

Spectroscopic investigation of Cappadocia proto-Byzantine paintings

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Abstract

The present contribution focuses the attention on the mural paintings of two among the oldest Cappadocia churches, belonging to the group of “proto-Byzantine paintings.” These materials have never been extensively investigated before and represent a starting point of paramount importance to understand the evolution of both materials and techniques during the ages in this extraordinary region of central Turkey. Specifically, among the several investigated churches and after the synergic work of art historians, conservators, and scientists, we selected the church of St. John the Baptist at Çavuşin, whose architectural structure is dated back to fifth–sixth century, and Church nr. 5 (Süslü church, sixth–ninth century) in Güllü Dere. A limited but exhaustive number of samples was carefully selected and then collected during the on-site campaign in Cappadocia. Samples were investigated with a multianalytical approach by using cross-section examination, X-ray fluorescence spectroscopy (XRF), Fourier-transform infrared (FT-IR), and micro-Raman spectroscopy to characterize materials, execution technique, and conservation state. The wall paintings in the church of St. John the Baptist are characterized by the presence of superimposed or adjacent layers ascribable to different historical periods, as it occurs in many of the Cappadocia churches. Their discrimination has been based on the mortar/ground layer. Pigments have been successfully identified and are mainly based on iron earths and ochres; the presence of gypsum and anhydrite, oxalates, and organic materials have been highlighted on the surface, thus suggesting alteration processes. The church nr. 5 at Güllü Dere shows a unique pictorial phase. Pigments are applied on a gypsum based ground layer and exhibit alteration patterns being made of lead based compounds, such as lead oxides and carbonates. A peculiarity of this church is the presence of anatase, detected in correspondence of red and yellow areas of the samples.

KEYWORDS

anatase, Byzantine wall paintings, Cappadocia, lead-based pigments, Rock-Hewn churches

1 | INTRODUCTION

The rupestrian churches in the Turkish region of Cappadocia have been included by UNESCO in the World Heritage List due to their extraordinary uniqueness.^[1]

Given the relevance of this complex, since 2006, the University of Tuscia started the project named “Rock painting in Cappadocia. For a project of knowledge, conservation and enhancement” that concerns the phenomenon of rock hewn painting, in its entire lifetime and in its various aspects, following an interdisciplinary methodology, which links humanistic knowledge with scientific and technical investigations. In this framework, the archaeometric research line has developed. It represents the backbone of the studies concerning the knowledge of the techniques of the Byzantine wall paintings in Cappadocia and for the researches on their state of conservation.

Since the beginning of the project, more than 50 churches have been investigated to gather a deep knowledge of the materials used and to study the degradation phenomena.^[2–4] Before this, few studies of the execution techniques used in the Cappadocia paintings had been carried out, and there had been very little investigation of the pigments and binders. In 1967, Marcel Restle published a first work reporting materials and techniques used in 13 churches.^[5] Beginning in the 1970s, as mentioned, during the United Nations Educational, Scientific and Cultural Organization (UNESCO) and International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM), conservation-restoration campaign at the Churches of Tokalı and Karanlık in the Göreme Open Air Museum research was conducted on the techniques used, which provided essential information for the restoration interventions.^[6–8] Art history scholars, such as Nicole Thierry and Catherine Jolivet, have illustrated the great variety of Cappadocia painting, sometimes including a discussion on aspects of the techniques in an attempt to identify chronological periods; however, such chronological characterization has until now been very broad.^[9,10]

Because a detailed treatment of the whole lot of Cappadocia rupestrian churches can result dispersive both for the abundance of sites and for the temporal extension of their realization, which ranges from to sixth to 13th century, here we focus our attention on the proto-Byzantine rupestrian settlements (Figure 1). These materials have partially been investigated before within our research^[2] and, to deepen their study, the group of the Raman Spectroscopy Laboratory of Roma Tre University joined this collaboration. This represents a starting point of paramount importance to understand the evolution of both materials and execution techniques during the ages. These are the oldest churches of the area and deserve a

specific attention due to the interesting painting technique they show, which seems to involve a *secco* method on a gypsum ground layer, often representing preiconoclastic patterns. A large number of pictorial contexts of Cappadocia belong to the chapter of proto-Byzantine painting whose chronological boundaries are controversial and oscillate between the sixth and ninth century. These are well-preserved paintings characterized by several patterns as nonhomogeneous figurative installations, large white backgrounds painted with a synthetic color range or the coexistence of iconic and aniconic structures and of palimpsest paintings.^[11,12] They were made by different workshops that worked in the Cappadocian region offering interesting solutions in terms of execution technique and use of materials. The examination of this group of paintings will make it possible to weld the historical-artistic studies and offer new elements useful for supporting questions relating to dating or chronological groupings.

In particular, we discuss the wall paintings belonging to two churches, the ones of the St. John the Baptist church in Çavuşin, Figure 2a,b, whose architectural structure dates back to fifth–sixth century, and the ones of “nr. 5” Süslü church in Güllü Dere, sixth–ninth century, Figure 2c,d.

While the former results characterized by the presence of superimposed or adjacent painted plasterworks ascribable to different historical periods, as it occurs in many of the Cappadocia churches, the latter shows only wall paintings pertaining to a more recent single phase.

Hence, their choice is of particular interest because it allows to get information on the evolution of both materials and executive technique employed in this specific historical time span. This helps in characterizing other churches of the region for which their temporal location is not straightforward on the basis of the iconographic analysis, also providing important elements for the construction of a map of the workshops active in Cappadocia in the proto-Byzantine period.

Some parts of these paintings also exhibit clear color alterations that will be here discussed. A digression on the possible incorrect assignment of Raman bands located at low wavenumber is given.

Microstratigraphic analysis, X-ray fluorescence spectroscopy (XRF), Fourier-transform infrared (FT-IR), and micro-Raman spectroscopy were used as combined techniques to obtain information on the morphological features of the samples to chemically characterize the painting materials and to distinguish the different pictorial layers superimposed on the walls of the investigated churches.

