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The Characterization of a Fragment of a Medieval Fresco from Corbii de Piatră Cave Church

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Abstract: The fresco of the Corbii de Piatră Cave Church, dating from the end of the 13th century and the beginning of the 14th century, is applied to the sandstone wall. The degradation of the fresco on large surfaces, with many areas of detachment, has been determined by the infiltration of meteoric water through the sandstone wall on which it is applied, as well as temperature variations, and repeated wetting/drying processes. However, there are small portions of fresco that show good adhesion to the wall. The present research, aimed at providing scientific data to restorers and historians, involves the advanced characterization of a fragment of fresco with good adhesion to the wall and is being carried out by an interdisciplinary team. The stratigraphy, microstructure, compaction defects, chemical composition, and variation of chemical composition in the fresco from the pictorial surface to the mortar-sandstone interface were determined. Correlations were established between degradation processes and wall adhesion.

Keywords: fresco; mortar; meteoric water infiltration; degradation; microstructure; chemical composition; adhesion

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1. Introduction

Corbii de Piatră Cave Church, an important medieval monument on the territory of Romania, was built on an old Dacian site by the founder of Wallachia, voivode Basarab, at the end of the 13th century. The church was painted in a pure Byzantine style between the end of the 13th century and the beginning 14th century [1,2]. The church is unique in Romania due to its antiquity, the pure Byzantine style of painting, and its architecture, with two altars located in the same nave.

Some historians have explained the presence of the two altars in the nave through the desire to meet the needs of the Orthodox and Catholic faiths. The wife of Basarab I, Margareta, was Catholic. She founded the Catholic monastery Negru Vodă in Câmpulung (the first royal residence of Basarab I, located near Corbii de Piatră) and the Orthodox Church of St. Nicholas in Curtea de Argeș (the second princely residence). This explanatory version assumes that the architecture of the church is the result of its consecration of two saints corresponding to the two confessions, Mother of God for the Orthodox and St. Peter for the Catholics [3].

The shape of the church, as it was excavated in the sandstone rock from a pre-existing enclosure, and the decorative details are typical of oriental cave architecture and do not allow the analogy with the specific occidental art of the 13th century. Its architecture is derived typologically from the hall churches, with two altars dedicated to a double patron, specific to the Byzantine world from the 10th century.

The pictorial ensemble in the Corbii de Piatră cave church could be the first evidence of Byzantine painting in Romania. During that period, while Europe was embroiled in the Hundred Years' War, art underwent a renewal, and painting transitioned from the rigid and formal Byzantine style to a more effective narrative style featuring realistically depicted material characters. The votive painting of Basarab I, fragmentarily preserved in the central niche of the southern wall of the nave, may represent his earliest known mural depiction [2,4].

Due to the infiltration of meteoric water through the sandstone wall in which the church was carved and the prevailing climatic conditions within the church, exacerbated by microbiological action, the fresco within the church has undergone significant degradation (Figure 1). Large portions of the fresco have come off the wall. The biological colonization, facilitated by the cave church's environmental conditions, resulted in the growth of bacteria and algae, which covered the pictorial surfaces, particularly those on the northern wall. Eventually, this led to the deterioration of the frescoes, as veils and crusts formed. Parts of the fresco were still visible 12 years ago [4].

Upon initial examination with the naked eye, the existing frescoes were found to have two types of support mortars: friable mortars that easily detach, even when touched, and strongly adherent, hard mortars. The purpose of the research is to advance the characterization of the fresco element with good adhesion to the sandstone wall, to highlight and explain the factors that can be correlated with adhesion, and to make available the scientific data obtained to restorers. The research presented in the paper had been carried out by an interdisciplinary team. An experimental program for achieving the objectives was established, considering the strategies used nationally and internationally in the characterization of old frescoes. Taking into account the factors that give stability to the fresco and the mineralogical nature of the pigments used, it was particularly important to make decisions regarding the conservation or restoration of the painting in the monument. Identifying the materials used in constructing the fresco also provides insight into commercial exchanges and pigment trades that took place in the region during the painting of the church. This includes whether the pigments used were of local origin or rare pigments acquired through commercial exchanges. Understanding the nature of the pigments used enables us to draw associations with the fresco painting found in other churches established by Basarab I.

