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Abstract

This paper focusses on the archaeometric investigation of wall paintings of the St. Maria Veterana archaeological site in Triggiano (Bari, Southern Italy) finalised to support the hypothesis on the historical reconstruction of the site based on iconographic interpretations. The site is an original and relevant example of medieval art in Apulia and in Southern Italy and includes a medieval church surrounded by several additionally architectural elements (chapels, crypts, tombs), nowadays buried below by a Renaissance church. Here, the presence of different pictorial cycles, only partially dated, and the evidence of re-use of painted blocks in Renaissance structures pertaining to medieval structures, suggested a complex scenario in which different artisans and clients were possibly succeeded. The site is also framed in a wider regional context, the Apulian region, currently object of an intense archaeological and scientific debate due to widespread action of valorisation of the cultural patrimony as an essential link between the territory and the cultural identity of the citizens. The study of the site involved the sampling and the analysis of 48 samples of painting fragments, investigated by optical microscopy, scanning electron microscopy with EDS microanalysis (SEM-EDS) and micro-Raman spectroscopy. The obtained results allowed a complete material characterization of mortars and pictorial layers, highlighting the use of precious and rare pigments as cinnabar and verdigris, along with more common recipes based on natural ochres and earths more commonly used in other similar sites through the Apulia region. The combined data obtained from the analysis of mortars and pigments allowed to finally propose a reliable hypothesis on the construction and decorative phases of the site, in agreement with the dating based on iconographic interpretations. Up to now, St. Maria Veterana Church was considered a minor site, mainly due to the scarcity of the written sources. However, the new stylistic interpretation of the pictorial cycles, the preciousness of the used materials, the quality of the manufacture technique and the numerous artistic executive phases identified through five centuries (11th-16th) suggest a continuous attendance of the site by artisans and client carriers of high cultural and artistic values.

Keywords	Wall paintings; pigments; mortars; Apulia; archaeometry; chronological dating

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Dear Professor Howard and dear professor Hunt,

we would like to publish our study in your journal, so please consider the manuscript I'm sending.

The research concerns the archaeometric investigation of wall paintings of the St. Maria Veterana archaeological site in Triggiano (Bari, Southern Italy), as original and relevant example of medieval art in the territory. This research focus belongs to a wider research project (TRIVIANUM, Study and conservation of Triggiano (Italy) cultural heritage) entirely founded by a private organisation, the Pasquale Battista Foundation. The project involves several local Institution, Universities (University of Bari and University of Pisa), no-profit organisations and researchers from different specialisations and provenances.

We believe that our research is suitable for publication in the *Journal of Archaeological Sciences: Report* as it is based on a multidisciplinary approach that merges scientific knowledge (petrography, mineralogy) with archaeological and artistic ones to obtain important results that allowed the dating of the construction phases of the site and contribute to the study of wall paintings in archaeological sites and medieval churches in the Apulia region and southern Italy.

Thanks for your attention

Best Regards

Giovanna Fioretti

Simona Raneri

Daniela Pinto

Marcello Mignozzi

Daniela Mauro

The archaeological site of St. Maria Veterana (Triggiano, Southern Italy): archaeometric study of the wall paintings for the historical reconstruction

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Abstract

This paper focusses on the archaeometric investigation of wall paintings of the St. Maria Veterana archaeological site in Triggiano (Bari, Southern Italy) finalised to support the hypothesis on the historical reconstruction of the site based on iconographic interpretations. The site is an original and relevant example of medieval art in Apulia and in Southern Italy and includes a medieval church surrounded by several additionally architectural elements (chapels, crypts, tombs), nowadays buried below by a Renaissance church. Here, the presence of different pictorial cycles, only partially dated, and the evidence of re-use of painted blocks in Renaissance structures pertaining to medieval structures, suggested a complex scenario in which different artisans and clients were possibly succeeded. The site is also framed in a wider regional context, the Apulian region, currently object of an intense archaeological and scientific debate due to widespread action of valorisation of the cultural patrimony as an essential link between the territory and the cultural identity of the citizens.

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1. Introduction

The characterization of raw materials (pigments, binder and aggregate fragments) and painting techniques in ancient wall paintings represents a relevant task in studying complex figurative cycles

and allows to better define chronology, artisan knowledge, receipts and technology used over time, especially in the case of archaeological sites and historical buildings involved in subsequent construction and frequentation phases (Piovesan et al. 2012; Regazzoni et al. 2018).

In the overall Mediterranean area, and in particular in the Apulia region (South Italy), outstanding examples of medieval wall paintings were found in different contexts, from natural caves to hypogea, to Romanesque churches. Although numerous sites were exhaustively studied from the stylistic, figurative and historical point of view, providing a considerable contribute to the history and art history of the region, a limited number of reports concerning the archaeometric characterization of the materials used in the wall paintings and the definition of production techniques are currently available.

Generally, researches are focused on rupestrian settlement and mural painting set into the numerous local natural and artificial caves set underground or alongside riverbeds. As examples, the study of wall paintings at the rupestrian hypogeum of St. Marco in the territory of Fasano (Brindisi, Southern Italy) showed the use of pigments based on natural red/yellow ochres and carbon black, as well as a mixing of them to give different colour shades (Pinto et al. 2008). Capitanio et al. (2005) carried out a study on the paintings of the St. Nicolò all'Arena hypogeum in Monopoli (Bari), revealing the presence of minium and hematite, in red pigments, and yellow ochres rich in iron oxides mixed with clay minerals and (once) almandine-garnet in yellow pictorial layers. Very interesting is the case of St. Angelo *in cryptis* cave in Santeramo in Colle (Bari), where the presence of cinnabar as red pigment was pointed out by archaeometric analysis, beside the use of natural earth pigments (Fioretti et al. 2017). Other interesting cases include studies on wall paintings preserved in Apulian medieval churches. For example, in the paintings of the Seppannibale temple in Fasano (Brindisi), colours were obtained by using natural red and yellow ochres, as reported in Calia et al. (2011) and Pinto (2011), by using organic binder. In the case of St. Maria delle Cerrate (Lecce), the archaeometric investigations highlighted the application of pigments, in some cases highly precious as lapis lazuli, both by *fresco* and egg-based tempera, suggesting the presence of two different and independent artists, in term of artistic tradition and dating (De Benedetto et al., 2012). A noteworthy variability of pigments was observed in the St. Stefano crypt in Vaste (Lecce), where the wall paintings, analysed thanks to a combined analytical approach, showed the presence of many natural and artificial pigments including kaolinite, calcite, carbon black, hematite, massicot, goethite, indigo, azurite, phthalocyanine blue and chrome yellow (Fico et al., 2015). In some cases, the study of raw materials allowed establishing chronological correlations among different environments. As an example, Eramo et al. (2012) analysed Castel Fiorentino and the Castle of Lucera sites (Foggia, Italy); in these cases, the petrographic investigation of mortars, supported by the mensiochronology, allowed to correlate different structures and then to deduce the chronological stratification.

The presented research aims to contribute to the knowledge of the Apulian medieval context by adding new data collected from the St. Maria Veterana archaeological site, being a significant evidence of the Apulian Romanesque style and medieval painting art, despite the extremely poor and backward context of the neighbour *Locus Triviani* (Battista 1983, Battista 1996). In detail, the present archaeometric investigations on mortars and pictorial layers of this site, intend to contribute to the scattered knowledge about raw materials, production and execution techniques in the area, supplying also data useful for the better understanding and the reconstruction of the social, cultural and economic contexts of the region.

2. Historical and artistic framework

The church of St. Maria Veterana, located in the historical centre of Triggiano (Bari), represents one of the most interesting examples of urban archaeology in the central Apulia (Figure 1). The

excavations of the site carried out between the late ‘70s and the beginning of the ‘80s of the 20th century returned several findings, including ceramic fragments, funeral goods, coins, and supported the reconstruction of the different phases of its architectural and artistic history (Rescio 2015).

