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A Case Study of Renaissance Wall Paintings in Granada (Spain): Historical–Artistic Analysis, Materials Characterization, and State of Conservation

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Abstract: The research carried out on the wall paintings of Hernán Pérez del Pulgar's Palace chapel in Granada (Spain) was aimed at determining its historical–artistic, stylistic, technical, and compositional aspects. For this, a 16th century frieze and an 18th century pendentive were studied. The mineralogical, chemical, and textural characterization of the constituent materials and the study of the state of conservation of the paintings have helped to determine the pictorial technique used, identify the nature of the salts present in the paintings, and other pathologies including a dormant fungal attack. To this end, optical microscopy (OM), X-ray diffraction (XRD), Field emission scanning electron microscopy with microanalysis (FESEM-EDS), and micro-Raman spectroscopy (MRS) were used. The information obtained helps clarify important aspects of the painting technique used, laying a basis to ensure effective and suitable conservation and restoration measures on the paintings that will ensure their durability over time.

Keywords: wall painting; tempera; pigments; conservation; efflorescences; fungi attack

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1. Introduction

Rendering mortars have constantly been used to protect the internal structure of buildings from exposure to environmental factors and deterioration agents (e.g., condensation, rain, direct sunlight, contaminants, etc.). In some cases, and depending on the historic period, renders and plasters were provided with an aesthetic value that reflected the social level of the house's patron, as is the case of Roman and Medieval wall paintings [1–3]. Wall paintings are regarded as one of the oldest pictorial manifestations of artistic heritage, understood as any type of decoration made on a wall using plaster, mortar or stucco, and pigments [4], as well as a valuable historical document. Therefore, research on wall paintings has become a growing issue for its relevance in art history and in the conservation and enhancement of cultural heritage [5].

The traditional masonries upon which wall paintings are found are varied, from mud brick and fired bricks, to natural stone [6–8]. When covering them, lime plaster has been one of the main coatings used since ancient times, as also found in Spanish architectural heritage, enabling a huge variety of applications, and providing great textural and chromatic results [4,6,9]. Regarding the wall pictorial techniques, two seem to be the most recurrent: (i) the fresco technique, executed when the lime mortar is still wet, where pigments are mixed with water and fixed to the surface by the carbonation of the lime, and (ii) the tempera technique, carried out on a dry mortar, not necessarily lime, where pigments are fixed by means of an organic binder (e.g., rabbit glue or egg) [2,3,8,10,11].

The Renaissance was a period of great advances in artistic techniques, including developments and experimentations regarding pigments and their mixtures [12]. In Spain, the 16th century was a relevant historical period due to the formation of the modern state and the assimilation of the Italian Renaissance [13,14]. Cities such as Granada underwent important artistic, political, and social developments, adapting the old Muslim city to the Christian one with the creation of new buildings [15–17]. Andalusian workshops such as those of Julio Aquiles and Alexandre Mayner, together with painting collaborators such as Gaspar Becerra and Antonio Sánchez Ceria, favored the dissemination of the Italian Renaissance style in Granada [17–20]. For instance, in the Alhambra palaces, Pedro Machuca conceived space in a way inherited from the Italian Rafael and Peruzzi [14,20].

Mural decoration underwent a considerable rise at the end of the 17th century and especially in the first half of the 18th century. The custom of covering walls went beyond religious spaces, reaching urban areas, hence giving rise to a considerable sensitivity for mural decoration particularly on the façades of the main buildings and palaces in Granada [21]. The following period (19th century) was the scene of the French invasion by Napoleon's troops. This resulted in the lootings of many religious artistic heritage sites, including those that took place during the occupation of Granada (1810–1812) [22,23]. In addition, this period went through artistic changes in which late Baroque and Rococo trends were developed, and the adaptation of the French neoclassical style was encouraged [24].

The wall paintings studied in this paper are located inside Hernán Pérez del Pulgar's Palace, also known as the Viceroy Palace. The palace is a building from the 16th century, considered as a typical Renaissance palace since it follows the Castilian architecture canons of the time [25,26]. The palace was owned by Hernán Pérez del Pulgar, marquis of Salar, an important figure who took part in the expulsion of the Moors in 1492 [27]. The palace is located in a privileged area of the town center of Granada, following the course of the world heritage UNESCO Darro River Street (number 5, Carrera del Darro, Granada) (Figure 1). This street preserves important historical buildings from the 17th century (e.g., Church of San Gil and Santa Ana, and Church of San Pedro and San Pablo) and others including the Arabic baths (11th century) and buildings from the beginning of the 20th century [28,29]. This street also preserves wall paintings whose colorfulness has encouraged their conservation in recent decades [28,30–32].

From the archaeological study and testing carried out by Álvarez García and Raya Praena [26] and Arroyo Terán [25], it is known that the building has a coffered ceiling in wood whilst the masonry of the wall paintings was made with perforated bricks and a lime mortar with washed river sand, as is commonly found on Andalusian historical buildings [33–36]. However, while an exhaustive archaeological and architectural study of the palace has been carried out [25,26], no studies have been conducted on the wall paintings. Before performing any kind of intervention on the paintings, conservators and restorers must be aware of their documentary nature (historical, iconographic, morphological, stylistic, aesthetic, and spiritual references) [37]. The wall paintings in question, of unknown authorship, are found in the chapel of the first floor of the palace. This room presents, on the one hand, an anteroom decorated with two decorative friezes and, on the other hand, the chapel itself composed of a small dome with its cornice and four pendentives.

Since wall paintings are integrated in the masonry, they are subjected to specific environmental and deterioration agents. The delicate state of conservation to which the wall paintings belong is due to the widespread deposition of saline efflorescences that have given rise to the loss of the original painting and must be solved to preserve the paintings over time. Therefore, to be able to carry out an effective and respectful conservation–restoration intervention, it is important to know the composition of the materials used in the wall paintings, as well as the possible causes of deterioration [38,39].

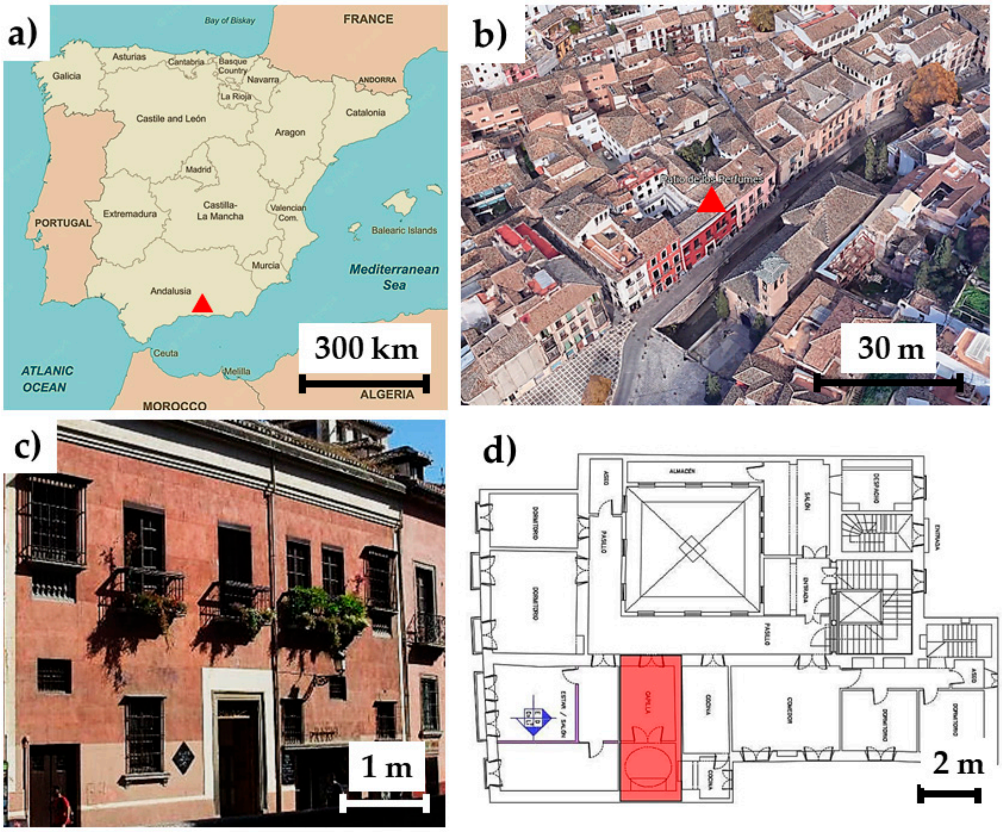

Figure 1. Localization of Hernán Pérez del Pulgar's Palace chapel. (**a**) Map of Spain with the province of Granada marked in red. (**b**) Image of the location of the palace in the historical center of Granada, marked in red. (**c**) Main façade of the Palace on street Carrera del Darro, number 5. Photo credit: D. Jiménez-Desmond. (**d**) First floor plan of the palace, with the chapel marked in red. Scale 1:150 m. Photo credit: J.D. López-Arquillo.

The general objective of this study is to collect information about the paintings in question to provide a basis to carry out successful conservation and restoration treatments. For this, the following specific objectives were pursued:

- Thorough historical research and study of Renaissance wall paintings in Granada to collect new data about the wall paintings in Hernan Pérez del Pulgar's chapel, giving continuity to the previous studies of the palace complex [25,26];
- Chemical, mineralogical, and textural characterization aiming to determine the constituent materials of the paintings, as well as the nature of the present salts, so that professionals of the field can carry out effective conservation–restoration treatments.

2. Analytical Procedure

2.1. Historical–Artistic Study and State of Conservation of the Wall Paintings

Firstly, a historical–artistic study of the wall paintings in Hernán's Pérez del Pulgar's Palace chapel was carried out. This included the most relevant data on their material history and the interventions detected on them, together with those described in documentary sources. The wall paintings in the anteroom (Figure 1d) of the chapel consist of two friezes (Figure 2a,b), the south-west frieze and the north-west frieze, the latter one in a poorer state of preservation. The south-west frieze has dimensions of 1.46 m high by 3.18 m wide, while the paintings on the north-west frieze have the same height but wider, 4.13 m. On the other hand, in the chapel, we found a small dome with dimensions of 2.62 m in diameter and 1.14 m in height. The dome rests on a cornice and four pendentives, richly decorated (Figure 2c). Next, a study of the state of conservation of the wall paintings was performed by means of visual examination, identifying pathologies and possible deterioration agents.

For the sake of facilitating the work of conservators and restorers, a series of degradation maps were drawn up using Adobe Photoshop software CC 2018.