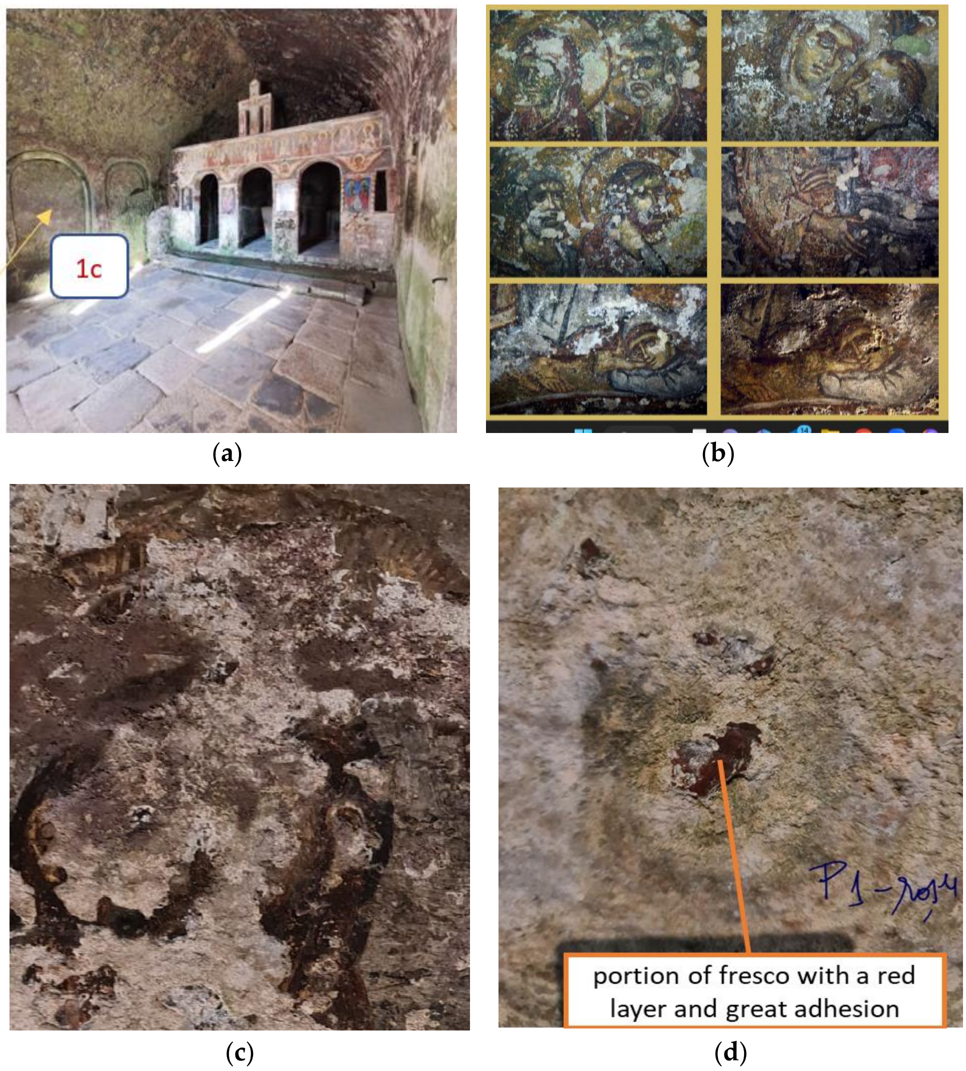

Figure 1. Corbii de Piatra Church: (**a**) an overview of 2022; (**b**) the layout of the mural paintings in 2011 [2]; (**c**) the state of the painting in 2022; and (**d**) the place where the fragment of the fresco with the red paint layer was taken.

2. Materials and Experimental Techniques

The fresco sample was taken from the northern wall of the church. The authors, who are specialists in sacred art and materials engineering, assessed the current state of the fresco painting and analyzed the degradation processes by comparing images from previous years. Based on this analysis, they determined the location for taking samples, the minimum sample size required, and the elements that needed to be highlighted through their characterization. The deontology of the conservation and restoration of historical monuments was respected during the sampling [5,6]. The mortar sample was taken from the wall of the Corbii de Piatră cave church, especially from the second floor where the fresco support is most exposed to water infiltration processes through the sandstone wall. The sample was taken from an area with high adhesion that was covered with a red paint layer at a height of 1.75 m. The analysis of the pigments used for the red color was performed on the sample taken from this area (Figure 1d).

A single sample was taken for all the analyses performed. The fresco sample was characterized using various methods, including optical microscopy in polarized light, cathodoluminescence, atomic force microscopy, X-ray diffraction, and scanning electron microscopy with the energy dispersive fluorescence spectroscopy module for elemental chemical analysis.

The analyses were performed in polarized light with the help of a Zeiss Observer A1 m optical microscope, which allows magnification up to 1000×, visualization in bright field, dark field, polarized light, and acquisition of images with a Canon camera.

The cathodoluminescence analysis was carried out with a Nikon E400 optical microscope, a cold cathode cathodoluminescence device (CL 8200 MK 3A), and a COOLPIX 950 digital microphotography device. The parameters required to perform the technique are as follows, according to the standard in use an average vacuum value of 0.5 Torr, a current–voltage on the beam ranging from 15 to 17 kV, and a current intensity on the electron gun ranging from 350 to 400 mA. The mineralogical composition of the mortar components, compared with the geological maps, allows the identification of the original raw materials' provenance.

Atomic force microscopy (AFM) was carried out with EasyScan II Nanosurf equipment using a non-contact mode, a CTR10 tip, and Nanosurf software to evaluate the scans to use the fresco sample embedded in the resin for flatness, with the surface mechanically polished at a very low speed without removing the external paint layer. The experiments followed the determination of the surface layer morphology of the material constituents and the analysis of the intimate contact between them at their interface.

The X-ray diffraction analysis (XRD) was used to identify the crystalline phases of the components in the mortar [7,8]. The analysis was conducted using an XPERT PRO MPD 3060 X-ray diffractions device from Panalytical (Almelo, Netherlands) equipped with a Cu X-ray tube ($K\alpha$ = 0.154051 nm) and set to scan 2Theta values between 20°–70°, with a step size of 0.13° and a time/step of 51 s, at a scan speed of 0.065651 °/s.

The SEM–EDS electron microscopy characterization was carried out using the HITACHI SU5000 electron microscope equipped with a backscattered electron detector and the energy dispersive fluorescence spectroscopy module for elemental chemical analysis.

3. Experimental Results

Microstructural characterization by optical microscopy is a frequently used method for the characterization of heritage materials and assets [2,7–12]. The aim was to identify the morphology, size, and type of aggregates, binders, additives, apparent porosity, cracking, and degradation processes, and the characterization of the interfaces between the constituents.

To enable its characterization, the fresco sample was embedded in resin and sanded with abrasive paper until it achieved a roughness of 2000. The optical microscope examination was performed on the entire surface of the sample, which allowed an overall characterization.

The analyzed sample shows a continuous red pictorial layer, which in certain areas penetrated through the existing cracks in the mortar before its application (Figure 2a). The matrix has inclusions, cracks, pores, and even voids (Figure 2b). The cracks observed are short in length, with some of them appearing some are detached from the tip of the straw insert, as shown in Figure 2c,d. The quality of the inlay-mortar interface is good, as no cracks have developed along its length that extends from the interface to the interior of the mortar. An area of carbonic residue can be observed following the degradation of the straw inserts used in the preparation of the mortar (Figure 2a,c). The microstructure shows open, yellow–orange, large, rounded phases inside the mortar (Figure 2c,d), while others are small and globular and located near the compaction defects. The observed light separations may be attributed to the presence of precipitates or the use of organic additives, such as sheep tallow or mineral oil, which were commonly utilized during that time period to enhance the quality of the mortar.

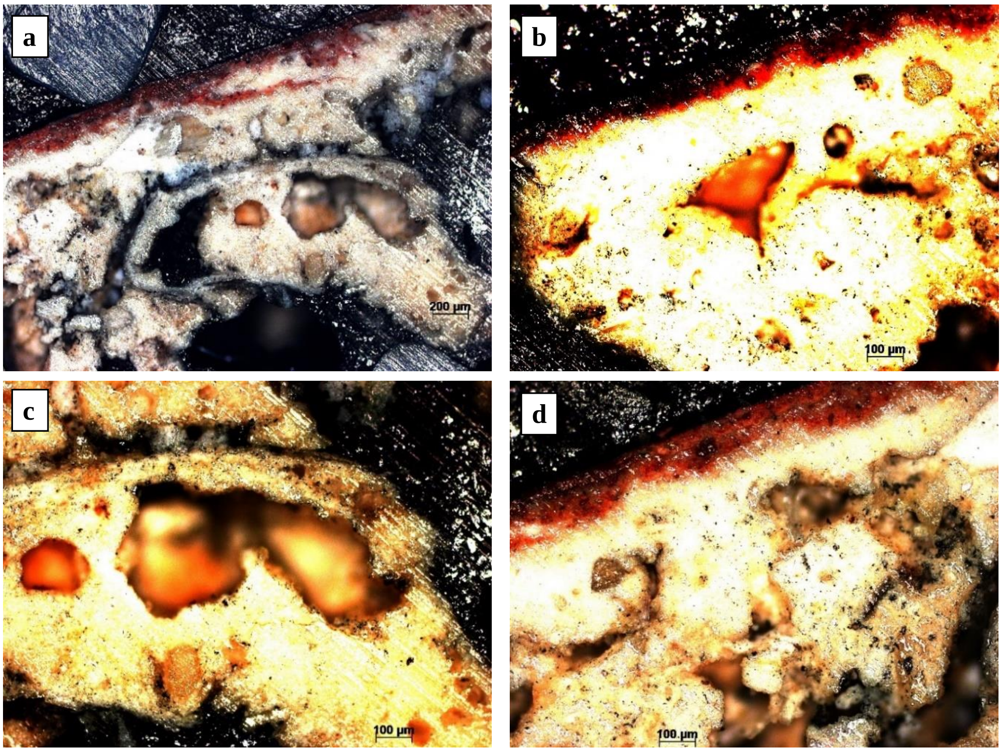

Figure 2. Fresco microstructure by polarized light microscopy (OMPL).