The primitive church was founded in the last quarter of the eleventh century (probably in 1080), as demonstrated by an epigraph (Battista 1987; Magistrale 1987). Over the following centuries, the site was interested by numerous burials directly in the bedrock, according to a common *modus operandi* having comparison with other interesting Apulian contexts, such as *Madonna della Grotta* in Modugno and *San Nicola* in Cisternino (Mignozzi 2015). On the walls of the medieval church and on some pillars, cut at about 1.50 meters from the ground by the building structures pertaining to the modern structures (dated to 1580), the archaeological investigations brought to the light traces of wall paintings, useful for the reconstruction of the Angevin art history in the Bari suburbs (Crudele, Di Gioia 2010; Gelao 1987; Mignozzi 2018).Today, the complex consists of an original medieval nucleus, perfectly preserved in its dimensions and shapes, single-aisle with three naves bounded by two pairs of central pillars and two other couples leaning against the counter-façade and the apse wall. Around it, the environment is marked by hypogea and burial rooms of complex stratification and coeval to the construction of the upper church of the Renaissance age.

As far as the painted remains, the oldest phase dating back to the first half of the 15th century, is mainly recognized in the presbytery area that includes the apse, the north and east walls of the last aisles and the two nearest pillars to the altar. Here, panels with saints, among which St. John the Baptist figure, an anonymous bishop, a Dominican saint with dark sandals and an ashlar painted with the face of Christ Child originally placed in the centre of the apse, on the legs of His Mother, an *Odegitria dexiokratousa*, can be recognised. On the southern wall, near the façade, St. Leonardo and the enthroned Virgin with a child was painted in the early 15th century structures. Above this last, on the left, St. Vito was painted in the half of the 16th century. Between the ‘30s and ‘40s of the 15th century a new panel was realised on the northern wall, overlapping the 15th century layers, with a long but fragmentary inscription in refined Gothic characters, related to another Virgin with Child. To the right of this panel, there is another one with St. Anthony Abbot, particularly interesting, because in the lower frame the name of the saint and the coat of arms are reported, suggesting that the client was Giovanni Antonio of the *Orsini del Balzo* family, Duke of Bari and Triggiano between the ‘40s and ‘60s of the 14th century. Other pictorial traces are visible on all the walls, pillars and reused blocks, in some cases ascribable to the 16th century, just before the medieval church was demolished and covered.

[MM]



Figure 1. The archaeological site of St. Maria Veterana, Triggiano (Bari). In the foreground the remains of the tombs along the central nave; on the sides the original pillars of the medieval church.

3. Paintings and sampling

The internal walls of St. Maria Veterana archaeological site show different remains of pictorial decorations sometimes occurring in almost well-preserved conservation state (Figure 2), sometimes presenting only pictorial traces. Specifically, on the northern wall (area A in Figure 2) close to the apse, there are four overlapping pictorial cycles (dated to 11th-14th centuries): the oldest layer is hidden by successive paintings and it is visible only in the centre and on the margins (area A/I); the second pictorial cycle shows two orange red frames, one of which showing orange background and the lower part of a Dominican saint with a light tunic and dark sandals (area A/II); on the left there is a third pictorial layer in which the bottom of the Virgin figure with red mantle is assumed (area A/III); on the right, the last pictorial layer (area A/IV) displays dark red frame reporting symbols and a writing referring to St. Antonio. Pictorial traces of a continuous orange red frame with orange background are also present on the side wall of the apse (area B in Figure 2), whereas in the apse area (C in Figure 2) only an orange red band is present. The north pillar closest to the apse shows the St. John' foot (area E) and an orange red frame (area F). On the counter façade (area L) an orange red frame is visible. In the south wall nearest the façade (area N) the lower part of two superimposed pictorial cycles (dated to 13th-14th centuries) are well-preserved: the most ancient one (area N/I) shows the lower part of St. Leonardo with chains and blue, pink and green tunic and the enthroned Virgin with a child; the most recent cycle appears on the left and displays St. Vito with a yellow and red tunic and two dogs (area N/II). In the first southern chapel (area O) red frames with emblems and symbols are painted. Other not identified pictorial traces were founded on the pillar against the apse wall (area D), on a side of the north pillar closest to the apse (area G), on the south pillar (area H), on the northern wall closest to the façade (area I), on the central part of the north wall (area S) and in the second southern chapel (area R). Traces of colour are also visible in some reused blocks in the Renaissance pillar against the counter façade (area M) and in the wall curb outside the medieval church (area P).

For this study, a total of 48 fragments of plasters with pictorial decoration were collected from wall painting traces observed in the above described 17 different areas corresponding to both medieval and Renaissance structures of the church, as illustrated in Table 1.



Figure 2. On the left top, the plan of the archaeological site of St. Maria Veterana in Triggiano (Bari): painting areas are marked by capital letters. In the boxes some of the most significant pictorial layers.

Area	Pictorial cycle	Visible decorative elements and figures	Sample	Colour	Sampling point
A	I (no dating, probably 1080-1325)	-	SA1	Pink	Hand skin
			SA2	Red	Painting traces
			SA3	Black	Painting traces
	II (1325-1350)	Dominican saint with dark sandals in a red frame and yellow background	SA4	Black	Tunic edge
			SA5	Black, red, yellow	Background
			SA11	Orange red	Frame
			SA13	Orange red	Frame
			SA14	Yellow	Background
	III (1430-1440)	Red tunic of the Virgin with rombic decoration, a writing	SA6	Pink, dark red	Virgin tunic, decoration edge
			SA7	Dark red	Virgin tunic, background
			SA8	Red, yellow	Virgin tunic, decoration
			SA9	Greyish yellow	Background
			SA15	Red, dark red	Virgin tunic, background
	IV (1440-1460)	St. Anthony Abbot in a red frame and grey background, a writing	SA10	Grey	Background
			SA12	Red, dark red	Frame
B	-	Red frame	A1	Orange red	Frame
			A4	Yellow	Background
C	-	Frame	A2	Orange red	Frame
D	-	-	A3	Red	Painting traces
E	-	St. John the Baptist foot and tunic	PS1	Pink	St. John the Baptist foot skin
			PS6	Pink	St. John the Baptist foot skin
F	-	Frame	PS2	Red	Painting traces
			PS3	Orange red	Frame
G	-	-	PS4	Red	Painting traces
			PS5	Black	Painting traces
H	-	Frame	PD1	Orange red	Painting traces
			PD2	Orange red	Frame
I	-	-	S1	Red	Painting traces
L	-	Frame	S2	Orange red	Frame
			S3	Yellow	Background
M	-	-	RP1	Dark red	Painting traces
			RP2	Red, dark red	Painting traces
			RP3	Green	Painting traces

			RP4	Green, red	Painting traces
N	I (1410-1440)	St. Leonardo and the enthroned Virgin	SL3	Red, dark red	Virgin tunic, background
			SL4	Green	Virgin mantle
			SL5	Pink, red	St. Leonardo tunic, edge
			SL6	Green	St. Leonardo tunic
	II (1525-1550)	St. Vito	SL1	Yellow, black	Background
			SL2	Red	St. Vito tunic
O	-	Emblem in a frame	C1	Red, black	Background, frame
			C2	Pink	Background
			C3	Grey, black	Frame
			C4	Yellow, pink	Frame
P	-	-	RV1	Green	Painting traces
			RV2	Red, green	Painting traces
R	-	-	CC1	Black	Painting traces
S	-	-	G1	Yellow	Painting traces

Table 1. Details on samples, colour surfaces and sampling areas with indications of pictorial cycles and their dating based on iconographic analysis.

4. Analytical methods

All the selected samples were observed under a stereomicroscope for a preliminary identification of macroscopic features. Thus, cross sections were obtained on representative samples for in deep analytical studies. For a complete description of stratigraphy, thickness and morphological features of pictorial layers, microstratigraphic observations were carried out under optical microscope (in reflection mode) using a Nikon Eclipse80i microscope equipped by a camera for digital image acquisition. The characterization of mortars was obtained by minero-petrographic analysis on thin sections following classification method proposed by Pecchioni et al. (2018) by using a Zeiss Axioscope 40 optical microscopy. Data were complemented by the chemical analysis of aggregates, binder and painted layers using a scanning electron microscope equipped with X-ray analysis (SEM-EDS, LEO, EVO50XVP model coupled with an X-max Silicon drift Oxford equipped with a Super Atmosphere Thin Window; operation conditions: 15 kV accelerating potential, 500 pA probe current and 8.5 mm working distance). Further investigations on pictorial layers representative of different cycles and colour palette were carried out by micro-Raman spectroscopy; data were collected on polished cross section and small samples chips by using a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a 532 and 785 nm excitation sources and an Olympus BX41 microscope with a 10, 50 and 100× objective lenses. The minimum lateral and depth resolution was set to a few μm. The system was calibrated using the 520.6 cm^{-1} Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions with counting times ranging from 30 to 180 s. Optical filter were used to minimise the power at the sample to avoid damage effects. Backscattered radiation was analysed with a 1200 mm^{-1} grating monochromator.