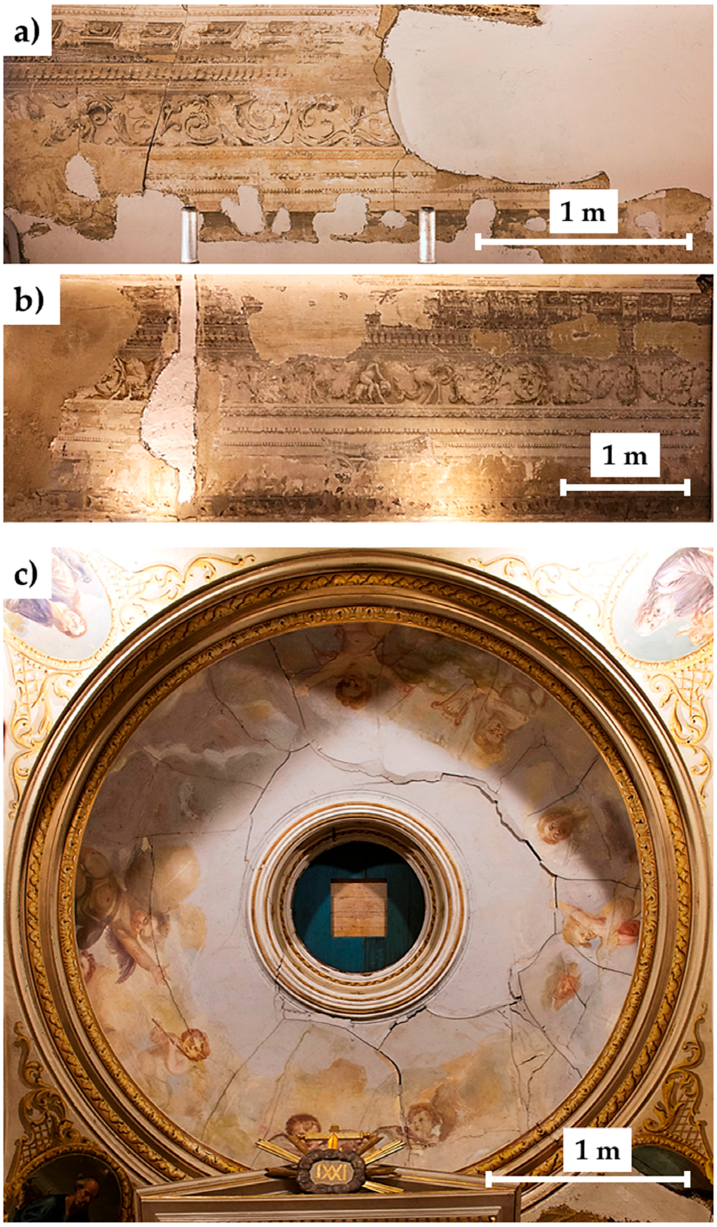

Figure 2. Wall paintings from the chapel of Hernán Pérez del Pulgar's Palace. (**a**) Frieze from the anteroom (SW). (**b**) Frieze from the anteroom (NW). (**c**) Dome, cornice, and four pendentives of the chapel.

2.2. Materials

Nine micro-samples (Table 1) were taken from the wall paintings to be characterized from a compositional and textural point of view. The sampling procedure was guided considering the diverse colors present at the surface of the paintings and their state of conservation.

Table 1. Paint samples taken from the 16th century wall paintings in Hernán Pérez del Pulgar's palace chapel.

Sample	Description	Location
FR-GB-W	Greyish blue and white polychromy	NW frieze
FR-B	Brown polychromy	NW frieze
FR-EF-M	Mortar with efflorescences	NW frieze
FR-EF	White polychromy with efflorescences	NW frieze
FR-SEF	Grey polychromy with subefflorescences	NW frieze
C-EF-M	Mortar with efflorescences	Cornice of the dome, above Saint Mark's pendentive
CP-EF-Y	Yellow polychromy with efflorescences	Saint Mark's pendentive
CP-EF-BL	Blue polychromy with efflorescences	Saint Mark's pendentive
CP-EF-R-B	Red and brown polychromy with efflorescences	Saint Mark's pendentive

FR: frieze; GB: greyish blue; W: white; B: brown; EF: efflorescence; M: mortar; SEF: subefflorescences; C: cornice; CP: chapel; Y: yellow; BL: blue; R: red.

2.3. Analytical Techniques

Sampling must be carried out in a careful and respectful manner towards the wall paintings. Therefore, samples were taken with a scalpel from the north-west frieze since it presented the worst state of conservation, with detachments of the pictorial layer that facilitated the sampling. The same occurred in the taking of samples from the chapel itself, where one of the pendentives presented many deteriorations (Saint Mark's), making the process easier without the need of taking samples from well-preserved areas.

For this study, the macroscopic observation and photographic recording of samples were carried out by using a Nikon SMZ 1000 stereoscopic microscope with a 30× maximum magnification.

The mineralogical composition of the samples was analyzed by means of X-ray diffraction (XRD) using the random powder method. Samples pieces were ground in an agate mortar, with a size of less than 50 µm. An X'Pert Pro diffractometer with copper radiation was used, equipped with an automatic slit and continuous sample rotation system. Experimental conditions were as follows: voltage of 45 kV; intensity of 40 mA; Cu Kα radiation (λ = 1.5405 Å); scanned zone between 4 and 70° 2θ; goniometer speed of 0.1° 2θ/s. Data interpretation was conducted with the aid of Xpert Highscore 2.0 (PANalytical), Xpowder10, and Xpowder 12 software, all of them equipped with the Joint Committee for Powder Diffraction Standards (JCPDS) PDF-2 database.

The microstructure, texture, mineralogical composition, and state of conservation of selected painting samples were studied by optical microscopy (OM) used with both transmitted light (TL) and reflected light (RL) in plane-polarized light (analyzer removed) or crossed polarizers (analyzer inserted). A Carl Zeiss Jenapol U instrument (Germany) equipped with a Nikon D-7000 digital camera was employed to this end. Samples were prepared as polished thin sections to study their cross sections.

The elemental composition and microtexture of the paintings were studied by means of two field emission scanning electron microscopes (FESEM) coupled to an X-ray energy dispersion spectrometer (EDS). The microscopes used (Carl Zeiss, Germany) were a Zeiss Supra 40 Vp microscope with a X-Max 50 mm Aztec 3 detector and an AURIGA microscope coupled with a microanalysis system INCA-200. Both FESEMs were equipped with detectors of secondary (SE) and backscattered electrons (BSE) that analyze elements with an atomic number Z > 4 (Be). Single-point and area analyses were acquired in selected areas from bulk samples and polished thin sections. For the latter, X-ray maps were also obtained which highlight the morphology and location of the pigments in the paint stratigraphy (cross section). The SEM-EDS working conditions were 20 keV beam energy, 500 pA filament current, 10 eV/ch resolution for pinpoint and area analyses, and 20 eV/ch resolution for map acquisition.

Micro-Raman spectroscopy (MRS) analysis was performed in the paintings' cross sections using a Jasco NRS-5100 confocal Raman spectrometer to identify the nature of organic binders and pigments. Spectra were recorded by placing the thin section on the microscope (OLYMPUS) stage and observing them with 20× and 100× objectives. Paints were excited with a 785 nm laser (solid-state Torsana Starbright). Five spectra were collected from each sample spot and averaged, with exposure times of 15 s (25% power). The Raman spectra were recorded in 3000–150 cm^{-1} and 1500–150 cm^{-1} ranges with a spectral resolution of 1.6 cm^{-1}. The software JASCO Spectra Manager™ II was used to process the Raman spectra.

3. Results and Discussion

3.1. Historical–Artistic Study

Around the first half of the 16th century, the formal solutions of Italian classicism were introduced in Spain, and it was not just adopted by royalty, but practically all of the nobles and lords adopted these new aesthetic models when building their houses. Therefore, this tradition of covering walls with paintings was not exclusive to religious spaces since it was also present in urban areas and civil buildings where this new taste was emerging [17–21]. Although authorship of the wall paintings is unknown, according to the current owners, the anteroom (SW and NW friezes) and the dome and cornice paintings were executed in the 16th century Castilian Renaissance style. However, they went through aesthetic changes during the 18th century, when they also executed the paintings present in the four pendentives.

The wall paintings are in a precarious state of conservation, presenting detachments of the polychromed layer (among other pathologies), an indication that the artist might have followed the tempera technique. Despite the current owner's claim that they follow the fresco technique, the typical *giornata* (artistic term originated from an Italian word meaning "a day's work". During the execution of a wall painting, the necessary amount of mortar for a day's work is applied, leaving a mark between every day's work, known as *giornatas* [8].) found on fresco paintings was not distinguished here. This might be due to the small dimensions of the paintings, which could have been painted in a single day. Moreover, the presence of remains of the preparatory drawing in the upper left part of the north frieze, apparently made with graphite, does not agree with the traditional fresco technique in which the preparatory drawing would have been made with a brush and pigments mixed with water [4,8,40,41]. These peculiarities, among others, have given rise to questioning the pictorial technique, considering other possibilities.

Regarding the iconographic analysis of the wall paintings of Hernán Pérez del Pulgar's Palace chapel, we can observe two very different styles. Both, however, follow the classical Spanish Renaissance style: on the one hand, the style known as *Grutesco* (grotesque) in the two friezes of the anteroom and, on the other, a religious theme in the paintings of the dome and pendentives. The iconographic programs of the time were dictated by the known *Concejos*, and lastly approved by the Royal Council, highlighting painter ordinances in cities such as Seville, Cordoba, Granada, or Málaga (South Spain) [18]. These same characteristics can be observed in other Spanish Renaissance works [42].

The grotesque style is characterized by symmetry and repetition of decorative motifs. They usually form vertical bands, a structure that we know as *candeliera* (typical decorative motif based on plant or fantasy elements, marking the compositional axis, thus creating symmetry [43].) decoration. These motifs also create movement by including motifs based on scrolls and garlands. To this, we must add the anthropomorphic motifs [43–45]. Therefore, on both friezes of the anteroom, we can observe the typical decoration of 16th century palaces, with a decoration that mixes plant motifs with mythological or human figures and, as in this case, representations of architectural motifs [14,20,43,45]. Thus, the friezes present a linear distribution in which plant motifs (e.g., lianas and acanthus leaves) (Figure 3a), some fictive architectural elements (Figure 3b), and disjointed human faces are distributed (Figure 3c) mixing white, brown, and greyish-blue tones, following the guidelines of the grotesque style. This style is often found in the Renaissance style of the city of Granada, associated with aesthetic and prestigious values, very much following the Italian style where it comes from [14,18,20,26]. Grotesque art was a fundamental language from the Proto-Renaissance up to the Mannerism, a decoration that fully introduced the Italian classicism [46]. Moreover, it is a style present on the facade of houses, palaces, and even civil buildings of the city of Granada and other Andalusian cities that demonstrated the emergence of a conscience aimed to execute wall paintings in consonance with the modernization of the city [14,20,47,48].

