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A combined analytical approach applied to Medieval wall paintings from Puglia (Italy): The study of painting techniques and its conservation state†

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A combined analytical approach has been applied to the wall paintings, dated from 10th to 14th centuries, of the Santi Stefani crypt at Vaste (Lecce, Southern Italy). These paintings are a precious testimony of Medieval art in Southern Italy. However, the church shows problems of damp as well as clear evidences of flora, fungi and mold presence, and there is little knowledge of the pictorial methodologies used. Raman spectroscopy allowed to determine the palette and to reconstruct the worksite and the chronological sequence of the various paint layers. Kaolinite, calcite, carbon black, hematite, massicot, goethite, indigo and azurite were identified as pigments along with synthetic pigments, like phthalocyanine blue and chrome yellow. Attenuated total reflectance-Fourier transform infrared spectroscopy suggested the presence of egg as a binder in some pictorial layers. The conservation state of the crypt is poor, and detachments of pigmented layers are frequent because of the presence of subflorescence and efflorescence: nitrate, sulfate and chloride salts have been identified spectroscopically and quantified by ion chromatography. The extensive use of kaolinite in Santi Stefani, actually not uncommon in Medieval art, is observed for the first time in a crypt of Puglia: its use to stabilize some pigments and to improve their adhesion on substrate is proposed. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: kaolinite; Medieval wall paintings; pigments; conservation state; ion chromatography

Introduction

The rupestrian civilization is a historical phenomenon of remarkable importance in many Mediterranean countries, and it is of considerable importance in various regions of Southern Italy. In Salento (Southern Italy) extensive evidence of medieval rupestrian settlements are still preserved, most of which have been dated to the 10th and 13th centuries. During this period, the artistic products were very close to the Mediterranean and Greek culture: Santi Stefani at Vaste is one of the most precious examples of Medieval crypts in the Salento.[1]

The crypts, which can still be visited in the territory of the provinces of Lecce, Brindisi and Taranto (Puglia), were the results of the activity of Italo-Greek monks: they decorated the walls of the crypts, which now preserve much of the medieval paintings of Salento, with images of the Virgin, Christ, bishops and other decorations referring to the style in vogue in the other provinces of the Byzantine Empire (Greece, Macedonia, Thrace and Anatolia).[1–3]

The Santi Stefani crypt (length 11.40 m; width 9.60 m; height 3.10 m), 1 km from the village of Vaste, is a rock-cut church which owes its name to the presence of three different representations of *Santo Stefano* in the iconographic program. The façade presents three entrances surmounted by arches, and the church has a basilica plan composed of three apsed aisles. The decoration extends into central and lateral apses and into the aisles, where detachments of the later pictorial layer made visible the oldest one. Its apse, like much of interior painted in the years 1379/80, suggests that a Greek textual source could coexist harmoniously with practice usually associated with the Roman rite.[4] The study carried out by A. Jacob,[5] about the inscription dated in 1379/80 of the central apse, and researches conducted by Castelfranchi are particularly important also for the dating of the wall paintings, which were made at different time from the 10th to the 14th century.[1]

Santi Stefani crypt is an important place from an artistic point of view and for the local tourism; nevertheless it was neglected for long, so the conservation state is critical; moreover, poor use in the past as well as vandalistic actions caused the loss of many parts of the paintings.[6]

The study of the crypts is very important in order to preserve them. Diagnostic analyses can be useful to reveal the principal causes of degradation and to understand how to properly restore

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† *Dedicated to Professor Pier Giorgio Zambonin on the occasion of his 80th birthday*

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these monuments; among the analytical tools, micro-Raman spectroscopy, compared to other similar methods of analysis, has numerous advantages such as specificity, sensitivity, short analysis time, immunity to interference, high lateral resolution, not or micro-destructivity and the possibility to make measurements outside the laboratory with transportable instruments, even in severe conditions.[7]

Different researches have been conducted on the Medieval wall paintings, especially in Greece:[8,9] Raman spectroscopy in combination with other analytical techniques has been used to identify colors and painting techniques,[10] products of degradation[11] and, in a recent research, the plaster and its dating.[12] In Italy the Medieval frescoes are found mostly in the rocky churches and crypts of the southern regions (Puglia, Basilicata and Campania) and, whereas archaeometric studies are few,[13–15] the contexts have been better investigated from the historical and artistic point of view.[1–4,16–18]

In this study different areas of the pictorial layers were first analyzed *in situ* using visible reflectance and Raman spectroscopies. Few samples were taken from selected scenes of the crypt, cross-sectioned and studied by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and microRaman spectroscopies, in order to identify binders and the stratigraphic sequence of pigments. Finally the conservation state of the Medieval wall paintings of Santi Stefani crypt at Vaste was assessed by ion chromatography.