5. Results

5.1 Mortars characterization

The petrographic and chemical characterization of plasters layers beneath the painting layers allowed the discrimination of nine types of mortar mixtures based on composition and texture of the

binder, grain size distribution, shape and sorting of the aggregates and on the porosity. The obtained results are summarised in Table 2, whereas a selection of representative pictures for each mortar type are reported in Figure 3.

Mortar type	Binder		Aggregate				Other characteristics	Sample	Sampling area
			Volume	Size (Mode)	Composition				
	Structure Texture	Porosity			Minerals	Other			
L	Non-hom. (nodular, fractured) Micritic	Angular, rounded 5-10%	<5%	80 µm	mQtz, K-fsp	-	Lime lumps, underburnt relicts	SA4 SA5 SA11 SA13 SA14	A/II
								A1 A4	B
								A2	C
								PS1 PS6	E
								PS2 PS3	F
								PS4 PS5	G
								PD1 PD2	H
								S2 S3	L
CP	Hom. Micritic	Angular 5%	10%	50-800 µm	mQtz, K-fsp	Cocciopesto	Lime lumps, underburnt relicts, iron oxides	SA6 SA7 SA8 SA9 SA15	A/III
								A3	D
HA	Hom. Micritic	Stretched 5%	45-50%	90 µm (well sorted)	mQtz, pQtz, K-fsp, Ol	-	-	C1 C2 C3 C4	O
CC	Hom. Micritic	Angular 5 %	5-10%	150 µm	mQtz, K-fsp	Clay clumps, cocciopesto	-	RP1 RP2 RP3 RP4	M
								RV1 RV2	P
STR	Non-hom. (nodular) Micritic	Angular >5%	-	-	-	-	Straw fibres, underburnt relicts	CC1	R
CRN_R	Non-hom. (nodular) Micritic	Angular 5-10%	<5%	200 µm	mQtz	Calcarenite fragments	Underburnt calcarenite relicts	SA10 SA12	A/IV
								S1	I
CRN	Non-hom. Micritic	Angular 5%	5-10%	200 µm	mQtz	Calcarenite fragments	Iron oxides	SL1 SL2	N/II
HFA	Non-hom. Micritic	Rounded, angular 10%	20%	200 µm	mQtz, Ol	Calcarenite fragments, fossil sand	-	SL3 SL4 SL5 SL6	N/I
								G1	S
Q	Hom. Micritic	Subrounded 5%	5%	120 µm	mQtz, K-fsp	-	Fossil structure relicts in the binder	SA1 SA2 SA3	A/I

Hom.: homogeneous**; Non-hom.:** eterogeneous**; mQtz**: monocrystalline quartz; **pQTZ**: polycrystalline quartz; **k-fsp**: K-felspar; **Ol**: olivine.

Table 2. Petrographic characterisation of mortar types.

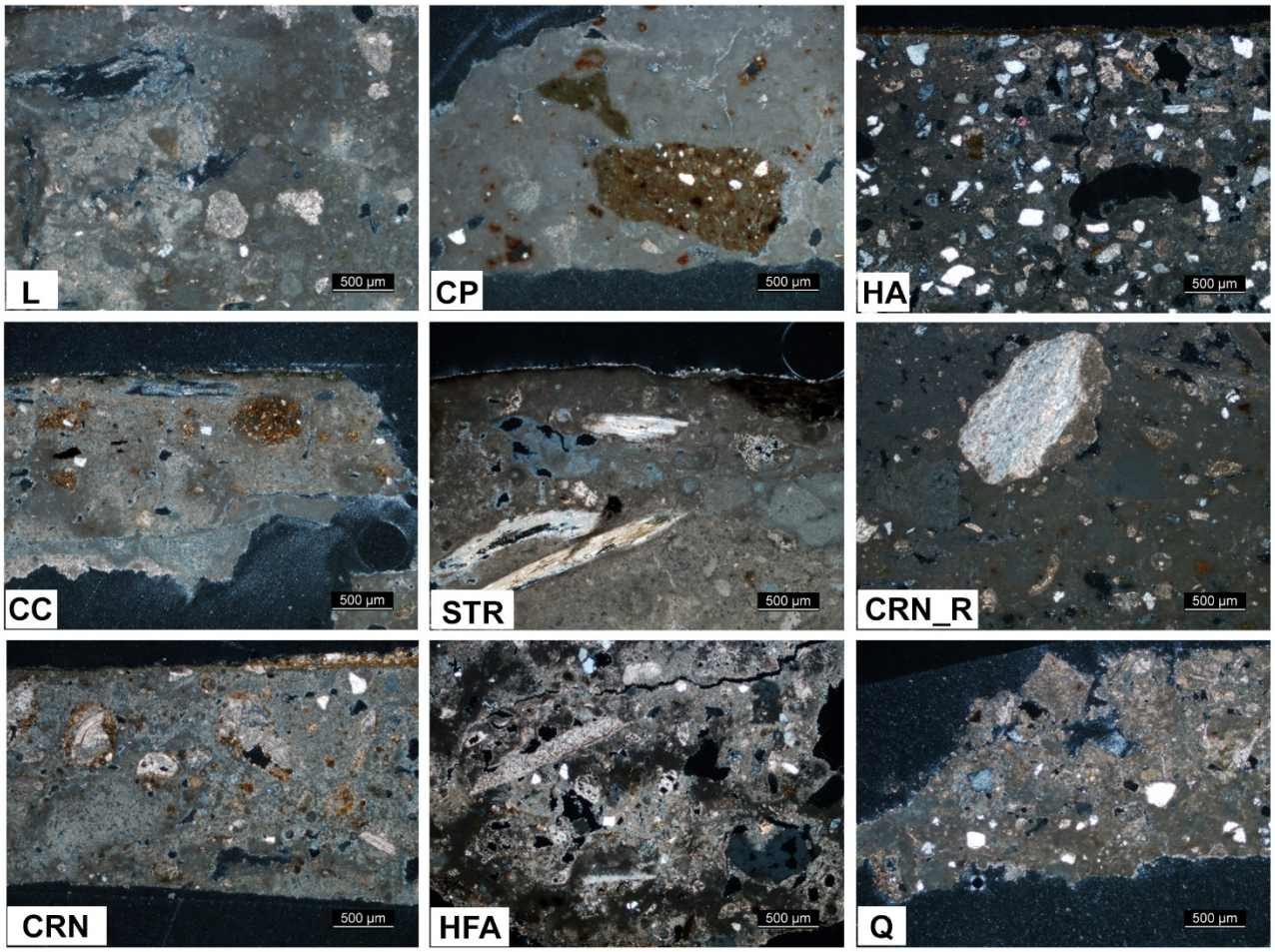


Figure 3. Microphotographs of representative samples in thin section for mortar types L (sample SA14), CP (sample A3), HA (sample C1), CC (sample RP4), STR (sample CC1), CRN_R (sample SA10), CRN (sample SL1), HFA (sample G1) and Q (sample SA2).

Type L (lumps) includes 18 samples, coming from areas A/II (samples SA4, SA5, SA11, SA13, SA14), B (samples A1, A4), C (sample A2), E (samples PS1, PS6), F (samples PS2, PS3), G (samples PS4, PS5), H (samples PD1, PD2) and L (samples S2, S3). The petrographic analysis revealed a very fat mortar with very low content of aggregate (<5%), consisting of sporadic fine sand grains (about 80 µm) of quartz and feldspar. The binder is micritic, high fractured, showing a nodular appearance with a porosity of about 5-10%, due to fine and rounded pores, locally angular. The mortar appears very rich of large (about 600 µm in size) lime lumps and underburnt relicts. SEM-EDS analysis confirmed the silicate nature of the aggregate and revealed the presence of silica, magnesium and sodium in the lime binder.

