The study of the mural painting in the 12th century monastery of Santa Maria delle Cerrate (Puglia-Italy): characterization of materials and techniques used

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A multidisciplinary research was conducted by the University of Salento in collaboration with the Lecce Provincial Museum, in order to study different forms of art widespread in the Salento peninsula (Southern Italy) very valuable from an artistic point of view and important as driving force for the tourism of the area. In this research, the archaeometrical analysis was used to study the first cycle of paintings of the church of Santa Maria delle Cerrate, an italo-greek monastery located in the country about 15 km north-east of Lecce, probably built in the 12th century. Microscopic, chromatographic and spectrometric techniques were used: optical microscopy was used to study samples and the relevant stratigraphy, micro-Raman Spectroscopy to identify pigments and Gas Chromatography with Mass Spectrometric Detection to investigate the techniques masters used to decorate the monastery church. Further information on organic and inorganic materials present in the samples were obtained from Fourier transform infrared analysis in attenuated total reflectance. Materials and techniques were clearly ascertained, and, interestingly, pigments were applied both by fresco and egg-based tempera. Among the various pigments detected, the identification of both lapis lazuli and lead white opened new perspectives both from the historical and conservative points of view. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: lapis lazuli; lead white; palette; Byzantine wall paintings; fresco-secco techniques

Introduction

The Abbey of Santa Maria delle Cerrate is located a few kilometers from Lecce in Puglia (Italy). It is an italo-greek monastery founded in the 12th century by Tancred, count of Lecce.[1] There are few historical documents known: the monastery is mentioned in a document dated in 1133, in a colophon of 1154 and in the manuscript of 15th century.[2] Although a few remains of the monastery, today the church of Santa Maria delle Cerrate is a testimony of the artistic language of the time, born from the encounter between the eastern and western culture, the main feature of the Salento (South Puglia). The decoration of the church is very important; it was decorated with several cycles of paintings: the oldest decoration is *in situ* while the subsequent cycles were removed and exposed in the museum of the monastery since 1975. The surviving paintings decorate the walls of the nave, apse and arches. The first painting cycle (the centre of this research) is of high quality to consider the way in which it develops the iconography and its stylistic and morphology features: it includes figures of Bishops and Ascension in the apse and scenes of the Virgin and Saints in the nave.[3]

The archaeometrical analysis is of great help in the study of mural paintings, especially when the bibliographic sources and studies are few, as in our case. In particular, the micro-Raman spectroscopy, compared to other similar methods of analysis, possesses numerous advantages such as specificity, sensitivity, short analysis time, immunity to interference, high lateral resolution and non-destructive or micro-destructive analysis. Some research has been done on the Byzantine wall paintings, especially in Greece[4,5]: Raman spectroscopy in combination with other analytical techniques have been used to identify colors and painting techniques,[6] products of degradation,[7] and a recent research of 2011 has concerned the study of the plaster and a possible its dating.[8] In Italy, the Byzantine frescoes are found mostly in the rocky churches and crypts of the southern regions (Puglia and Basilicata), and archaeometric studies conducted are few, but the context has been better investigated from the historical and artistic point of view.[9–11]

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According to historians, the oldest pictorial cycle of the church of Santa Maria delle Cerrate could date from the end of 12th century to the beginning of 13th century.[1] The art historian Pace, who described for the first time the frescoes, mentions two churches (Santa Maria di Anglona and San Demetrio Corona) that were painted several years after the construction, and Santa Maria delle Cerrate could be the third case.[3]

Dating is not the only intriguing question: the contrast between the Romanesque architectural structure and Byzantine iconography, the peculiar and characteristic pictorial repertoire of church (Fig. 1), which masters worked the pictorial cycle and from where they came are other puzzling issues. A letter dated between 1220 and 1235 evidences the presence of a greek painter in San Nicola di Casole, a monastery (now almost completely destroyed) located about 40 km south of Lecce.[1] Greek masters developed Santa Maria delle Cerrate frescoes as well?