The pictorial layer in Figure 3 has a thickness between 71.7 and 81.5 µm (Figure 3a). Above it, a remnant of the carbonation layer formed during the drying of the fresco can be identified (Figure 3b, top right). The carbonation layer on the surface of the pictorial layer has a protective role and determines the transparency of the color and a decrease in its intensity [11]. Under the red pictorial layer, there is a thick area of pink color from the diffusion of the red pigment in the wet mortar (Figure 3b) [7,11].

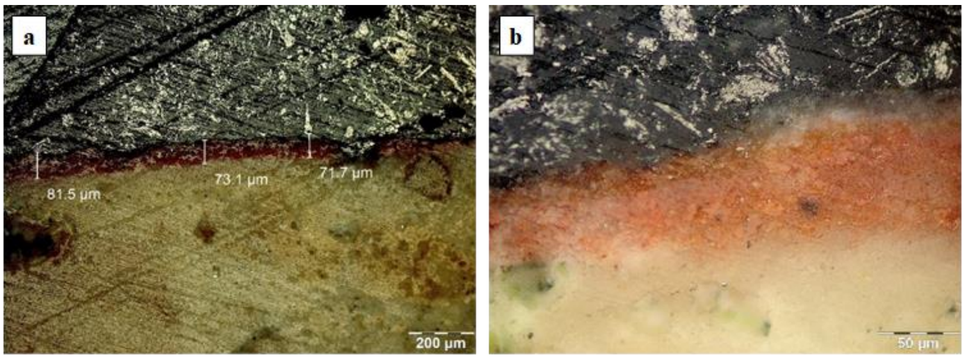

Figure 3. The pictorial layer in section through the fresco (OMPL).

The microscopic analysis of the investigated fresco fragment using the cathodoluminescence technique [13–15] revealed the presence of two distinct areas: an outer, unaltered layer, and a strongly altered internal layer. The outer layer (Figure 4a,b) is unaltered and has orange luminescence, specific to calcite-type carbonate minerals. The thickness of this layer ranges from 0.3 to 0.5 mm, and it is composed of a mixture of sedimentary particles, ranging in size from very fine arenite (63–125 µm) to silty particles (3.9–63 µm), that are poorly sorted and have subrounded contours. These particles are trapped in an extremely fine matrix, possibly composed of calcitic lime (CaO or $Ca(OH)_2$).

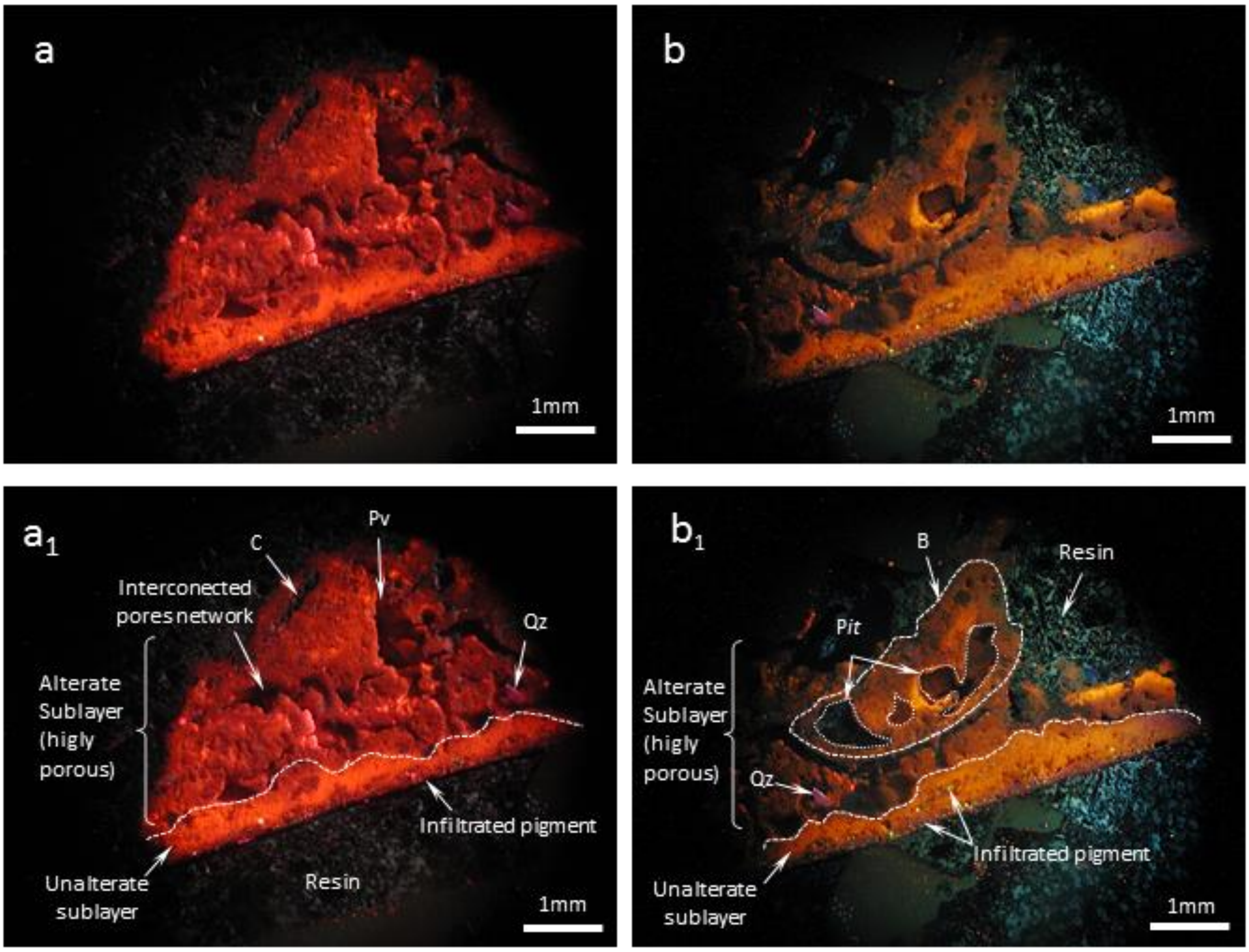

Figure 4. Cathodoluminescence analysis. Fragment of the fresco with two distinct areas: an external unaltered sublayer and an internally altered layer with high porosity. (**a1**) interpreted image of image (**a**,**b1**) interpreted image of image (**b**) Qz-quartz; C-fragment of carbonized plant (straw); PV-vacuolar porosity; B-bioclast; Pit-intraparticle porosity.