Type CP (cocciopesto) was recognised in 6 samples from areas A/III (samples SA6, SA7, SA8, SA9, SA15) and D (sample A3). The observation under optical microscopy indicated a fat mortar with micritic binder, rich in iron oxides, with an aggregate volume of about 10%. Aggregate has a bimodal distribution and consists mainly of cocciopesto fragments about 800 µm in size (at least four different cocciopesto types were recognised) and minor fine grains of quartz and feldspar (50 µm). Pores (5%) are angular. Few lime lumps and underburned fragments were also recognised in the pastes.

Mortars of type HA (high aggregate content) was recognised in 4 samples from area O (samples C1, C2, C3, C4). The mortar is homogeneous, very lean and contains about 45-50% of aggregate consisting of sorted fine grained sand composed by monocrystalline and polycrystalline quartz, feldspar and subordinate olivine crystals. The porosity is very low, due to stretched pores of about

400 x 100 μm. SEM-EDS analysis confirmed the presence of silica in the aggregate and indicated the calcic composition of binder.

Type CC (clay clumps) was recognised in 6 samples collected from areas M (samples RP1, RP2, RP3, RP4) and P (samples RV1, RV2) from painting traces on reused blocks in Renaissance pillars. The binder displays a micritic texture with angular pores (5%). The aggregate (5-10%) includes rare and fine sand grains of quartz and feldspar and fragments of cocciopesto as in the mortar of type SS. However, in this case some peculiar yellowish rounded agglomerates of clay (up to 600 μm) are also present. Rare fossils were also observed. SEM-EDS analysis revealed the presence of few amounts of silicon, aluminium, magnesium and sodium in the calcitic binder.

The mortar of type STR (straw) was recognised in 1 sample from area R (sample CC1) and is characterised by a very fat mixture without aggregate, with numerous underburnt relicts (500-2000 μm). Pores are angular (porosity <5%). Mortar contains long (up to 2000 μm) remains of straw fibres completely filled by calcite.

Three samples coming respectively from areas A/IV (samples SA10 and SA12) and I (sample S1) show a nodular mortar mixture (type CRN_R, calcarenite relicts) characterised by a non-homogeneous binder with micritic texture and with several underburnt relicts. The latter preserve the original structures of the calcarenite used as raw material. Calcarenite fragments (about 200 μm) are also present among the aggregate fraction, along with very fine grains of quartz (~10%). SEM-EDS analysis revealed the presence of calcium and small percentages of magnesium in the lumps, suggesting a further dolomitic character of the lime stone.

Type CRN (calcarenite) mortar was recognised in 2 samples from area N/II (samples SL1 and SL2); it is characterised by a non-homogeneous calcitic binder, very rich in iron oxides, with micritic texture and aggregate volume of 5-10%. Pores are very angular and about 300 μm large. Lumps are absent. Aggregate consists of calcarenite fragments (500-800 μm) showing still well preserved fossil tests.

Samples from area N/I (samples SL3, SL4, SL5 and SL6) and area S (sample G1) are grouped in type HFA (high fossil aggregate content). Likewise to the latter mortar mixture, this group is characterised by an aggregate consisting of calcarenite rock fragments (about 100 μm in size) with well preserved fossil tests. However, the aggregate content in samples from this group is higher (about 20%) than in type CRN, as higher is the number of single fossils grains, which reach up to 2,8 mm in size. The porosity is also higher (about 10%) and consists of both rounded and angular pores with a size ranging from 50 to 500 μm. An additional significant difference of this mortar group with respect to mortars of type CRN is the almost absence of iron oxides.

Type Q (quartz) mortar was recognised in 3 samples from area A/I (samples SA1, SA2, SA3). It is characterised by non-homogeneous binder composed by micritic calcium carbonate. The aggregate content is about 5% and the porosity (5%) consists of rounded pores (70-90 μm). The aggregate shows unimodal grain size distribution and includes very fine sandy grains of quartz and feldspar. Fossil structure relicts are visible in the binder. SEM-EDS analysis revealed the presence of silicon, aluminium, sodium, magnesium and potassium in the calcic binder.

5.2 Pictorial layers

The studied pigments include pictorial layers exhibiting different shades of yellow, red, pink, orange, green, blue, grey and black. The microscopic, chemical and spectroscopic analysis of selected samples allowed to provide details on the stratigraphy and composition of raw materials.

As a first remark, pigments can be discriminated based on their stratigraphy, consisting in one or in multiple pictorial layers, the latter employed to obtain peculiar chromatic hues. Moreover, in some cases, the colour is due to the use of a single pigment, while in others different pigments were mixed

together in order to obtain particular chromatic effect. All recognised recipes observed for studied samples, including major and minor pigment components, are summarised in Table 3.

| | | | | Area - samples | | | |

In detail, concerning red pigments, four different recipes were detected, all based on the use of red ochre, variably mixed with other pigments. The most common recipe recognised in red pictorial layers (recipe R1) is characterised by a fine grained and opaque pigment, locally translucent; the Raman analysis revealed bands at 226, 292, 411, 612, 1320 cm^{-1}, attributable to pure hematite (Zoppi et al. 2005), testifying the use of hematite-rich red ochre; data are confirmed by SEM-EDS analysis, giving back the typical elements proper of natural ochres, such as iron, silicon, aluminium and potassium. This recipe was recognised in several red colours throughout the site because of its common use in the medieval buildings, namely in all the four cycles of the area A paintings (11-15th century), in the apse (area C), near the apse (areas B and D), in the decorations on pillars in the areas E, F, G and H (unknown dating), in the two overlapped paintings in the area N (15-16th century) and in other unidentifiable coloured traces in areas I, L and S. Moreover, the use of hematite-rich ochre was recognised in wall paintings of the areas O and R (chapel, unknown dating) and in the reused blocks of the Renaissance pillars in areas M and P (unknown dating). In two samples, C1 and SA12, collected respectively from the decoration of the chapel in area O and from the red frame around St. Antonio in the most recent cycle of area A, the chemical composition of ochre revealed by SEM-EDS included very small amount of manganese and titanium oxides.

The darker shades of red observed in the third and fourth pictorial cycles in area A, in both cycles in area N and in the reused blocks in the area M pillar, were obtained by mixing red ochre with fine and opaque particles of carbon black (recipe R2), as revealed by the Raman analysis of the pictorial layers and the presence of black spots into the red layers (Figure 4).

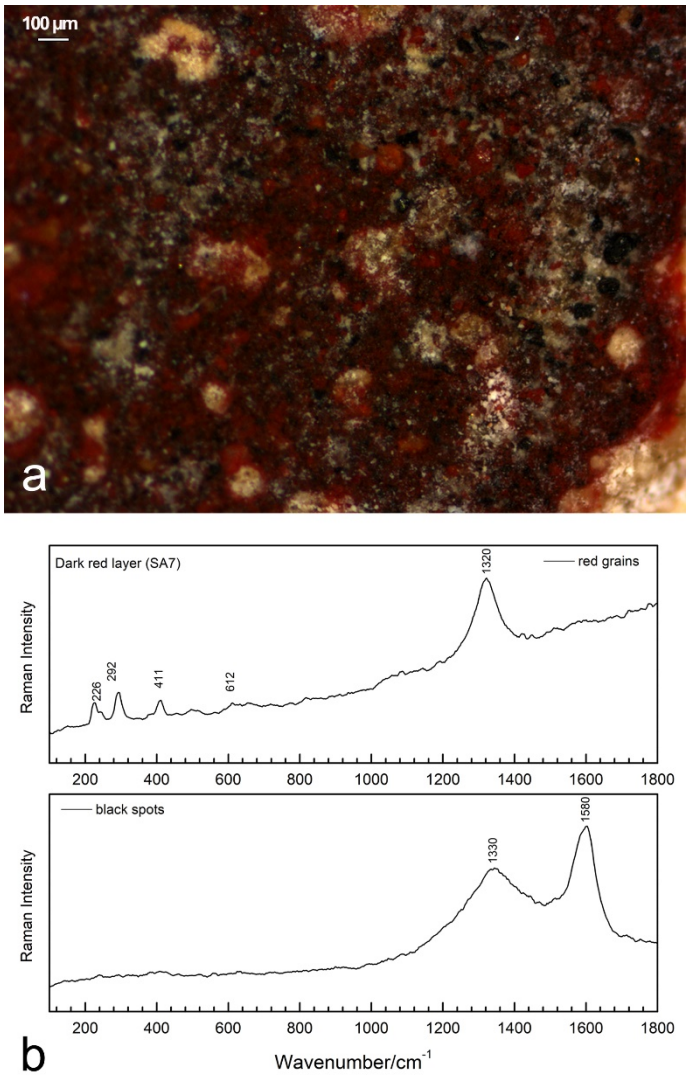


Figure 4. On the top, a macro-photographs of sample SA7 and, on the bottom, the Raman spectra revealing the mixtures of carbon black particles in a red ochre matrix.