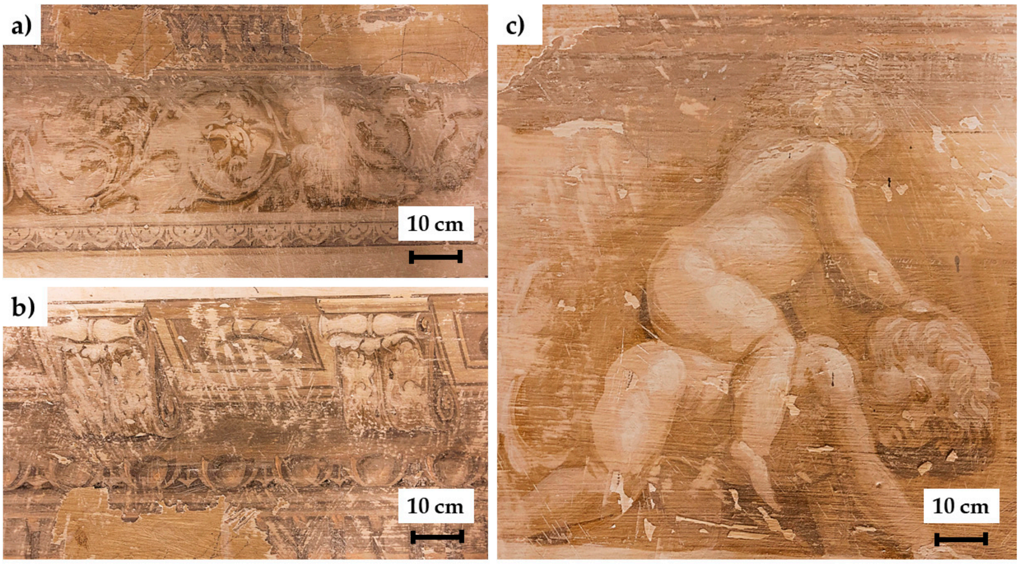

Figure 3. Iconographic details of the wall paintings from the north-west frieze. (**a**) Plant motifs based on lianas and acanthus leaves. (**b**) Architectural motifs based on a cornice decorated with plant motifs. (**c**) Human motifs based on a child riding the back of another.

Regarding the wall paintings of the dome in the chapel, the main theme of its iconographic program is of a religious nature. The dome presents in its main scene the representation of a sky covered with clouds. On this, cherubs are painted playing a variety of musical instruments (Figure 4a), simulating the Christian Paradise [49]. The dome rests on a double cornice richly decorated with acanthus leaves and other plant elements painted in a golden-yellowish tone. This cornice, in turn, rests on four pendentives where we find one of the most representative images of Christianity, both from the artistic and devotional point of view, as well as from the iconic or liturgical point of view: the four evangelists. These are represented with their corresponding allegorical forms: Mark (lion) (partly lost due to efflorescences) (Figure 4b), Mathew (angel) (Figure 4c), Luke (bull) (Figure 4d), and John (eagle) (Figure 4e) [50,51]. They are generally all represented with a pen and a book, alluding to their work as writers of the Gospels [50].

3.2. State of Conservation

The visual inspection of the wall paintings reveals intense deterioration affecting their structural nature and aesthetic appearance. This poor state of conservation is due to the 19th century Napoleonic invasion, recent historical events and state of abandonment, as well as the impact of different degradation agents that have worsened the situation [26]. After the naked-eye examination of the paintings, which allowed us to develop a first diagnosis, humidity appears as one of the main causes of decay, driving certain chemical reactions that modify the composition of the painting compounds [4,10,52–55].

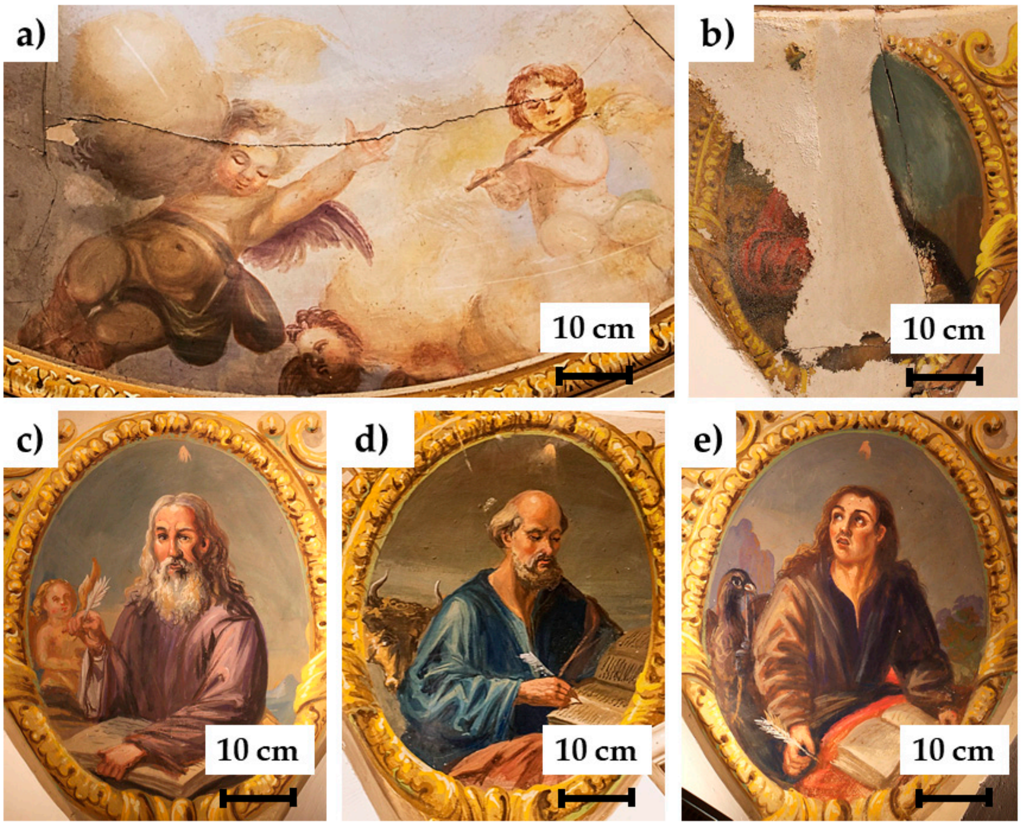

Figure 4. Iconographic details from the wall paintings of the dome and the pendentives. (**a**) Lower part of the dome where we can see cherubs playing musical instruments. (**b**) Representation of Saint Mark, with his allegorical form (lion). (**c**) Representation of Saint Mathew, with his allegorical form (angel). (**d**) Representation of Saint Luke, with his allegorical form (bull). (**e**) Representation of Saint John, with his allegorical form (eagle).

Saline efflorescences are one of the major deterioration forms present here and arise as a result of humidity filtration, both on the surface of the paintings and in depth. Salts are very destructive because they have a great water absorption capacity (i.e., hygroscopicity) and end up modifying the water behavior of the wall and giving rise to chromatic alterations [4,10,53,54,56,57]. When the wall dries, the saline solution can undergo a crystallization process that triggers further degradations: the salts present in the pores crystallize and may destroy the internal structure of the materials that can be manifested as a loss of painting, detachment of the pictorial layer, swelling, and pulverulence (among others), very common in the deterioration of wall paintings [7,53,54,56,58,59], all of which are present in the wall paintings that are studied here (Figure 5a,b).

On the other hand, as a consequence of the state of abandonment and near-ruin in which the building was found in previous decades [26], the paintings show other deteriorations such as the presence of cracks and fissures that give rise to losses and detachments, as seen in Figure 5c. The formation of cracks was mainly due to a problem with the central wooden beam of the hall's ceiling, prior to the rehabilitation of the building, which contributed to this situation [26]. This condition has also favored the infiltration of rainwater and, therefore, the appearance of salts (Figure 5d).

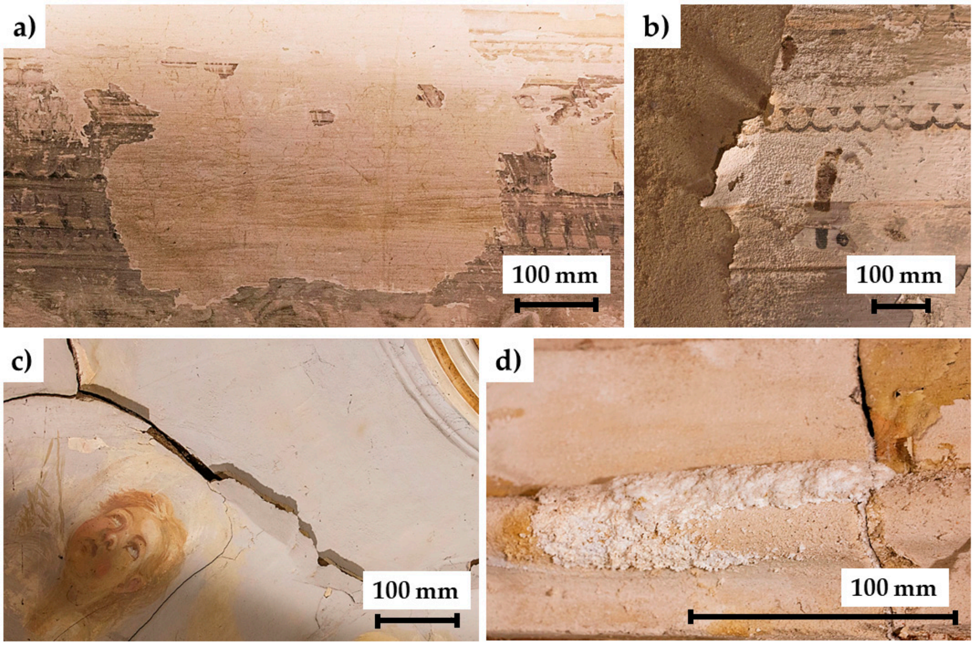

Figure 5. Images of specific deteriorations. (**a**) Detail of paint loss and the intervention with lime mortar. (**b**) Detail of detachment of the paint layer from the substratum in the north-west frieze. (**c**) Detail of a crack on the dome. (**d**) Detail of the accumulation of efflorescences on the cornice of the dome.

Therefore, cracks and salts (efflorescences and subefflorescences) are the two main deterioration forms of the wall paintings in the chapel (anteroom and dome). The characterization of the salts allows conservator–restorers to understand the type of degradation and its causes and, therefore, carry out appropriate and effective treatments, while respecting the integrity of the wall paintings [4,7,10,54]. In addition, it is also important to point out that during the rehabilitation of the palace, the paintings of the anteroom (SW and NW friezes) were subject to intervention. The large lacunas they presented, compromising the integrity of the paintings, were filled in by applying a lime-based mortar (Figure 5a). Although this has provided some stability, the paintings are still in a precarious state mainly due to the presence of salts.

Several degradation maps have been drawn out (Figure 6) to facilitate the work of professionals, indicating the location and extension of the different deterioration forms.