Due to the scarcity of information and the importance of the church of Santa Maria delle Cerrate and its decoration, in order to characterize the materials and painting techniques used and to test the hypotheses above said, chromatographic, optical and spectroscopic techniques were carried out of some samples taken from wall paintings of the first painting cycle.

Experimental

Material

A total of 21 samples were taken from different scenes of the church of Santa Maria delle Cerrate for the purpose of identifying the material and techniques of the wall paintings. The samples 2, 9 and 20 were also cross sectioned, and Fig. 2 shows the stratigraphy of the sample 20.

Methodologies

Optical microscope

A Nikon microscope ECLIPSE 80i equipped with a fluorescence source X-Cite 120, a high sensitivity digital camera, and Nikon B-2A and UV-2A filter blocks has been used to carry out optical
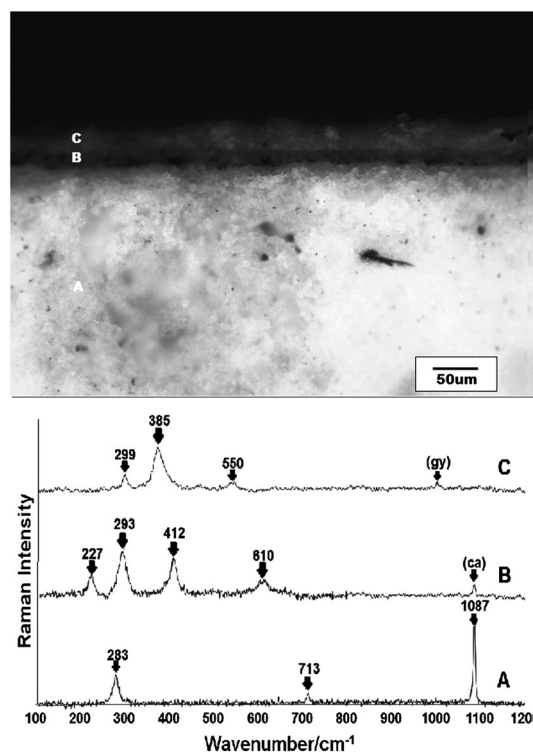

Figure 2. Optical microscope photograph of the cross section of the sample 20 (visible light and objective of 20 ×) and related micro-Raman spectra of the different layers. All the Raman spectra are baseline corrected: (gy) corresponds to the gypsum peak and (ca) to calcite peak.

observations under visible, blue and UV light of cross sections in order to identify the stratigraphic sequence and the presence of fluorescent materials.

Micro-Raman spectroscopy

The micro-Raman measurements were carried out with a Renishaw inVia instrument equipped with a diode laser (maximum power on sample of about 200 mW) with excitation wavelengths of 785 nm, an holographic notch filter, a Leica DMLM microscope with motorized xy stage and a 50X objective permitting a spatial resolution of 2 μm. The 442 line of a He–Cd laser source was also used on the same apparatus and the elastic backscattering removed with a dielectric filter. Neutral density filters were employed to keep the laser power at a low level (0.1–2 mW) on the samples, to avoid undesired heating effects such as laser-induced transformations, which are well known to occur, for example, on iron oxide or hydroxides. The spectra were collected with repeated acquisitions (three to five according to the signal/noise ratio) each of 10–20 s. The calibration of the spectrometer was checked using the most intense pure silicon Raman peak at 520.5 cm^{-1}. The spectral resolution is 3 cm^{-1}. All the Raman spectra are baseline subtracted.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra were obtained using a Agilent Technologies FTIR spectrometer, model Cary 600. The spectrometer was connected to a microscope model Cary 610 (Agilent Technologies) equipped with a nitrogen-cooled MCT detector and Germanium ATR. The measures carried out in ATR, and the ATR-FTIR spectra were obtained in the spectral region 400– 4000 cm^{-1}. The resolution

Figure 1. Overview of the painting cycle of the church of Santa Maria delle Cerrate.

was 4 cm^{-1}, and the number scans was 64 for each spectrum. All the spectra presented are baseline corrected.