In the case of brilliant and light shadows of red, translucent grains in an opaque red matrix were observed. Raman analysis revealed the combined presence of hematite and a Pb-based red pigment, as claimed by Raman bands detected at 220, 280, 410, 615, 1310 cm^{-1}, attributable to hematite, and strong bands at 145 and 380 cm^{-1}, suggesting the use of minium. The absence/weakened of some diagnostic bands can be related to the use of Pb-based pigments in mixtures; actually, the spectral features of these compound might be modified in function of the relative molar amount of the used compounds (Howell et al. 1999). Beside the already detected phases, in deep SEM-EDS investigation indicated (Figure 5) the occurrence of orpiment and very fine and rare particles of cinnabar (recipe R3). This recipe was detected in samples belonging to Renaissance pillars in the areas M and P.

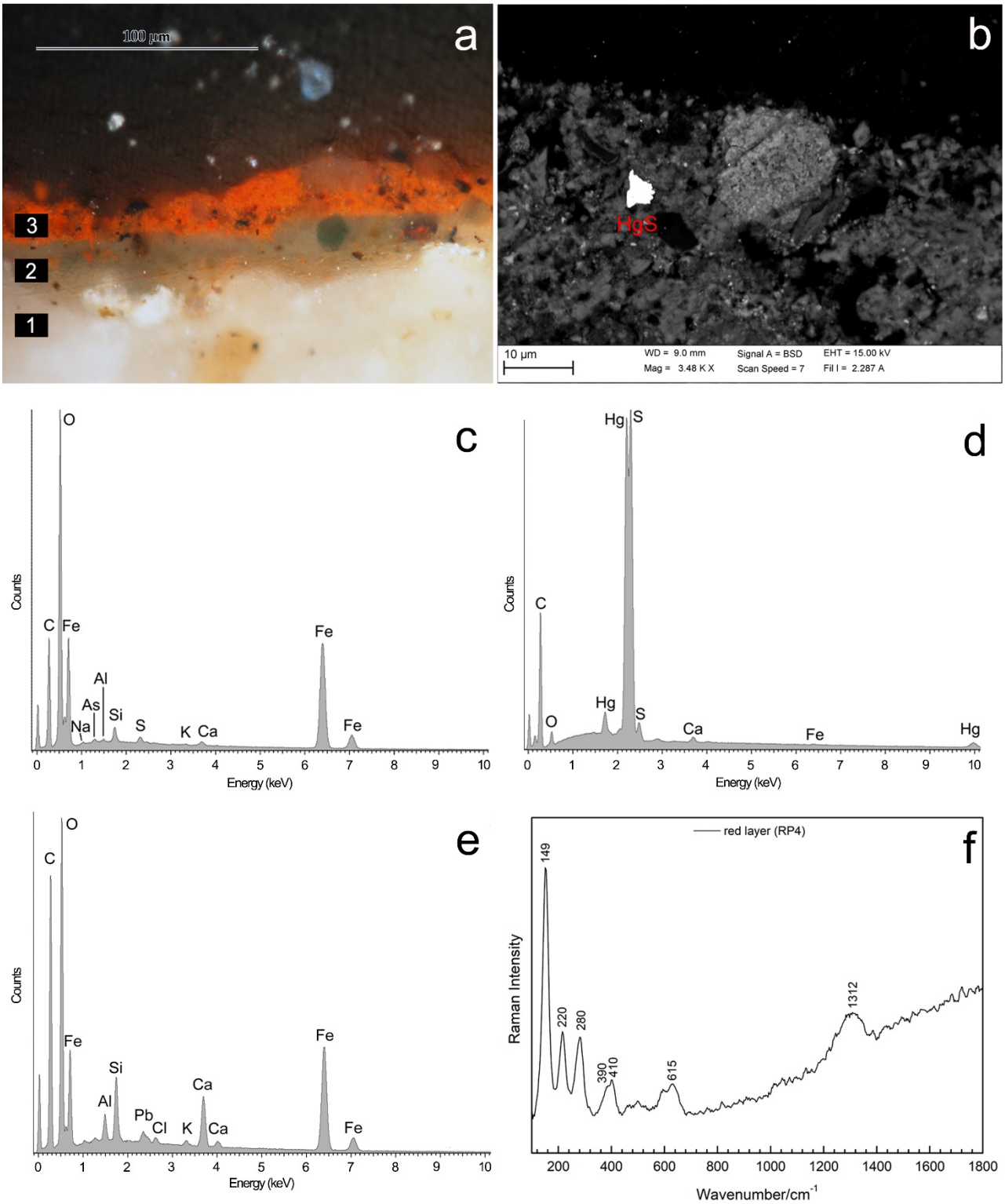


Figure 5. Micro-photograph (reflection mode) showing the mortar, the green layer (2) and the red layer (3) in RP4 sample (a); BSE-SEM image of red layer showing a very lucent and small fragment of HgS, cinnabar pigment (b); the spectra obtained by SEM-EDS on different pigment particles revealed the presence of orpiment (c), cinnabar (d) and minium (e) in the red layer. In all the spectra the presence of elements such as Fe and Ca confirmed the presence of natural red ochre in the recipe (R3); (f) Raman spectrum collected on brilliant red areas revealing the mixture of minium and hematite.

A mixture of red and yellow ochre (recipe R4) was detected by Raman and SEM-EDS analyses in samples from the orange-red paintings from the second cycle in area A, the orange red frame in the

apse areas (areas B, C and D), the decoration of medieval pillars (areas E, F, G, and H) and paint traces in the I, L and S areas.

Concerning pink pictorial layers, two different recipes were detected. In the first one (recipe P1), the colour is due to few amounts of red grains and rarer yellow pigment particles dispersed in lime-based binder; in this case, both Raman spectroscopy and SEM-EDS analyses revealed the use of iron oxide and silico-aluminates, typical of red and yellow ochres. This recipe was used for the first and third cycles in the painting area A (Virgin tunic), for the St. Leonardo tunic (first half of the 15th century) in the first cycle of the painting area N and for the background in the painting in the chapel (area O). The second recipe (recipe P2) was recognised in the pink layer in correspondence of the St. John foot skin (medieval pillar in area E). It consists of a mixing of small amounts of red ochre and massicot scattered in lime, as showed by SEM-EDS and Raman analysis; in detail, Raman spectra exhibit a band at ~150 cm^{-1} attributable to Pb-based pigments (Smith, Clark 2004), bands at 292, 411, 517, 647 and 1320 cm^{-1} attributable to hematite (Zoppi et al. 2005) and a band at 1086 cm^{-1} related to calcite (Figure 6).

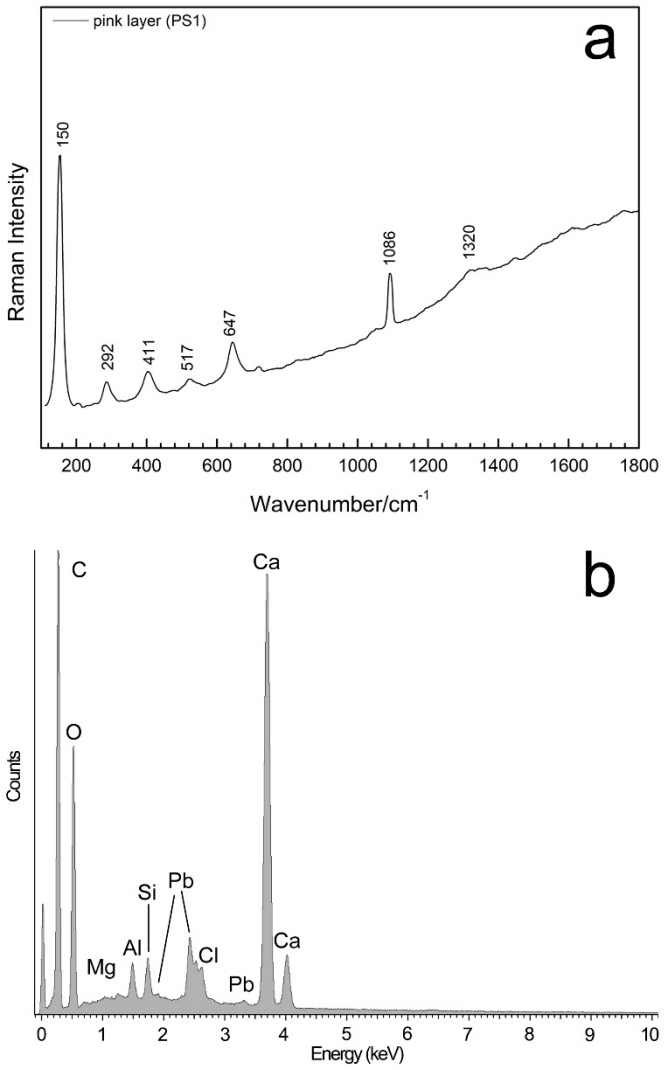


Figure 6. Raman spectrum (a) and SEM-EDS spectrum (b) collected on pink layer in sample PS1 showing the presence of hematite and massicot.