Beneath the unaltered layer, the mortar shows a faint red luminescence that is characteristic of carbonate minerals such as dolomite ($CaMg(CO_3)_2$). This suggests that lime of dolomitic origin (CaMgO) was used in the preparation of the fresco.

At this level, the component sedimentary particles are found in low percentages. Carbonate particles are not observed in the internal layer, these being completely dissolved. However, in contrast to the fine sedimentary particles observed in the altered layer, large bioclasts of carbonate, possibly gastropods, are present and are millimeters in size. These bioclasts exhibit partially dissolved tests and a dull orange luminescence (Figure 4b_1). Quartz grains appear in low concentrations, showing purple luminescence colors, specific to quartz of volcanic origin (Figure 4b_1). There are also fragments of non-luminescent carbonized plants (possibly straw) present (Figure 4a_1), which were likely used as an additive in the preparation of the mortar. The development of intraparticle, vacuolar, and channel secondary porosity (Figure 4) is a result of pronounced processes of selective dissolution of calcitic carbonate particles in ambient environments with normal temperatures (20 °C) after exposure to meteoric waters characterized by a slightly acidic pH [13–15].

The pores in the internally altered layer of the fresco are large, irregular, and interconnected, which facilitates the infiltration/circulation of meteoric fluids. It has to be mentioned that the selective dissolution process did not affect the mortar because the dolomite in its composition is a carbonate mineral that is resistant to dissolution under normal temperature conditions (20 °C) [16–18]. It dissolves when the ambient temperature exceeds 40 °C, at an acidic pH of 4 (conditions not reached inside the Corbii de Piatră cave), with activators (Mn^{2+}) and inhibitory minerals (Fe^{2+}) [17,18]. The dolomitic matrix that binds the mineral particles has a dull, reddish-brown luminescence and non-luminescence in some places. It can be the result of mortar preparation under exogenous conditions, in which case O_2 is the inhibitory element of luminescence [1]. Secondary carbonate recrystallizations can be observed on the internal pore walls. The bright red or orange luminescence of these minerals suggests re-precipitation of dolomite and calcite on the internal pore rim from percolating fluids under dysoxic conditions.

Atomic force microscopy is used in the analysis of construction materials and paints to highlight the surface profile and characterize the surface condition of these materials [19,20]. The main parameters that were monitored included the mean roughness (Ra) and the mean squared roughness (Rq) of a line on the investigated surface, as well as Sa and Sq, which represent the corresponding parameters for the entire analyzed surface [21]. The average roughness (Ra) represents the average value of the individual heights (surface asperities) and the depth of the arithmetic mean elevation of the profile. The root mean square roughness (Rq) is the square root of the sum of the squares of the individual heights and depths from the mean line of the investigated line.

The experiments were conducted on EasyScan II equipment from Nanosurf using a CTR-10 tip in non-contact mode. The purpose of the experiments was to determine the average surface roughness of ceramic materials, characterize their 2D and 3D appearance, and identify whether they comprise a unitary homogeneous agglomerate composed of a single material or a multi-component structure. The configuration of the fresco surface covered with a pictorial layer was also studied.

The fresco sample with red colored paint, an area shown in Figure 5a–c, was scanned with an atomic force microscope, and the surface profile given in Figure 6 for 24.8×24.8 μm^2 in a and 6.19×6.19 μm^2 in b. The main parameters for the median analysis area of the exposed surface have the following values: Ra is 80.146 nm, and Rq is 93.64 nm. The surface profile shows that the area has asperities/peaks below 10 μm and averages at the nanometer level (Sa = 85.05 nm and Sq = 102.58 nm). The directionality of the red paint layer applied through a brushing operation can be observed.

Figure 5. The composite material of the fresco with red paint applied on the outside in (**a**,**b**) and the area analyzed by atomic force microscopy in (**c**).

Both 2D and 3D AFM at 25×25 μm^2 surface scans present a homogenous material with no pores or microcracks at the microscale. At the microlevel (shown in Figure 6b with a size of 6×6 μm^2), no alternation of the constituent materials was observed in the surface layer. Only the arrangement of the paint on strips of 1–2 μm or less was detected, as depicted in the 3D image in Figure 6b.

The characterization of the pictorial layer was completed by SEM analysis and elemental composition determination.

