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Materials and Techniques of Selected Mural Paintings on the "Gothic Road" around 1400 (Slovakia)

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Abstract: Mural cycles in the churches of Plešivec, Čhyžné, and Štitnik from around 1400 were studied from the material and technical point of view. Stylistically, they show a mixture of Northern and Southern European stylistic currents, which were characteristic for the time around 1400 in East Central Europe. After a precise study in situ, an analysis of extracted samples was conducted by OM, SEM-EDX, and XRD. The plasters used for these murals were all made of lime and sand with different impurities; importantly, they different among each other in terms of their quality and stability. The pigments that were used in these murals were natural and organic: lime white, yellow and red earths, malachite, and azurite were identified, and some pigment degradations were also pointed out. The principal technique is *a fresco*, but all murals were finished *a secco* in different proportions, using an organic binder. Painting procedures and modelling were also studied, revealing a strong difference among all three cycles. The painting technique does not always correspond to the style.

Keywords: medieval mural paintings; plasters; pigments; painting techniques; material analysis

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1. Introduction

Around 1400, the geographical area of East Central Europe (Austria, Slovakia, Hungary, Slovenia, Croatia) was an important crossroad between political, economic, social as well as cultural and artistic currents from Northern and Southern Europe. This situation can be clearly observed through the complex style of contemporary artworks as well as in their technical execution and in the use of materials and painting procedures. The present research is centred on mural paintings in Slovakia, which provide a very good example of what was happening around 1400. It is a part of a wider project that is still going on that investigates the entire area mentioned above. Conserved artworks reveal a mixture of influences from the North—Bohemian, Hungarian, and Austrian art, as well as from the South, especially Italian Trecento, both of which are incorporated into the local style. This diverse artistic language can be appreciated in selected mural paintings from several localities in Slovakia, with a special interest on those found along the so called "Gothic road" in the area of Rožňava/Gemer: the former St. George church in Plešivec (1370-80), the church of St. Mary's Annunciation in Chyžné (end of the 14th and beginning of the 15th centuries), and in the Evangelical church in Štitnik (beginning of the 15th century), as the best examples.

There is no direct stylistic connection among the three of them, but they all show strong Italian Trecento influence. A lot has been published about the style and history of all three monuments, especially in Slovak literature [1–4]. In Plešivec, the whole presbytery is decorated with murals, and some fragments have also been discovered in the nave. In this research, only paintings in the presbytery have been taken into consideration. They count among the best examples of gothic art in Slovakia. In the presbytery, scenes from *Christ's childhood* and *Passion* are depicted, and these paintings were completed by two different

painters. On the north wall, a high-quality artist strong in the Italian Trecento tradition was active (Figure 1a), while on the south wall, a local painter of lower artistic quality was working and combining northern and southern influences (Figure 1b). The difference in their quality can be well observed not only from their style, but also from their painting technique and modelling, as explained in the Results section. Paintings in the presbytery were partially discovered and restored in 1977–1978 [2]; their full discovery was achieved in 2014, and the murals are being currently restored by P. Koreň.

Figure 1. Conserved paintings on the (**a**) north presbytery wall showing Italian Trecento influence and (**b**) on the south presbytery wall revealing Central-Northern European and local tradition. Red arrow points towards the *giornata* line. Plešivec.

The presbytery in Chyžné (Figure 2) was also entirely painted with murals, with *Christ's childhood* presented on the upper layer and the twelve Apostles on the lower layer of the walls, while on the ceiling, symbols of four Evangelists and four Church fathers are depicted. In addition, some other scenes such as *Imago Pietatis* or *Parabola of ten virgins* can be found. In the nave, the mural paintings are not preserved. The artist shows Italian Trecento influence, especially Rimini reminiscence [1,5,6], although with a strong local note. The church in Štítnik is covered with mural paintings from different periods between the 14th and the 16th centuries. In this research, the murals on the north side nave were chosen according to their style and date. On the upper layer of the north wall, *St. Barbara* and *Volto Santo* are presented, which were completed at the end of the 14th century by a painter with a strong Italian influence. From the same time or maybe some years earlier, paintings on the east and west walls were completed and show a large depiction of the *Crucifixion* (Figure 3a) and a beautiful Virgin Mary (Figure 3b), which is part of the *Annunciation*. On the lower layer of the north wall, a *Passion Christi* (Figure 3c) was completed at the beginning of the 15th century; the *Passion* probably covered older paintings related to the *Annunciation* and the *Crucifixion*.

Figure 2. *Apostles*. Presbytery, Chyžné.

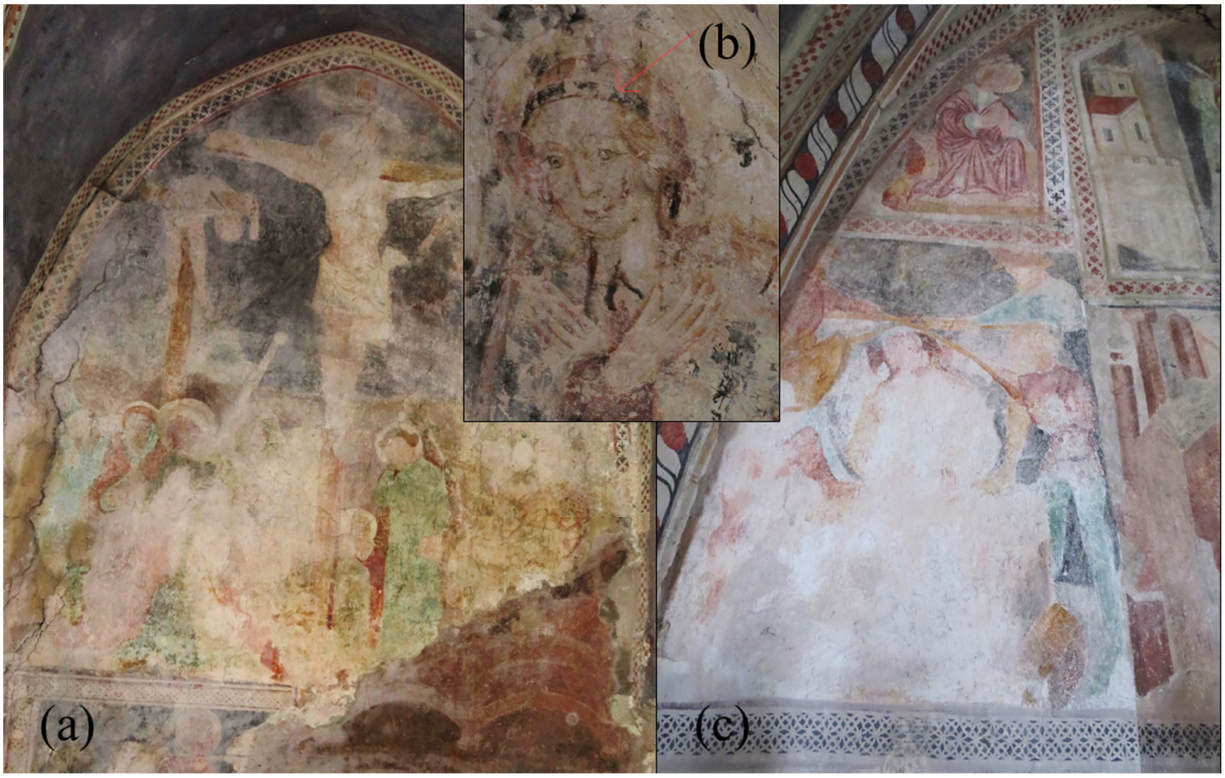

Figure 3. Mural paintings of the north side nave: (**a**) *Crucifixion*, east wall. (**b**) Virgin Mary from *Annunciation*, west wall; fine modelling can be observed as well as the blackening of some areas due to probable degradation of a lead pigment, which is pointed out with the red arrow. (**c**) *Coronation* and other scenes, north wall, Štitnik.

These paintings are in a bad conservation state, which makes it difficult to read and understand them. The murals from the 14th century show strong Italian Trecento influence, while those from the 15th century have a more local impact, combining Italian trecento with northern stylistic currents [2,4,5]. Murals were discovered in different restoration phases between 1874 and 1914, with the most important one in taking place in 1908–1909 by I. Groh [2].