Yellow layers, in different shades, are characterised by three different mixtures, mainly based on the use of iron-based ochres as revealed by the presence of iron and silico aluminates minerals by SEM-EDS analysis. One of these recipes (recipe Y1) was revealed in the background of the St. Vito painting (first half of the 16th century) in the area N and in a chapel (area O) in the frame decoration and it is based on a mix of yellow ochre, massicot and lime, as shown by Raman bands at 145 cm^{-1} attributable to massicot, 299 and 387 cm^{-1} attributable to goethite (Figure 7.a, c). A different recipe was used to obtain a greyish yellow shade for the background in the third cycle of area A and in the traces from area S. It consists of very few amounts of yellow ochre mixed with lime and carbon black, as revealed by SEM-EDS analysis. The last yellow recipe (recipe Y3) was detected in the second and third cycles in the area A and in some coloured traces of orange yellow shadow in the background (areas B and L). Raman analysis (Figure 7.b, d) revealed a mixing including hematite (bands at 292, 410, 1310 cm^{-1}), massicot (band at 145 cm^{-1}) and lime (bands at 1086 cm^{-1}).

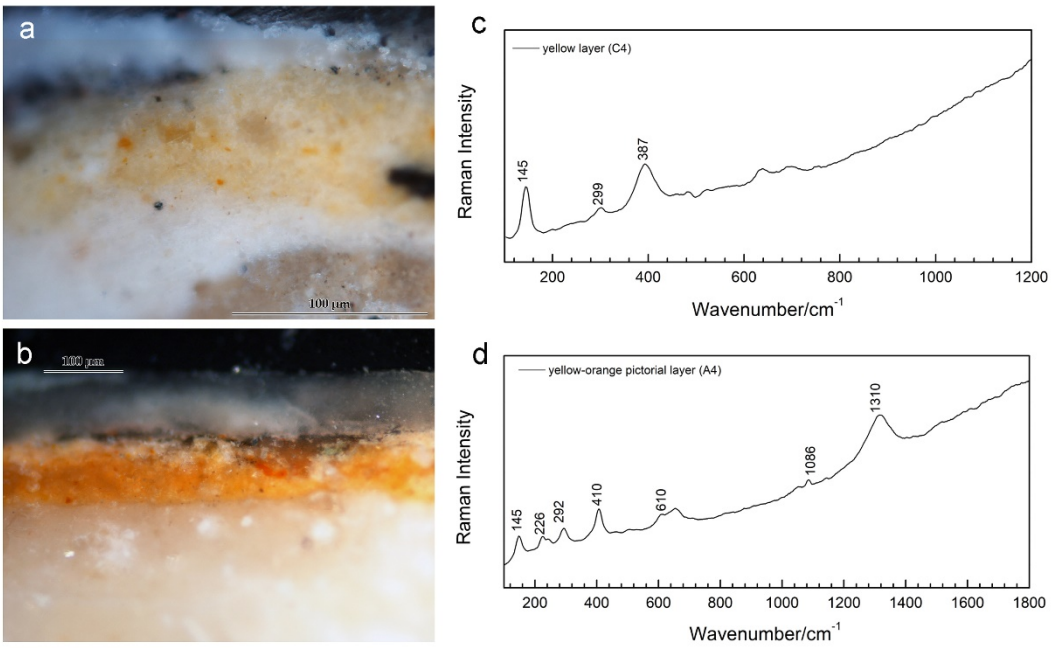


Figure 7. On the top, microphotograph of sample C4 (a) and Raman spectrum (c) showing the presence of a mixture of goethite, massicot and lime (a); on the bottom, microphotograph of sample A4 (b) and Raman spectrum (d) showing the presence of hematite, massicot and lime.

Green pictorial layers seem to be mainly due to natural green earth, as testified by the results obtained by both spectroscopic and chemical analysis, revealing Raman bands attributable to green earths (Coccato et al. 2016) and the presence of silicon, aluminium, calcium, magnesium and iron, respectively (Figure 8.a,b,d,e) detected by SEM-EDS analysis. This mixing (recipe G1) was used to produce green colour in the medieval pillar (area E), as background under pink layer to enhance the effect of St. John skin, and in the first cycles of St. Leonardo painting (area N). In reused blocks of the Renaissance pillars (areas M and P) the chemical and spectroscopic analyses of translucent grains present in the pictorial layer suggest the adding (recipe G2) of copper-based pigments, possibly identified as verdigris (Coccato et al. 2016) (Figure 8.c,f).