Experimental

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

Visible diffuse reflectance spectrometry

Diffuse reflectance intensity measurements for visible wavelengths were carried out using a Minolta CM 2600d. The system operates with an internal integrating sphere of 52-mm diameter, in reflectance geometry d/8, with 3 Xenon pulsed lamps; the spectral range is 360–740 nm, with spectral resolution of 10 nm. The Specular Component Excluded mode was used in order to eliminate any bias due to specular reflection. Analyses were carried out using a D65 illuminant, which corresponds to average daylight, with a color temperature of 6504 K, and a 3-mm (SAV) measurement aperture.

Reflectance spectra were measured for each color, so as to identify only different chromatic areas and minimize micro-destructive sampling.

Raman spectroscopy

The paintings were analyzed in non-destructive mode with a transportable Renishaw Raman Analyzer 100 equipped with a 785-nm diode laser, a 1200 lines mm^{-1} diffraction grating and a Peltier-cooled CCD detector. It was connected to the measuring probe by means of a fiber-optic cable. The probe was mounted on a X–Y manual stage on a tripod and a microcamera allowed to focus on the sample. To avoid any possible damage, the laser power at the painted surface was kept at about 10.0 mW. Two long working distance microscope objectives, 20× and 10×, were used to focus the laser beam on the painted surface and to collect the backscattered Raman signals.

The laboratory 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 DM LM microscope with motorized xyz stage and a 50× objective permitting a spatial resolution of about 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 and laser induced transformations, which are well known to occur, for example, on iron oxide or hydroxides.[19–21]

The spectra were collected with repeated acquisitions (3–5 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 spectroscopy (ATR-FTIR)

ATR-FTIR spectra were obtained using an Agilent Technologies FTIR spectrometer, model Cary 680. The spectrometer was connected to a microscope model Cary 610 (Agilent Technologies) equipped with a nitrogen-cooled broad band MCT detector and Germanium ATR. The measurements were carried out in ATR, and the ATR-FTIR spectra obtained in the spectral region 500–4000 cm^{-1}. The resolution was 4 cm^{-1}, and 64 scans were averaged for each spectrum. All the spectra presented are baseline corrected.

Ion chromatography

The ion chromatograph was a Dionex DX500 system (Sunnyvale, CA USA) equipped with conductivity detector. Separation of ions was carried out on a Dionex IonPac AS14 column, 4 × 250 mm, attached with a AG14 guard column, 4 × 50 mm, to prevent column poisoning. Conductivity was suppressed with Dionex ASRS II suppressor. The suppressor voltage, flow rate and run time were set at 50 mA, 1.2 ml/min and 15 min, respectively. Instrument control and data reduction were carried out with Dionex Peaknet 5.1 software. Data collection rate and cell temperature were set at 5 Hz/s and 35 °C, respectively. The eluent concentration was: 3 mM Na_2CO_3 and 1 mM $NaHCO_3$. Injection volume was of 50 μl. The standards were prepared from a 1000 mg/l IC Standard Solution (Fluka). The range was investigated with three level point and the fitting with linear curve (not forced to pass through the origin). The samples were treated following the Italian norm NORMAL-13/83 (Roma, Italy). The standards and samples were injected three times. The statistical parameters calculated for each anion are reported in Table S1 (Supporting Information).

Results and discussion

Painting materials and artistic techniques

The Raman analysis of the Santi Stefani paintings was preceded by a preliminary diffuse reflectance study with the specific purpose of measuring the color space and highlighting any differences in the visible range to choose the painting points to be analyzed. These investigations have been carried out by a portable Raman spectrometer directly *in situ*, therefore in a totally non-destructive and non-invasive mode, and most of the pigments have been identified by this mode (Table 1). Although, sometimes some problems of fluorescence occurred, and the spectra exhibited a more or less complex background. Only a few micro samplings, which were cross sectioned and polished for microscopic and spectrometric detailed analyses, were carried out and herein described.

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Table 1. List of the samples of the Santi Stefani crypt and pigments identified by the Raman analysis: hematite (he), goethite (go), carbon (cb), massicot (ma), chrome yellow (cy), indigo (in), azurite (az), phthalocyanine blue (pb), kaolinite (ka), capuut mortum (cm), calcite (ca) and gypsum (gy)