Gas chromatography–mass spectroscopy (GC–MS)

An Agilent GC–MS system made up of a 6890 N gas chromatograph and a 5973inert quadrupole mass spectrometer detector was used to separate and identify the organic compounds. Chromatographic separations were performed on a chemically bonded fused silica capillary column DB-35MS (i.d. 0.25 mm, film thickness 0.25 μm, length 30 m) with a 5 m deactivated silica pre-column. GC conditions for amino acids were: initial temperature 100 °C, 2 min isothermal; 6 °C/min up to 280 °C, 15 min isothermal; carrier gas He; constant flow rate of 1.2 ml/min. GC conditions for fatty acids: initial temperature 80 °C, 2 min isothermal; 10 °C/min up to 200 °C; 6 °C/min up to 280 °C, 8 min isothermal; carrier gas He;

constant flow rate of 1.3 ml/min. As to the sample preparation, a procedure adapted from M. P. Colombini et al. was followed.[12]

Results

Palette

As to the pigments, Raman spectroscopy has again demonstrated a valuable and fast method for the identification of the pigments used. The analysis showed some peculiar results related to the materials used. Table 1 shows the identified pigments in the different samples. Natural and artificial colors were used, Fig. S1 (Supporting Information).[13,14] The red and black pigmented layers did not reserve any unusualness as hematite and carbon, widely available and stable, were the only minerals identified; the main Raman peaks identified of hematite

Table 1. List of the samples of the church of Santa Maria delle Cerrate and pigments identified by the Raman analysis: hematite (he), goethite (go), carbon (cb), massicot (ma), lapis lazuli (ul), celadonite (ce), calcite (ca), gypsum (gy) and lead white (lw)

Sample	Collocation	Sampling points	Stratigraphy	he	go	cb	ma	ul	ce	ca	gy	lw
1	central apse	Saint-arm	1	•	•		•			•		•
			2						•	•		
2	central apse	Deacon	1			•						
			2				•			•		•
			3	•	•	•						•
			4				•					
3	central apse	Saint-book	1	•	•					•		•
			2							•		
4	left wall	Staked Saint	1			•						
			2							•		
5	left wall	Saint-arc	1			•				•		
6	central apse	Saints-background	1			•				•		•
			2							•		
7	left wall	St. George and the Dragon-horse	1	•						•		
8	right apse	Saint-aura	1	•	•	•	•			•		•
9	central apse	Bishop-dress	1	•	•	•				•		•
			2	•			•			•		
10	left wall	Joachim and Anna-background	1			•			•	•	•	
11	right wall	Saint	1			•			•	•		
			2						•	•		
12	left wall	Joachim and Anna-background	1						•			
			2	•	•	•				•		
			3							•	•	
13	right wall	Saint with head upside down	1		•					•		•
14	right wall	Bishop-dress	1	•	•	•				•		•
15	right wall	Military Saint	1	•	•	•	•			•		•
			2	•					•			•
16	left wall	Joachim and Anna-foot	1	•		•				•	•	
			2	•						•		
17	left wall	Staked Saint-background	1	•		•				•		
			2	•						•		
18	left wall	Staked Saint	1	•		•	•			•		
19	left wall	Joachim and Anna-mantle	1	•						•	•	
			2						•	•		
20	left wall	Staked Saint-background	1			•				•		
			2	•	•					•		
			3	•	•						•	
21	right wall	Saint with head upside down-face	1	•						•		

are at 225, 293, 412, 498 and 610 cm^{-1}, while the carbon shows characteristic Raman peaks at 1350 and 1590 cm^{-1}. Yellow pigments used in the frescos are yellow ochre and lead monoxide, called massicot; the first is a natural pigment which yields characteristic peaks at 299, 385 and 550 cm^{-1}, the second is a lead oxide which yields characteristic peaks at 145 and 280 cm^{-1}. This pigment is obtained by heating to more than 300 °C (600 °C for 45 min) of the lead white in non-oxidative conditions.[15]