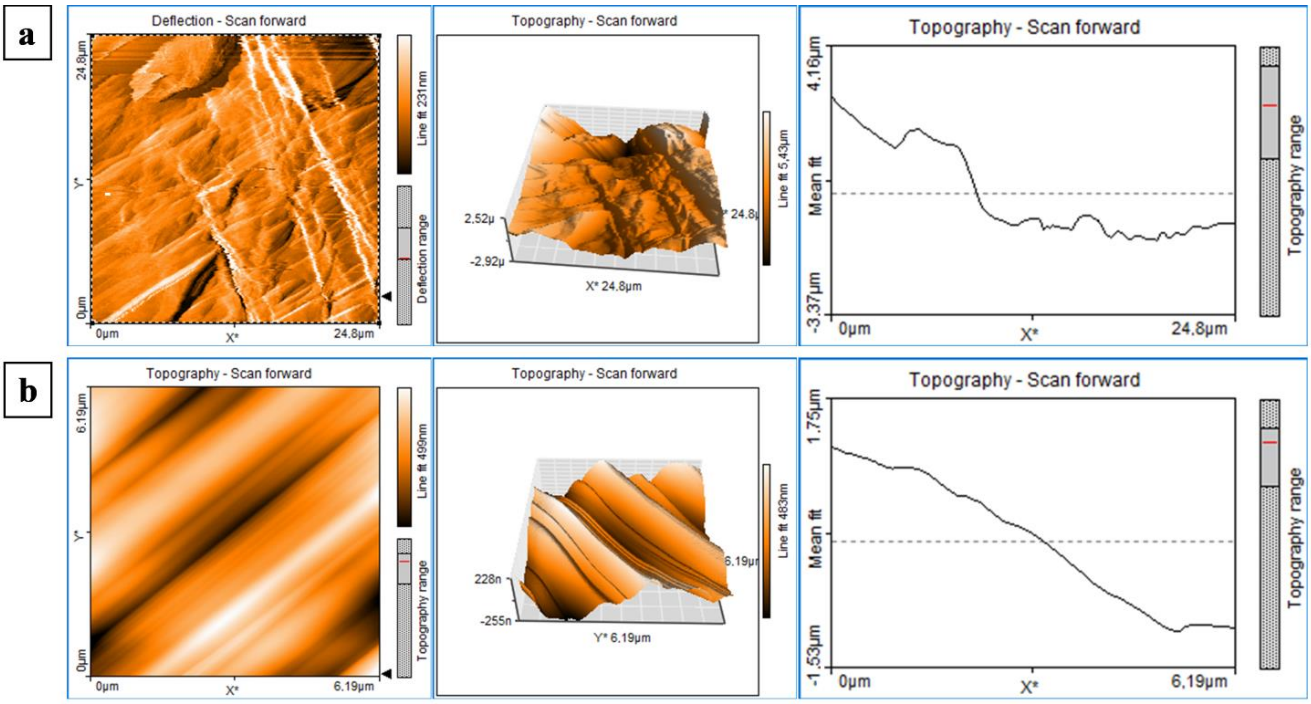

Figure 6. AFM images of the surface of the red painted layer material: (**a**) on a 25 × 25 µm^2; (**b**) on 6 × 6 µm^2 analyzed area.

The SEM analysis was used to examine the morphology and interface quality of the phases, which exist as small separations and cannot be observed through optical microscopy. It was also used to identify the layers present in the fresco section, including the carbonation layer that formed during the fresco drying process, the pictorial layer, and the intonaco layer [8,10,21,22]. The thickness of the pictorial layer is 6.7–14.5 µm, and the thickness of the plaster layer is between 15.9 and 41.6 µm (Figure 7). Above the pictorial layer, the carbonation layer is visible.

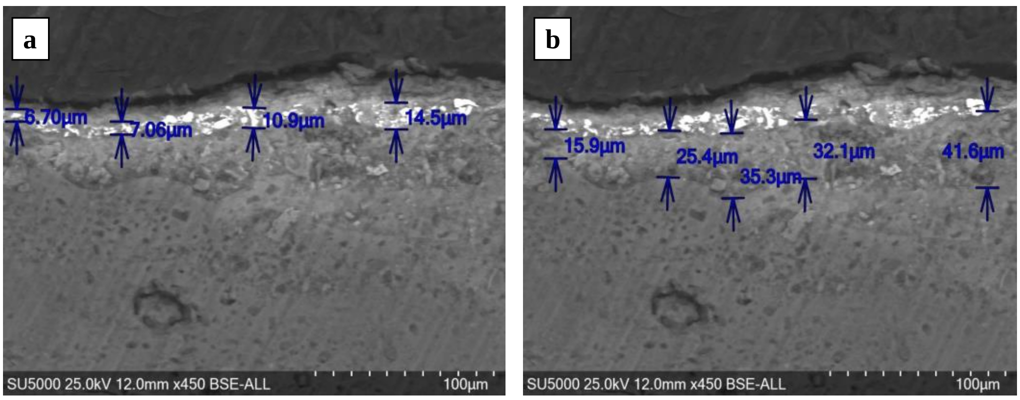

Figure 7. Determination of layer thicknesses from cross-section SEM analysis at ×450 magnification: (**a**) pictorial layer; (**b**) intonaco layer.

The EDX spectra allow the elemental analysis of the mortar components, which complements the XRD analysis and enables correlation between the microstructure and composition of the layers and areas that have undergone advanced degradation. The variation of the sulfur content on the thickness of the sample (Figure 8) and the EDS mapping (Figure 9) shows the presence of sulfur on the surface of the sample. The superimposed spectra drawn at different points concerning the surface (Figure 10 showed the variation of the sulfur content from the pictorial layer toward the inside.

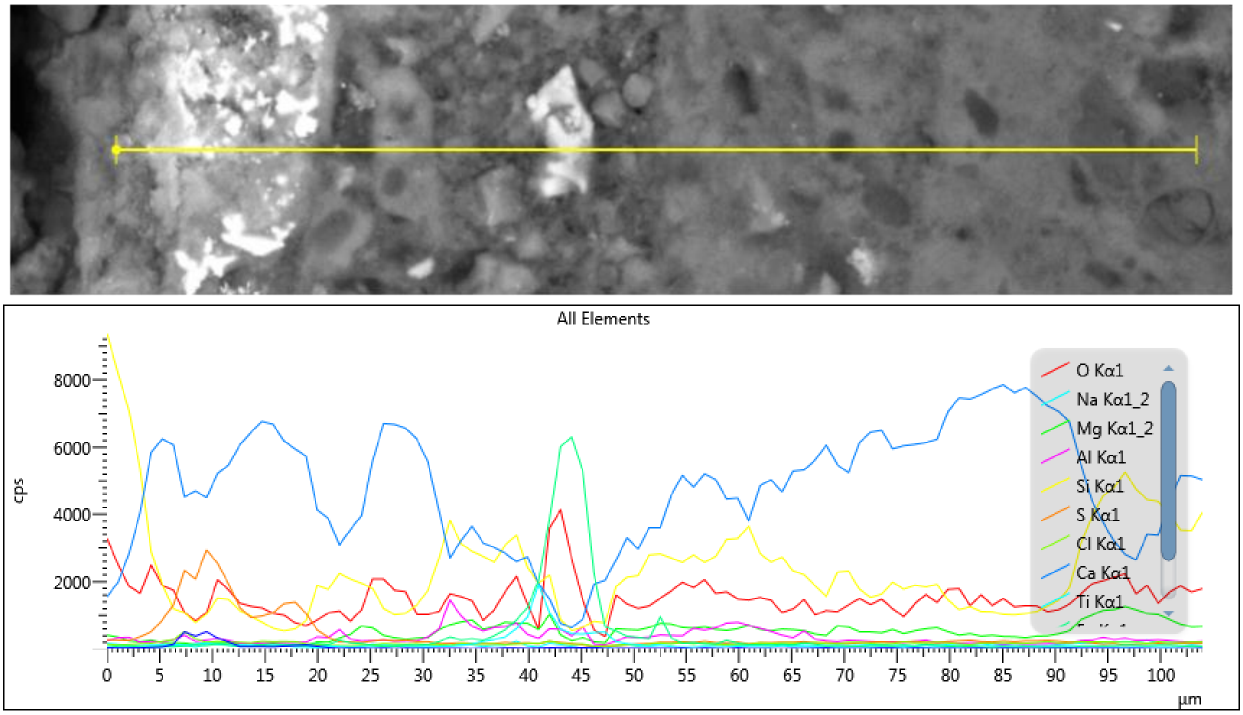

Figure 8. EDS line-scan analysis for the fresco with the red pictorial layer.