It should be stressed here that the choice of the samples to be exported to Italy for laboratory analysis has

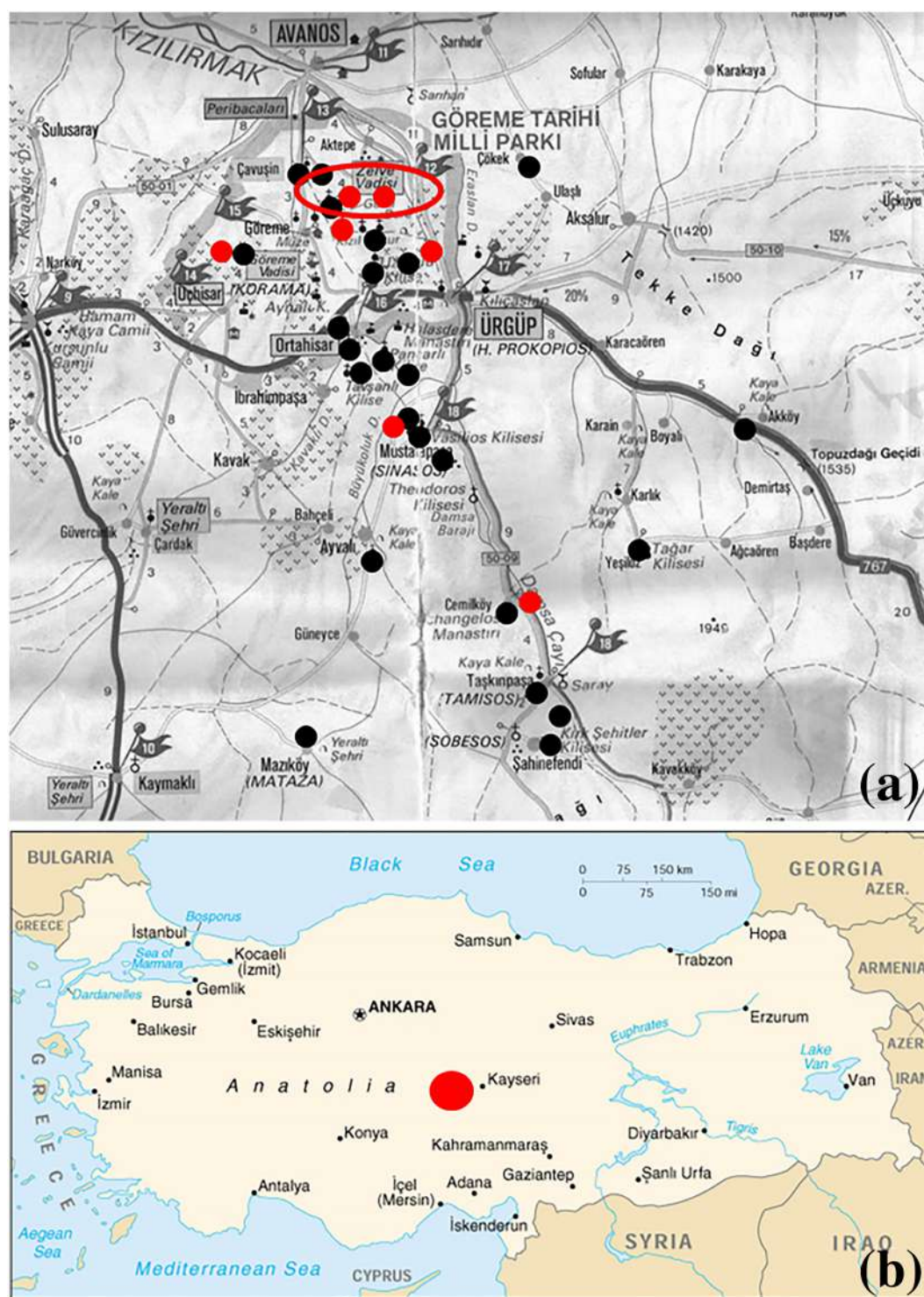


FIGURE 1 (a) Map with the churches (red and black dots) surveyed during the campaigns in Cappadocia, in red the churches with proto-Byzantine wall paintings (sixth—early ninth century). The two investigated churches are circled in the upper part of the map. (b) A map of Turkey with the region of Ürgüp highlighted by a red dot

been always made accurately, after a deep examination of the church and of the painted surfaces. This was performed by art historians, conservators, and scientists synergically in order to guarantee that the samples were representative of all pictorial phases. Our goal

was to take as few as possible samples, to guarantee the permission for exporting them to Italy, and contemporary to have significant samples for investigating the constituent materials, the realization techniques and the conservation state.



FIGURE 2 Photographs of the two investigated churches: St. John the Baptist, outer (a) and inner (b) view; Süslü Kilise, outer (c) and inner (d) view

2 | EXPERIMENTAL

2.1 | Cross-section preparation and microscope observation

During the campaigns in Cappadocia, microsamples have been taken from the wall paintings of the investigated churches. The choice of the sampling points was performed after a careful on-site observation of the surfaces, of the painted layers, and of their conservation state, often affected by iconoclastic interventions (ancient and recent) and by unsuitable restoration. Each precious sample was selected after a deep observation, with the use of a portable video-microscope, by art historians, conservators, and scientists working synergically.

Each sample point is marked with a number and carefully documented by photograph and a specific card describing its characteristics, as summarized in Table 1. Samples are labeled with two letters referring to the Church name (SJ for Saint John, SU for Süslü) followed by a progressive number.

Cross sections were prepared from the samples according to traditional techniques by embedding micro fragments in polyester resin and, after

polymerization, by polishing the surface with micro-abrasive paper (P4000).

Six cross-sections were prepared from the seven different samples for the St. John the Baptist, whereas three cross-sections were realized from the eight samples belonging to the Süslü church, as reported in Table 1.

The cross-section samples were observed and photographed using a Zeiss Axioskop polarizing microscope equipped with a Zeiss AxioCam digital camera. The cross-sections were also studied under UV lighting, using a mercury vapor lamp directly connected to the microscope in order to observe the fluorescence of the materials. A filter with the following characteristics was interposed between the mercury lamp and the sample: excitation BP 365/12, beam splitter FT 395 and emission LP 397.