2. Objectives

Most of the murals have already been studied from the art history point of view, as can be well observed from the existing literature ([1–6], with additional bibliography). Nevertheless, their material and technical aspects are not well known, but this information is as important as the study of a piece of artwork's style is. For this, the interdisciplinary collaboration between Humanities and Natural Sciences is vital, offering much better and complete comprehension. The principal objectives of this study are therefore to obtain information on the materials and painting techniques applied in all three of the selected mural cycles. Therefore, (a) the characterization of supports (plasters), including their composition (binders and aggregates); (b) the number of layers and the application of *giornatae* (daily portions of plaster limited to one scene or one figure) or *pontatae* (larger horizontal stripes of fresh plaster that can cover the entire wall width); (c) the possible use of lime-wash; (d) the identification of specific pigments (organic, inorganic) and their possible degradation; (e) the identification of specific binders (organic, inorganic); (f) the sequence of the colour layers; (g) the colour modelling and brushes used (fine, thick); (h) the painting process from the preparatory work (under-drawings, incisions, pouncing, under-paintings) to the final colour modelling (shades, highlights); and (i) the painting technique (*a fresco*, *a secco*, lime technique) are of interest in the current work.

The information obtained here offers an understanding of the materials and painting procedures applied in the chosen murals as well as their comparison to other artworks, as planned in the near future. On this basis, the coexistence of Italian Trecento features and contemporary Central-Northern influence, as stated in art-historical analyses, can be confirmed or rejected.

3. Materials and Methods

For the material analysis, invasive and non-invasive techniques were used [7–14]. The first and most important step was a precise examination with the naked eye, which was helped by a straight and ranking light. In mural paintings, it is possible to distinguish preparatory drawings, colours, colour modelling, and brush strokes; therefore, painting procedure can also be determined. On damaged areas, we could observe the number of plaster layers and their basic composition and texture, and we could sometimes also determine the use of lime wash.

Next, small samples of the colour layers and plasters used in the murals were extracted for laboratory analysis. Samples were prepared depending on the analytical technique that was chosen; most of them were embedded in resin for cross-section preparation. Cross-sections were studied under optical microscopy (OM) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). For the optical microscopy, a polarised microscope Carl Zeiss JENAPOL with coupled with a Canon EOS 6D camera were used. For SEM-EDS, a scanning electron microscop JEOL JMS-6060LA with an energy dispersive spectrometer EX-23000BU was applied, and the samples were analysed under 15 Pa pressure and 15 kV accelerating voltage. A few samples from Plešivec were analysed with another piece of equipment, environmental scanning electron microscope-energy dispersive X-ray spectrometry (ESEM-EDX) under ESEM FEI XL30 with a BSE-Detektor//SE Detektor in high-vacuum microscope mode between 5.0×10^{-5} mbar and 3.0×10^{-6} mbar, and these samples were previously observed with a digital optical microscope Keyence VHX-6000 with 100–1000× magnification. The optical microscopy revealed the sequence of the colour layers and the painting technique applied, sometimes facilitating optical

pigment identification based on the morphology of the particles in the sample. SEM offers additional morphological characterization, as it provides higher magnifications compared to OM, while the EDS detector is able to identify the chemical elements in the analysed point or area, and therefore, the materials applied during the painting process can also be identified. Morphological characterization by OM and SEM in the case of mural cross-sections is critical for wall painting technique identification and can be conducted through microstratigraphic analysis [12–15]. For plaster composition, samples were ground into fine powder and were analysed by X-ray diffraction (XRD) using a Bruker AXS, Germany D8 Advance model. Samples were prepared in silicon-single crystal-sample trays and were measured using Bragg–Brentano geometry, Cu-Kα_1: 1.54056 Å, Cu-Kα_2: 1.54440 Å, 40 kV, 40 mA, 5–80° 2θ, and a 0.02° increment of 2 s per step (count). Although other techniques such as FTIR, Raman or GC-MS could offer important additional results, at the moment, the use of these methods is not possible.

4. Results and Discussion

The results and the discussion are organized according to mural cycles corresponding to each church and always follow the same four sections for a better comparison among them, which explains the composition of plaster, preliminary painting procedures, the materials and techniques used, and the colour modelling. The last one can tell us a lot about the painting skills of an artist, as it allows us to observe his application of thin or thick brushes; smooth or rough transitions between colours; the way of giving shape to objects and figures by sequence of the colour layers, shades and highlights; as well as the thickness and colour of the final contour.

4.1. Plešivec

4.1.1. Plaster

Only paintings in the presbytery were taken into consideration at this point. These are quite damaged due to their later overlaying with a new plaster after having been previously hammered; also, several areas are lost. On damaged areas, the thickness of the plaster can be observed, which is about 5 mm. Togner was the first to observe a clear separation between *arriccio* and *intonaco* [2,3]. The *intonaco* was applied fresh on a daily basis as *giornatas*, which had to be painted in one day, when the plaster was still wet. Nevertheless, due to fragmentary condition of the murals, it is not always possible to determine their size, form, or sequence. However, on the *Crucifixion* (south wall), it can be clearly observed that *giornatas* was applied from right to left (new portion of plaster goes over the border of the old one) and followed the form of a figure or a group of figures (Figure 1b). The analysis of the plaster confirms that it is made of lime as a binder and sand as an aggregate. The lime was not mixed with the sand well; therefore, white lumps of uncarbonized lime can be observed on the cross-sections (Figure 4a). The sand is mostly composed of quartz, but it also contains alumosilicates and grains with iron compounds, as analysed by XRD (Figure 4c).

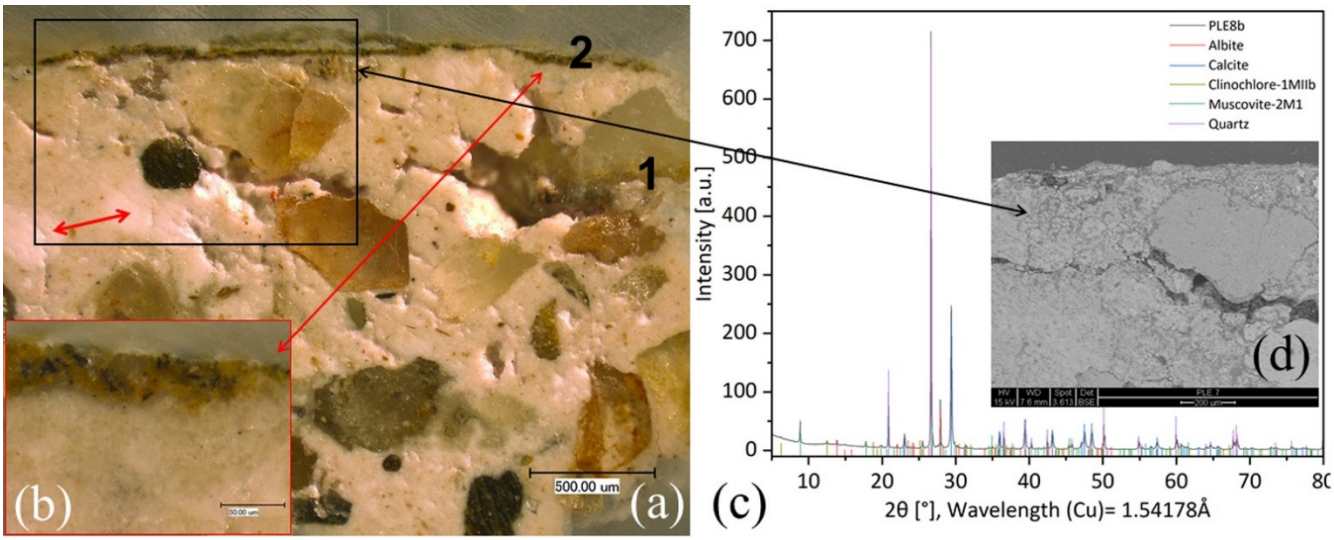

Figure 4. (**a**) OM image of a cross-section. (1) plaster made with lime and sand; (2) thin brownish colour layer on top applied *a fresco*. A short red arrow points at two lime lumps. (**b**) OM image of the same cross-section under higher magnification showing detail of the colour layer applied *a fresco*. Its location is pointed out with a large red arrow. (**c**) XRD graph with plaster composition. (**d**) SEM image of the upper left part of the cross-section marked with black rectangle on the OM image. Presbytery, Plešivec.

4.1.2. Preliminary Paintings Procedures

In the fresh plaster, strong and deep incisions were made for several straight lines (architecture, scene limitation, ornamental borders) and haloes (made with compass). The haloes are also decorated with incisions, which were probably made using a thin triangle-formed piece of wood that had been pressed into a fresh mortar. Both artists also used the same form of haloes. Togner mentions the existence of *sinopia*, a preparatory drawing in red c on *arriccio* that is later covered by *intonaco*. He makes an interesting observation—there is one on the north wall but not on the South wall [2,3], which reveals one of the differences between both artists, as *sinopia* is very characteristic for Italian Trecento painting but not so much for the Central European style of painting [16,17]. Preparatory drawings on *intonaco* in red and yellow are also visible with the naked eye, mostly where the colour layers fell off. It seems that the artist who worked on the north wall used red, while the artist working on the south wall only used red for drawing the straight lines which limit the scenes, while for the figures, he preferred yellow. Corrections of figures or other elements can be observed in some areas, and the brushstrokes seem confident and quick. Some underpaintings (uniform color layers applied as the basis for another colour layer to give them intensity [16,17]) can also be observed with the naked eye—the blue colour for the sky seems to be painted on top of a grey underlayer on the north and south walls. This is surprising due to the fact that the style of these paintings is related to the Italian Trecento style; underlaying the azurite with grey *veneda* was typical for Central and Northern European-style painting [17,18], while Italian painters generally used the reddish *morello* [16,17,19]. Samples could not be extracted from the area to confirm this.