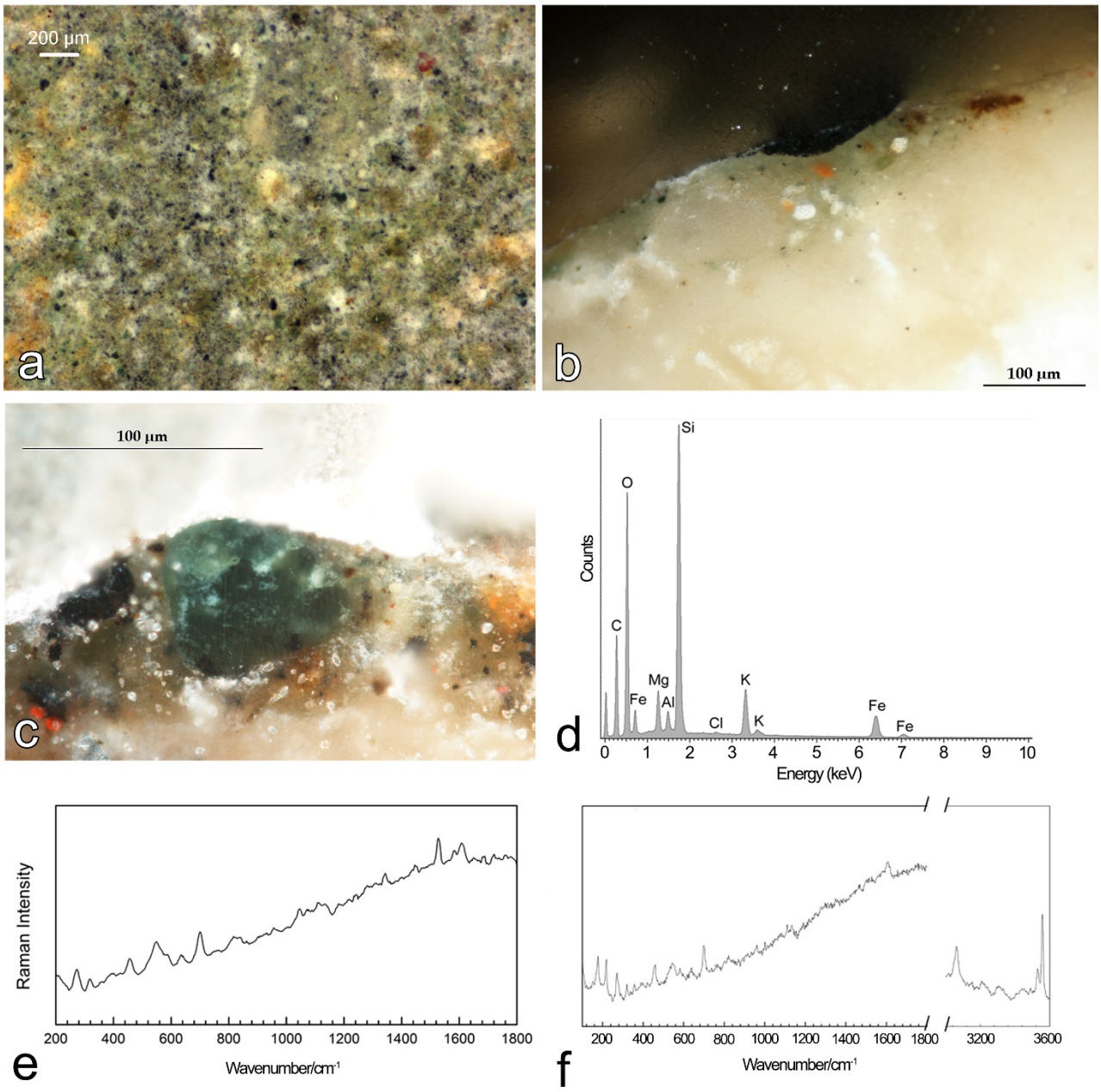


Figure 8. Macrophotograph of green surface of sample RP4 (a) and its RL-microscope photograph (b) showing the typical features of recipe G1, rich in silico aluminates of calcium, magnesium and iron, as displayed in the correspondent SEM spectrum (d); RL-microscope photograph of sample RP4 (c) showing a green particle present in the recipe G2; the Raman spectrum of green earth of the recipe G1 (e) and pigment in box c, identified as verdigris (f).

Concerning black and grey colours, the Raman analysis showed the use of carbon black with typical broad bands at ~ 1325(br) and 1580(br) cm^{-1} (Coccato et al., 2015); the pigment was used alone (recipe B1) in the background of the Dominican saint panel (area A/II), in black traces on the medieval pillar (area G), for the background of St. Vito painting (area N/II) and for frame in the decoration of a chapel (area O). In other cases, green earth was mixed with variable amounts of lime (recipe B2) to turn in lighter grey shadows, i.e. the St. Antonio frame in the area A/IV and in the decoration of the two chapels (areas O and R). Finally, fragments exhibiting black-brownish colour recognised in the first cycle of the area A were obtained by mixing three different pigments, identified by SEM as carbon black, yellow ochre and green earth (recipe B3).

Concerning the painting technique, the observation of cross section both under light microscope and by SEM-EDS analysis allowed supporting possible discrimination among “a fresco”, lime-paint and

“a secco” techniques. Looking at some diagnostic features such as the presence/absence of carbonatation layer between the pictorial film and the underlying plaster, the accumulation of pigment on the interface, the thickness of the pictorial layer (Mugnaini et al, 2006; Piovesan at al., 2011; Piovesan et al. 2012; Regazzoni et al. 2018), some hypothesis can be proposed.
Overall, in St. Maria Veterana paintings, the pictorial layers exhibit an irregular surface contact with the substrate; these evidences would suggest the application of the pictorial layer on a wet support, claiming for the use of a fresco technique. Only in some cases (samples RV1, RV2, RP1, RP2, RP3 and RP4), namely in the reused blocks in the pillars (areas P and M) pertaining to Renaissance structures, a sub-horizontal but discontinuous layer of intonaco was observed; BSE-SEM (backscattered electron image) images revealed in this case the presence of a weak carbonation layer (Figure 9). Finally, in samples referring to greyish yellow, pink and grey colour recipes (samples SA9, G1, SA1, SA6, SL5, C2, PS1, PS2, SA10, C2 and CC1) the presence of lime was recorded in the mixing, possibly claiming the use of lime-paint technique, even if the widely use of lime as white pigment to lightening the coloured shades has to be considered.

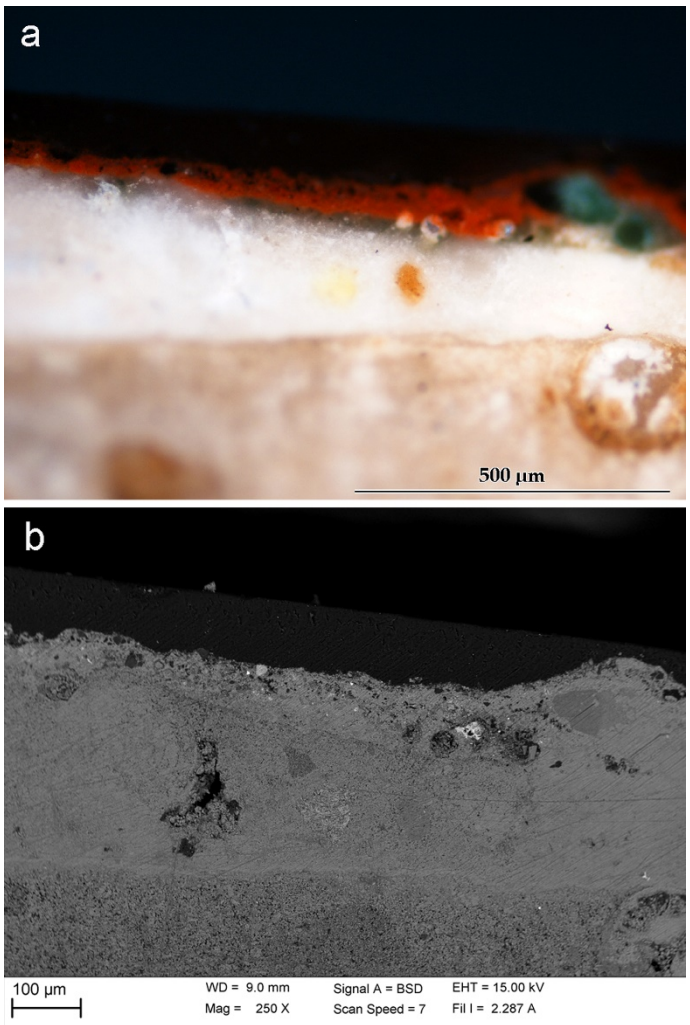


Figure 9. Microphotograph (a) of sample RP4, showing the intonaco layer. SEM-BSE image (b) suggesting fresco technique due to the absence of the carbonation layer.

6. Discussion

The petrographic analysis of mortars in thin section displayed the presence of different preparation mixtures, discriminated in terms of both raw materials and production techniques, attesting the subsequent frequentation of the site by different artisans and clients.

Specifically, the mortar type L is the most common and interests several areas of the site: the Dominican painting (area A/II), the apse (area C) and its nearest wall (area B), all the sides of the two central medieval pillars (areas E, F; G, H) and the counterfaçade (area L). In virtue of this affinity, it is possible to suppose that during the phase of the realization of the second cycle of the fresco in the area A, dated thanks to the iconographic analysis to the first half of the 14th century, also all the other listed areas were decorated. The analysis of the pictorial layers and the subsequent comparison of the used recipes seems to support this hypothesis; in particular, the use of mixtures of yellow and red ochre (Table 3, recipes Y3 and R4) was identified in paintings of areas A/II, B, L and areas A/II, B, C, F, H, L respectively. Similarly, areas D and A/III show the use of the same mortar (type CP), based on the use of cocciopesto as aggregate. The iconographic study of the painting in the area A/III dated the tunic of the Virgin to about the half of the 15th centuries, thus suggesting a possible common dating for painting traces in area D. Other similarities were observed in samples of areas A/IV and I, where mortars show calcarenite relicts (type CRN_R) in the binder, suggesting a possible contemporaneity in the decorations of these two areas. Finally, the S. Leonardo painting in area N/I dated to the first half of the 15th century, shows the same mortar mixture (type CRN) of pictorial traces in the area S, suggesting a contemporaneity of the decorations despite pigments exhibit a variety of recipes.

The use of the same mortar mixture (type CC) in the reused blocks of the Renaissance pillars (areas M and P) allows to assess their affinity with the same painting cycle. This hypothesis is further confirmed by the occurrence of peculiar recipes in the paint traces, due to the use of more precious pigments such as cinnabar, minium and orpiment (recipe R3) in the red layers and verdigris (recipe G2) in green layers. However, the use of such pigments and mortar mixture do not find comparison in other paintings of the studied pictorial cycles, so that a reasonable hypothesis would attribute these blocks to not preserved structures of the medieval church.