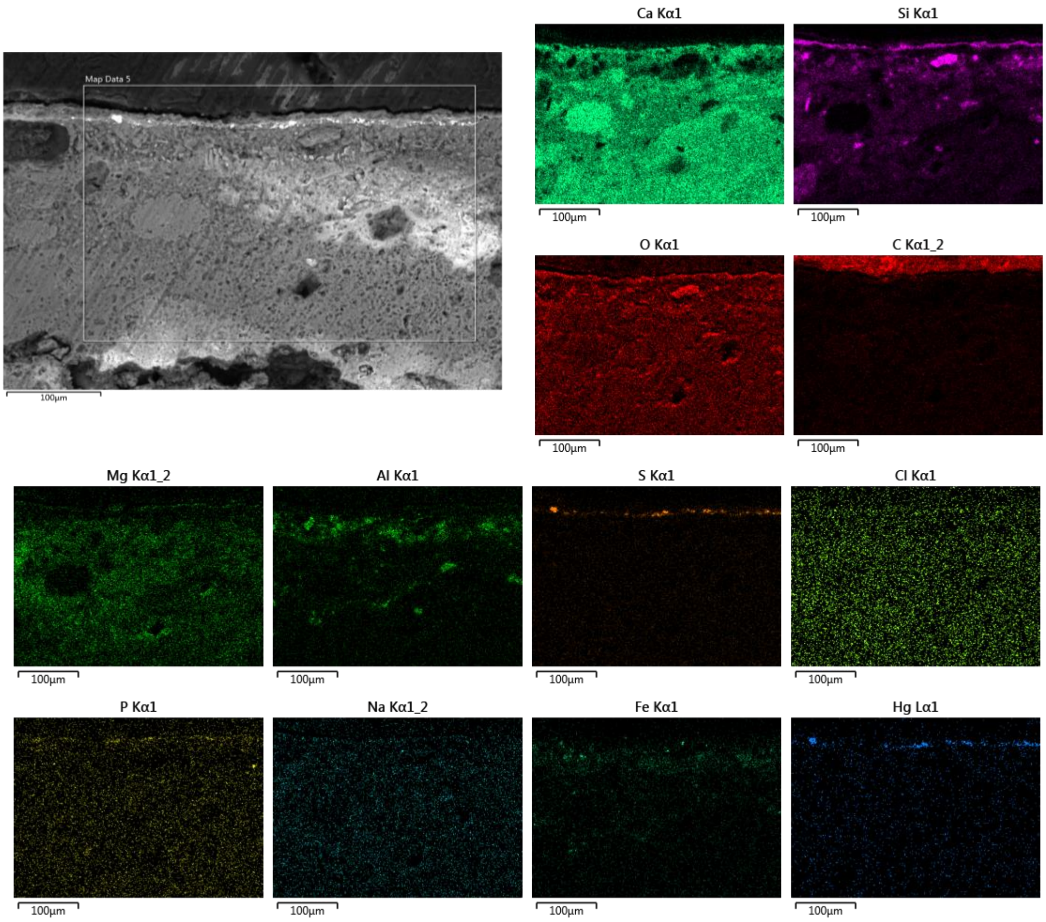

Figure 9. The pictorial layer in section through the fresco.

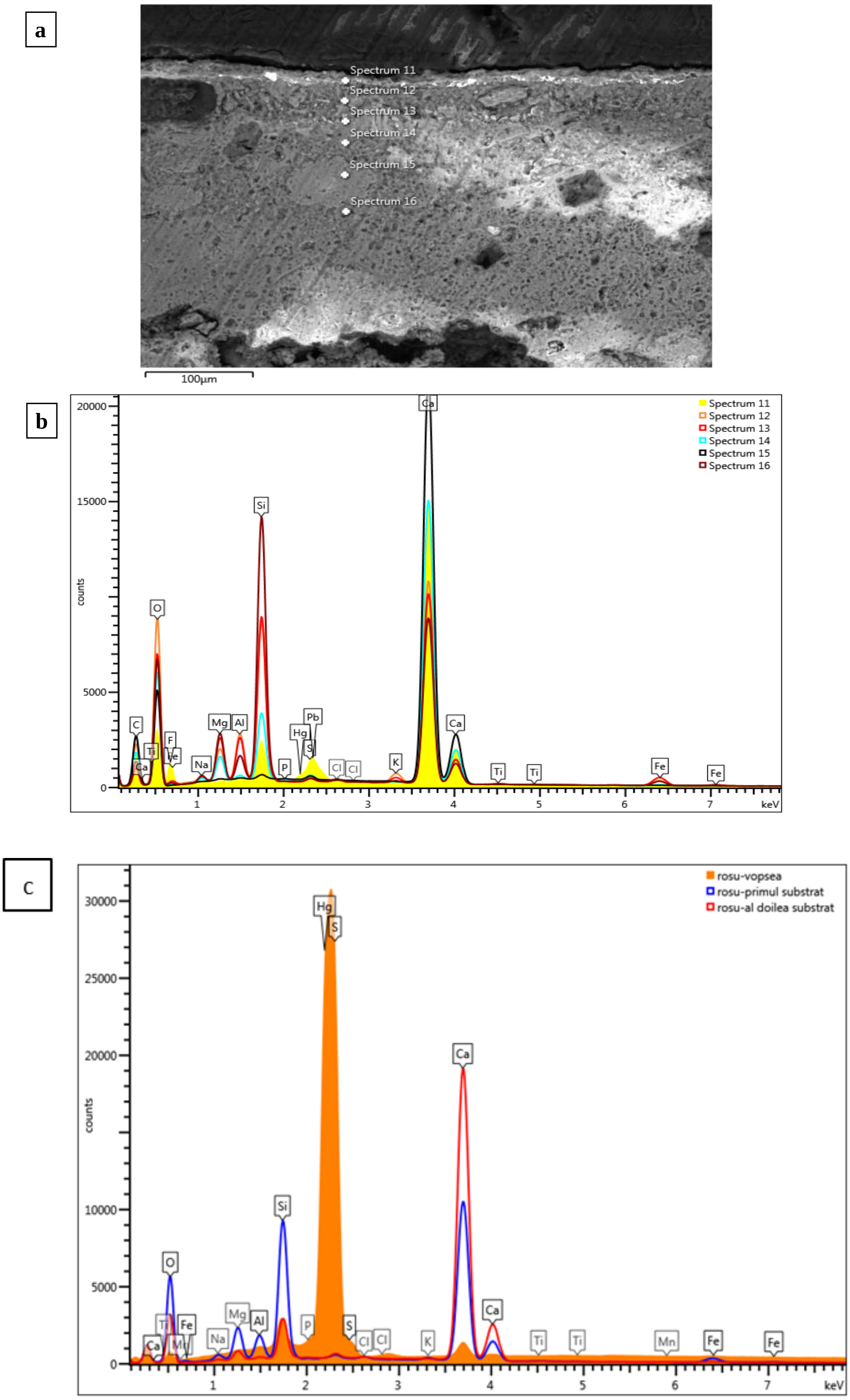

Figure 10. Superimposed EDS spectra in two areas of the section. (**a**) MEB image; (**b**) the evolution of the concentration of the elements on the thickness of the fresco fragment Figure 10a, 11-pictorial layer (with the presence of Fe-hematite, Hg, and S-cinnabar), 12-intonaco layer, 13-interface intonaco–arriccio, and 14-15-16-arriccio; (**c**) composition in three points (for another area in the fresco) orange for the pictorial layer (with the presence of Hg and S-cinnabar and Fe-hematite), blue for the intonaco layer, and red for the arriccio layer. For the mortar layers in both figures, the presence of specific chemical elements can be noted.