4.1.3. Materials and Techniques

Several samples were extracted from the murals and were analysed under OM and ESEM-EDX. The results showed that the pigments are of natural inorganic origin, making them suitable for *a fresco* painting. Due to humid and alkaline environment of the fresh lime, only inorganic pigments are stable in the fresco technique [17,20–24]. The palette included lime white (identified by Ca as its characteristic chemical element), yellow and red ochres and iron clays (Fe), malachite (Cu), azurite (Cu), and carbon black (C). Furthermore, malachite (Figure 5a,c) was partially identified as containing spherulites of malachite,

which were probably mixed with normal malachite, as observed on the SEM images (Figure 5b), something that is characteristic for Slovakia, as it was mined in the Špania valley [25,26].

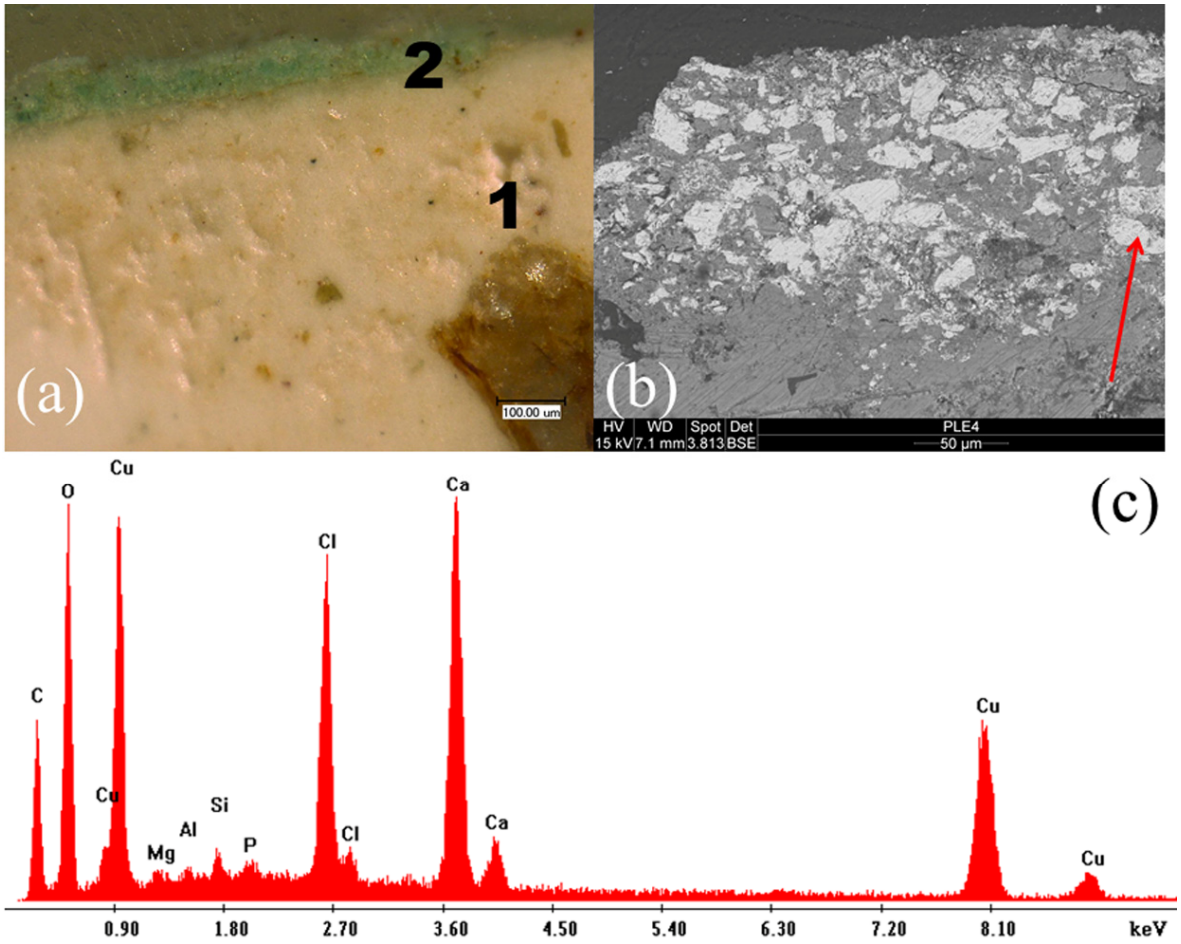

Figure 5. (**a**) OM image of a cross-section. (1) Plaster and (2) green layer *a secco*; (**b**) ESEM image of a smaller part of the green layer with one spherulitic particle pointed out with a red arrow. (**c**) EDX spectrum shows important Cu, Cl, and Ca peaks identifying malachite, which has probably transformed to (para)atacamite, on lime-based plaster. Presbytery, Plešivec.

This form of malachite occurs in the nature when it develops without an obvious point of nucleation; it starts crystallizing freely in solution. This leads to an invisible cluster of a few molecules, which becomes the centre around which needle crystals grow. They radiate out in all directions, forming what we commonly call a "spherules" [27]. EDX analysis (Figure 5c) also shows presence of Cl, probably a degradation of malachite to atacamite or paratacamite, two of four polymorphs of copper hydroxychlorides, which can form as a corrosion product by the action of NaCl salts in the wall or plaster [26–28]. However, this chemical degradation cannot be proven by EDX analysis alone and is only able to be determined here by the presence of Cl. Despite this, it is a very common change that can occur with malachite in wall paintings.

Besides this green mineral, most ochres and clays were also found locally; the Gemer hills are rich with this material, and mediaeval artists had them within their reach due to their proximity [3,25,28]. Pigments were mostly applied on a fresh mortar using the *fresco buono* technique [16,17,22–24], as observed from the cross-sections (Figure 4b,d). The line between the plaster and colour layer is blurry and is not straight and well defined because the lime penetrates the colour layer in the process of carbonatization, which also makes it the principal binder for pigments. During this chemical process, the plaster and colour layers merge together [17,22,23]. This was the principal painting technique.

However, both painters also used *a secco* colour applications in order to conclude the final modelling and contours as well as for the application of azurite and malachite of the final works (Figure 5a).

The much better conservation state of the colour layers on the north wall reveals that the bigger part of the murals was completed *a fresco* by the first painter who worked in the Italian tradition, while the second one had to finish a bigger portion *a secco*—the plaster was already too dry, and the lime could not work sufficiently as a binder anymore. This is why the colour layers fell off in a wider range; they were not as resistant to temperature, humidity, etc. The binder in the *fresco* technique is the lime from the plaster, which is sometimes also added to pigments in the form of lime water to strengthen the binding power. However, for *secco* additions, an organic binder, such as egg yolk or casein, must be used [17,20,22], the latter of which was already mentioned by Togner [2,3]; however, there has been no analysis on organic compounds used for this purpose that has been conducted so far. Organic binders were used when the plaster was dry or for certain pigments because of their chemical characteristics and instability in humid and alkaline lime [17,20,23,24]. On some of the cross-sections, two colour layers can be still distinguished: the basic one applied on a fresh mortar, and the second one was applied on an already dry surface, where a straight, well-defined line between both layers is generally very clear (Figure 5a).

4.1.4. Colour Modelling

There is a clear difference in the modelling between the north and the south wall, which also confirms the stylistic differences between both principal artists. On the north wall, where the painter with a higher skill level and who was based in the Italian Trecento style was working, we can appreciate a combination of thin and thick brushes and the smooth transition between lights and shades; all in all, this artist had much higher technical skills than the artist working on the south wall. Despite the bad conservation state of the paintings in general, the colour layers are well preserved, confirming the execution of the in fresco technique for most of the painting. Faces, drapery, or architectural details are still well readable and show very high artistic skills (Figure 6a). The modelling goes from light to dark and shows examples of final highlights and dark contours. The artist who worked on the South wall was not skilled in smooth colour transition. He mostly used thick brushes and only chose thin ones for final details as contours (Figure 6b). The faces and draperies are flat, there is no special modelling for the faces or drapery folds, and there is no attempt to individualize the figures.