3.3. Compositional, Structural, and Textural Characterization of the Paintings

Macro- and Micro-Stereoscopic Study

The naked-eye and stereoscopic microscope observations confirmed the poor state of conservation of the paintings which present cracks, detachments, and pulverulence. There is a generalized chromatic alteration due to the accumulation of superficial dust on the surface. As we can see in the study of the CP-EF-Y sample (Figure 7a,b), there has been a detachment of the polychromy layer exclusively. Note that in the fresco technique, pigments become part of the intonaco (i.e., lime-based substrate) because of the carbonation process; therefore, as Figure 7b shows, these paintings have been made with another painting technique (e.g., tempera). However, what is most striking is the formation of salt efflorescences on both front and back of the yellow polychromy (Figure 7a,b).

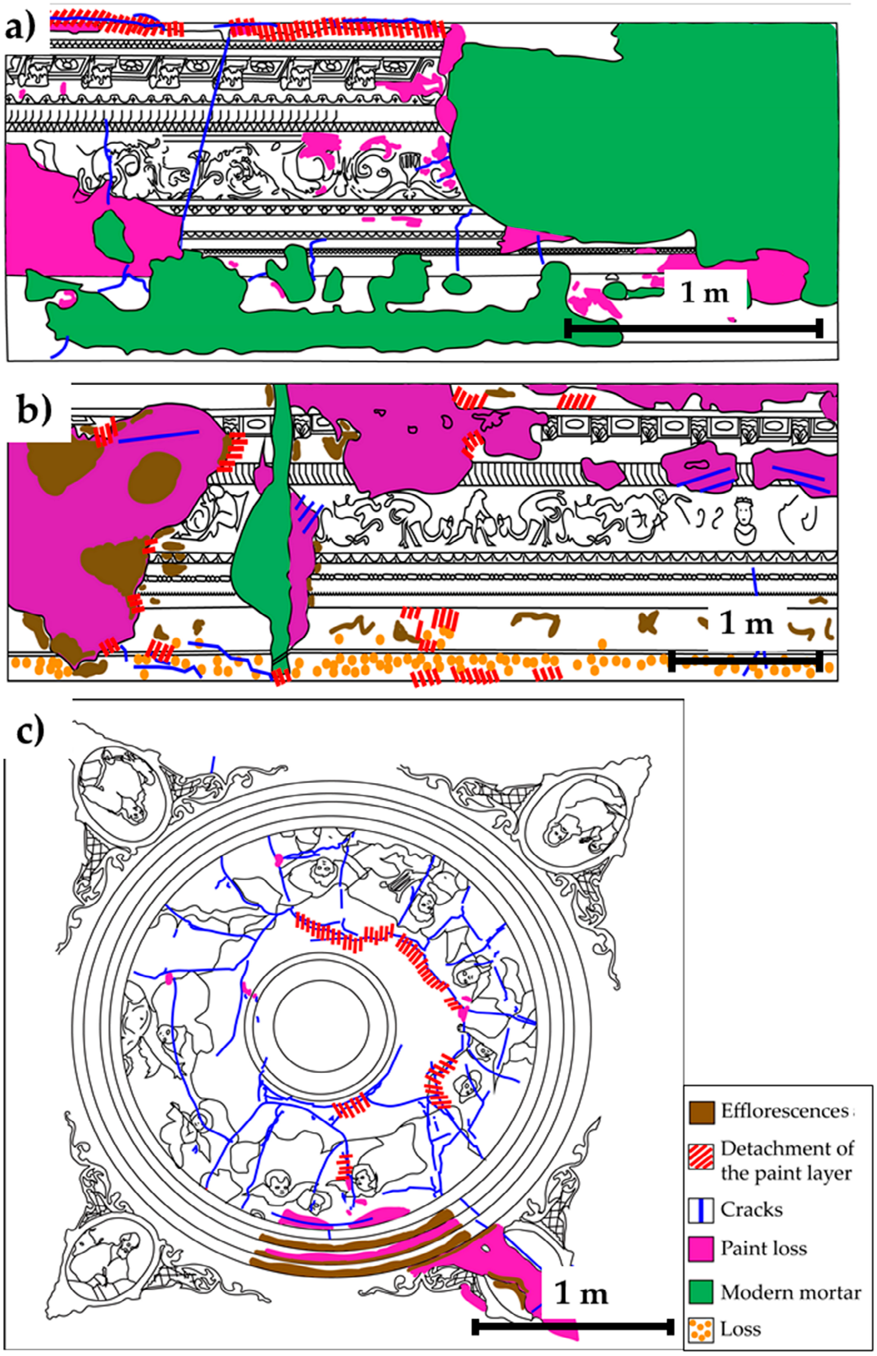

Figure 6. State of conservation and degradation maps. (**a**) Frieze from the anteroom (SW), (**b**) Frieze from the anteroom (NW), and (**c**) Dome, cornice, and four pendentives.

In the CP-EF-R-B sample (Figure 7c,d), we can observe decohesion of the outer most mortar layer and superficial fissures that cover the entire surface. This sample shows efflorescences disseminated over the entire surface in the form of a "spiderweb", forming a veil. When observing it with higher magnifications, we can see the small losses of red polychromy and the formation of salts between the pigment particles, which should exert pressure and favor its detachment, giving the pigment a powdery character (i.e., pulverulence). On the back of this sample (Figure 7d), part of the detached substrate can be seen together with the polychromy. It displays a fine-textured matrix with whitish hue, microfissures, and efflorescences that have favored its detachment. The FR-GB-W sample (Figure 7e,f) shows dust accumulations on the surface that causes a chromatic alteration by darkening the original colors. Small deposits of subefflorescences are also observed, playing a determining role in the detachment of the brown polychromy, thus leaving exposed the mortar substrate. Similarly, in the FR-B sample, accumulation of dust and chromatic alteration (Figure 7g) are observed, as well as a general presence of salts covering the mortar/stucco substrate (Figure 7h).

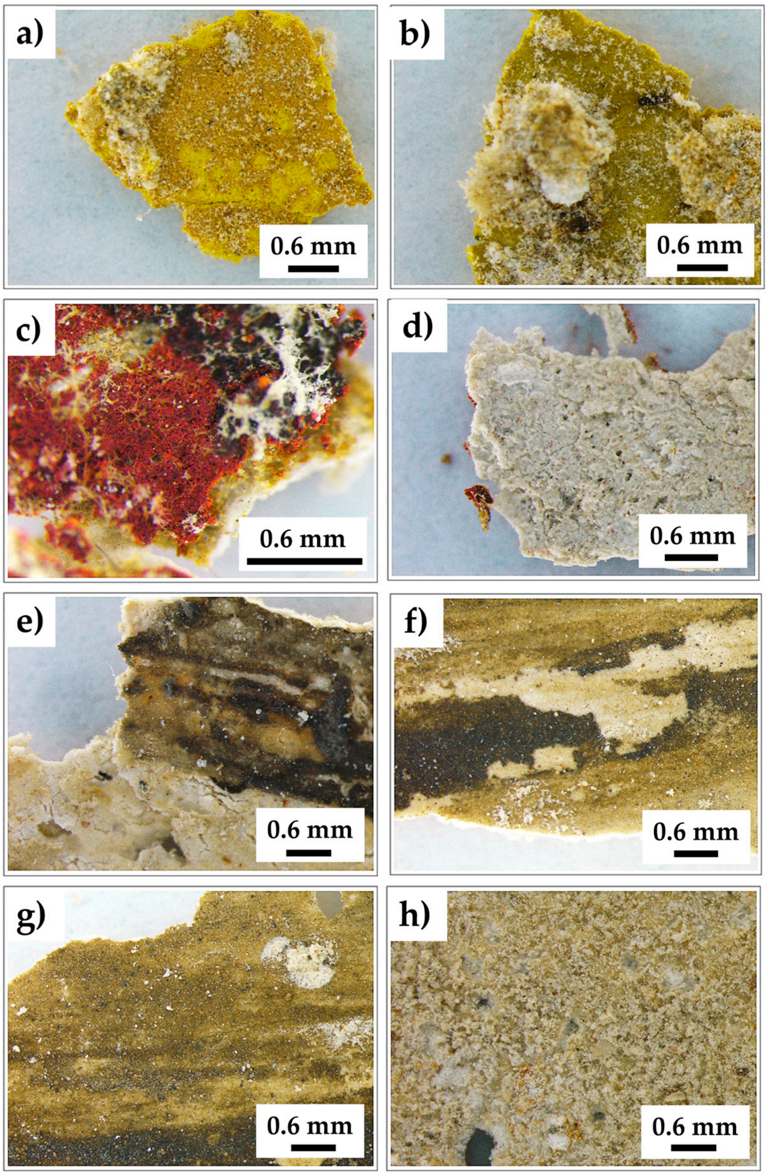

Figure 7. Stereomicrographs. (**a**) CP-EF-Y sample showing efflorescences on the front, on top of the painting layer, and (**b**) on the back, under the painting layer, causing detachment from the substrate. (**c**) CP-EF-R-B sample showing efflorescences on the front, on top of the painting layer, and (**d**) the detachment of the same fragment with part of the substrate. (**e**) FR-GB-W sample displaying the degradation of the greyish and white layers. (**f**) Detail of the efflorescences and paint loss. (**g**) FR-B sample showing chromatic alteration, and (**h**) the painting substrate covered with subefflorescences.

Mineralogical Study under Powder X-ray Diffraction

The semi-quantification results of the mineral phases found in the selected painting samples using powder XRD analysis are presented in Table 2.

Table 2. Semi-quantitative mineralogical composition by means of power XRD of seven samples. +++++: >50%; ++++: 30%–50%; +++: 10%–30%; ++: 3%–10%; +: <3%.

Samples	**Mineral Phases**				
	+++++	**++++**	**+++**	**++**	**+**
FR-EF-M	Gypsum	Calcite	Quartz	Muscovite	
FR-SEF	Gypsum	Hexahydrite	Quartz	Calcite	
FR-EF	Gypsum	Hexahydrite	Quartz		
C-EF-M	Hexahydrite	Gypsum	Epsomite	Calcite	Quartz
CP-EF-Y	Gypsum	Hexahydrite	Epsomite	Quartz	Calcite
CP-EF-BL	Gypsum	Calcite	Hexahydrite	Epsomite	Quartz
CP-EF-R-B	Gypsum	Cinnabar	Calcite	Cerussite	Hexahydrite

Gypsum ($CaSO_4{\cdot}2H_2O$); Calcite ($CaCO_3$); Quartz (SiO_2); Muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$); Hexahydrite ($MgSO_4{\cdot}6H_2O$); Epsomite ($MgSO_4{\cdot}7H_2O$); Cinnabar (HgS); Cerussite ($PbCO_3$).

