16,27,28]. As seen in the Results section, a possible organic binder was suggested by FTIR analyses, however we cannot confirm that it is an original material. According to previous studies, azurite mixed with animal glue changes to green and yellow hues due to conformational structural changes in the binder [27]. Therefore, glue was probably not the binder in these murals. If azurite is mixed with egg tempera, the pigment–binder interaction lowers the thermal stability of the pigment. When exposed to NO_x/SO_x pollutants, nitrates/nitrites and sulphates can form on the surface of the paint [25]. However, darkening is most frequently documented as degradation of Cu-containing glazes based on oils, resins, and proteins [19]. Therefore, the darkening in Ormož could have also occurred—besides the transformation of copper-based pigments to tenorite—because of the alteration of a hypothetical protein binder added to those pigments.

Having all three possibilities in mind, the most probable cause of the darkening is the degradation of basic copper carbonates (azurite and malachite) to tenorite due to their small granulation and their direct contact with the alkaline plaster. However, the fact that they must have been mixed with an organic protein binder, probably egg yolk, could have attributed to this large blackening as well.

Similar blackened colours but limited to selected areas such as the coats of holy figures, haloes, banners, etc, were found on gothic murals in two other locations in northern Slovenia: in the subsidiary church in Ribičje and the subsidiary church of Mary on the Stone in Vuzenica, where some faces also turned black. The analysis of black vestments in Vuzenica revealed a combination of azurite and a lead-based pigment, whereas in Ribičje there were no conclusive results. In Vuzenica, we cannot be sure whether the blackening of the original colour happened due to the degradation of azurite or lead-based pigment, which is more common and happened on the aforementioned faces. The question for all these murals, but especially in Ormož where almost all colours changed to black, remains: how did these paintings look originally? Answering this question seems even more difficult, since we cannot distinguish between the original blue and green areas, while many of the other coloured areas are lost. Our best suggestion is that the black vestments were blue or green, the figures were situated in front of a light blue background, while the landscape must have been in different green hues.

5. Conclusions

Early gothic mural paintings in the nave of St. Jacob´s church in Ormož, Slovenia (1350–1370) are almost totally black. The principal objective of this research was to discover why and when they degraded to this point, as they are a unique case in Slovenia. After a detailed study in situ, several samples, mostly from the blackened areas, were extracted and studied as cross sections under an optical microscope. Most samples were then analysed by Raman and FTIR spectroscopy and one by SEM-EDS to identify pigments and possible chemical changes, while XRD was used for plaster characterization. Analyses identified a plaster made of a high quantity of aggregate—mostly quartz—with some impurities, and a lower quantity of binder (lime), resulting in a relatively bad plaster consistency. As pigments, haematite, green earth, malachite/(para)atacamite, azurite, and tenorite were identified. Furthermore, an organic material was identified by FTIR that could present a binder added to pigments or a consolidant applied in later interventions. Based on these results, we can conclude that the blackening is caused by degradation of copper-based pigments (probably mostly azurite) to tenorite, which can occur in an alkaline environment (e.g., a fresco painting) and/or due to the exposure to high temperatures (e.g., fire). Keeping in mind these pigments' small granulation and their direct application on fresh plaster without any underpainting, this situation seems to be the most probable cause for the alteration of the copper-based pigments. Although historically, some fires are documented in Ormož as a possible source of high temperatures that could have damaged the paintings. There is also the possibility that the addition of a protein organic binder influenced the final blackening of the paintings. On the other hand, malachite (and perhaps also azurite before turning to tenorite) degraded to copper hydroxychloride, probably paratacamite, as a result of chloride salts in the wall. Similar cases of blackened pigments but limited only to some special areas such as vestments, haloes, or banners were found in two other churches in northern Slovenia, but at least in one of the churches, azurite was mixed with lead-based pigment; its degradation is probably the cause of blackening. Obtained information can help us to visually reconstruct the original aspect of Ormož murals, showing intense blue and green colours. The results are an important part of the larger nationwide project dedicated to the art historical and material re-evaluation of mediaeval murals that is currently going on in Slovenia.

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References

1. Stelè, F. *Gotsko Stensko Slikarstvo [Mediaeval Mural Painting]*; Ars Sloveniae; Mladinska knjiga: Ljubljana, Sovenia, 1972.
2. Höefler, J. *Srednjeveške Freske v Sloveniji: Vzhodna Slovenija [Mediaeval Frescoes in Slovenia: Eastern Slovenia]*; Družina d.o.o.: Ljubljana, Slovenia, 2004; pp. 13, 146–148.
3. Cocciato, A.; Moens, L.; Vandenabeele, P. On the stability of mediaeval inorganic pigments: A literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments. *Herit. Sci.* **2017**, *5*, 12. [CrossRef]
4. Feller, R.L.; Roy, A. *Artist's Pigments. A Handbook of Their History and Characteristics*, 2nd ed.; National Gallery of Art: Washington, DC, USA; Archetype Publication: London, UK, 2012; Volumes 1 and 2.
5. Mikuž, J. Ormož. Conservation report. *VS* **1977**, *21*, 355–357.