2.2 | Fourier-transform infrared spectroscopy

Infrared spectra were obtained using a Nicolet Avatar 360 Fourier transform spectrometer. For each sample, 128 scans were recorded in the $4000\text{--}400\text{ cm}^{-1}$ spectral range in diffuse reflection modality (DRIFT), with a

TABLE 1 List of samples with the description made before analysis, by observing the micro-fragments and the powders under a stereo-microscope

Church	Sample number	Cross-section	Fragment (F) /powder (P)	Sampling area	Color	Pictorial phase
St. John the Baptist	SJ_1	X	F	Apse: In correspondence of the Baptist, right of the carved cross	Yellowish	1st
	SJ_2		P	Apse: Transfiguration, in correspondence of a vein in the hand of lower apostle	Red	2nd
	SJ_3	X	F	Apse: In correspondence of the frame under the transfiguration, right side	Green and black	2nd
	SJ_4	X	F	Apse: Between the mandorla and the angel, south side	Green	2nd
	SJ_5	X	F	South wall: Lower frame of the beheading of St. John the Baptist	Red	2nd
	SJ_6	X	F	Background under the beheading scene	White ground layer	2nd
	SJ_7	X	F	St. John the Baptist, on the right of the cross	Red (traces)	1st
Süslü	SU_1		P	Lower painting register: Right side, between the first and second circular decorative element	Light green	
	SU_2	X	F	Lower painting register: Right side, between the first and second circular decorative element	Light green (apparently a secco technique)	
	SU_3	X	F	Vault: In correspondence of a flower decorating the clypeus with a cross	Reddish/yellow with darkened areas	
	SU_4		F	Left wall: In correspondence of a cross clypeus	White ground layer	
	SU_5		P	Apse: Lower register, right side, in a raceme of vines	Red	
	SU_6		P	Apse: Background, right side	Yellow	
	SU_7		P	Lower register: In correspondence of a leaf.	Red-purple	
	SU_8	X	F	Vault: Decoration of the cross in correspondence of black triangles.	Black	

resolution of 4 cm^{-1} . Spectral data were collected using the OMNIC 8.0 (Thermo Fisher Scientific Inc.) software. To investigate the different parts of the samples, they have been separated manually with the aid of a stereo microscope. Then, the sample parts were weighted in order to use the same quantity for each analysis; then, they have been ground with spectrophotometric grade

KBr (1 w/w% sample in KBr) in an agate mortar. As background, the spectrum of the KBr powder was used.

The study and interpretation of the FT-IR spectra was carried out by comparing the experimental results with literature data^[13–15] and spectral databases—the IRUG Spectral Database, 2014 edition (<http://www.irug.org>) and other databases supplied with the Omnic 8.0 software.

2.3 | Raman spectroscopy

An InVia Renishaw Micro-Raman spectrometer equipped with a Leica DM2700 M confocal microscope has been used to collect unpolarized Raman spectra. Two solid-state diode laser sources, one at 532 nm (output power ~ 50 mW) and the second one at 785 nm (output power ~ 200 mW), provide the excitation energy. Neutral filters were used to decrease the power at the sample, taking into account its nature and composition thus avoiding degradation processes. A Leica 50X LWD and a couple of Olympus, 20X LWD and 100X, objectives allow focusing the excitation beam down to few microns and collecting the backscattered light. Holographic edge filters give the high-contrast rejection for elastically scattered component. The anelastic contribution is then dispersed by a diffraction grating (1800 grooves per millimeter for 532 nm excitation wavelength, 1200 grooves per millimeter for the 785 nm case) achieving a spectral resolution of ~ 1 cm^{-1} . Light is collected by a 1024×256 pixel charge coupled device (CCD) detector, and Peltier is cooled to reduce the interference of dark counts to a negligible level.

Several different points were measured on each layer of the investigated sample. Only the most representative spectra are here reported. The investigated spectral range is bounded between 100 and 3200 cm^{-1} , suitable to collect the fingerprint region of inorganic compounds and to unravel the presence of organic ones, if any. To achieve a suitable statistics, nearly 20 scans with an integration time of 5–10 s have been collected. Wire (Renishaw) and Origin (OriginLab Corporation) software were used to treat the raw data (background subtraction when necessary).

2.4 | X-ray fluorescence spectroscopy

The analysis of the chemical elements in the samples was performed through XRF Surface Monitor II spectrometer (Assing). The XRF spectrometer was equipped with an Ag anode tube and Amptek X-123 Si-PIN detector, resolution 145 to 260 eV at 5.9 KeV, optimum energy range 1–50 KeV. The measuring conditions were voltage 50 kV, distance of 94 mm from the analyzed surface, spot of 2 mm, current beam 76 μA , and acquisition time 60 s for each measured point. Spectra were collected by Gonio software by Assing, which was used also to gather the counts per second (cps) of each detected element.

3 | RESULTS AND DISCUSSION

Ground layers, pigments, alteration products, and inclusions of all the samples from the two selected churches

were investigated, and the results are discussed in detail in the following paragraphs. In Tables 2 and 3, respectively, the FT-IR and Raman results are summarized. Table S1 reports the XRF data.

A first aspect that must be stressed is that the complete characterization of organics in the wall paintings of Cappadocia's churches is a difficult task. This is as a consequence of (a) past restoration works using materials similar to the original binder (for example the calcium caseinate employed by ICCROM in the 80s of the 20th century to consolidate some churches)^[6]; (b) the fires lighted inside the churches by shepherds that produce carbon black and organics, especially fatty substances; and (c) presence of other surface protectives applied in undocumented restoration.

3.1 | Ground layer

The characterization of the ground layer could give important information both on the study of the execution techniques and to investigate if there was an evolution during times that could help in the dating.

3.1.1 | St. John the Baptist church

As previously mentioned, the St. John the Baptist church, whose architectural asset can be dated back to fifth–sixth century, hosts two different pictorial phases: (a) the former (sixth–seventh century) consists of an iconic panel painted in the apse of which only the figure of the Baptist remains; (b) the latter is a more extensive pictorial cycle (seventh/eighth–middle ninth century) where Christ is in glory in the apse and Christological cycle is painted in the presbyterial area. This interpretation pairs with a difference in the materials used for the preparatory layer.

Two out of the seven cross-sections we have analyzed are ascribed to the first, and more ancient, phase, namely, samples SJ_1 (Figure 3a,b) and SJ_7 (data not shown). The observation of these microsamples cross-sections is particularly useful in this investigation because it makes possible to reveal the stratigraphic pattern, to measure the layer thickness, to highlight the possible presence of organic materials exhibiting fluorescence under UV irradiation, among the other.^[2,3] Concerning the organic substances mentioned, FT-IR revealed their presence in almost all the examined samples. These are proteins and lipids for the most, as summarized in Table 2. To obtain a spatially resolved mapping of such substances, FT-IR spectra were collected by separating the different parts of the microsamples under a stereo-microscope.