Also, the irradiation of the lead white with a laser source, as occurs during the Raman analysis, may cause the passage of the this basic lead carbonate and of its degradation products (PbO_2 and PbS) in massicot, through a process of thermal degradation.[16] In our case, massicot was employed voluntarily by the artists as a yellow pigment, and it is not derived from this transformation: in fact, through the use of the microscope connected to the instrument, we have observed the yellow layer before and after the Raman analysis; moreover, a slightly red-shift of the massicot Raman peaks to 84, 138, and 274 cm^{-1} was not observed, as reported by the literature in the case of massicot derived from thermal degradation laser.[16]

The green color is conferred by the presence of green earth based on celadonite. This is a hydrated silicate of iron and magnesium, a green mineral used since ancient times. The green earths were used to make the incarnate or the background very often, as reported in well-known Medieval texts of monk Theophilus[17] and Cennino Cennini.[18] The main Raman peaks of the celadonite are 202, 273, 391, 545 and 701 cm^{-1}. Calcite and lead white are the pigments used for the white areas that show characteristic Raman peaks at 283, 713 and 1087 cm^{-1} the first, while at 1050 cm^{-1} the second. Lead white is an inorganic pigment based on basic lead carbonate. Known since ancient times due to its high covering power, the lead white was the most widely used white pigment until the 19th century.[19]

Overall, the pigments used in the frescoes of Santa Maria delle Cerrate were common and easily available, except for blue. The blue color identified, according to the Raman analysis, was, indeed, the natural ultramarine blue (lapis lazuli). This inorganic rare blue pigment was produced from the mineral lapis lazuli present in nature, through an expensive and long processing.[18]

The name lapis lazuli denotes a complex rock mixture rich in a blue cubic mineral called lazurite $[(Na,Ca)_8[(SO_4,S,Cl)(AlSiO_4)_6]$, but usually it also contains two isomorphous minerals of sodium-alumino-silicate group, haüyne (sulphate group) and sodalite (chloride).[20] In fact, the blue pigment of the lapis lazuli rock arises from the trapping of S3 - and S2 - radical anions in cavities of the lazurite, a sodalite (feldspar-like) mineral. The first chromophore gives the blue pigment and the second the violet hue. The relative proportion of these chromophores leads to a variety of hues. The spectrum is the resonance Raman spectrum of S3 (260 and 285 cm^{-1} bending, 548 cm^{-1} stretching) and S2 (583 cm^{-1}) multi-atomic ions.[21] The lapis lazuli rock also contains some other minerals such as diposide ($CaMgSi_2O_6$), quartz (SiO_2), calcite ($CaCO_3$) and pyrite (FeS_2).[22] This was a very expensive pigment, used in the tempera and fresco techniques. In the tempera technique, lapis lazuli was generally applied with an emulsion of egg yolk, water and vinegar.[18] In the fresco technique, its use as a pure pigment spreads between the 6th and 9th centuries in areas of the Silk Road (from Tokaristan to China) and in Sassanide or Buddhist paintings, in 10th century in the Christian Georgian and Armenian churches and in the medieval period in European and Islamic paintings.[22] The discovery of lapis lazuli is peculiar. The lapis lazuli in general has been

replaced by other blue pigments because of its high price often. In the monastery of Santa Maria delle Cerrate, lapis lazuli has been used not only in the clothes, even in the background, and this result confirms the richness of its clients. In fact, the background is made always by lead white and lapis lazuli, as can be seen in the Fig. 3 that shows the Raman spectra of the lead white and lazurite and the microscopic photograph of the sample 1. The simultaneous presence of the two pigments in the samples was also attested by ATR-FTIR analysis: Fig. 4 shows the characteristic FTIR peaks of the lapis lazuli at 1155, 1037 and 466 cm^{-1} of the sample 8 and at 1234, 1150, 1021, 970 and 466 cm^{-1} of the sample 1.[23,24] Furthermore, the FTIR peaks at 1404 and 689 cm^{-1} sample 1 are characteristic of lead white.[25]

To our knowledge, this mixture has never been used in Byzantine frescoes.[4,26] Although the use of lapis lazuli is attested in ceramics from the 13th and 14th centuries,[21] in the Byzantine miniatures[27] and only in a Byzantine fresco in the church of Mileseva of the 13th century (Greece),[20] there are no sources on its use in Byzantine wall painting in Italy. The only known example so far of its use in Italy before the 14th century is the frescos of Sant' Angelo in Formis to Capua, in southern Italy: personal communication not published by Prof. Lucinia Speciale of Università del Salento.