The superimposed spectra in Figure 10a show the evolution of the elemental composition on the thickness of the fresco. The red pictorial layer exhibits specific elements (spectrum 11). The intonaco layer shows an increasing content of Ca and Si, as seen in spectra 12 and 13. The support layer, depicted in spectra 14 and 15, has high levels of Si, indicating the abundance of quartz in the sedimentary rock. The elemental composition and the superimposed EDS spectra highlighted the presence of high concentrations of calcium and oxygen on the surface, which are associated with the carbonation layer formed during the drying of the fresco. Additionally, the presence of iron, sulfur, and mercury in the pictorial layer was observed (Figure 10c).

The elemental composition, determined in four points on the surface of the red pictural layer (Figure 11, Table 1), shows the presence of iron.

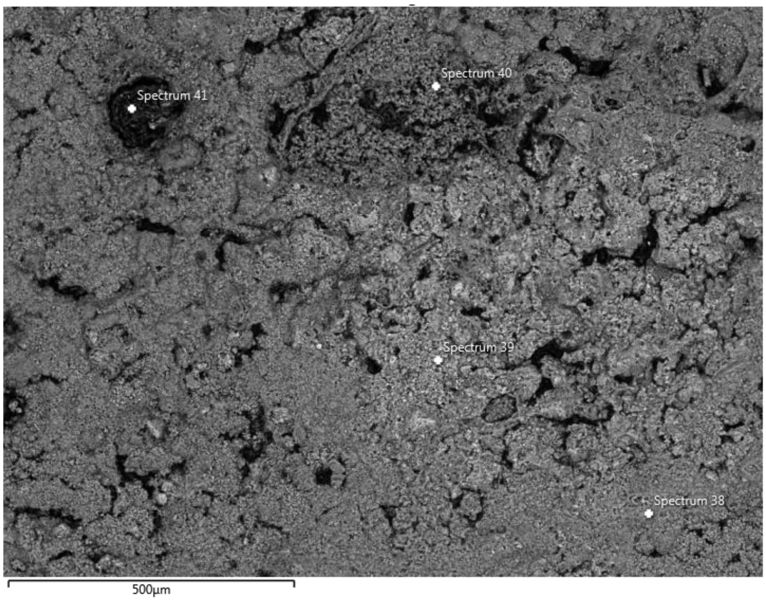

Figure 11. SEM–EDS scan on the surface of the red painting layer.

Table 1. Elemental chemical compositions on the front of the painting layer are determined at four points shown in Figure 11.

Spectrum Label	Concentration in wt%—Figure 11 Point Scans										
	O	Na	Mg	Al	Si	P	S	K	Ca	Mn	Fe	Total
38	55.54	0.11	0.43	0.97	21.33	0.13	-	0.25	15.43	0.10	5.72	100.00
39	38.96	-	0.52	1.64	28.70	0.25	-	0.52	7.45	0.51	21.45	100.00
40	51.69	-	0.24	0.48	41.39	-	-	0.17	5.01	-	1.01	100.00
41	57.57	2.43	1.95	0.23	4.96	-	19.52	1.39	11.32	-	0.63	100.00

The two sets of results obtained for the composition of the pictorial layer, as shown in Figures 9 and 10, and on the surface (Figure 11 and Table 1), indicate the presence of the elements (Hg, Fe, and S) that correspond to the presence of cinnabar (HgS) and red iron ochre (hematite Fe_2O_3). The analyzed pictorial layer was made with a mixture of cinnabar and red iron ochre.

In general, in fresco painting, silicon reveals the presence of quartz in the support, but this can also be determined by the use of coal rich in silicon, such as the one from the vine. In the present case, the association with carbon is relevant.

The presence of sodium, associated with Ca, Al, Si, and S, without Cl, suggests the use of sodium aluminosilicate with sulfur or ultramarine blue $(Na, Ca)_8$ $(AlSiO4)_6$ $(SO_4, S, Cl)_2$. An interdisciplinary study conducted by the National University of Art under the direction of Professor Mocanu [2] suggested the possible use of blue color but did not identify it. This viewpoint must be confirmed by future pigment analyses.

The qualitative phase analysis [23,24] was carried out using the PDXL2 program (Rigaku) and the PDF4+ 2022 database (International Center for Diffraction Data).

The qualitative phase analysis (Figure 12) highlighted the presence of the following polycrystalline phases:

- for the mortar support (Figure 12a): calcium carbonate ($CaCO_3$) and calcium and magnesium carbonate (($Mg_{0.03}$ $Ca_{0.97}$) O_3), with a small amount of monoclinic silica. Other components were identified by cathodoluminescence, which can be explained by the fact that these compounds are below the detection limit by XRD, or they can be found in the composition of the mortar in an amorphous state.
- for the pictorial layer (Figure 12b), two pigments were highlighted: cinnabar (α-HgS), hematite-red iron ochre Fe_2O_3, and elements from the mortar support, quartz (α-SiO_2), and calcium carbonate ($CaCO_3$).
- Calcium, magnesium, and silicon are chemical elements characteristic of the composition of the supporting mortar of the fresco.

The positions of the diffraction peaks from the PDF cards used for qualitative phase analysis (having the lowest figure of merit) are presented in Supplementary Materials (Figures S1 and S2).