4.2. Chyžné

4.2.1. Plaster

The wall is very uneven, which also causes an uneven surface for the paintings. The plaster is made of lime and sand, as already observed by the naked eye as well as on the cross-sections (Figures 7a and 8a). In a Chyžne plaster sample that was extracted in the presbytery, the always colour layers are always together; therefore, only SEM-EDS analysis was conducted, not XRD (Figures 7b,c and 8b,c, Tables 1 and 2). One cross-section revealed two plaster layers (Figure 7a): one underlaying *arriccio* that is quite thick and a very thin (30–90 µm) upper layer, which is often referred to as *intonaco*. The latter one has less sand and tends to peel off, which damages the colour layers. However, due to high amount of dolomitic lime (suggested by the common presence of Ca, and Mg), both layers are generally quite solid. It is not clear if the paintings were completed using *giornatas* because no junction in the *intonaco* portions can be discerned. It is possible that each figure or scene was completed on an individual layer of a fresh plaster portion.

Figure 6. Colour modelling. Comparison between the paintings on the north (**a**) and on the south (**b**) wall. Presbytery, Plešivec.

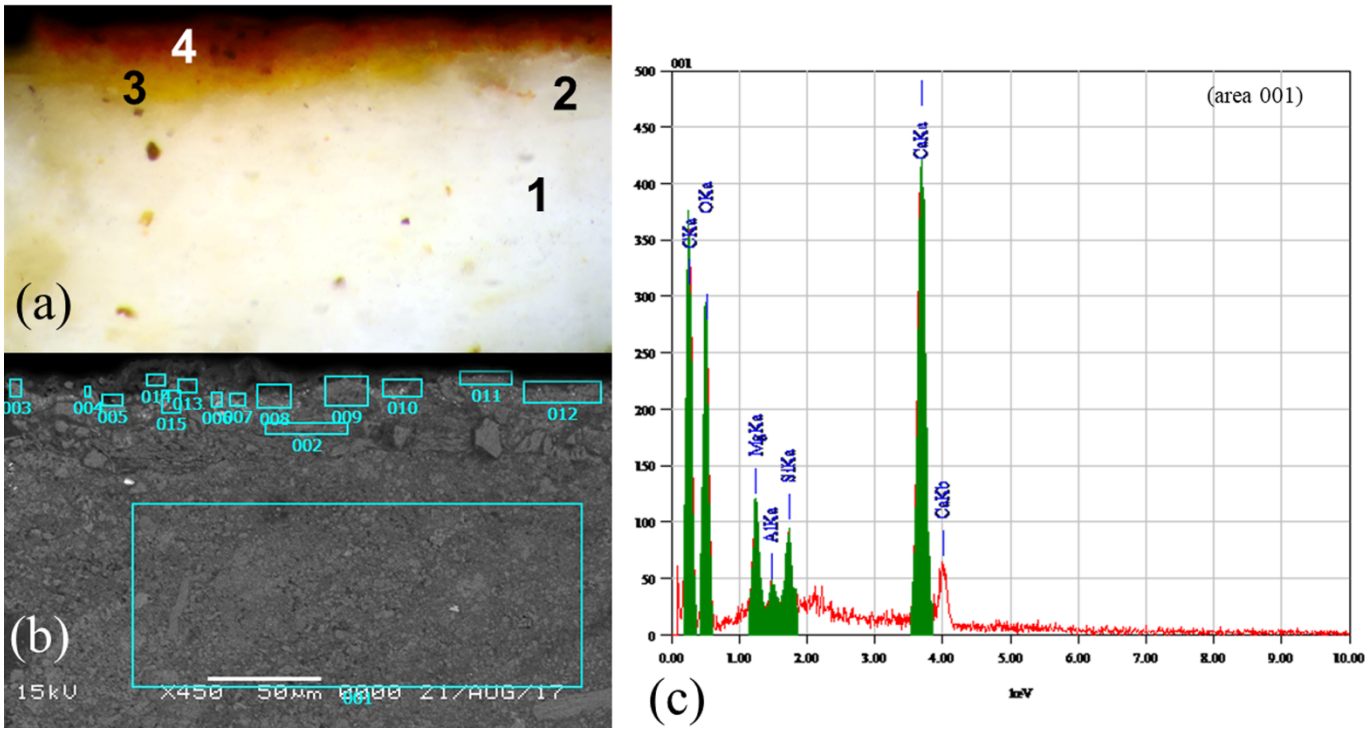

Figure 7. (**a**) OM image of a cross-section. (1) thick plaster, (2) thin plaster, (3) thin yellow layer *a fresco*, probably preparatory drawing, and (4) red colour layer *a fresco*. (**b**) SEM image of the same cross-section with areas analysed by EDS, as shown by blue rectangles (Table 1). (**c**) EDS graph of the 001 area of the plaster that identifies dolomitic lime (Mg, Ca) with a low amount of sand (Si, Al). Presbitery, Chyžné.

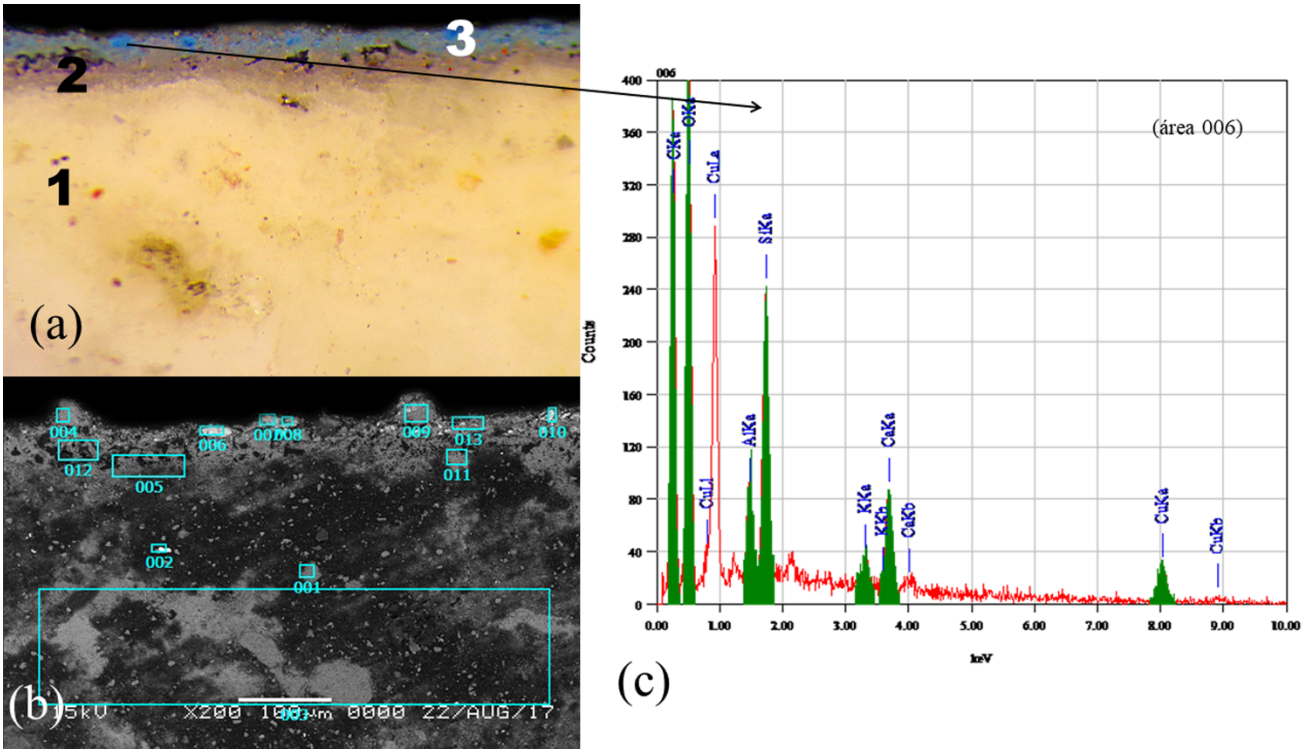

Figure 8. (**a**) OM image of a cross-section. (1) plaster, (2) grey layer *a fresco*—underpainting, (3) blue layer *a secco*—azurite. (**b**) SEM image of the same cross-section with areas analysed by EDS shown by blue rectangles (Table 2). (**c**) EDS graph of the area 006 of the blue grain, identifying azurite (Cu). Presbytery, Chyžné.

Table 1. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 7b.