TABLE 2 Overall results of FT-IR analysis on the samples from ST. John the Baptist at Çavuşin and of Süslü Kilise at Güllü Dere

	Sample	Description	Gypsum	Calcium carbonate	Oxalate	Silicates	Other materials
Çavuşin St. John the Baptist	SJ_1	Plaster		+++			Organic substances (protein?)
		Plaster, brown paint layer, coherent white powder	++	+++			Organic substances (lipids?)
		Coherent white powder	++	+++		+	Organic substances (lipids?)
	SJ_3	Red paint layer	++		++		Organic substances traces
		Green paint layer	++		++	Tr	Organic substances
	SJ_4	Green paint layer	+	+	++	++	Organic substances (probably lipids or waxes)
	SJ_6	Brown	+++	+	++		Organic substances
Güllü Dere, church nr. 5 (Süslü Kilise)	SU_1	Green paint layer	+++	+++	++	+++	
	SU_3	Plaster	+++	Tr	+		
		Grey and red paint layer	++	+++	++		
	SU_4	Plaster with red paint layer traces	+++	++	+		
	SU_5	Paster with red paint layer	+++	+++	++	Tr	
	SU_6	Plaster with yellow paint layer	+++	+++	++	Tr	Organic substances traces
	SU_7	Plaster	+	+++	+	Tr	Organic substances traces
		Red paint layer with plaster traces	+	+++	+		Organic substances traces
	SU_8		+	++	+		Organic substances traces

In some spectra of the first phase samples from the church of St. John the Baptist, intense bands at $2850\text{--}2920\text{ cm}^{-1}$, due to the stretching vibrations of C-H bond, suggest the presence of lipid compounds, probably oils or waxes (Figure S1).

Here, the analysis of the cross-sections of the first pictorial phase highlights the combination of two mortars: one (Figure 3a, layer 1) results rich in limonitic aggregates and contains only calcium carbonate (main bands at $2981, 2873, 2512, 1795, 1432, 875, 712\text{ cm}^{-1}$), as inorganic binder. The second, which acts as a ground layer (Figure 3a, layer 2) for the paint film (Figure 3a, layer 3), is made of a white inorganic binder (probably gypsum according to the morphological appearance, then confirmed by spectroscopic techniques) with the addition of organic binders, probably proteins. Lastly, on the surface of the sample cross-section, a black soot layer is clearly

visible (Figure 3a, layer 4). The protein presence has been hypothesized only on the base of the light blue fluorescence under UV exposure (Figure 3a,b, sample SJ_1), as no FT-IR signatures have been detected due to the strong bands of gypsum in the surface layer (see Figure S1). In a previous paper,^[2] it was highlighted that oldest churches are generally characterized by paintings applied over a thick transparent layer, made by gypsum that is superimposed to a second white plaster layer also made of gypsum with traces of organic material. This material has been widely used in Cappadocia and may be associated to the use of the rock from the Sivas quarries, near to the region of Nevşehir, rich of calcium sulphate,^[16] and its application directly on the rock surface seems to be a characteristic of the oldest churches in Cappadocia, the so-called “churches of the origins.” However, the interpretation of the stratigraphy is still far from appearing

TABLE 3 Summary of the Raman analysis on samples from St. John the Baptist at Çavuşin and Süslü Kilise at Güllü Dere churches

Church	Sample number	Raw fragment or powder	Cross-section
St. John the Baptist	SJ_1	Anhydrite	Mortar: calcite and gypsum Pictorial layer: goethite Sulfates, carbon (soot layer)
	SJ_2	Gypsum, hematite	
	SJ_3		Mortar: gypsum Pictorial layer: hematite
	SJ_4		Mortar: gypsum
	SJ_5		Mortar: gypsum Pictorial layer: hematite Weddellite, carbon (soot layer)
	SJ_6		Mortar: gypsum Anhydrite, Weddellite
	SJ_7		Mortar: calcite and gypsum Pictorial layer: hematite Weddellite, carbon (soot layer)
Süslü	SU_1	Calcite, glauconite, goethite with anatase	
	SU_2		Mortar: calcite and gypsum Pictorial layers: goethite (underneath) and Glauconite (on top)
	SU_3		Mortar: calcite and gypsum, Pictorial layer: hematite with anatase, litharge
	SU_4	Gypsum, hematite	
	SU_5	Hematite	
	SU_6	Calcite, gypsum, hematite, and goethite with anatase	
	SU_7	Calcite, gypsum, hematite with anatase, litharge, plattnerite, feldspar, quartz	
	SU_8		Mortar: calcite and gypsum Pictorial layer: litharge Superficial patina: plattnerite

Note: The relative intensity of FT-IR reflectance are highlight by using “tr” for traces, “+” for low intensity, “++” for medium, and “+++” for high.

simple due to the presence of superimposed painting layers, in some cases three or four, such as in the church of the Forty Martyrs in Şahinefendi.^[3]

On the other hand, the second decorative phase in St. John the Baptist is characterized by a completely white homogeneous ground layer, without any presence of aggregates (Figure 3c,d, sample SJ_4, layer 1). In this phase, the painting layer is thin and partially penetrated in the ground setting (Figure 3c layers 2–3, where 2 is the paint layer penetrated in the ground and 3 is the surface green painting).

In the FT-IR spectra of samples from the second phase, some weak bands can be associated to proteins, that is, 1642 cm^{-1} , 1547 cm^{-1} , and 1463 cm^{-1} (Figure S2). By combining these results with the ones from cross-section analysis, it can be hypothesized that protein

binder has been used in the plaster and painting, whereas lipids were applied as surface protective layer, possibly also in past restoration works. Lipids can be due also to the residues of burnt material with the lighting of fires inside the churches.