Technique

The stratigraphic analysis of sample 19 taken from the mantle of Joachim in the scene of Joachim and Anna (left aisle) showed the presence of a unique pictorial layer made of a mixture of hematite, ultramarine blue (lapis lazuli) and calcite. The abundant presence of calcite on the surface of the sample 19 suggested the use of lime water as a binder.[26] As to the plaster, macroscopic investigation of the wall painting surface permitted to detect at least two different layers of plaster and the inner, the so-called arriccio, contains straw. A different situation comes out from Fig. 2 showing the cross section of sample 20 taken from the left aisle: the first layer A is the white preparation based on calcite, the second orange layer B measures 27 μm and it consists of hematite, the third yellow layer C is thick about 42 μm and it contains yellow ochre but not calcite. It is possible to see the
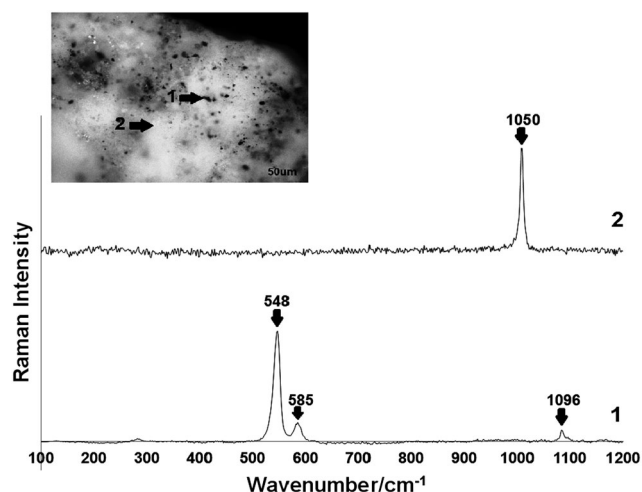

Figure 3. Optical microscope photograph and Micro-Raman spectra of the preparatory layer of the sample 1: lapis lazuli crystals (1) are present in the lead white layer (2). Operating conditions of Raman analysis: He–Cd laser operating at 442 nm, 2 mW at the sample, 50 × objective, integration time 20 s, 5 scans. The Raman spectra are baseline corrected.
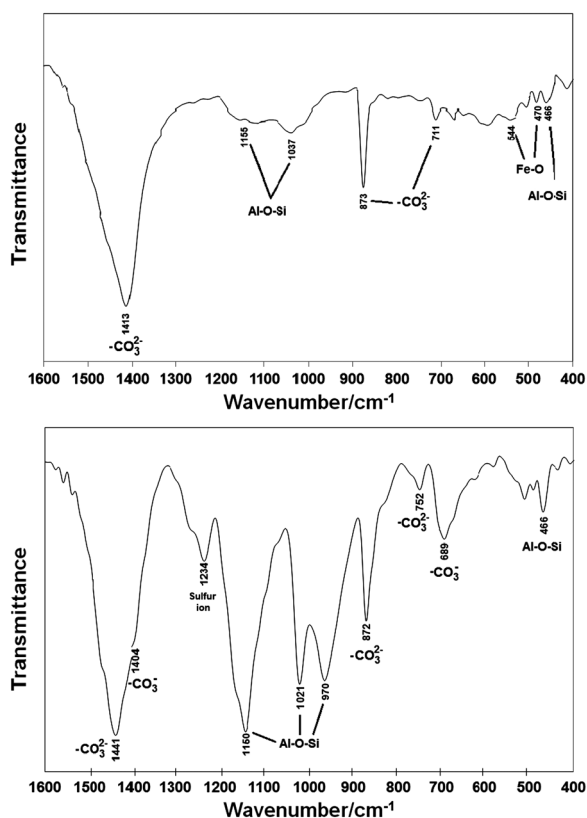
Figure 4. Representative infrared spectra of different inorganic pigments present in the sample 8 (left) and in the sample 1 (right). In addition to the infrared peaks of lapis lazuli and lead white, the CO_3^{2-} peaks refer to the presence of calcite, and the Fe–O peaks refer to hematite.