Number	Sampling points	Identified materials	Raman spectroscopy		Sample collected
			In situ	In laboratory	
1	Vergine con Bambino	he, go, ma, ka, bc, ca, gy	X	X	SS4, SS5, SS6
2	Santo Stefano (right)	cm, go, ca	X		
3	Sant'Antonio Abate	he, go, ma, cb, ca, gy	X		
4	Santa Caterina d'Alessandria	he, la, ca, in, bc	X	X	SS10
5	San Nicola di Myra	he, ma, ca, gy, bc	X	X	SS1, SS2
6	Santo	he, cm, go, ma, ca, az, bc	X		
7	Santo Martire	he, ma, ca, fta,gy, bc	X		
8	Apostolo	fta, ca, gy, he, go	X		
9	Santo Stefano	he, go, ca, in, cb	X		
10	Fragments	he, cb, ca	X	X	SS12
11	Monaco	he, ca, cb, az	X		
12	San Pantaleone	go, ca	X		
13	Apostolo	he, ca, bc, fta	X		
14	Sant'Andrea	he, go, ca, ma,yc, bc	X	X	SS7
15	Sant'Eligio	he, go, ca, az, cb	X		
16	San Filippo	he, go, ca, ma	X		
17	Arcangelo Michele	he, ca, cb	X	X	SS11
18	Santi Basilio, Nicola e Giovanni Crisostomo	he, ca, fta, in, az, cb	X	X	SS3
19	Cristo fra gli Angeli	he, ma, ca	X		SS13
20	Vergine dal nimbo stellato	he, go, ma, ka, ca, gy, bc	X	X	SS8, SS9

The palette of Vaste paintings includes red, yellow, pink, violet, blue, black, brown and white pigmented layers (Fig. 1). Red pigment is extremely popular because it covers a wide range of different colors. Because of the heterogeneity of its grains, indeed, it can be found in a variety of colors, beginning from light red to violet or deep purple. Preliminary diffuse reflectance data showed the same spectral profile in all the analyzed samples suggesting the same pigment was employed (data not shown): Raman spectra confirmed this result showing the peaks at 225, 293, 410, 498 and 610 cm^{-1} of hematite (α-Fe_2O_3),[19] main chromophore of red ochers and earth.[20] These bands ascribed to haematite occur at the same positions in all the spectra and no shift is observed that can be attributed to heating or mixing of the pigment,[21] as well as the band at ~1300 cm^{-1}, assigned to a two-magnon scattering band and derived from the antiferromagnetic behavior of the specimen, is visible in all the red points.[19–22]

The violet color is also based on *caput mortuum*: the characteristic Raman peaks are located at 223, 292, 405, 610 and 659 cm^{-1}.[19] Raman spectrum is very similar to that of the iron oxide Fe_2O_3, but the band at 659 cm^{-1}: in many papers this band is assigned to magnetite, which sometimes occurs together with haematite in natural ochres.[21,22] The color difference between red and violet areas of the paintings is due not only to the mixture of different minerals (iron oxide or hydroxide, kaolinite…) but also to the particles' size.[23]

In the *Vergine con bambino* in Santi Stefani crypt (right wall) kaolinite was also identified thanks to the peaks at 410, 511 and 636 cm^{-1} (Fig. 2).[19,24] Possibly kaolinite was used in mixture with Fe_2O_3 of *caput mortuum* to increase the adhesion of the pigment to the plaster and to obtain the desired violet tint as attested for mural paintings in a Roman site in England, dated to 200 A.D.[24]

The artists of Vaste made a great use of the yellow pigments, both on large backgrounds and for the details of representations such as haloes or to produce flesh tones although here in mixture. A noteworthy feature is the high quality of the yellow pictorial layers that seem extremely stable, showing a very limited drop of the paint film, and the vividness of the color is unchanged. Colorimetric analyses showed the presence of two different yellow coloring mixtures and Raman spectroscopy permitted to identify two different pigments, goethite (α-FeOOH) and massicot; the first is a natural pigment which yields characteristic peaks at 299, 385 and 550 cm^{-1}, main chromophore of yellow natural pigments,[20] the second is a lead oxide which yields characteristic peaks at 145 and 280 cm^{-1}.[19,25] The absence of the slightly red-shift of Raman peaks to 138 and 274 cm^{-1}, reported in the case of massicot derived from laser thermal degradation,[26] confirms that this unusual lead yellow was employed voluntarily by the artists.

The study showed that the lead yellow was used only on selected images whereas yellow ocher was generally used for the backgrounds and other large paintings. In most cases yellow pigments have been used alone, and the relevant layers are vivid and homogeneous, lacking crystals of different color. However, a few exceptions are there for the massicot related to the concurrent presence of kaolinite: the haloes of the saints (sample SS4) in *Vergine con bambino* on the right wall of the crypt, for instance, were painted with a mixture of massicot and kaolinite (Fig. 2, B–C).[27] Considering that massicot is produced from white lead, and this pigment was known to be not stable in alkaline condition, painters could have attributed the same stability problems to it and produced this unusual, for a lead-based pigment, mixture with a very stable clay mineral like kaolinite. Kaolinite mixed with massicot was also used to produce some flesh tones and brown hairs but with substantial differences: to produce the pink of the *Vergine con bambino* (right wall, sample SS5) the fresco painters laid down first a yellow layer made of massicot and kaolinite, then the red layer containing hematite (Fig. 2, D). This can