Chyzne 7	C	O	Mg	Al	Si	K	Ca	Fe
1	30.61	22.15	3.71	1.01	2.49	-	40.03	-
2	32.39	27.29	1.93	7.8	10.64	2.14	12.51	5.3
3	45.22	20.28	3.03	3.57	6.51	1.02	14.58	5.78
4	41.2	20.41	1.58	2.7	5.63	-	21.24	7.25
5	41.39	18.59	0.94	1.72	3.24	-	26.37	7.74
6	30.83	19.89	1.41	1.12	2.59	-	20.91	23.25
7	30.35	23	2.11	1.49	5.66	-	27.72	9.66
8	41.75	19.53	1.64	2.7	4	-	24.67	5.7
9	42.61	23.39	1.91	6.63	9.29	-	9.09	7.07
10	42.1	18.89	1.19	2.24	3.83	-	23.54	8.21
11	51.05	21.05	-	4.73	11.33	2.77	6.86	2.21
12	40.7	20.78	1.4	3.55	5.8	1.21	19.88	6.67
13	52.92	17.94	0.62	1.35	7.7	1.09	18.39	-
14	73.95	9.14	1.19	0.84	2.69	1.67	10.53	-
15	36.38	23.31	2.02	3.02	8.17	-	19.75	7.35

Table 2. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 9b.

Chyzne 9	C	O	Mg	Al	Si	K	Ca	Fe	Cu
1	43.32	29.52	-	-	25.24	-	1.92	-	-
2	52.82	17.12	0.59	0.87	8.53	-	4.38	15.7	-
3	50.82	18.54	1.62	0.8	7.43	-	20.8	-	-
4	40.2	29.42	-	2	22.55	1.92	3.92	-	-
5	49.21	16.38	1.04	-	3.2	-	30.17	-	-
6	44.63	18.21	-	2.72	7.07	1.48	6.16	-	19.73
7	45.48	17.81	0.97	1.68	6.07	1.23	11.27	2.9	12.59
8	53.32	15.5	-	2.56	5.21	1.3	9.84	-	12.26
9	38.54	30.23	-	2.06	23.44	1.19	2.02	-	2.52
10	48.73	14.69	0.65	1.75	2.69	-	11.64	-	19.84
11	38.86	19.64	-	-	4.16	-	37.34	-	-
12	59.28	12.5	-	-	1.68	-	26.54	-	-
13	53.04	16.82	-	1.57	6.6	1.23	16.54	-	4.2

Figure 9. (**a**) Yellow predrawing under red final contour, right hand, detail of the Apostol. (**b**) Red horizontal line made with a rope dipped in red and splashed on the wall. Presbytery, Chyžne.

4.2.2. Preliminary Paintings Procedures

Yellow preparatory drawing on *intonaco* can be clearly observed, which can be distinguished in several places, even under the final red contour (Figure 9a) and on a cross-section (Figure 7a). Besides yellow, the artist used also red for straight lines for the decorative borders limiting the scenes.

For bottom lines he used a ruler, while for other straight lines he preferred to use a rope dipped in red colour and splashed on the wall. Signes of this procedure are still documented on several areas (Figure 9b).

The rope was probably splashed on already dried plaster—there are no small holes in the surface, which would have been caused by the rope being pressed into a fresh material. The artist also used incisions as the preparatory procedure, which are quite thin and shallow and difficult to find. On the paintings in the presbytery, the painter used basic colour layers for consecutive colour modelling; nevertheless, there is also a grey underpainting under blue azurite, the so called *veneda,* which was observed in Plešivec. It can be distinguished by the naked eye, but it is also confirmed by a cross-section of a sample taken from a blue background on the south wall (Figure 9a).

4.2.3. Materials and Techniques

Pigments were identified by OM and SEM-EDS (Tables 1–3). The palette was made of natural earth and mineral pigments: lime white (Ca), yellow and red ochres and iron clays (Fe), malachite (Cu), azurite (Cu) (Figure 8c), carbon black (C), and vine black (C, Na, K). As in Plešivec, the spherulites of malachite were also identified in Chyžne, with its characteristic forms being observed under the optical microscope (Figure 10, Table 3). Cross-sections also revealed that the principal painting technique was *a fresco* (Figures 7a,b and 9a,b—grey layer); however some pigments such as azurite were applied *a secco* (Figure 9a,b—blue layer), as were the final parts of the painting. The principal binder is therefore lime resulting from the fresh plaster, with some additional lime water probably being added for better pigment application, while for the *a secco* parts, an organic binder must have been used, but no analysis for the organic materials has been conducted so far.

Table 3. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 10b.

Chyzne 10	C	O	Mg	Al	Si	S	Cl	Ca	Cu
10	37.61	14.87	2.88	-	1.39	-	-	3.44	39.81
11	39.42	13.08	1.88	-	-	-	-	2.44	43.17
12	43.03	16.81	-	-	-	5.38	-	-	34.78
13	34.93	14.92	1.65	-	1.5	-	-	1.99	45.01
14	41.69	15.11	1.92	1.43	2.21	-	-	3.95	33.69
15	31.16	15.58	1.04	0.76	0.92	-	-	3.02	47.51
16	32.51	16.05	1.72	1.1	1.55	-	-	2.16	44.91
17	33.19	16.94	2.56	1.35	2.23	-	-	3.43	40.3
18	29.74	15.79	1.15	-	0.93	-	-	5.3	47.1
19	34.63	15.18	2.53	-	1.25	-	-	2.75	43.67
20	36.64	18.82	4.01	-	-	-	-	40.54	-
21	26.45	21.92	1.78	-	1.14	-	-	48.71	-
22	37.69	19.25	4.12	-	1.34	-	-	37.6	-

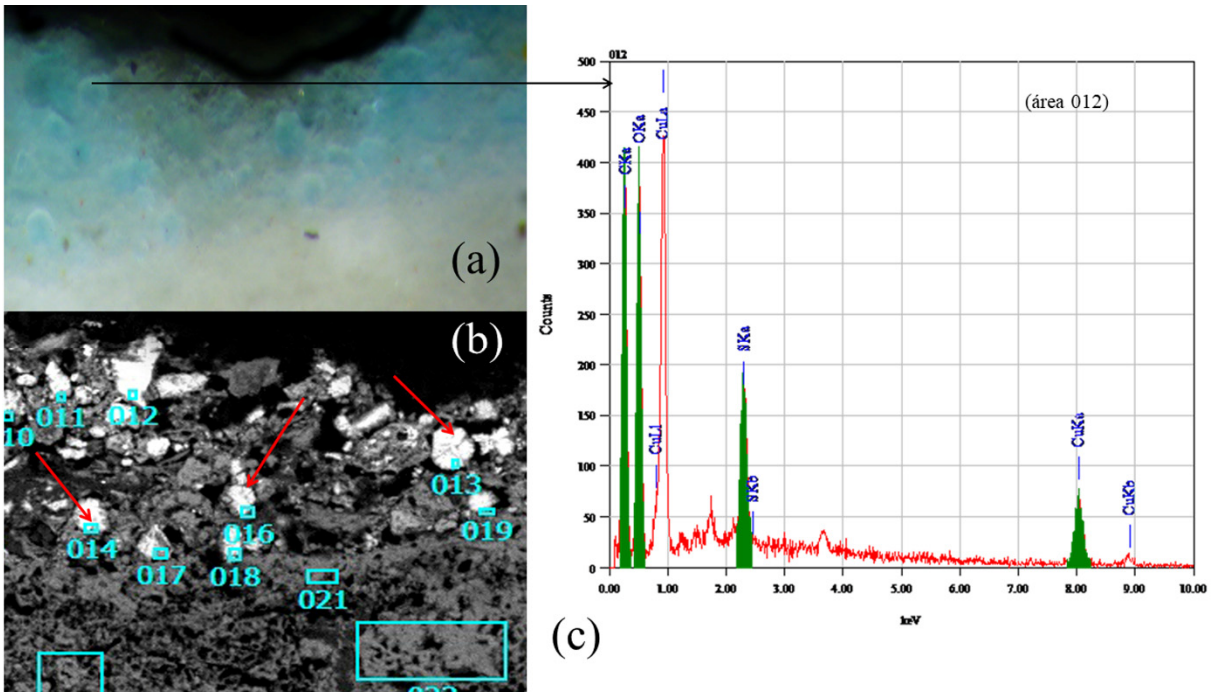

Figure 10. (**a**) OM image of a cross-section. (1) plaster, (2) turquoise layer with characteristic forms of spherulitic malachite. (**b**) SEM image of the same cross-section, where typical circular forms of the spherulitic malachite can be observed; some of them are pointed out by red arrows. Analysed EDS areas are shown by blue rectangles (Table 3). (**c**) SEM spectrum of the area 012 showing the presence of Cu.

4.2.4. Colour Modelling

Wide brushstrokes characterize this anonymous painter. No fine transitions between colours and shades/lights were obtained, which shows that the artist was trained locally. The colour modelling goes from dark local colour layers towards light modelling on top (Figures 2 and 8). For the white draperies, the painter used the white plaster support and designed drapery folds with quick schematic brushstrokes. Reddish final contours conclude the figures and objects in rather schematic way. The haloes of the saints are not formed with incisions and puncing as they are in Plešivec but are created with colour alone—yellow for the center and dark red for the external circle and decorated with white spots.