6. Vnuk, B. Stavbnozgodovinski razvoj ormoške župnijske cerkve [Buiding and historical development of the parish church in Ormož]. In *Ormož skozi Stoletja [Ormož through Centuries]*; Hernja Masten, M., Korpič, N., Kresnik, Z., Eds.; Občina Ormož: Ormož, Slovenia, 2005; Volume 2, pp. 592–618.
7. Peskar, R. Arhitektura in Arhitekturna Plastika okrog Leta 1400 in Slovenija [Architecture and Architectural Sculpture around the Year 1400 in Slovenia]. Ph.D. Dissertation, Faculty of Arts, University of Ljubljana, Ljubljana, Slovenia, 2005; pp. 235–239.
8. Zimmermann, T. Stensko Slikarstvo Poznega 13. in 14. Stoletja na Slovenskem [Mural Painting of the Late 13th and 14th Centuries in Slovenia]. Ph.D. Dissertation, Faculty of Arts, University of Ljubljana, Ljubljana, Slovenia, 1996; pp. 84, 92, 163, 205.
9. Knoepfli, A.; Emmenegger, O.; Koller, M.; Meyer, A. *Reclams Handbuch der Künstlerischen Techniken*; Wandmalerei, Mosaik; Philip Reclam jun.: Stuttgart, Germany, 1990; Volume 2.
10. Mora, P.; Mora, L.; Philippot, P. *La Conservazione delle Pitture Murali*, 11th ed.; Editrice Compositori: Bologna, Italy, 2001.
11. Bell, I.M.; Clark, R.J.H.; Gibbs, P.J. Raman spectroscopic library of natural and synthetic pigments (pre-1850 AD). *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1997**, *53*, 2159–2179. [CrossRef] [PubMed]
12. Bouchard, M.; Smith, D.C. Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2003**, *59*, 2247–2266. [CrossRef] [PubMed]
13. Azurite. *Database of ATR-FT-IR Spectra of Various Materials: ATR-FT-IR Spectra of Conservation-Related Materials in the MID-IR and FAR-IR Region*; Institute of Chemistry, University of Tartu: Tartu, Estonia, 2024. Available online: https://Spectra.Chem.Ut.Ee/Paint/Pigments/Azurite/ (accessed on 3 April 2024).
14. Svorová Pawełkowicz, S.; Rohanova, D.; Svora, P. Gothic green glazed tile from Malbork Castle: Multi-analytical study. *Herit. Sci.* **2017**, *5*, 27. [CrossRef]
15. Spring, M.; Grout, R.; White, R. 'Black earths': A Study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century. *Natl. Gallery Tech. Bull.* **2003**, *24*, 96–114.
16. Costantini, I.; Lottici, P.P.; Castro, K.; Madariaga, J. Use of Temperature Controlled Stage Confocal Raman Microscopy to Study Phase Transition of Lead Dioxide (Plattnerite). *Minerals* **2020**, *10*, 468–487. [CrossRef]
17. Piovesan, R.; Mazzoli, C.; Maritan, L. Fresco and Lime-paint: An experimental Study and Objective Criteria for distingushing between these painting techniques. *Archaeometry* **2012**, *4*, 723–736. [CrossRef]
18. Ragazzoni, L.; Cavallo, G.; Biondelli, D.; Gilardi, J. Microscopic analysis of wall painting techniques: Laboratory replicas and romanesque case studies in Southern Switzerland. *Stud. Conserv.* **2018**, *63*, 326–341. [CrossRef]
19. Švarcová, S.; Hradil, D.; Hradilová, J.; Čermáková, Z. Pigments—Copper-based greens and blues. *Archaeol. Antrhopol. Sci.* **2021**, *13*, 190–219. [CrossRef]
20. Theophilus. *On Diverse Arts. The Foremost Medieval Treatise on Painting, Glassmaking and Metalworking*; Hawthorne, J.G., Smith, C.S., Eds.; Dover: New York, NY, USA, 1979.
21. Broecke, L. *Cennino Cennini's Il Libro Dell'arte. A New English Translation and Commentary with Italian Transcription*; Archetype Publication: London, UK, 2015.
22. Mattei, E.; de Vivo, G.; de Santis, A.; Gaetani, C.; Pelosi, C.; Santamaria, U. Raman spectroscopic analysis of azurite blackening. *J. Raman Spectrosc.* **2008**, *39*, 302–306. [CrossRef]
23. Liberti, S. Sulle alterazioni deli dipinti murali. *Boll. ICR* **1950**, *3–4*, 31–45.
24. Frost, R.L.; Ding, Z.; Kloprogge, J.T.; Martens, W.N. Thermal stability of azurite and malachite in relation to the formation of mediaeval glass and glazes. *Thermochim. Acta* **2002**, *390*, 133–144. [CrossRef]
25. Rickerby, S. Heat alterations of pigments painted in the fresco technique. *Conservator* **1991**, *15*, 39–44. [CrossRef]
26. Cardell, C.; Yebra-Rodríguez, A.; Álvarez-Lloret, P.; Guerra, I.; Martín-Ramos, J.D. An in situ X-ray powder thermodiffraction study of azurite decarbonation. *Macla* **2009**, *11*, 47–48.
27. Cardell, C.; Herrera, A.; Guerra, I.; Navas, N.; Simón, L.R.; Elert, K. Pigment-size effect on the physico-chemical behavior of azurite tempera dosimeters upon natural and accelerated photoaging. *Dye. Pigment.* **2017**, *141*, 53–65. [CrossRef]
28. Odlyha, M.; Cohen, N.S.; Foster, G.M.; West, R.H. Dosimetry of paintings: Determination of the degree of chemical change in museum exposed test paintings (azurite tempera) by thermal and spectroscopic analysis. *Termochim. Acta* **2000**, *365*, 53–63. [CrossRef]