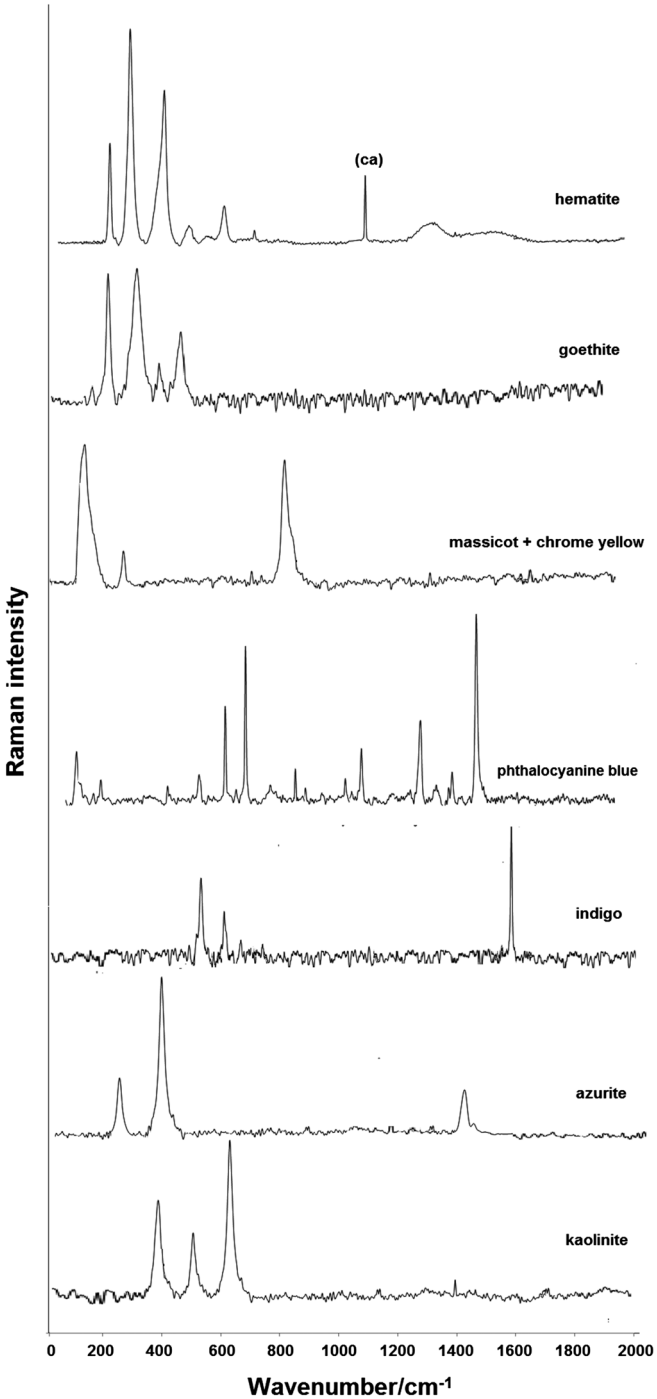

Figure 1. Raman spectra of pigments identified in the samples.

be clearly seen by macroscopic examination as the red hematite crystals are rare and superficial while the yellow layer emerges still in perfect state of conservation underneath. On the contrary the brown on the same figure (sample SS6) is a unique mixture of hematite, yellow massicot and kaolinite (Fig. 2, E).

As to the blue, in the mural paintings of Santi Stefani crypt two different pigments have been identified, indigo and azurite. The former was detected thanks to its characteristic Raman peaks at 546, 599 and 1576 cm^{-1}[19] and seems more used. Indigo, or *woad*, is a natural pigment formed by enzymatic or acid hydrolysis of indican (indoxyl glucoside) to give indoxyl (3-hydroxyl-indole) which is subsequently oxidized by atmospheric oxygen to give leucoindigo (dihydro-indigo) and then indigo.[28] In antiquity indigo was imported from India, but as reported by *Capitulare de villis* and *Mappae Clavicola*, in Europe and in Italy the same pigment was extracted from the indigenous plant *Isatis tinctoria*.[28] *Santi Basilio, Nicola e Giovanni Crisostomo* (sample SS3) in the left apse of Santi Stefani crypt, for example, all belonging to the 11th century pictorial cycle, shows the background divided into three bands, two of which are blue: Raman spectroscopy permitted the identification of indigo above a gray layer made of carbon black and calcite. Indigo was also found on the 14th century Santi Stefani pictorial cycle, in the panel representing *Santa Caterina d'Alessandria* (sample SS10), an interesting painting because, as occurs elsewhere in the crypt, the possible donor is represented as a kneeling woman at the saint's feet. Azurite, a basic carbonate of copper $2CuCO_3{\cdot}Cu(OH)_2$, which yields characteristic Raman peaks at 250, 403, 767, 839, 1098, 1432 and 1580 cm^{1}[29] is the other blue pigment used to decorate wall paintings of Santi Stefani crypt. It was very common during the Middle ages, and it was often used as a substitute of the more expensive ultramarine.[30] Azurite was found spread over a dark layer composed of carbon black, probably in order to obtain a higher shine.