Indeed, for these specimens, Raman spectra, reported in Figure 4, highlighted the use of a mixture of calcite and gypsum in the preparatory layer of the first pictorial phase (a), while revealing a preparatory layer uniquely made by means of gypsum, on the case of the more recent phase (b). Raman spectroscopy was not able, in this case, to give information about the presence of organic compounds probably due to the nature and the ageing of these materials. This last phase finds exact comparisons also with the paintings of other proto-Byzantine churches as Üzümlü, St. Basil (second phase) and Karşıbecak.^[2]

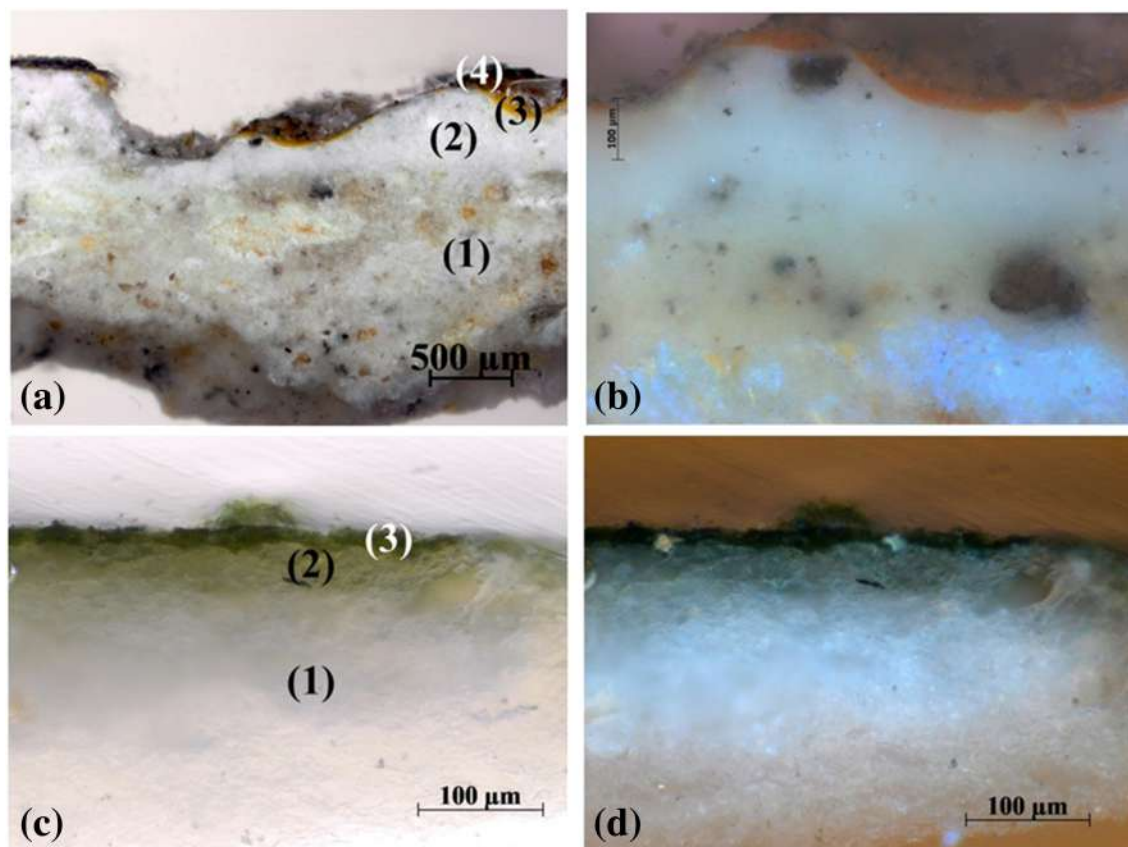
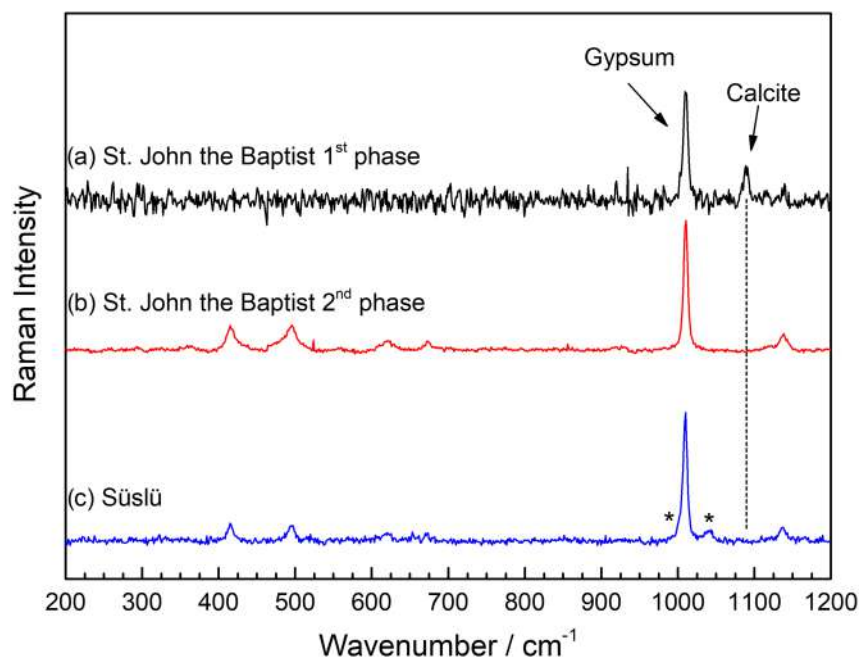


FIGURE 3 Microphotographs of the cross-sections from samples SJ_1 (upper) and SJ_4 (lower) of the church of Saint John the Baptist. (a) First phase, reflected light and (b) UV fluorescence; (c) second phase, reflected light and (d) UV fluorescence. The reported numbers underline the different layers

FIGURE 4 Raman spectra of the mortar/ground layers. (a) Black line, from sample SJ_1, first phase and (b) red line, from sample SJ_2, second pictorial phases of St. John the Baptist. The symmetric stretching mode of Calcite, CaCO_3 , and Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are marked by arrows. (c) Blue line, from sample SU_3. The two bands around 1000 and 1039 cm^{-1} , marked with an asterisk, are due to the polyester resin. The dashed line is a guide for the eyes



3.1.2 | Süslü church “nr. 5” in Güllü Dere

The Süslü church presents only one pictorial phase, instead, characterized by decorative aniconic patterns whose dating is very complex due to the absence of precise comparisons with other paintings. Interestingly, the stratigraphic analysis of the wall painting in Süslü church revealed an enhanced complexity, and the presence of a unique white ground layer based on gypsum (see spectrum (c) in Figure 4 and stratigraphy in Figure 5, layer 1) directly applied on the rock substrate whose traces are visible in the lower part of the cross-section (see arrows in the Figure 5a). The cross-section in Figure 5 shows also the presence of a yellow pictorial layer, over the ground (layer 2 in Figure 5a), and lastly, a red surface finishing with blackened particles (Figure 5a layer 3).