Table 2. GC-MS results of the analysis of the samples 1, 10 and 20

Amino acids	Sample		
	1	10	20
AA	µg/g	µg/g	µg/g
ALA	67.72 ± 2.14	13.37 ± 0.24	31.19 ± 1.33
GLY	84.11 ± 1.32	27.04 ± 1.89	46.56 ± 2.13
VAL	32.82 ± 0.76	15.24 ± 0.57	19.92 ± 1.02
LEU	85.28 ± 1.57	19.68 ± 2.00	17.06 ± 0.88
ILE	17.06 ± 0.23	9.18 ± 0.35	9.18 ± 0.23
PRO	87.48 ± 2.15	18.42 ± 0.76	17.27 ± 0.68
MET	0	0	0
SER	54.65 ± 1.23	13.66 ± 0.57	13.66 ± 0.98
THR	8.34 ± 0.12	7.15 ± 0.43	5.96 ± 0.19
PHE	16.52 ± 0.17	6.61 ± 0.30	4.96 ± 0.07
ASP	19.97 ± 1.20	6.66 ± 0.51	18.63 ± 0.30
HYP	1.31 ± 0.02	0	0
GLU	52.96 ± 0.86	11.77 ± 0.78	19.12 ± 0.82
LYS	0	0	0
ARG	0	0	0
TYR	0	0	0
wt (µg/g)	528.22 ± 23.01	148.78 ± 13.45	203.51 ± 16.71
Azelaic/palmitic	0	0	0
Cholesterol	Yes	Yes	Yes

layered structure, the superposition of paint layers which is an important characteristic of Byzantine wall painting: the painted surfaces are well separated from each other, and there is not a diffusion of pigments from a layer to the next one, typical characteristic of the dry technique, so suggesting the use of organic binders that actually have been extensively used in byzantine frescoes.[4,26–29] The identification of organic binders has been carried out by GC-MS on samples coming from four different scenes and areas of the church. In particular, sample 1 was collected from the second Saint's dress pictured in the central apse. The sample 10 is taken from the background of the scene of Joachim and Anna and the sample 19 from the mantle of Joachim. The sample 20 was taken from the background near the saint upside down on the left wall of the church.

The low protein content, the small content of amino acids (about 20 micrograms) and the absence of lipidic binders confirmed for sample 19 the use of lime water, already hypothesized by microscopic observation of the cross section.

Conversely the other samples contained significant amounts of organic materials: Table 2 shows the mean values of the relative percentage content of amino acids in the samples 1, 10 and 20 of Santa Maria delle Cerrate. The values obtained were compared with reference substances (egg yolk, animal glue and casein). The quantitative determination of the percentage content of five monocarboxylic fatty acids (lauric, miristic, palmitic, oleic and stearic acids) and of three dicarboxylic acids (suberic, azelaic and sebacic acids) allows us to distinguish between different triglycerides sources (drying oil or egg) on the basis of characteristic parameters: A/P (azelaic over palmitic acid ratio), P/S (palmitic over

stearic acid ratio), ΣD (sum of dicarboxylic acids)[12]: in the samples 1, 10 and 20, the amino acid profile, the presence of cholesterol, the absence of azelaic acid and the value of the ratio A/P equal to zero suggested the use of egg yolk as a organic binder. The presence of egg yolk in the sample 1 is also confirmed by the ATR-FTIR spectrum in which peaks appears at 2923, 2823, 1733, 1649 and $1550\,cm^{-1}$.

Discussion

The archaeometric analyses conducted on samples from the mural painting of Santa Maria delle Cerrate showed a peculiar situation.