4.3. Štítnik

4.3.1. Plaster

The paintings on the north wall of the nave are quite damaged, there are many lacunas, and the upper colour layers have mostly fallen off. On the lacuna next to the window on the north wall, very thick plaster can be observed; this plaster is actually composed of two layers: a thick *arriccio* and a thin layer (only 3 mm) of *intonaco*. The analysis of the plaster composition was conducted on cross-sections using SEM-EDS identification (Figure 11b,c, Table 4). The plaster on the north wall (*Passion*) is quite dark and yellowish (Figure 11a). The chemical analysis shows that it is made of lime and sand. Furthermore, the common presence of Mg and Ca enables the deduction that the lime is dolomitic and was mixed with high amount of fine-grained filler, which was composed mostly of silica sand (quartz), (area 022, Table 4).

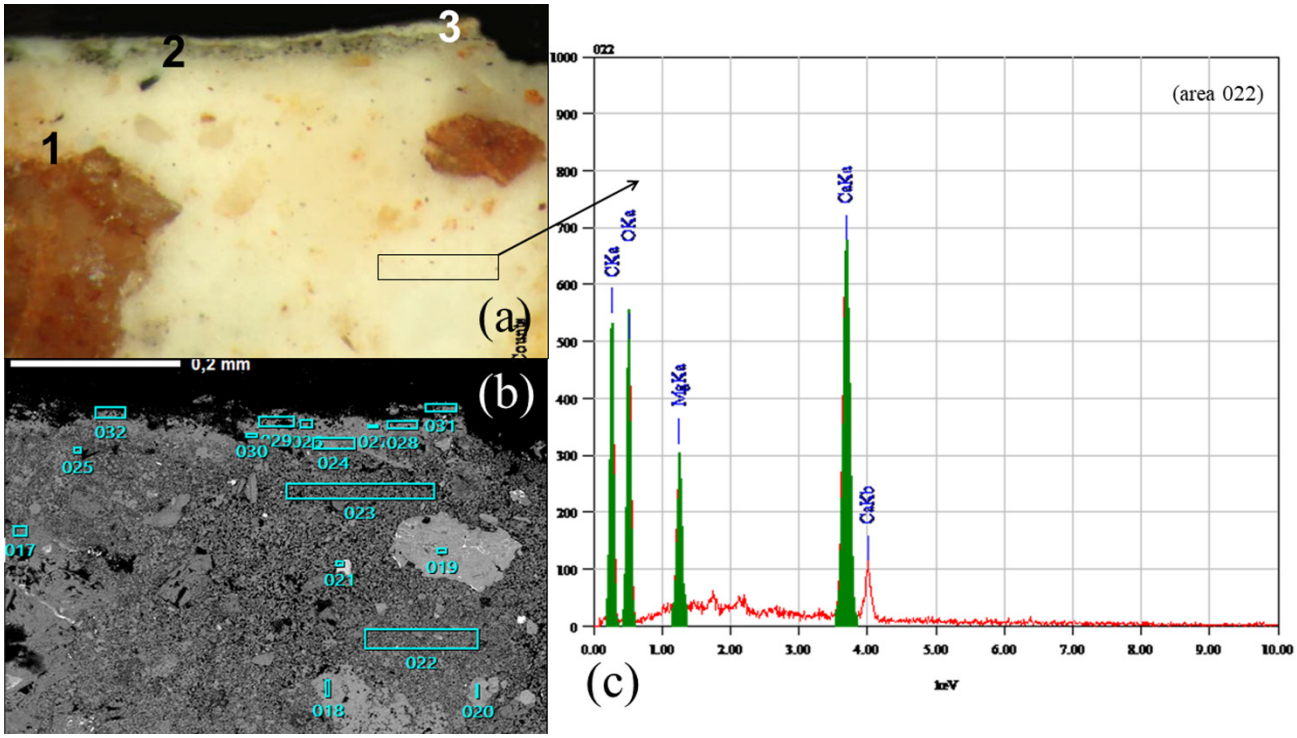

Figure 11. (**a**) OM image of a cross-section. (1) plaster (2) grey *a fresco* layer, and (3) white lime layer; (**b**) SEM image of the same sample with areas analysed by EDS shown by blue rectangles (Table 4). (**c**) EDS spectrum of area 022 of the plaster with Mg and Ca presence, indicating dolomitic lime. *Coronation of Christ*, north wall, north side nave.

Table 4. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 11b.

Stitnik 11	C (%)	O (%)	Na (%)	Mg (%)	Al (%)	Si (%)	P (%)	Ca (%)
17	30.46	22.64	-	15.15	-	-	-	31.75
18	19.3	23.55	-	2.85	-	-	-	54.3
19	24.09	21.66	-	-	-	-	-	54.26
20	21.81	22.57	-	1.45	-	-	-	54.17
21	21.05	30.04	-	1.33	-	-	11.41	36.17
22	32.54	20.56	-	7.08	-	-	-	39.83
23	33.63	20.09	-	6.21	-	-	-	40.07
24	24.82	23.28	-	5.6	-	1.5	-	44.8
25	36.79	19.16	-	6.09	-	-	-	37.96
26	33.85	20.36	0.7	3.05	-	1.8	-	40.23
27	27.84	21.78	-	3.62	-	0.99	-	45.78
28	35.34	19.15	-	3.82	-	-	-	41.69
29	45.36	16.76	-	3.26	-	1.06	-	33.56
30	27.62	22.2	-	5	-	1.17	-	44.01
31	48.44	16.9	-	3.03	1.41	2.14	-	28.08
32	47.09	16.18	-	2.8	-	1.08	-	32.85

Due to the darker colour of the sand grains observed on the OM image, there must be some ferric minerals and other impurities that are present, but this hypothesis could only be confirmed by additional XRD or Raman analysis. The lime binder is weak, as the plaster tends to pulverize, and therefore, the support for the paintings/colour layers is damaged. This is one of principal reasons why the *Passion* is in such a bad state. On the contrary, according to the analysis, the plaster under the *Crucifixion* on the east wall of the north side nave (paintings from the end of the 14th century) is of higher quality and has a whiter colour (Figures 12a and 13a); the plaster made as a mixture of slaked lime and silica sand with potassium feldspars, as deduced from EDS elemental analysis (Table 5, area 022, Figure 13d, Table 6, area 018). It has less impurities and is more solid, which can also be observe on the better conserved colour layers. This plaster composition is similar to those used in Italian Trecento, which was made normally of lime and *marmorino* [17,20,22,23]. This confirms that the *Crucifixion* on the east wall was painted during a different time period than the *Passion* scenes on the north wall by a painter influenced by Italian Trecento, as already stated by art historians on the basis of his style. On the north wall, the plaster was probably applied following the *giornatas* system; however, only horizontal contacts between the plaster layers can be really distinguished as in the *pontatae* in the area of the decorative borders, which limit the scenes and narrative belts.