The mineralogy of the studied samples is discussed below, although only the XRD patterns of C-EF-M (Figure 8a), CP-EF-R-B (Figure 8b), and FR-EF-M (Figure 8c) samples are shown here. Gypsum ($CaSO_4{\cdot}2H_2O$) is the main mineral phase, even in higher amounts than calcite ($CaCO_3$). The high content of gypsum suggests that the substrate of the wall paintings was gypsum, or a mixed mortar made with gypsum and lime which was very common during the Renaissance period [60–63]. For instance, Vasari (16th century) recommended the addition of gypsum on the last mortar layer to help the setting of the plaster [64]. Even Vitti [65] stated that in lime–gypsum mixed mortars, the advantages of one compensates the disadvantages of the other. This again indicates that a tempera technique was used for the wall paintings rather than a fresco one, in which a lime mortar would have been used instead. Different amounts of calcite and quartz (SiO_2) were also found in all samples, the former likely to come from the binder or/and the aggregate, with the latter added as sand (i.e., aggregate). In FR-EF-M sample, muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$) was also found, likely to come from the aggregate of the plaster substrate.

Hexahydrite ($MgSO_4{\cdot}6H_2O$) and epsomite ($MgSO_4{\cdot}7H_2O$) were found in all samples. These are among the most damaging soluble salts as they promote the formation of cracks and pose a significant threat to architectural heritage [66–69]. The crystallization pressure exerted by soluble salts when they precipitate often result in the detachment of paint layers and/or the disintegration of the wall support. In this last scenario, the painting would disintegrate, losing itself completely [7,10,54,66]. This is probably the cause of the major paint loss of Saint Mark's pendentive painting (Figure 4b). Moreover, the abundant sulfate-based efflorescences occurring in our wall paintings also play a key role in their discoloration [57,58,70], as observed in the paintings of the chapel (Figures 5 and 7). Mg-sulfate salts are abundant in historic buildings and monuments in the city of Granada built with Mg-based calcarenite ashlars and dolomite-rich structural mortars and renderings [66].

Table 2 also reveals the presence of pigments in some samples. In the CP-EF-R-B sample (Figure 7b,c, showing red and brown color), the main mineral phase identified, apart from gypsum, is cinnabar (Figure 8b), a red HgS pigment used since Ancient Greece until the 20th century [60,71] depending on its nature (natural or artificial, the latter used in Europe since the medieval period) [71]. Another mineral phase identified in this sample is cerussite ($PbCO_3$), whose presence can be related to a lead carbonate pigment (i.e., white lead, $(PbCO_3)_2{\cdot}Pb(OH)_2$) used since antiquity until the mid-19th century, but traditionally not recommended for the fresco technique [71,72]. This fact also supports our hypothesis that the fresco painting technique was not used here. On the other hand, in the CP-EF-Y sample (showing yellow color at the surface, Figure 7a,b), none of the mineral phases found can be related to a yellow pigment. Hence, its nature could not be determined by XRD. Most likely they must be present in minor quantities, below the detection limit of the XRD technique (ca. 3 wt%).

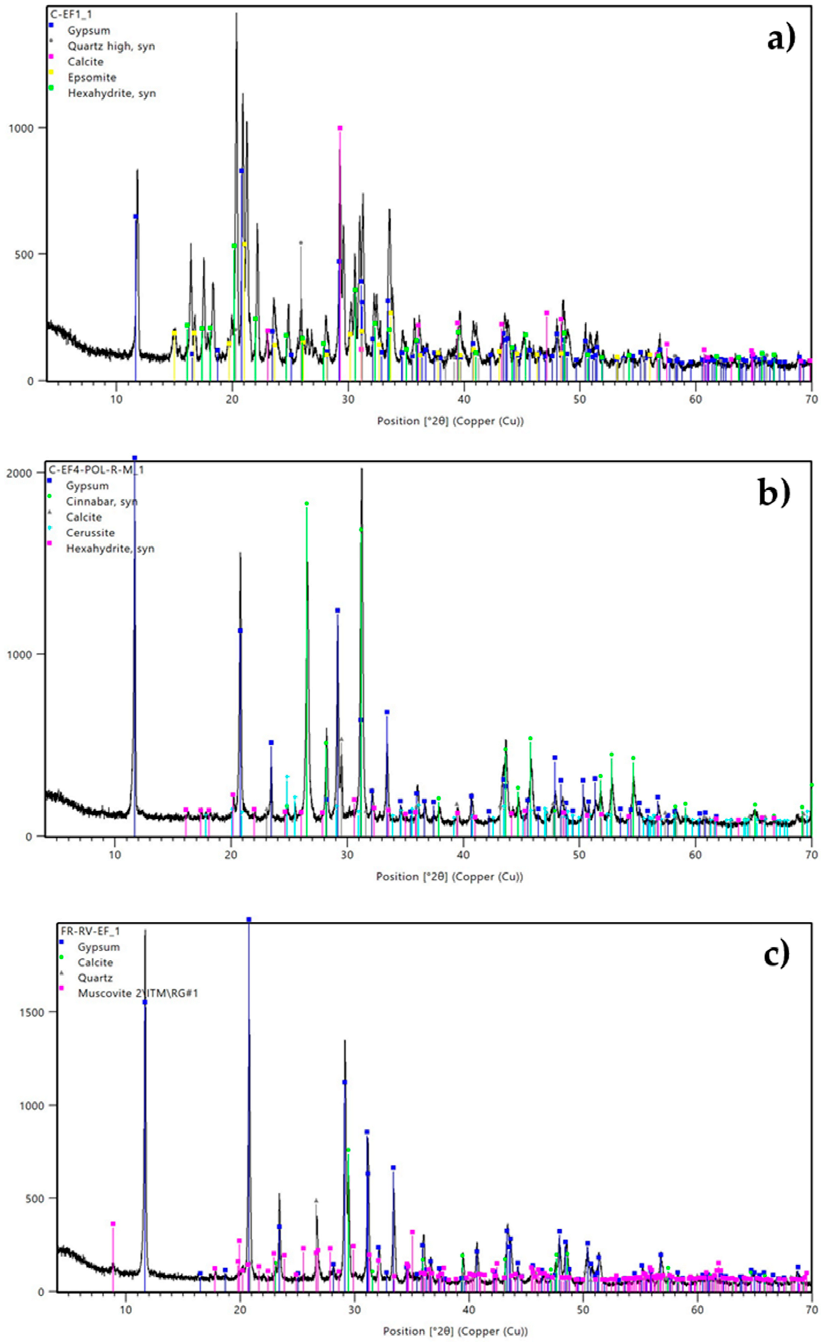

Figure 8. XRD patterns of selected polychromy samples. (**a**) C-EF-M sample with the presence of gypsum, quartz, calcite, epsomite, and hexahydrite. (**b**) CP-EF-R-B sample with the present of gypsum, cinnabar, calcite, cerussite, and hexahydrite. (**c**) FR-EF-M sample with the presence of gypsum, calcite, quartz, and muscovite.

Optical Microscopy Study

Next, certain paint stratigraphies (cross sections) were analyzed with OM and FESEM–EDS. The OM study of samples from Saint Mark's pendentive (CP-EF-Y and CP-EF-R-B) and from the NW frieze (FR-B and FR-GB-W) showed that the gypsum base (according to MRS as shown below) of the polychromy was applied using several layers, as seen under RL with crossed polarizers (Figure 9a). Moreover, the study with TL (crossed polarizers) revealed that, at present, this gypsum base contains crystals of diverse morphology and composition. Indeed, in addition to gypsum (main component), quartz is also recognized according to optical features, as well as abundant strongly birefringent crystals (Figure 9b) that most likely should correspond to the sulfate-based salts identified with XRD. Elongated and sub-rounded voids and sub-parallel fissures are common. Rhombic gypsum crystals are also present, which denote dissolution–recrystallization processes. All these features are indicative of the poor state of conservation of the polychromy (Figure 9b).

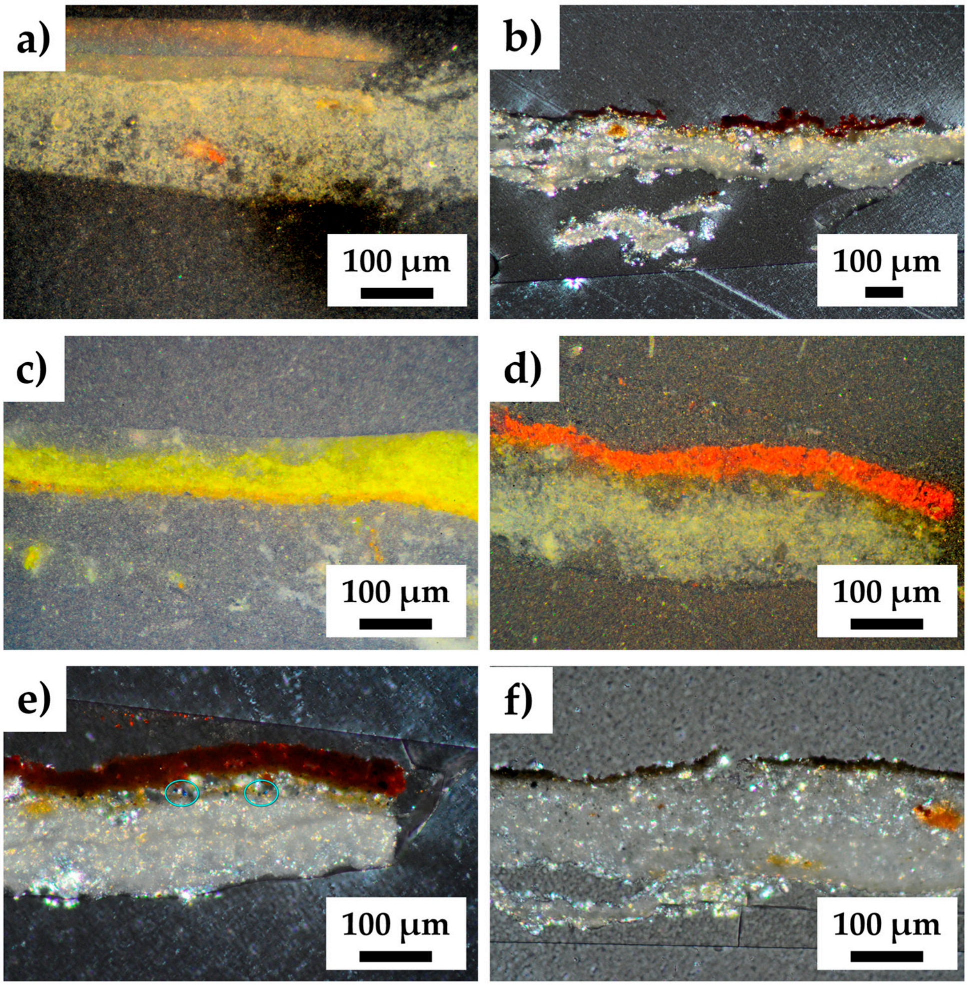

Figure 9. Optical microscopy photographs showing the cross section of painting samples. (**a**) FR-B sample. Note the application of several base layers (RL with crossed polarizers). (**b**) CP-EF-R-B sample showing copious voids and fissures, and birefringent crystals, likely sulfate-based salts (TL with crossed polarizers). (**c**) CP-EF-Y sample composed of two yellow layers (RL with crossed polarizers). (**d**) CP-EF-R-B sample displaying an intense red layer at the surface (RL with crossed polarizers). (**e**) CP-EF-R-B sample observed using TL with crossed polarizers where isolated anisotropic blue crystals (blue circles) are seen under the red layer. (**f**) FR-B sample displaying a dark brown layer at the surface (TL with crossed polarizers).