Due to the morphological analogies revealed in the plaster of the second layer from St. John the Baptist at Çavuşin and in that of Süslü church at Güllü Dere, it can be hypothesized a common workshop and chronology for this phase, that is, between eighth and ninth century. So, the church of St. John the Baptist at Çavuşin, due to its architectural structure can be dated back to the fifth–sixth century with a first painting decoration characterized by the stratigraphy shown in Figure 3a,b and a later second decorative phase that could be dated back to eighth–ninth century, Figure 3c,d. In the samples from the Süslü church, FT-IR measurements revealed both gypsum (bands at 3546, 3406, 2241, 2114, 1623, 1146, 1121, 671, 604, 466 cm^{-1}) and calcium carbonate in all examined samples, with different relative amounts in the plaster and in the painting layers, if considering the main

bands reported here for these two compounds (Figure S3). In the spectrum of Figure S3, referred to sample SU_6, the bands at 2924 and 2854 cm^{-1} are due to C–H stretching vibration of organics, but these two bands are not enough to make hypothesis about composition. Particularly, micro-Raman investigations revealed the presence of an “adhesive” layer between the gypsum ground and the pictorial film made by gypsum with inclusions of iron oxides (Figure S4).

To summarize, from the FT-IR analysis (Table 2), it is confirmed the presence of gypsum in all the investigated sample, apart from the plaster layer of SJ_1 of St. John the Baptist, referred to the first pictorial phase.

3.2 | Pigments of the pictorial layer

The evolution over time of the executive technique can be also traced by inspecting the materials employed in the pictorial layer of these wall paintings.

3.2.1 | St. John the Baptist church

While the preparatory layer allows for a discrimination between the two phases identified in the St. John the Baptist church, conversely, no differences have been found in its color palette. This is rather bare and consists of only three pigments, namely red, yellow, and green. Such simplicity could be the manifestation of the fact that this church is among the oldest in the lot, thus material and executive techniques as well represent the

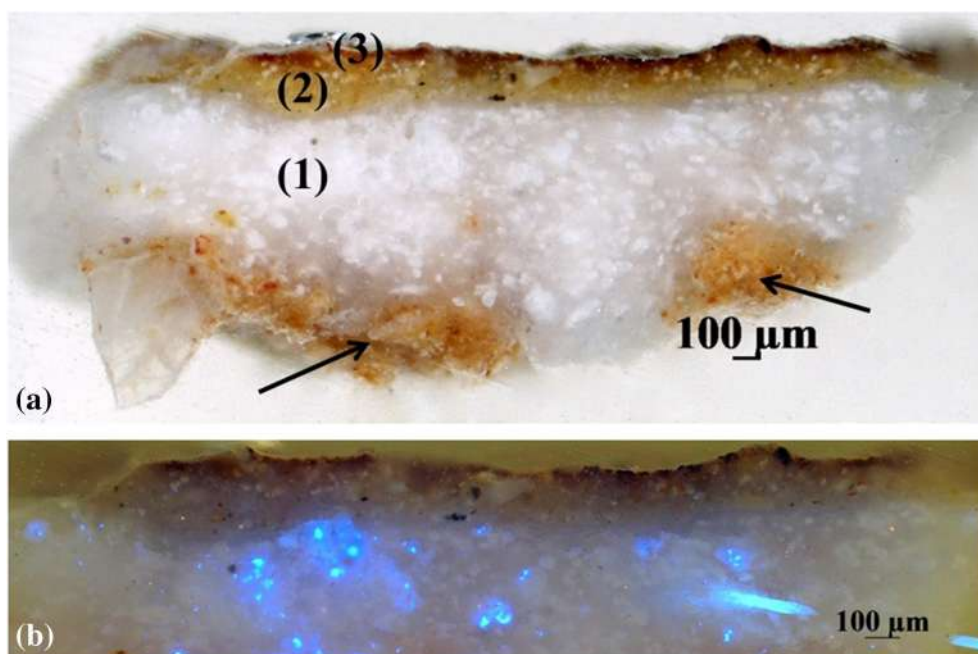


FIGURE
5 Microphotographs of the cross-sections from the wall paintings in the church “nr. 5” Süslü Kilise, sample SU_3. (a) Reflected light and (b) UV fluorescence. The reported numbers underline the different layers. Arrows highlight the areas commented in the text

foundation of the local pictorial expression. A detailed analysis of the materials has been conducted identifying all the pigments as based on iron minerals. Raman spectroscopy revealed the use of hematite (bands at 226, 246, 297, 412, 491, 557, and 612 cm^{-1})^[17] and goethite (only recognizable by the two main and broad bands at 297 and 380 cm^{-1} because of an intense fluorescence background)^[17] for red and yellow areas, whereas green earth (bands at 176, 248, 306, 370, 420, 486, 540, 696, and 908 cm^{-1})^[18] for green fields, accordingly to the detection of Fe by means of XRF in all the paint films (Table S1). XRF detected also the presence of Sr that is frequently associated to calcium compounds.^[19]

3.2.2 | Süslü church “nr. 5” in Güllü Dere

To appreciate an evolution in the pigments, if any, we have considered the paint film of the Süslü church, which is considered a couple of centuries later. In this case, XRF and Raman spectroscopy identified the presence of not only iron-based pigments, but highlighted the introduction of lead-based ones. Hence, along with the most commonly diffuse hematite, goethite, and glauconite, Raman spectra of litharge (PbO —bands at 143, 286, and 337 cm^{-1})^[17] have been collected from orange/red layers. Particularly, traces of iron oxides have been also detected in the rear side of the specimens, the one in contact with the bare rock. Indeed, the Süslü church has been built in the so called “Rose Valley” since the pinkish hue of the rocks, which is probably due to the presence of these oxides.

These results, combined with the findings on the ground layer, unravel that the evolution in the executive techniques and pigments employed were not simultaneous.