It is interesting that in different backgrounds the optical perception of a blue hue is just suggested: micro-Raman analysis has identified the composition of a 'fake blue' present in a few samples: it was obtained mixing together black carbon and a few crystals of hematite.[31]Also Vitruvius[32] reports of a mixture based on a pigment obtained by burning vine wood and applied in wall decoration as imitation of blue color. An example of use of 'fake blue' can also be found in Puglia (Italy), in the image of the *Vergine col bambino* in the Crocifisso crypt of Ugento (Lecce, Italy), where the dark background, similar to that of Vaste, was identified as 'black carbon with the addition of granules of red ocher'.[13]

Another example of black pigment with red ocher is situated in a Soleto church, dedicated to St. Stephen and decorated with a fine pictorial cycle of fresco, dated to the 14th century; even here, the mixture is used as background for the eponymous saint, where the black carbon is also replaced by black bone.[1]

This hypothesis cannot be overrated considering that during the 1992 restoration, the only one acknowledged for the crypt, a solution of B52 (an all purpose alkaline cleaner/degreaser containing ethylenediaminetetraacetic acid (EDTA)) was used to clean frescoes, and the azurite layers could have been irreparably lost. As the relevant report affirms that frescoes were cleaned with B52 solution and the lacunae filled,[33] the synthetic pigments identified in Santi Stefani crypt, phthalocyanine blue ($CuC_{32}H_{16}N_8$), which yields characteristic Raman peaks at 592, 681, 1450 and 1527 cm^{-1}[22] and chrome yellow ($PbCrO_4{\cdot}PbO$), peaks at 824 and 844 cm^{-1}[34] were probably used in the same circumstances.

Optical microscopy observations of cross sections and ATR-FTIR analysis provided additional information on the pictorial methodologies used in this crypt.

In the cross section of the sample SS3 taken from the dress of a saint (*Santi Basilio, Nicola e Giovanni Crisostomo*, dated to 11th century and located in the left apse), the stratigraphic analysis shows a presence of three layers: a first preparatory layer (a) composed of calcite, a second layer (b) characterized by carbon black, a third layer (c) composed of hematite and calcite (Fig. S1, A–B, Supporting Information). It is possible to see the layered structure, the superposition of paint layers which is an important element of Byzantine wall painting: the different painted layers

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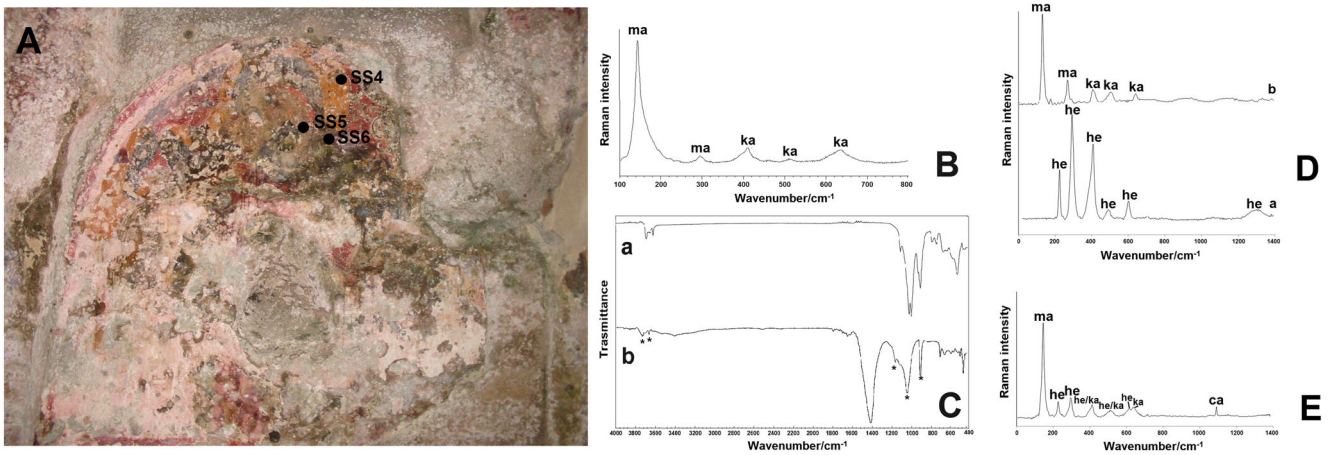