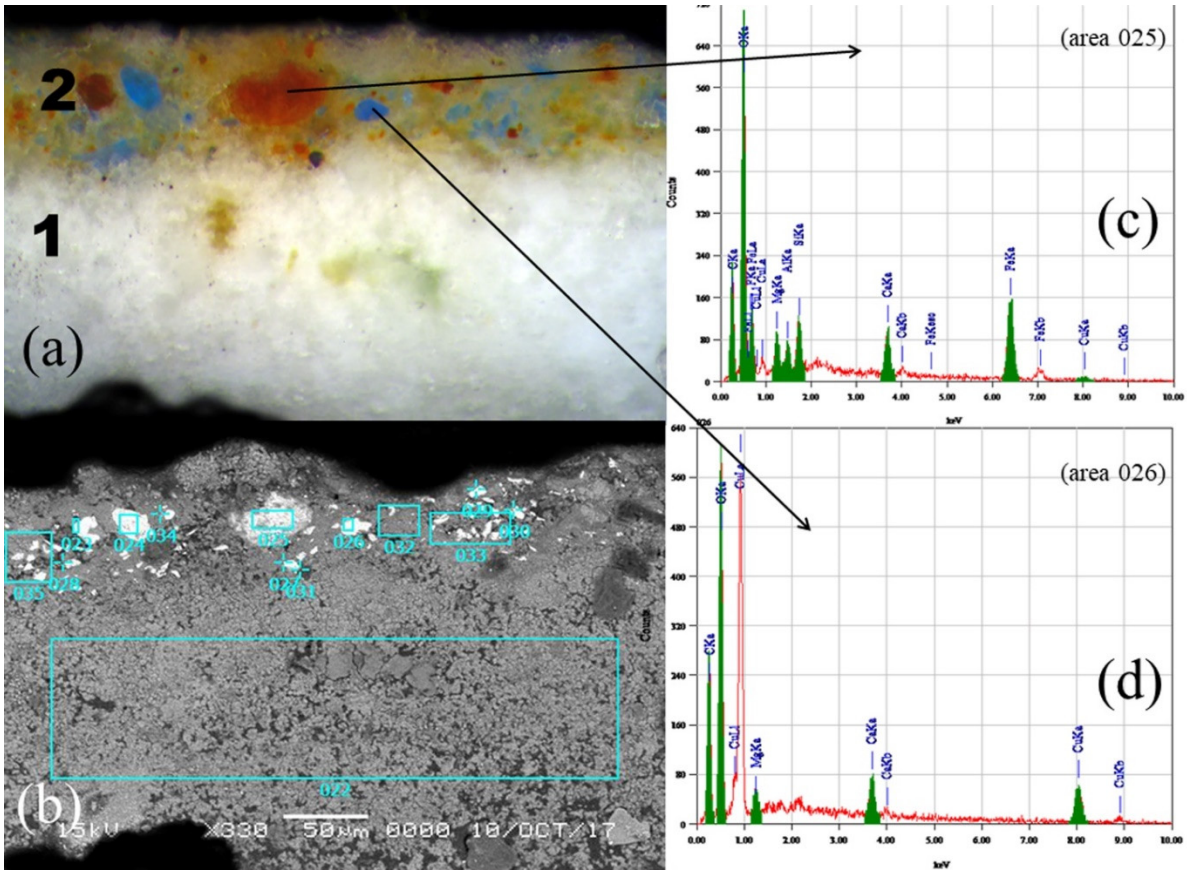

Figure 12. (**a**) OM image of a cross-section. (1) white plaster and (2) green colour made of white, yellow, red, and blue pigments. (**b**) SEM image of the same sample with areas analysed by EDS shown by blue rectangles (Table 5). (**c**) EDS spectrum of the area 025 of the dark orange grain, identifying iron oxide (Fe). (**d**) EDS graph of the area 026 of the blue grain, identifying azurite (Cu). St. John Evangelist's coat, *Crucifixion*, east wall, north side nave.

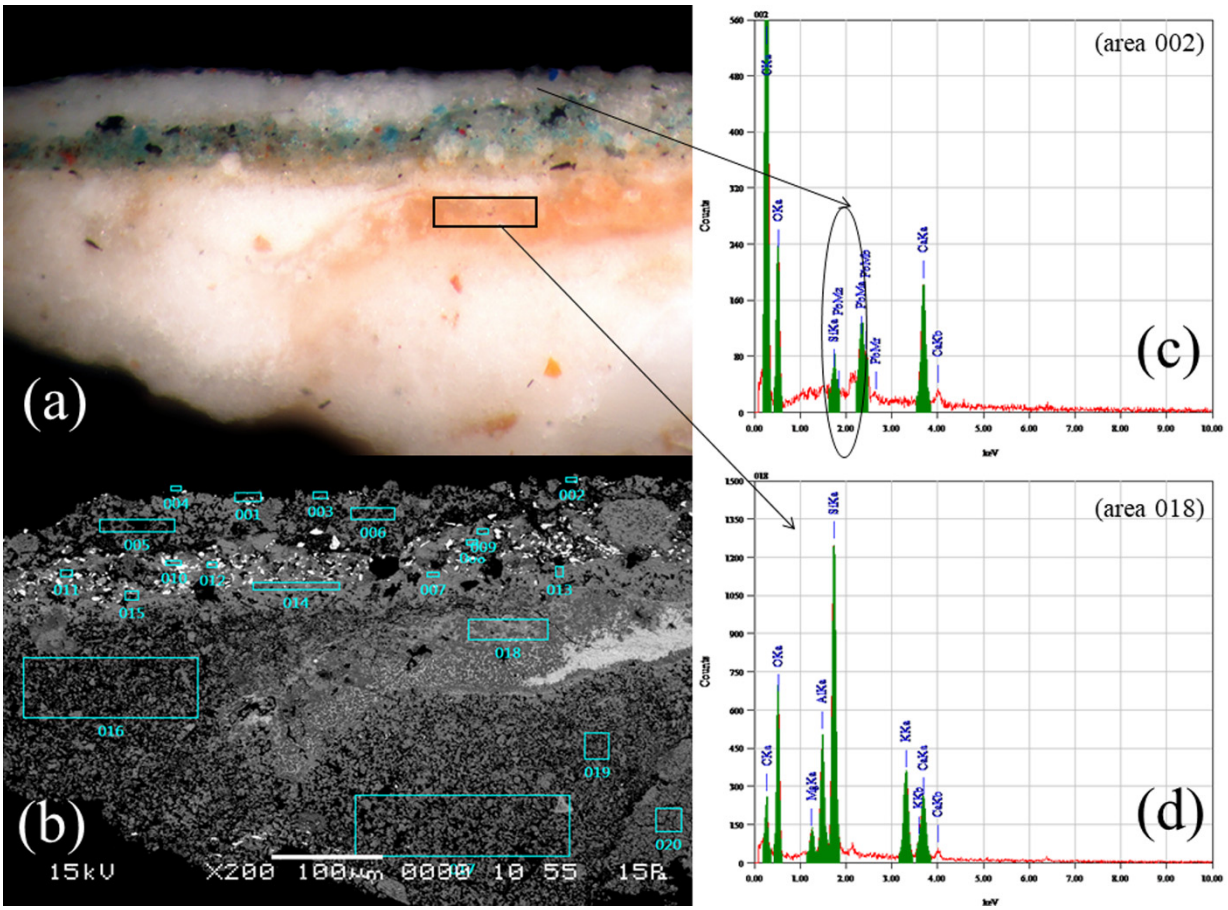

Figure 13. (**a**)OM image of a cross-section. (1) white plaster, (2) blue azurite layer with some iron oxide particles, and (3) white layer. (**b**) SEM image of the same sample with areas analysed by EDS shown by blue rectangles (Table 6). (**c**) EDS spectrum of the white layer containing lead and lime whites. (**d**) EDS spectrum of the yellowish area in the plaster, containing high amount of Si. Christ's coat. *Christ's Baptism*, north wall, north side nave, Štítnik.

4.3.2. Preliminary Paintings Procedures

No incisions or pouncing can be observed, not even for the haloes or decorative stripes, which is an interesting difference in comparison to the paintings in Plešivec and Chyžné. The predrawing is also very difficult to find due to the bad conservation state of the paintings. It seems that the painter of the scenes on the north wall combined red and black, while the *Crucifixion* it has more orange-pinky tone, another confirmation of different artists and periods. On the blue background, grey underpainting can be observed; however, no samples could have been taken from this area, so *veneda* cannot be confirmed.

4.3.3. Materials and Techniques

As in the other two studied monuments, the pigment palette is also composed of inorganic pigments, earths, and minerals in Štítnik: lime white (Ca), yellow and red ochres and iron clays (Fe), malachite (Cu), azurite (Cu), and carbon black (C) [17,21,23,24]. An interesting finding was that the green colour from St. John Evangelist´s green coat on *Crucifixion* was not made with malachite but was instead composed of a mixture of yellow ochre and azurite with red grains of cuprite and ferric clays, lime white, and barite grains (Figure 12, Table 5). On other green areas of the same scene as well as on the north wall, malachite (in some cases confirmed as spherulite one) was identified.

Table 5. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 12b.

Štítnik 12	C	O	F	Mg	Al	Si	S	Ca	Fe	Cu	Ba
22	39.83	18.29	-	3.49	-	0.9	-	37.5	-	-	-
23	25.29	18.33	1.53	2.17	-	1.71	-	4.04	43.97	2.95	-
24	42.4	13.02	-	1.98	-	-	-	6.69	-	35.91	-
25	22.77	20.68	1.99	2.63	1.67	2.99	-	5.63	38.05	3.57	-
26	36.6	13.88	-	1.56	-	-	-	5.32	-	42.63	-
27	20.65	20.09	-	2.36	-	2.15	-	4.37	47.84	2.54	-
28	28.4	16.27	-	1.11	-	-	-	12.36	2.08	39.78	-
29	18.69	22.58	-	0.45	-	-	10.85	1.85	-	-	45.59
30	26.67	20.17	-	1.62	-	0.53	8.1	3.89	-	2.07	36.94
31	75.85	7.63	-	2.65	-	0.48	-	13.39	-	-	-
32	40.64	18.85	-	6.86	0.95	1.22	-	28.33	-	3.14	-
33	43.63	16.91	-	4.74	-	1.19	0.56	21.58	3.25	8.14	-
34	32.45	18.6	-	2.76	-	-	3.43	20.62	1.45	4.31	16.37
35	42.57	17.34	-	2.95	-	2.47	1	21.9	1.89	4.85	5.04

Table 6. Chemical elements identified by EDS in the sample and their presence in % according to the areas analysed, which correspond to blue rectangles on the SEM image of Figure 13b.