The OM study using RL with crossed polarizers of sample CP-EF-Y (Figure 7a) shows two well-defined layers of different yellow colors and thickness (Figure 9c). The thinner layer of yellow mustard color appears below the thicker bright yellow color layer seen at the surface. In both layers, the pigments are closely mixed with the binder, such that neither the morphology of the pigment particles nor their optical features are discernible, making it difficult to determine their composition. It should be noted that in all the studied samples, the pigments are closely packed with the binder; consequently, they are difficult to recognize based on their optical properties.

In sample CP-EF-R-B (Figure 7c), a discontinuous layer of intense red color under RL with crossed polarizers made of small and evenly sized particles appear at the surface of the polychromy (Figure 9d). The study using RL with plane-polarized light reveals that the pigments are highly reflective. Again, the intimate mixing of the colored particles with the binder hinders the red pigment's identification. Voids and fissures are abundant, mainly below the red layer, causing its detachment from the polychromy (Figure 9b,d). A close inspection of this sample using TL with crossed polarizers and plane-polarized light has revealed the occurrence of isolated anisotropic blue crystals under the red layer (Figure 9e). Their analysis studied by FESEM–EDS and MRS is discussed below. On the other hand, the OM study of samples FR-GB-W and FR-B (Figure 7e,g) using TL with crossed polarizers has revealed that both paintings display a very thin dark brown layer at the surface, made of protruding angular crystals (Figure 9f).

Field Emission Scanning Electron Microscopy–X-ray Energy-Dispersive Microanalysis and Micro-Raman Spectroscopy Study

The FESEM–EDS study was conducted for both bulk samples and cross sections. Regarding the FESEM–EDS study of the bulk samples, it should be noted the intense microbial attack by fungi, with hyphae penetrating deeply in the CP-EF-Y sample (Figure 10) that resulted in the typical detachment and disintegration of original materials [58,73–75]. Even though it appears to be an inactive focus, this situation means that the paintings, at least the ones on the dome, present a worse state of conservation than was originally thought. It must be considered that with an increase in humidity (>65%) and a temperature of 20–35 °C, fungi grow rapidly [76]. There have been cases of biological colonization on wall paintings that have resulted in the loss of large fragments [73,74,77], also favoring the formation of efflorescences and subefflorescences [76,78,79] and pigment discoloration [56,75,80]. Additionally, for fungi to grow, organic compounds are needed [76], and this could be related again to the use of organic binders in the tempera painting technique.

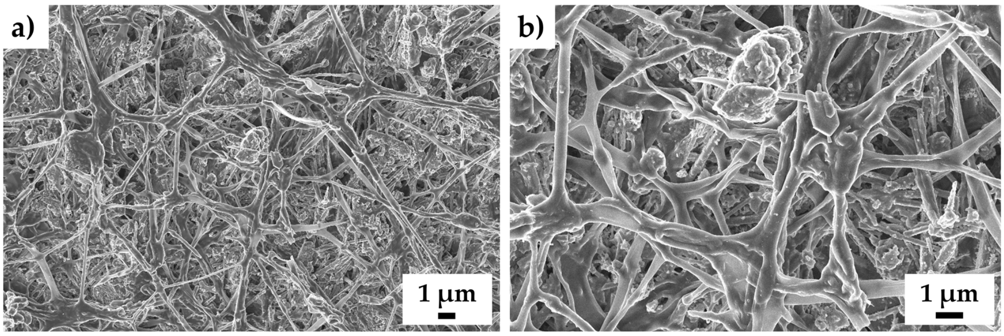

Figure 10. (**a**,**b**) SE micrographs showing the fungal hyphae penetrating the CP-EF-Y painting sample.

Moreover, many acicular crystals of gypsum (Figure 11a) and hexahydrite/epsomite salts were observed over the fungi, as the EDS found sulfur (S), calcium (Ca), and magnesium (Mg) (Figure 11b,c), in agreement with XRD data.

In sample CP-EF-Y, under the fungi, thin elongated crystals composed of lead (Pb) and chromium (Cr), according to EDS, were observed (Figure 12a,b). Both the composition and morphology of this phase are consistent with the presence of chrome yellow (lead chromate, $PbCrO_4$), a pigment from the 19th century [71,81,82]. Arsenic (As) and sulfur (S) have also been identified below the lead and chromium, assigned to yellow orpiment (arsenic trisulfide, As_2S_3), a pigment commonly used in the 16th century [71,81,82]. Based on these findings, the following interpretation can be raised: the original painting from the 16th century used orpiment as the yellow pigment and later, in the 19th century, Saint Mark's pendentive was repainted with chrome yellow. This can be extrapolated to the rest of the paintings of the chapel.

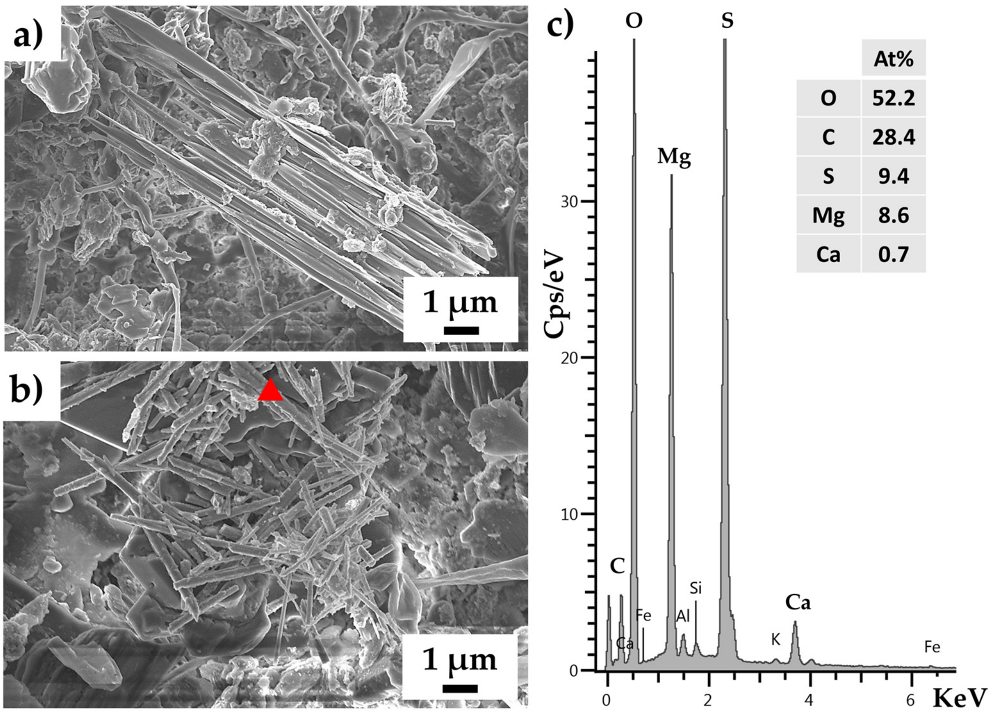

Figure 11. FESEM–EDS analysis of sample CP-EF-Y. (**a**) SE micrograph of the calcium sulfate crystals showing acicular shape. (**b**) SE micrograph of the magnesium sulfate crystals (the red arrow shows the single-point EDS analysis). (**c**) EDS spectrum showing the presence of S and Mg.

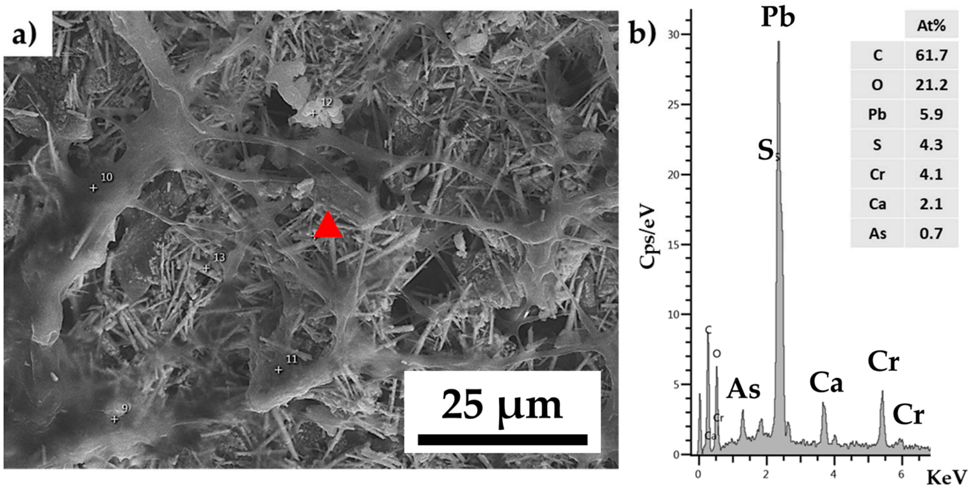

Figure 12. FESEM–EDS analysis of sample CP-EF-Y. (**a**) SE micrograph (the red arrow shows the single-point EDS analysis). (**b**) EDS spectrum with the presence of Pb, S, Cr, As, and Ca.

In sample CP-EF-BL, we observed a severely cracked surface (Figure 13a), also covered with fungal colonization. The EDS analysis identified calcium (Ca), silica (Si), magnesium (Mg), sulfur (S), sodium (Na), potassium (K), aluminum (Al), iron (Fe), zinc (Zn), mercury (Hg), barium (Ba), sodium (Na), chlorine (Cl), and copper (Figure 13b). According to this complex chemical composition, we suggest the presence of the following compounds: calcium and magnesium sulfates (as identified by XRD), halite (NaCl), K-rich aluminosilicates that would correspond to mineral dust (seen at naked eye), and oxy-hydroxides of Fe. The Hg indicates the presence of the red pigment HgS (also identified in sample CP-EF-R-B), whose origin is discussed below and is connected to the presence of Zn and Ba. Regarding the identification of copper (Cu), it could be related to the blue pigment observed at the surface of this painting sample. The presence of copper can be ascribed to (anisotropic) azurite ($Cu(CO_3)_2(OH)_2$), a pigment used since ancient times until the 17th century, meaning it could be the blue pigment used on these Renaissance wall paintings [71,78,81,82]. On the other hand, the different elements identified can also be related to lapis lazuli (natural) or ultramarine (artificial) ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$). However, synthetic ultramarine is optically isotropic whilst the pigment studied here, according to the OM study, is anisotropic [81].