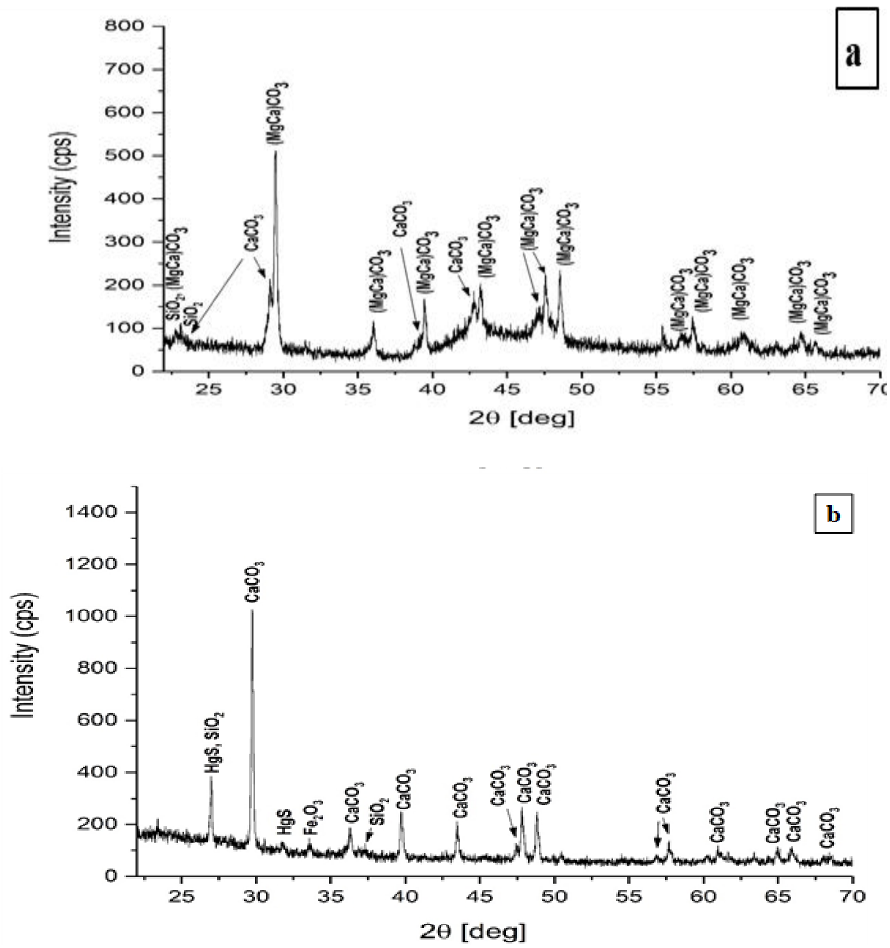

Figure 12. Qualitative phase analysis by X-ray diffraction of the fresco sample covered with a red painting layer, whose mortar shows good adhesion to the sandstone wall: (**a**) analysis of the mortar; (**b**) analysis of the pictorial layer.

4. Conclusions

Considering the advanced degradation of the whole fresco mural painting in Corbii de Piatra cave church, including the significant detachment of large portions of the fresco due to the friable mortar and small areas with high adhesion to the sandstone wall, this study aimed to characterize an element with high adhesion in the fresco and to establish correlations with factors that contribute to the stability to the fresco. The analyzed fresco sample was collected from an area with high adhesion on the northern wall of the church, which has the highest humidity due to water infiltration through the sandstone.

The research facilitated the identification of the structural constituents, the determination of the elemental composition for the supporting mortar and the red painting layer, the identification of the inserts and their role in the propagation of cracks, and the identification of compaction defects in the fresco layers.

The red paint layer appears to be continuous and unaltered, with an uneven thickness. It adheres well to the mortar support and, in some areas, appears to have penetrated the pre-existing cracks in the mortar.

On its surface, a thin layer of carbonation, thick layers of deposits, and areas of surface degradation were identified.

The roughness of the surface shows that the method of application was brushing.

The pigments used for the red color in the pictorial layer were identified through X-ray diffraction and EDS elemental analysis as cinnabar (HgS) and red iron ochre (Fe_2O_3, hematite). These compositions are consistent with those discussed in the work [4]. A mixture between the two pigments could also have been used.

The DRX qualitative phase analysis highlighted the presence of calcium carbonate ($CaCO_3$) and calcium and magnesium carbonate $(Mg_{0.03}Ca_{0.97})O_3$ in the mortar.

The thickness of the intonaco mortar layer is uneven and varies between 15 and 41 μm. The layer's characterization using OM and CL allowed the identification of the structural and petrographic constituents that originated from the mortar's preparation as well as from the dissolution/deposition processes under the action of meteoric water.

The straw inserts identified by the carbon residue in the mortar are well integrated into the matrix, and the quality of the insert-mortar interface is good. The tips of the inserts are tension concentrators, from which cracks start.

The cracks identified in the mortar are short. Some of them develop perpendicularly to the surface of the fresco due to repeated wetting/drying processes, while others occur inside the fresco. Part of the cracks originates from the top of the straw inserts. Rounded separations of fatty matter with yellow–orange light separations, were identified both in the mortar matrix and near the compaction defects. These separations may be deposits or may be associated with the addition of sheep tallow, a component used at that time to increase the quality of the mortar.

The presence of moldic and vacuolar secondary pores was observed in the mortar, in canal-like spaces. The pores are large, irregular, and interconnected, allowing the infiltration/circulation of meteoric fluids in the lower layer of the fresco and thus reducing the advanced action on the upper layers.

Mortar and pigments, the materials identified as being used for the fresco, are of indigenous origin.

The quality of the mortar matrix and the formation of an interconnected network of pores that allow the circulation of meteoric fluids in the mortar layer of the fresco without degrading or detaching the mortar can explain its good adhesion to the sandstone wall. In this situation, the mortar behaves as a drainage mortar.

Previous research led to the testing of a mortar with a similar composition. The research carried out by the authors regarding the behavior of the adherent mortar layer, the formation of drainage channels, and the documentation from the works of Marcus Vitruvius Pollio led to the restoration solution with a drainage mortar and an intonaco mortar with additives (sheep tallow or oil).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13084933/s1, Figure S1: XRD qualitative phase analysis of the mortar support, with displayed PDF cards peak bars (PDXL 2 software); Figure S2: XRD qualitative phase analysis of the pictorial layer, with displayed PDF cards peak bars (PDXL 2 software).

Author Contributions: A.E.V. participated in all study activities, including sample collection, characterization, and result interpretation; D.G. (Dorin Grecu) advised and participated in sample collection and result interpretation; I.M. performed cathodoluminescence analysis and result interpretation; A.D.N. contributed to the characterization studies using optical microscopy and MEB–EDS and result interpretation; N.C. performed AFM analysis and result interpretation; D.G. (Daniela Giugea) motivated the research theme and conducted the study presented at the Arhiepiscopia Argeșului și Muscelului to obtain a sample collection agreement; B.I. and C.M. contributed to the X-ray diffraction analysis; S.G.M. contributed to the interpretation of the X-ray results; D.-C.A. and A.D.R. contributed to the ceramic microscopic characterization and results interpretation; M.I.P. contributed to the mineralogy results interpretation; M.A. established the theme, conducted and coordinated the interdisciplinary team at the national level, and participated in all research activities. All authors have read and agreed to the published version of the manuscript.

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