3.3 | Alterations

The status of the wall paintings hosted in both these churches is characterized by the presence of an important level of degradation. This is not surprising because these are rupestrian settlements; thus, they are subjected to atmospheric agents. Moreover, these churches were often used as shelter for breeders and animals, and lighted fireplaces or candles that were lit inside these rooms constitute themselves a source of anthropic alteration. For these reasons, the surface of the painting results very irregular and covered by a black soot layer. This is of particular evidence for the case of St. John the Baptist church, where optical observation at the stereo-microscope revealed a black layer of several tens of microns (see Figure 3a, layer 4) from

which Raman spectroscopy detected the spectral signature of amorphous carbon (Figure S5).^[20] However, this is not the only alteration aspect we have found. As an example, on the surface of sample SJ_1 a coherent white powder has been detected that is made of both gypsum and calcium carbonate. Its origin can be found both in the crystallization of environmental humidity on the pictorial surface or in a superficial recarbonation process due to migration of calcium from the ground layers.^[21–27] As shown by the Raman spectrum in Figure 6a, superficial gypsum is also undergoing a dehydration process that leads it towards the formation of anhydrite, as confirmed by bands at 421, 497, 609, 626, 670, 1017, and 1114 cm^{-1} .^[28] The presence of the organic materials at the surface is also compatible with the high content of oxalates characterized by strong and defined bands at 1624 cm^{-1} (that overlaps with gypsum bands exactly at the same wavenumber), 1384, and 1320 cm^{-1} and also detected by means of Raman spectroscopy, as reported in Figure 6b where the spectrum shows the main bands of weddellite.^[29] In the case of Süslü church, the presence of lead-based pigments introduces an additional degradation process. As highlighted by the stratigraphy presented in Figure 5 (layer 3), also for these wall paintings, the pictorial film shows a black superficial patina. However, its nature is different with respect the one discussed previously, and it is due to a well-known oxidation process that alters bivalent lead-based pigments, as litharge and massicot, into plattnerite, a tetragonal dimorph of PbO_2 ,^[30,31] whose spectrum is reported in Figure 6c. Because the starting point of this process is a highly stable form of lead oxide, its conversion to the tetravalent state requires the action of a strong oxidant. This role can be played by the metabolism of microorganisms,^[32–35] whose presence on the surface layer is also corroborated by the detection with Raman and FT-IR spectroscopy of oxalates (see spectrum in Figure 6b), silicates, and feldspars (orthoclase), the decomposition of these latter involving the metabolism of heterotrophic bacteria.^[32] The oxidation process is also highlighted by the additional presence of the characteristic Raman bands of red lead (Pb_3O_4 —119, 234, 407, 539 cm^{-1} , as reported in Figure 6c and summarized in Table 3) characterized for a mixture of Pb in different (II, IV) valence state^[17]: the Pb_3O_4 is characterized by a strong Raman cross-section, thus its presence can be revealed even if present in traces, as the residual of an alteration process.

3.4 | Inclusions

Particular attention has to be dedicated to the discussion of the low ($<200\text{ cm}^{-1}$) wavenumber portion of the spectra in some specimens from Süslü church. Those

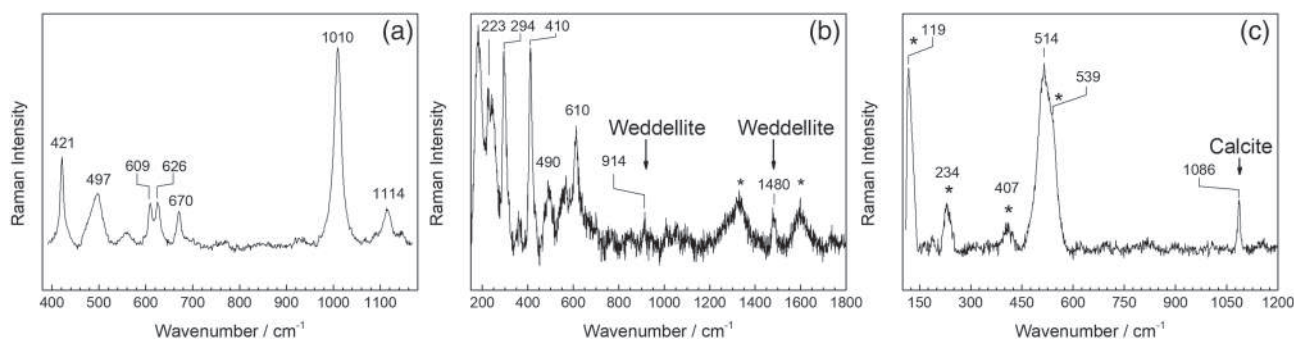


FIGURE 6 (a) Raman spectrum of the anhydride collected from the white superficial powder of sample SJ_1 from St. John the Baptist church (first phase). (b) Raman spectrum from the red grains in the pictorial film of sample SJ_7 from St. John the Baptist church (first phase). Besides the spectrum of Hematite, amorphous carbon (marked with asterisks) and Weddellite, a calcium oxalate (marked with arrows), are present. (c) Raman spectrum of the black superficial layer from sample SU_8 from Süslü church. Spectral signature of plattnerite is shown along with the one from red lead (Pb_3O_4 —marked with asterisks). The presence of calcite is also highlighted. Bands position wavenumbers are reported

spectra give us the opportunity to highlight the possibility of a wrong attribution of the bands at low wavenumber. It is well established that this spectral region hosts the stretching mode M—O (M: heavy metal, O: oxygen) of the most common oxides. Surely, their vibrational signature involves one or more additional bands that allows for an unambiguous identification of the molecular compound. However, these other bands are typically very weak if compared with the one arising from the M—O stretching mode, and they may not emerge from the noise level, thus the identification of the specific oxides is often based solely on the detection of the M—O stretching vibration, because a shift in wavenumber is driven by the reduced mass of the oscillator. This is a commonplace in the characterization of historical artwork, for which degradation processes or the presence of organics, among the others, are responsible for a relevant fluorescence, which prevents the detection of the whole pattern.