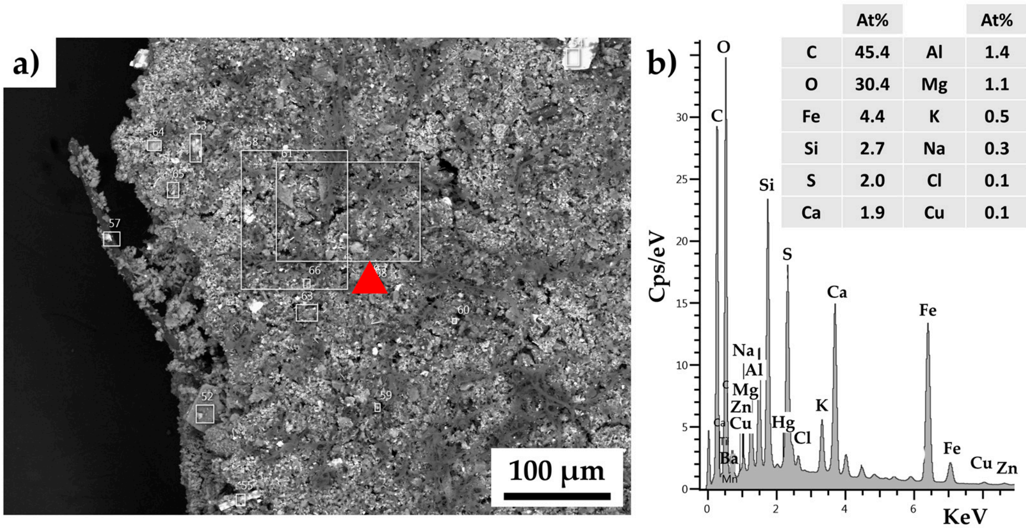

Figure 13. FESEM–EDS analysis of sample CP-EF-BL (**a**) SE micrograph (the red arrow shows the area where the EDS analysis was taken). (**b**) EDS spectrum with the presence of Fe, Si, S, Ca, Al, Mg, K, Na, Cl, and Cu.

With respect to the FESEM–EDS study of the cross sections, in addition to single-point analyses, X-ray maps from selected areas were acquired. The X-ray map of sample CP-EF-R-B revealed that the base layer was largely made of Ca and S (Figure 14a–c). Aggregates of K/Na/Mg-rich aluminosilicates (Figure 14d–g) were also recognized. At the surface, BSE analysis showed that the red layer is made of crystals of high atomic number, as indicated by their brightness (Figure 15a). Indeed, the X-ray maps showed that this layer is composed of Hg and Fe (Figure 15b,c). Often, expensive HgS pigment was adulterated with similar but cheaper red pigments, such as hematite, for cost saving [81]. Concerning the origin of the HgS pigment, i.e., artificial vermilion (wet/dry-process type) or natural cinnabar, the BSE image (Figure 15a) shows the diverse sizes of the HgS crystals (ca. 2–10µm) displaying both irregular and cubic shapes. Accordingly, the presence of the wet-process vermilion characterized by very fine and very even crystals (<1 µm) is excluded [81]. Hence, either the dry-process-type vermilion or cinnabar are likely the pigments used here. Although they are difficult to distinguish optically, the occurrence of impurities helps to identify the origin of the natural cinnabar. Among the minerals associated with cinnabar, pyrite/marcasite (FeS_2), realgar (As_4S_4), stibnite (Sb_2S_3), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$), barite ($BaSO_4$), and sphalerite (ZnS) can be found. Other impurities include selenium (Se), lead (Pb), and cadmium (Cd) [83]. Our FESEM microanalyses detected zinc (Zn), barium (Ba), and arsenic (As) in the red HgS-based layer (Figure 16). Consequently, the natural origin of the pigment can be suggested here.

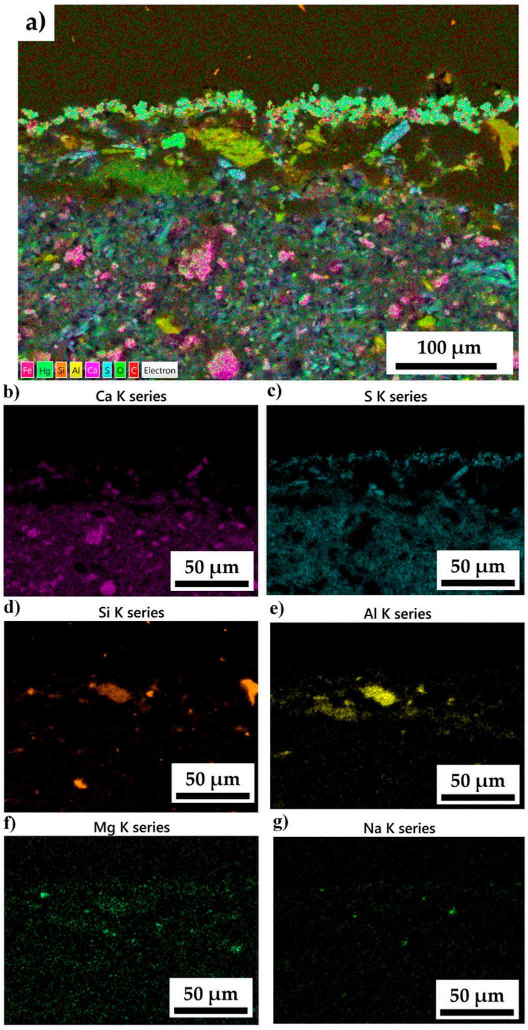

Figure 14. X-ray maps from the paint stratigraphy of CP-EF-R-B sample. (**a**) X-ray false color map displaying the elements Si, Al, Ca, S, O, and C. (**b**) X-ray map showing the distribution of Ca. (**c**) X -ray map showing the distribution of S. (**d**) X-ray map showing the distribution of Si. (**e**) X-ray map showing the distribution of Al. (**f**) X-ray map showing the distribution of Mg. (**g**) X-ray map showing the distribution of Na.

In the sample CP-EF-R-B, as mentioned above, the OM inspection with TL detected isolated anisotropic blue particles (see Figure 9e) whose composition could not be completely discerned with FESEM–EDS. Nonetheless, their MRS analysis (Figure 17) shows a composition compatible with lazurite (main mineral phase in lapis lazuli pigment) since a strong band at 549 cm^{-1} and a weaker band at 585 cm^{-1} are present [84–86]. These two bands are also encountered in artificial ultramarine Raman spectra [87]. As previously mentioned, OM detected anisotropic crystals, while lapis lazuli/ultramarine are typically isotropic, as they have a cubic crystal structure. However, in natural lapis lazuli, distortions and substitutions in the crystal structure can originate during phase changes which results in anisotropic crystals whereas its artificial equivalent ultramarine is isotropic [81]. Therefore, natural lapis lazuli seems to be the blue pigment found here. In addition, synthetic ultramarine is a pigment that was first manufactured in 1828 [71,82] and, thus, not related with the historical data of the wall paintings. Lastly, the presence of cinnabar was also confirmed by MRS (253, 284 and 343 cm^{-1}) [84], as well as gypsum in the mixed mortar substrate, since bands at 415, 494, 1009, and 1136 cm^{-1}, and weak calcite bands at 283 and 1087 cm^{-1} were detected [84] (Figure 17).

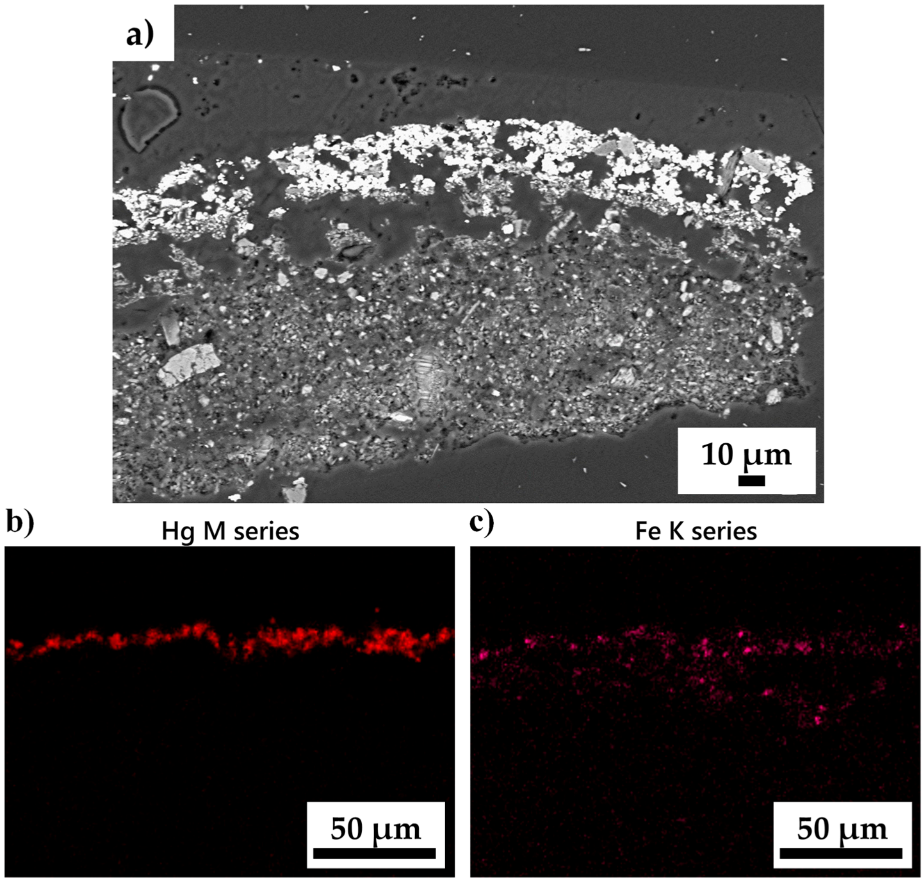

Figure 15. FESEM analysis of CP-EF-R-B sample. (**a**) BSE image showing the occurrence of pigments with high atomic number at the surface, as revealed by their brightness. (**b**) X-ray map showing the distribution of Hg. (**c**) X-ray map showing the distribution of Fe.

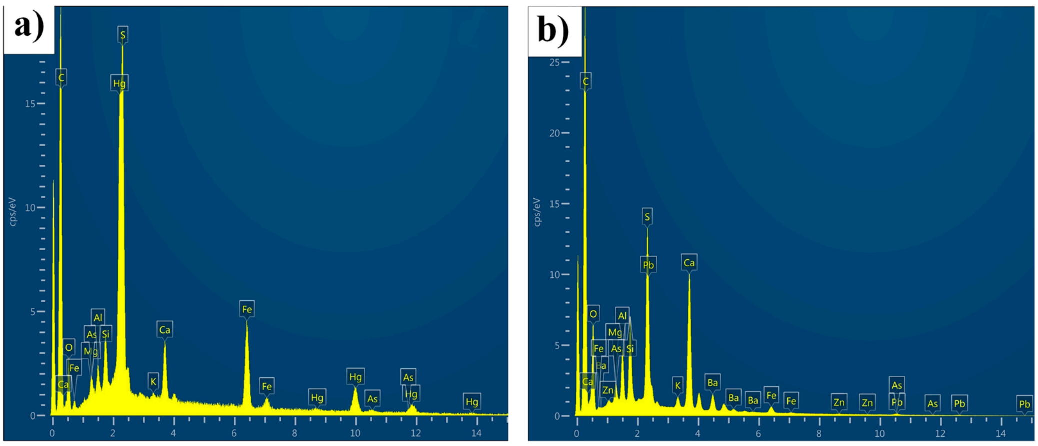

Figure 16. FESEM–EDS spectra of CP-EF-R-B sample. (**a**) Showing Hg and S indicating the use of a HgS pigment, and the occurrence of As. (**b**) Microanalysis from an area within the red layer showing the main presence of S and Ca (gypsum) and Zn, Ba, and As, possible impurities of the HgS pigment.