Figure 2. Photograph of *Vergine con bambino* of the Santi Stefani crypt, right wall (A); micro-Raman spectra of the sample SS4 (B) and ATR-FTIR spectra (C) of the standard of kaolinite (a) and of the same sample (b), in which are marked with the symbol * peaks attributed to kaolinite. Micro-Raman spectrum of cross section of sample SS5 (D), first layer (a) and second layer (b), and of sample SS6 (E). Ma, ka, he and ca correspond to massicot, kaolinite, hematite and calcite Raman peaks, respectively.

are well separated from each other, and there is no diffusion of pigments from a layer to the next one, typical characteristic of the secco technique.[11,14,15,35] The identification of peaks at 2972, 2870, 1750, 1640 and 1556 cm^{-1}, in the ATR-FTIR spectrum, compatible with the presence of egg, suggests the layers were applied on the dried plaster as often documented in Byzantine paintings, including in the nearby church of Santa Maria di Cerrate (Puglia, Italy) (Fig. 3, B).[14,15,36]

The stratigraphic analysis of the sample SS2 taken from the image of *San Nicola di Myra*, located in the right aisle of the crypt of the Santi Stefani and dated to the 14th century also permitted to distinguish three layers, a first preparatory layer (a) composed of calcite, a second yellow layer (b) characterized by massicot and a third layer (c) composed of hematite (Fig. S1, C–D, Supporting Information). The observation in visible and UV light, however, shows a significant spread of yellow pigment within the layer a, typical of the true fresco technique; these data were confirmed by ATR-FTIR analysis on the same sample showing pigments and calcite whereas organic binders were undetectable (Fig. 3, A).

Conservation state of the crypt

The study of the conservation state of Medieval paintings in the Santi Stefani crypt was done with the aim of having a condition survey and enable a diagnosis of the problems of the wall painting.

At first observation, some scenes are fragmentary, and what remained of the paint layer was seriously damaged, either completely lacking cohesion or detached. Moreover, the wall paintings of the crypt show clear problems of damp: Santi Stefani is carved into the tufa, a porous and highly hygroscopic material that easily absorbs water from the soil; there is also the clear presence of plants, fungi and molds, and the decorations are affected by craquelure and substantial losses of the paint layers, which often limit the interpretation of the iconography.

Planning the correct procedures for the restoration is necessary to prevent irreparable loss of the decoration: for example, if the restorers had known the presence of azurite in the crypt, possibly an EDTA based cleaner would have not been used. For these reasons, spectroscopic (Raman and FTIR spectroscopy) and chromatographic (IC) analyses were conducted. Specifically, the first ones

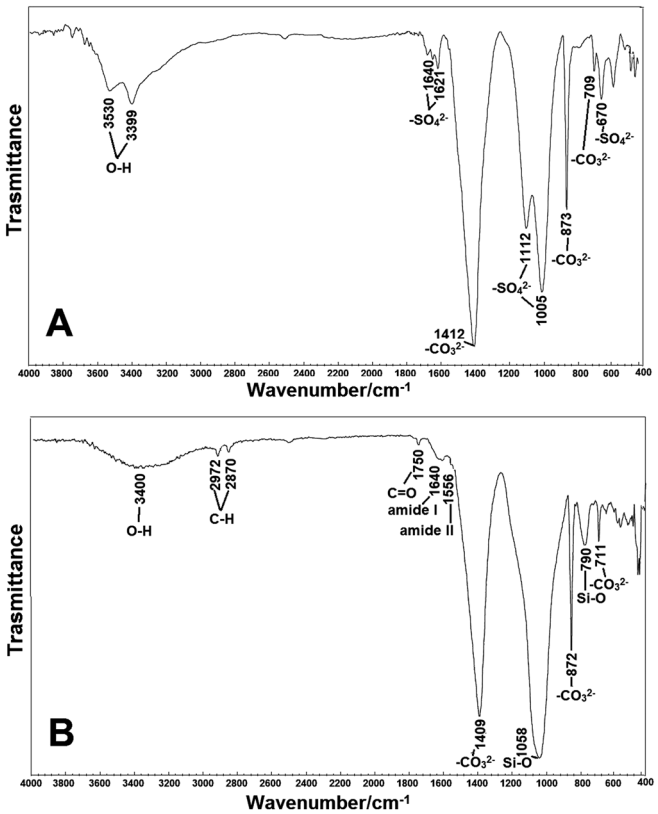

Figure 3. Representative infrared spectra of sample SS2 (A) and sample SS3 (B), in which the use of the fresco technique in A and probably the presence of egg in B could be ascertained; in addition to the infrared peaks of organic binder, the CO_3^{2-} peaks refer to the presence of calcite, O–H and SO_4^{2-} peaks refer to the presence of gypsum, Si–O peaks refer to silicates.

were performed on all samples analyzed (Table 1), while the quantitative determination of soluble salts by IC was made only on eight samples (Table 2) extracted from various points of the surfaces (Fig. 4), due to the significant amount of sample (about 100 mg) required by the Italian NORMAL.