Stitnik 13	C (%)	O (%)	Mg (%)	Al (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Fe (%)	Cu (%)	Pb (%)
2	73.96	6.07	-	-	0.94	-	-	-	10.95	-	-	8.09
3	60.27	15.7	-	-	4.83	2.3	-	-	16.89	-	-	-
4	73.68	10.19	-	0.59	1.59	2.48	-	-	7.52	3.96	-	-
5	52.5	13.55	-	-	-	-	-	-	33.95	-	-	-
6	40.31	19.34	1.11	0.77	1.46	1.35	-	-	35.66	-	-	-
7	21.47	24.16	-	1.69	4.05	-	1.18	1.31	41.8	-	4.34	-
8	22.86	23.36	-	-	2.55	-	-	-	51.23	-	-	-
9	25.76	21.99	-	-	1.54	-	-	-	50.71	-	-	-
10	29.17	22.01	-	-	6.93	-	-	-	24.22	-	17.67	-
11	36.47	24.16	-	1.04	12.05	-	-	-	19.58	-	6.7	-
12	24.88	28.04	-	-	14.25	-	-	-	24.04	-	8.79	-
13	22.32	23.7	-	-	2.91	-	-	-	51.07	-	-	-
14	24.32	25.05	0.83	-	6.25	-	-	-	43.55	-	-	-
15	42.63	20.31	-	-	7.45	-	-	-	29.62	-	-	-
16	44.37	16.46	-	0.23	0.96	-	-	-	37.98	-	-	-
17	40.11	17.09	-	-		-	-	-	42.81	-	-	-
18	15.66	35.69	1.61	6.56	20.04	-	-	11.26	9.18	-	-	-
19	35.71	20.39	-	1.48	2.88	-	-	-	39.54	-	-	-
20	30.02	20.41	-	-	0.85	-	-	-	48.72	-	-	-

Another interesting feature is the different azurite granulation used to obtain different hues—when this mineral is finely ground, its blue intensity decreases, but it is easier and cheaper to apply, meaning that less of it is used. Additionally, when bigger grains are used, a more intense blue colour is created, but more binder must be used in order for the pigment to bind well to the support [16,17,21,23,24,29]. Sometimes, azurite can turn black

due to chemical reactions if the colour layer is exposed to heat (candles) or H_2S vapours in the air [24,29–32], which is probably what happened with the once blue backgrounds of the murals in the north side nave (Figure 1a,c); this degradation was still not confirmed by chemical analysis because no samples could have been taken from the affected areas. Additionally, in some rare cases, lead pigment (probably lead white) was identified on the basis of its white colour being observed on the cross-section and by the presence of Pb on the EDS spectrum (Figure 13, Table 6); this pigment is not suitable for *a fresco* painting due to its instability in humid and alkaline environments [17,29–31,33]. However, artists still sometimes used it on mural paintings and usually applied on dry mortar and therefore mixed with an organic binder. In Štítnik, a lead-based pigment was only found in upper layers, probably *a secco*, but no analysis of the organic materials has been conducted on these murals, either.

On the other hand, the black areas observed by the naked eye can also point towards the use of a lead pigment, which tends to darken when it reacts with sulphuric acids in the air [24,31,33]. This can be well observed on the figure of Virgin Mary (Figure 3b) on the west wall of the north nave, where black lines and her hair belt must have been of a bright white, yellow or red colour (lead white, massicot, lead-tin yellow or minimum), but it has since turned black. No samples have been taken from this area; therefore, the use of lead pigment or its precise identification cannot be determined. The painting technique is a mixture of *a fresco* and *a secco*, the basic binder is the lime from the plaster, but an organic binder must have also been used; casein was suggested by Togner [3]. He also suggested the use of lime wash over the entire painting surface; however, cross-sections did not confirm this hypothesis.

4.3.4. Colour Modelling

Similar to preliminary painting procedures, the lecture of the modelling is very difficult because the upper layers have fallen off due to *a secco* finishing as well as due to plaster pulverization. There is a clear difference among the modelling on 14th century paintings (*Annunciation*, *Crucifixion*, *St. Barbara*, *Volto Santo*) and those from the beginning of the 15th century (*Passion* cycle). Earlier paintings that are closer to Italian Trecento style show high quality modelling in a perfect combination between thick and thin brushes, a smooth transition between shades and lights, and the fine execution of details, hair, drapery, and beautiful faces (Figure 3b).

On the other hand, the of the artist who painted *Passion* used basic colour layers and mostly thick brushes to model the faces, draperies, and architecture (Figures 3c and 14). He made an extensive use of the white colour of the proper plaster/support to create some draperies, all of which are modelled just with simple brushstrokes in different colours. Perhaps the final modelling, which would show higher artistic skills, has been lost due to the bad conservation state of these paintings.

Figure 14. Basic modelling of faces (**a**) and drapery (**b**) where most of the details have been lost. *Christ carrying the cross*, north wall, north side nave, Štítnik.

5. Conclusions

All of the results are gathered in Table 7. On the basis of the information gathered so far, we can conclude that from the technical as was as from the stylistical point of view, there is not much of a relationship among the three selected mural cycles in the Gemer region (Plešivec, Chyžne, Štítnik); however, they all present relatively high technical skills and show examples of *a fresco* technique execution as the principal composition method.

In all three cases, the artists finished with *a secco* applications for last details and contours, but only in small portion, showing that they managed to carry out most of the work on fresh plaster. All of the plasters were made of lime and sand had higher or lower binder-aggregate amount and variable impurity contents.

The plaster composition supports the stylistic characterization—painters with strong Italian influence (Plešivec—north wall, Štítnik—east wall) used better quality plaster than those with more local influence (Plešivec—south wall, Chyžné, Štítnik—north wall). The palette is similar in all three churches and was made of inorganic pigments, earths, and minerals and principally comprised lime white, yellow and red ochres and iron clays, malachite, azurite, and carbon black. Many of these pigments were obtained in local mines and hills, as is the case of spherulitic malachite and ochres. However, in Chyžné, vine black was also found, while in Štítnik, a synthetic lead pigment was applied for some details, probably *a secco*. The principal binder was lime from the plaster; however, the artists used also lime water to mix the pigments before their application on the wall. For the *a secco* parts (final details and sometimes malachite and azurite layers), an organic binder must have been used, but no analyses have been made so far. Research on mural paintings is ongoing. The results presented here still have to be completed and compared to other selected monuments in Slovakia and in other related countries in the East Central Europe, in order to better understand the materials applied and that painting techniques used by the artists as well as their possible connection from the material point of view.

Table 7. Comparison of materials and techniques used in selected churches with distinction between artist hands in Plešivec between the north (N) and the south (S) wall and in the workshop and dating between *Passion* (P) and other scenes (O) in Štitnik. Legend: Q = quarz; (>) = high amount/proportion; (<) = low amount/proportion; (>>) = very high amount/predominant; (<<) = very low amount/auxiliar; (x) = presence/use, (/) = no presence/use; (?) = not certain; (dol) = dolomitic; u. = under.

Location	Plešivec-N	Plešivec-S	Čhyžné	Štitnik-P	Štitnik-O
			PLASTER		
num. of layers	2	2	2	2	?
binder	lime	lime	lime (dol)	lime (dol)	lime (dol)
aggregate	sand (>Q, <Al, Si, Fe)	sand (>Q, <Al, Si, Fe)	sand (>Q, <Al, SI)	sand (>Q, <Si, Fe)	sand (>Q, <K)
			PIGMENTS		
lime white	x	x	x	x	x
lead white	/	/	/	x	/
yellow earth	x	x	x	x	x
red earth	x	x	x	x	x
malachite	x	x	x	x	x
mixed green	/	/	/	/	x
azurite	x	x	x	x	x
carbon black	x	x	/	x	x
cine black	/	/	x	/	/
			PAINTING TECHNIQUE		
a fresco	x (>>)	x (>)	x (>>)	x (>)	x (>)
a secco	x (<<)	x (<)	x (<)	x (<)	x (<)
lime technique	/	/	/	?	/
			PAINTING PROCEDURE		
giornata	x	x	?	x	?
sinopia	x	/	/	/	/
pre-drawing	red	red, yellow	red, yellow	red, black	pink
underpainting	grey u. blue	grey u. blue	grey u. blue	grey u. blue	grey u. blue
incisions	strong, deep	strong, deep	thin, shallow	/	/
pouncing	x	x	/	/	/
fine modelling	x	/	/	?	x
rough modell.	/	x	x	x	/

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