Overall, the wall painting is in a good state of conservation, in fact blackening, efflorescence and fractures are not observed from a visual analysis. These observations have been confirmed by microscopic and Raman analysis, Fig. S2 (Supporting Information): few degradation products have been identified, such as calcium oxalates (whewellite $CaC_2O_4 \cdot H_2O$ and weddellite $CaC_2O_4 \cdot 2H_2O$), that have Raman main peaks at 1475, 1465 and $1490\,cm^{-1}$,[30] and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, Raman main peak at $1007\,cm^{-1}$)[30,31] exclusively in the samples taken from the left wall.

The right wall of the church does not have traces of calcium sulphates and oxalate in the plaster, but only few traces of coal on the surface, derived from air pollution and only in the sample 13 lead sulfate ($PbSO_4$, Raman main peak at $970\,cm^{-1}$) coming from the degradation of the lead pigment used.[30]

Different characteristics were typical of the Byzantine mural paintings such as the use of a rich palette, the presence of both fresco and secco techniques and the overlap of several paint layers.[29,32] The use of tempera on byzantine frescoes is well documented[4,33]: as often wall paintings were constituted by superimposed pictorial layers, it was not possible to use only

the true fresco for all the layers. As a result, the use of an organic binder, egg yolk very often,[34,35] on the plaster almost dried was the way they worked to cope with the problem. In the samples available, indeed, it appears that the application of pigments has taken place using a mixture of lime water and egg yolk, so both iconography and technique were Byzantine. However, there are some peculiarities such as the use of lead white and lapis lazuli which are not usual in the frescoes.[4,26] The lead white does not belong to the Byzantine tradition[4,26,35], and it is usually not recommended in the fresco technique due to its deterioration.[15,16,18] Its use in wall painting was problematic due to its darkening.[18,19] Darkening of lead-based pigments can be caused by their reaction with sulfur-containig compounds and gases that produces black galena (PbS).

Another mechanism for the darkening of lead-based pigments is their oxidation to the black-brown mineral plattnerite (PbO2).[15] The mechanism of this conversion remains unclear. Giovannoni *et al.*[36] found that hydrogen peroxide turns lead white, applied by means of fresco technique, to a reddish-brown product in conditions of high humidity, but the formation of plattnerite was not clearly established. Petushkova and Lyalikova[37] have attributed the formation of plattnerite to the metabolic activity of microorganisms.[38] However, in paintings of the church of Santa Maria delle Cerrate, lead white was widely used in the background, probably in order to increase the brightness of the figures.

The lapis lazuli, as a pigment for painting walls, is not mentioned by the sources before 14th century, when the first 'recipes' for its preparation begin to appear. However, it seems to have been used in S. Angelo in Formis (Capua) near Caserta (Italy). Its presence indicates that, contrary to what emerges from the written sources,[38] the lapis lazuli has been used in the mural painting before the 14th century; its use also demonstrates the richness of the client, being a very expensive pigment. However, whereas lapis lazuli is widespread in all the sides of church, lead white could be identified only on the abside and the right wall. On the contrary, gypsum, which has been used by the Byzantines as white, has been identified on the left side wall and is absent in the apse and on the right side wall, both on the pictorial and the preparatory layers.

This evidence permit to hypothesize that the first cycle is actually the result of two different phases, the left wall being developed by byzantine masters, whereas the abside and the right wall were worked by local/italic masters. Unfortunately, there is no proof, either technical or iconographic, conclusive about the relative chronology of these two painting cycles; however, the picketing made in 15th century to attach the intonaco/ fresco layers now exhibited in the museum, which shows underneath a colored layer, could suggest the left wall to be later.

Conclusions

Raman spectroscopy clearly permitted the complete identification of the palette used to work out the very first cycle of wall paintings in Santa Maria delle Cerrate. The adopted multi-analytical approach, comprising optical, Raman spectroscopy, FTIR spectroscopy and GC-MS, permitted to assess material and techniques adopted by artisans in the church. Moreover, materials and techniques significantly differ between left wall and apse and right wall. This suggests the working of two artists belonged to different studios and traditions, which worked independently and possibly at different times.

Supporting information

Supporting information may be found in the online version of this article.

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