The FTIR (Fig. 3) and Raman analysis (Fig. S2, Supporting Information) showed the presence of sulfates, nitrates, oxalates and carbon

Table 2. Concentrations of soluble anions (mg kg^{-1}) in some samples and crusts; the reported error is the expanded uncertainty estimated in accordance with the EURACHEM/CITAC Guide CG4 'Quantifying Uncertainty in Analytical Measurement' with a coverage factor $k = 2$, corresponding to a level of confidence of about 95%

Samples	F^-	CH_3COO^-	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
SS2	<D.L.	10 ± 2	2.5 ± 0.3	0.5 ± 0.1	5 ± 1	4.5 ± 0.9	6.4 ± 0.8
SS3	<D.L.	<D.L.	5.1 ± 0.7	<D.L.	<D.L.	<D.L.	610 ± 50
SS4	0.05 ± 0.02	<D.L.	3.2 ± 0.4	<D.L.	18 ± 3	19 ± 3	510 ± 50
SS7	0.11 ± 0.03	13 ± 3	3.0 ± 0.4	0.9 ± 0.2	3.1 ± 0.8	1.6 ± 0.5	11 ± 1
SS8	<D.L.	<D.L.	3.6 ± 0.5	<D.L.	4.1 ± 0.9	3.9 ± 0.8	450 ± 40
SS11	<D.L.	0.9 ± 0.2	2.2 ± 0.3	0.28 ± 0.09	10 ± 2	9 ± 2	900 ± 70
SS12	<D.L.	<D.L.	1.7 ± 0.3	<D.L.	18 ± 3	19 ± 3	530 ± 50
SS13	<D.L.	<D.L.	2.6 ± 0.4	<D.L.	<D.L.	<D.L.	9 ± 0.9

<D.L.: below detection limit

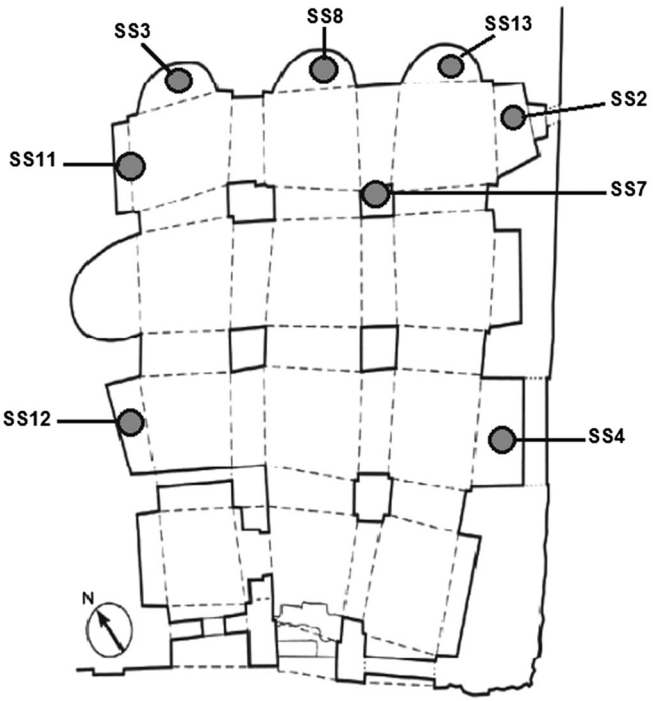

Figure 4. Planimetry of Santi Stefani crypt with sampling points for IC analysis.

black. In the evident and widespread white areas present on the wall paintings Raman (peak at 1007 cm^{-1}, Fig. S2, Supporting Information) and ATR-FTIR (infrared peaks at 3530, 3399, 1640, 1621, 1112, 1005 and 670 cm^{-1} assigned to gypsum) confirmed the presence of calcium sulfate dihydrate $CaSO_4{\cdot}2H_2O$, as seen for example from Fig. 3 relative to the sample SS2. Generally, sulfates derive from either the process of sulfation or the plaster itself:[37] the Raman data and the optical microscopic observation of cross sections (i.e. sample SS2) show that the gypsum layer does not exceed 60 μm below the surface affecting only the paint layers suggesting sulfation occurred in Santi Stefani crypt. The carbon black on the surface of the same sample SS2, as shown by the two Raman bands at 1600 and 1315 cm^{-1},[19] could be attributed to the soot from candles or oil lamps: the particulate matter produced by wax or oil combustion was embedded in the gypsum matrix, mechanism similar to the one occurring in black crust on stone in open air.[38]