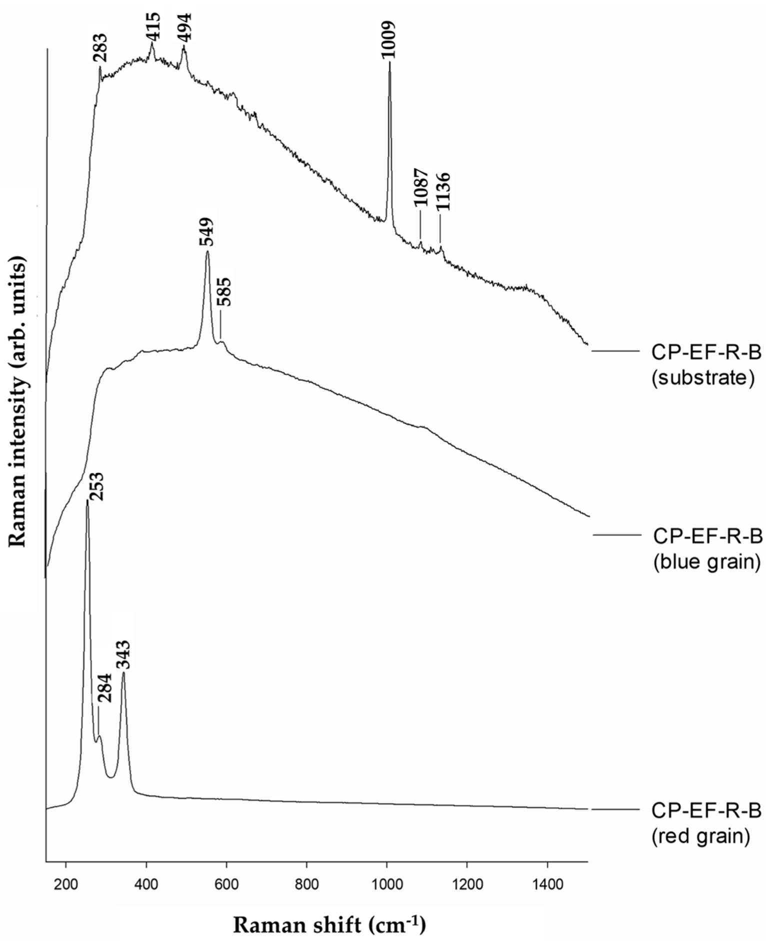

Figure 17. Raman spectra of the mortar (substrate), and the blue and the red crystals (grain) found in sample CP-EF-R-B.

The FESEM–BSE study of the cross section of sample FR-B (Figure 18a) revealed that the thin surface brown layer was obtained by mixing Mn and Fe oxides (Figure 18b). Here, K/Mg-rich aluminosilicate crystals were also recognized in addition to rhombic gypsum crystals (Figure 18a) that denote dissolution–crystallization processes and, thus, gypsum salt formation. NaCl and $CaCl_2$ were also identified, proving the severe problem that salt-induced damage represents in this case study (Figure 18c). The X-ray maps (Figure 18d–g) revealed that the black pigment is made of a Fe- and Mn-rich oxide, likely the pigment known as manganese black $(Fe,Mn)_3O_4$).

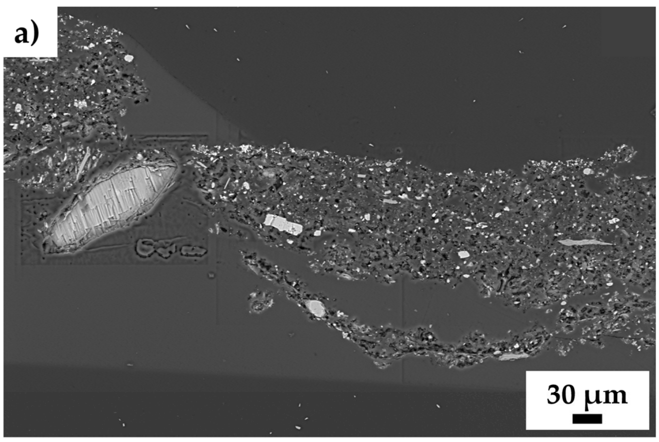

Figure 18. *Cont.*

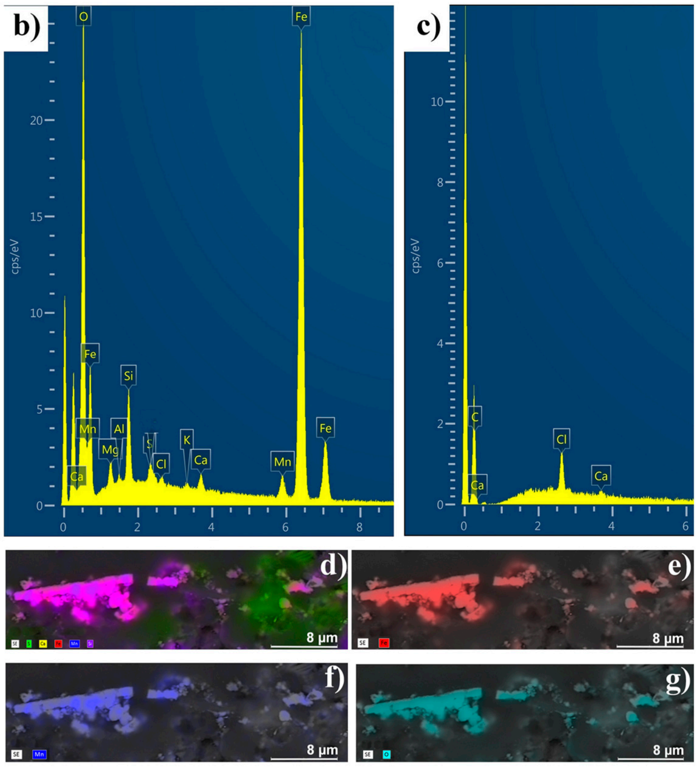

Figure 18. FESEM analysis of FR-B sample. (**a**) BSE image displaying dispersed bright tiny crystals at the surface. Note the rhombic crystal made of S and Ca (gypsum). (**b**) FESEM–EDS spectrum showing Mn and Fe (among other elements) indicating that Fe oxide and Mn oxide were used to obtain the brown/black layer at the surface. (**c**) EDS spectrum revealing the occurrence of $CaCl_2$ salt. (**d**) X-ray map showing the distribution of Fe, Mn, S, and Ca in a black pigment at the surface layer. (**e**) X-ray map showing the distribution of Fe. (**f**) X-ray map showing the distribution of Mn. (**g**) X-ray map showing the distribution of O.

4. Conclusions

The chemical–mineralogical and textural study carried out on samples collected from the wall paintings present in the chapel of Hernán Pérez del Pulgar's Palace in the city of Granada (Spain) has provided valuable data on the painting's composition and deterioration, as well as on the structural and conservation characteristics of the paintings themselves. The following conclusions have been drawn out:

- Regarding the pictorial technique, the high presence of gypsum in the mortar suggests that the pigments were applied on a gypsum plaster or on a mixed mortar with gypsum and lime, made with siliceous aggregates. This means that a tempera technique was used rather than a fresco technique, as was formerly thought. This conclusion is further supported by the fact that the paint layers are completely detached from the substrate in some areas, which is rare for a fresco, in which the pigments are completely embedded in the matrix of the mortar. Another indicator of the tempera technique is the use of graphite in the preparatory drawing, which was uncommon in the fresco painting technique. Additionally, the high presence of fungi, which need organic matter to survive, also supports the use of a tempera technique in these paintings. The fact that the studied wall paintings were made using the tempera technique agrees with the pictorial technique utilized on other wall paintings found in emblematic houses located in the same street (Carrera del Darro Street, Granada). However, the type of tempera binder employed here could not be clarified (either protein, e.g., egg yolk, rabbit glue, or polysaccharide-based binders, e.g., vegetable gums) due to fluorescence interference in the Raman spectra;

- With respect to the pigments, the identification of cerussite ($PbCO_3$) indicates the use of the lead white pigment (($(PbCO_3)_2 \cdot Pb(OH)_2$) for the white areas. The presence of HgS in the red polychromy and related impurities points to the application of cinnabar rather than vermilion, as well as its mixture with hematite, probably for cost saving. Concerning the nature of the blue polychromy, the results obtained are not fully conclusive due to the very scarce lapis lazuli crystals identified. Moreover, orpiment (As_2S_3) was the yellow pigment identified in these paintings, and black manganese for the black layers. The results support the initial approach of the historians that the wall paintings date back to the Renaissance period, considering that all the recognized pigments were used during the 16th century. However, the presence of lead chromate ($PbCrO_4$) above the orpiment layer in one of the pendentives, which is a yellow chromium pigment that began to be used in the 19th century, proves that the paintings were subject to intervention in the 19th century and not in the 18th century as the historical study suggested;
- As to the deterioration of the wall paintings, they are intensively affected by efflorescences, mostly composed of sulfate salts, e.g., gypsum, hexahydrite, and epsomite, which pose serious risks to the paintings since changes in relative humidity cause them to exert pressure under the pictorial layer, leading to detachment. Nonetheless, the source of Mg that gives rise to epsomite/hexahydrate salts could not be confirmed. It should be noted that despite the intense fungal colonization identified in the wall paintings, it is thought to be dormant. However, an increase in relative humidity could eventually reactivate this infection with irreversible consequences on the 16th century wall paintings.

After the characterization of the wall paintings, suitable and effective conservation and restoration measures should be applied to stop or delay the deterioration processes of these paintings. A former desalination treatment with cellulose pulp and deionized water is proposed to remove the calcium and magnesium sulfate efflorescences. Moreover, in those areas where the paintings are in danger of detachment, a facing intervention should be carried out by applying thin Japanese paper and an adhesive. Finally, to solve the problem of the fungal attack, the use of a fungicide in a low proportion (1%–3%) dissolved in a rapidly evaporating solvent is suggested. Since temperature and humidity determine the conservation of paintings, the placement of a monitoring system comprised by relative humidity and temperature sensors is also advisable, not only in relation to future fungal attacks that may occur but also related to the crystallization of other sulfates resulting from the substrate.

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Conflicts of Interest: The authors declare no conflict of interest.

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