Bearing in mind that wavenumber's shifts can also be induced by degradation of the bond, for aging or photo-damage, a certain level of ambiguity still remains. This is the reason why a multianalytical approach is always required by keeping in mind the specific sensibility of each used techniques that has to be carefully considered. To this end, an elemental analysis should be the proper tool to wash away every doubt. Nevertheless, “prudence is never too much,” all the more reason when we are dealing with the sensitivity of the techniques. Here, we report an example. In all the samples collected from the Süslü church, we revealed the presence of iron-based minerals mixed with the lead-based pigment, as detected by Raman spectroscopy and previously discussed. Such observation is supported by the XRF analysis, detecting both iron and lead in these specimens (Table S1). Systematically, Raman spectra collected from the ochre grains

dispersed in the pictorial layer, and just below it, revealed the presence of an additional band close to 143 cm^{-1} , as shown in Figure 7a,c. In the light of what mentioned above, it is quite natural ascribing it to litharge, identifying it as the Pb—O stretching mode. However, by optical inspection of the compound, white grains admixed with ochre one have been observed. Thus, combining these informations, we might be led to infer the presence of lead white. However, claiming the presence of a compound grounding the identification on a single band solely can result in a wrong attribution. Interestingly, the same signature was found in the rear side of the specimens, that is the one in contact with the bare rock, see Figure 5, where XRF does not detects any presence of Pb (cf. SU_3 in Table S1). Hence, ascribing that band to lead white or any other Pb-based pigment, how we would have been led to do, is no longer straightforward. To solve this puzzle, we focused the laser beam of the micro-Raman spectrometer down to few microns to isolate the contribution of the white grains, with respect to the ochre. The collected spectra, shown in Figure 7b,d, unambiguously revealed the presence of anatase (TiO_2) in both red and yellow areas, so we can affirm the presence of Ti instead.

This is not the first time that it is highlighted how Raman spectroscopy is highly sensitive to small amounts of oxides included in a matrix, completely missing the main phase, thus leading to misleading attributions. Examples are represented by recent investigation of Roman frescoes^[36] or clay-based pigments, such as kaolinite or ochres, particularly red ones.^[37,38] In these cases, while techniques sensitive to silicates as the X-ray diffraction can easily identify the main phase, Raman spectra could only reveal the Ti impurities thus suggesting an incorrect identification of the material composition.

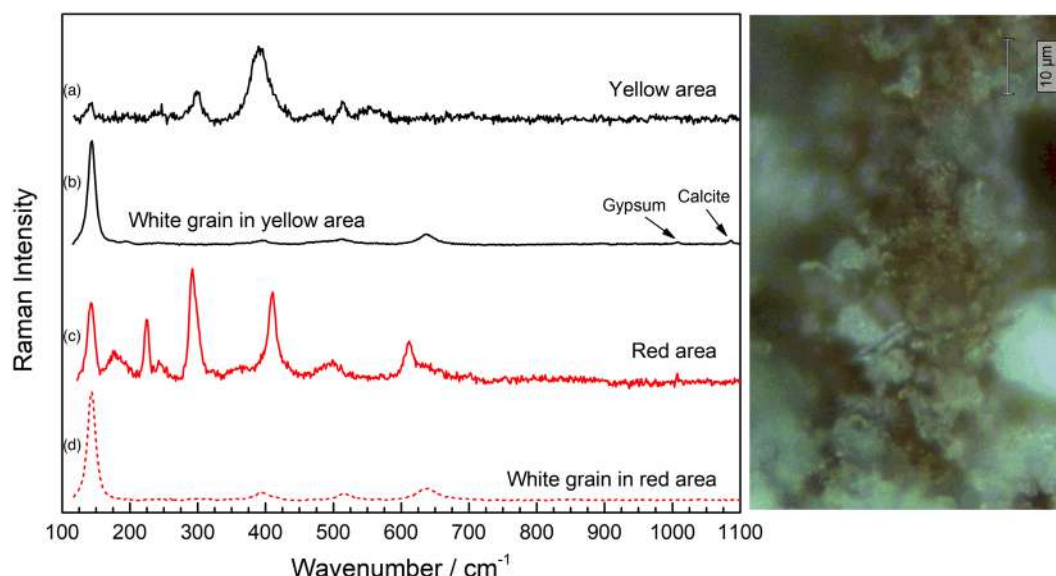


FIGURE 7 Raman spectra collected from sample SU_3. In particular, from (a) yellow area (b) white grains admixed to yellow area. Arrows show the presence of calcite and gypsum. (c) Red area and (d) white grain on red area. In the inset, the optical image of the yellow area investigated, showing the presence of both yellow and white grains

Because the presence of Ti resulted under the detection limit in XRF, we can assert that it is presence in traces as impurities in the rocks of the Rose Valley. It is worth noting that no trace of Ti dioxide has been found in the fragment coming from the St. John the Baptist church; thus, it seems to be a regional characteristic, in our case of the Güllü Dere area, that can be used to shed light on the provenance of materials used in the several settlements of the Cappadocian region.

4 | CONCLUSIONS

In this paper, the results of the analysis of samples taken from the proto-Byzantine churches of St. John the Baptist and Church nr. 5 (Süslü Kilise) in the region of Cappadocia have been reported and discussed. The focus was addressed to these two churches in order to compare materials and techniques for trying to define a possible evolution in paintings worksites of Cappadocia. The analysis revealed interesting results about ground layers and pigments.

The church of St. John the Baptist whose architectural structure can be dated back to the fifth–sixth century is characterized by two pictorial phases where all the pigments are iron based earths. The mortars of the two layers are quite different, the first one characterized by the presence of limonitic grains and the second made of gypsum without any inorganic aggregates.

In the church nr. 5 Süslü at Güllü Dere, only one pictorial phase has been detected. Pigments were applied

over a thin white gypsum layer with the presence of calcite suggesting the use of the so-called “sweet lime” from the quarries of Sivas, in the region of Nevşehir. The palette is composed of both iron-based pigments but also of lead-based ones.

Degradation compounds were also found such as oxalates, amorphous carbon, recarbonation surface layers, and plattnerite. This last compound was found only in the church nr. 5 Süslü at Güllü Dere, where lead-based pigments were widely used for the paintings.

At last, only in the church nr. 5 Süslü, anatase was detected through micro-Raman spectroscopy revealing the high sensitivity of this technique to determine small amounts of oxides included in a matrix. This is particularly relevant because allows for differentiate the materials and their possible provenance and use in the ages.

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SUPPORTING INFORMATION

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