Raman permitted also the identification of both calcium oxalates, whewellite ($CaC_2O_4{\cdot}H_2O$, 1490 and 1462 cm^{-1}, Fig. S2c) and weddellite ($CaC_2O_4{\cdot}2H_2O$, 1475 cm^{-1}, Fig. S2d).[38] Different theories about the formation of oxalates have been reported in recent years: air pollution phenomena, metabolic action of algae and lichens and degradation of organic materials used as binders or protective (original or applied in restoration operations) were claimed to justify their presence.[39,40] Due to the conservation state of the investigated frescoes, calcium oxalates possibly are products of the reaction between the oxalic acid excreted by the lichens, fungi, algae and other microorganisms and the calcite of the plaster.[37] The Raman spectra showed, indeed, peaks related to the presence of chlorophyll and carotenoids, suggesting the biological origin of calcium oxalates (Fig. S2a, Supporting Information). Nitrates were also detected spectroscopically thank to the sharp peak at 1384 cm^{-1} and in the region of 1040–1055 cm^{-1} in the infrared and Raman spectra, respectively.[38,41]

Table 2 collects the concentrations of soluble anions in the samples. Although deterioration of the wall paintings is commonly attributed to air pollution, a closer examination to these results reveals soluble salts as the main cause of the decay of the crypt.[42] The presence of chloride salts can be attributed to capillary rising,[42] but in the samples SS3, SS4, SS7 and SS8 their high concentration may rather be due to the application of chemical products as consolidant/protective, that lead to bleaching of polychromy.[43,44] The presence of nitrites and acetates salts in SS2 and SS7 samples (east side of the crypt, Fig. 4) is attributable to organic material decomposition and metabolic action of microorganisms[45] and perhaps to migration of water from a cesspool, in the past visible outside the entrance of the Medieval crypt. Nitrates and phosphates, abundant on both right (SS4) and left (SS11, SS12) sides could be due to the nearby agricultural activities.[44]

Sulfation is the prevalent mechanism of degradation in the western side of Santi Stefani crypt, as evidenced by the higher content of sulfates in the samples SS3, SS11 and SS12.[38] Among these, SS11 was a black crust taken from the figure of the *Arcangelo Michele* dated to the 11th century, in which black carbon and gypsum were identified by Raman spectroscopy and the ion chromatography has confirmed to be almost completely calcium sulfate. The same figure of the *Arcangelo Michele* presents considerable detachments of the paint surface, attributable to the fact that the decoration is placed below an opening in the ceiling and receives directly sunlight; this is also visible in *Santi Basilio, Nicola e Giovanni Crisostomo* (SS3, Fig. S1-A, Supporting Information): the heat of the direct radiation causes the gypsum crystallization and the

detachment of portions of the painting surface due to the resulting volume increase.

Overall, degradation of paintings in the Santi Stefani crypt originates from physical (mainly due to dampness and capillary rise of water), biological (due to the different micro and macroflora that are always active) and chemical (reaction of plaster and painting materials with environmental substances SOx, NOx, particulate matter, salts…) causes, so specific actions are necessary to preserve these memoirs of Medieval art in Salento for next generations.

Conclusions

A combined analytical approach, comprising optical microscopy, diffuse reflectance, Raman and FTIR spectroscopies, and ion chromatography, was used to study the palette and the conservative state of the Medieval wall paintings, produced between the 10th and the 14th century and located in the crypt of Santi Stefani at Vaste (Salento, Puglia, Italy), permitting the elucidation of different aspects of painting techniques and degradation products.

Different original pigments (kaolinite, calcite, carbon black, hematite, massicot, goethite, indigo and azurite) and some restoration products (phthalocyanine blue and chrome yellow) were identified.

The skill of the craftsmen who decorated the crypt is evident from the use of mixtures of different pigments to produce the desired hue, from the overlapping of layers of different colors and from the use of both painting techniques (fresco and secco), typical of Medieval art. Although the kaolinite is attested as pigment in Byzantine art, its use in the Santi Stefani crypt deserves attention, because it is the first occurrence recorded in a Medieval crypt of Puglia: mixed with other pigments (massicot, hematite) or overlaying the other colors, kaolinite permitted different shades to be obtained, ranging from violet (*caput mortuum*) to pink (e.g. in the flesh tones of the *Vergine*) or to brown (e.g. in the hair of the *Vergine*), to increase adhesion of the pigments to the substratum (e.g. of the purple pigment) and the stability of the materials (e.g. massicot in the haloes of the saints), and to use less expensive materials (e.g. avoiding the highly prized violet organic extracts).

However, the Santi Stefani crypt shows problems of damp as well as clear evidence of microflora, fungi and molds. Raman spectroscopy permitted the *in situ* identification of sulfates, nitrates and oxalates, which were also quantified along with chlorides, fluorides, nitrites and acetates by ion chromatography, thus obtaining a more clear picture of the poor conservation state. The study of the distribution of the anions in the crypt also evidenced the biological attack in the eastern wall of the church, and the prevalence of sulfation in the western wall, but the primary source of decay in the church is the significant dampness inside: this water provided the environment ideal for the migration of salts from the floor and from outside the walls, causing perhaps the worst effect possible on a wall painting such as its (fortunately partial) loss.

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