By summarizing, the material characterization of mortars and pictorial layers sampled from the all the fresco cycles of St. Maria Veterana, allowed to fix some reference points in the reconstruction of the decorative and chronological phases of the site. In detail, the following construction/decoration phases can be recognised:

- 1st phase, 1080-1325 (from the foundation of the medieval church to the second pictorial cycle): decoration of the northern wall closest to the apse with an unrecognizable subject (area A/I) and the north-west wall (area I).
- 2nd phase, 1425-1450: over the second pictorial cycle, displaying the Dominican (area A/II) and decoration of the wall near the apse (area B), the apse (area C), the central medieval pillars (areas E, F, G, H) depicting St. John and a bishop and the counter-façade (area L).
- 3rd phase, 1410-1440: execution of the painting of S. Leonardo (area N/I) and of the traces on the northern wall (area S) and overlapping of the third pictorial cycle in the northern wall closest the apse (area A/III), depicting the bottom of an enthroned Virgin and at the same time decoration of the pillar near the apse (area D); the areas N/I and S, equal to each other, do not show affinity in the materials and techniques used for the paintings of area D, therefore they cannot be considered strictly coeval or realised by the same workers.
- 4th phase, 1440-1460: execution of the fourth pictorial cycle depicting St. Antonio (area A/IV).
- 5th phase, 1525-1550: realization of the second cycle showing St. Vito (N/II).
- 6th phase, 1550-1580 (year of burial of the medieval basilica and construction of the Renaissance basilica above): execution of the paintings in the areas O and R.

- Reuse: reuse of pillars in the framework of the Renaissance church (area M and P) from an unknown and lost area pertaining to the medieval Church.

Concerning raw materials used for pigments and mortars as well as manufacturing and painting technique, relevant considerations can be added. Firstly, the stratigraphic analysis under reflected-light microscopy highlighted a variability of the recipes used for colours, which was also confirmed by the SEM-EDS and Raman chemical investigations. In recipes R1 and G1, red ochre and green earth respectively were used as natural ingredient to obtain red, green and black colours. In other cases, pigments are mixing with lime or carbon black to obtain lighter (recipe B2) or darker (recipe R2) shadows, or with both pigments (recipe Y2) to have the greyish yellow background of the area A/III. Only in few cases, the chemical and spectroscopic analysis revealed the use of rarer and more precious pigments to obtain special colour shades; the more interesting case encompasses the use of at least four pigments in the same recipe, as in the case of red pictorial layers of reused blocks in pillars of the areas P and M, where hematite, massicot, orpiment and cinnabar were used to obtain a very bright and intense magenta red hue. Also, in the case of green pictorial layers, the combination of green earth and verdigris, was clearly identified in the same samples of the area P and M. Noteworthy are the case of pink pictorial layers used to obtain the skin effect. In the oldest cycle of area A, the pink colour was simply obtained by mixing red and yellow ochre with lime (recipe P1). Instead, a very valuable expedient was recognised in the realization of the S. Giovanni foot skin, on the medieval pillar (area E), testifying the knowledge and expertise of the artist. Here a thicker yellow-orange layer, including lime, red ochre and massicot, was applied on a thin green layer consisting of natural green earth (Figure 11) following the well-known *verdaccio* technique, employed by experienced medieval Italian painters (Gargano et al. 2019; Frezzato 2011, Sfarra et al. 2016).

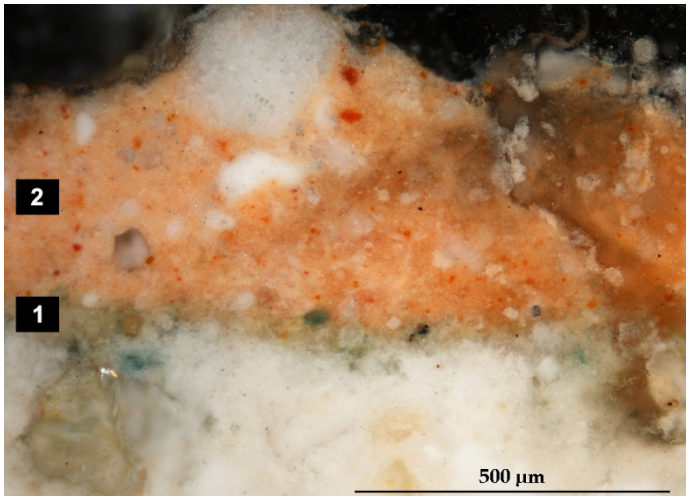


Figure 11 RL-microscope photograph showing the overlaying of green (1) and yellow-orange (2) layer to obtain the skin pink.

The use of some recipes to paint specific details of the scene was also observed in the pictorial cycles belonging to the same decorative phase, thus reinforcing the chronological correlation previous proposed: for example, to paint the red frames surrounding the Saint figures (where still visible) in areas A/II, B, C, F, H and L, the recipe R4, characterized by a mix of red ochre (major component) and yellow ochre (minor component), was used; besides, in the areas A/II, B and L, backgrounds were painted in yellow colour (recipe Y3) obtained by yellow ochre, as major component, mixed with little amount of red ochre. In all cases, the paintings were executed choosing “a fresco” painting technique, characterized by thin pictorial layers well adherent to the underlying support, rich in well-thickened pigment grains and by the absence of the carbonation layer. The

addition of lime was found in some recipes (P1, P2, Y2, B2) to lighten the colours in order to obtain pink, greyish yellow and grey colour hues. No preparatory layers between the mortar and the paint film was observed in almost all the investigated samples, with the exception of those belonging to the reused blocks of the pillars of areas M and P where a thin layer of intonaco is present.
The experience and the high technical level of the artisans involved in the different decorative phases of the site is not always supported by the quality of mortars, which conversely show mediocre production technology and poor accuracy. The presence of several underburnt relicts, sometimes keeping their original structures, suggests non-homogeneous distribution of temperature of the lime and fast calcination process. Moreover, non-adequate sieving of binder and differences in hydration times are testified by the presence of lime lumps. Although the majority of samples shows these typical markers, a better care in the preparation of support is evident in samples from the chapel in the O area, where the mortar (type HA) is characterised by high aggregate content (about 45-50%) of well sorted and selected quartz fine sand. Moreover, the use of cocciopesto as hydraulic component in type CP mortars (areas A/III and D) in order to accelerate the carbonatation process in wet environment might suggests an intentional manufacture routine.
Generally, the presence of calcium and magnesium in lime lumps and in the binder, testifies the use of limestone as raw material for lime production, reinforced by the wide availability of limestone outcrops (Calcare di Bari Fm.) in the areas close to Triggiano (Ciaranfi et al. 1988, Ricchetti 1975). Otherwise, in other mortars (types CRN_R and Q) the underburnt relicts consist in calcarenite fragments still exhibiting fossil tests (types CRN, CRN_R, HFA) suggesting the use of local calcarenites, belonging to the Calcarenite di Gravina Fm. (Azzaroli 1968, Iannone, Pieri 1979).

6. Conclusion

The presented research allowed to frame the hereinbefore unknown St. Maria Veterana archaeological site among the most relevant examples of the Apulian Romanesque style and medieval painting art. Moreover, the results of mineralogical and petrographic investigations performed on mortars and painting layers constitute a significant contribution in creating references for the better interpretation and understanding of raw materials, production and execution techniques in the Apulia region, to reconstruct social, cultural and economic ancient contexts.
The combination of stratigraphic and compositional data based on the analysis of painting layers and mortars allowed to identify several decorative cycles, contributing to the reconstruction of the main chronological phases of the site, with the support case of historical and iconographic information. Specifically, the characterisation of studied materials and its comparison with iconographic-based data allowed to define nine decorative phases spread in 500 years, from the 11th to the 16th century. Analogies among different decorated areas indicate an intense decorative works during 1325-1350, when Dominican painting, apse setting, central pillars and the counterfaçade were executed. Besides, the presence of pictorial traces, also found under the covering layers, suggested that the whole archaeological complex was almost completely painted. The different pictorial traces scattered also in subsequent settings denote a continuous attendance of the church and an artistic interest until the end of the 16th century, just before the church was replaced by the Renaissance building.
Moreover, the identification of cinnabar in the reused blocks proofs that in the church there was a precious medieval painting, nowadays lost; however, the memory of the valuable painting would be intentionally and symbolically preserved by inserting the frescoed blocks in the foundations of the new church. Although not always supported by the production technology of mortars, the use of more precious pigments (i.e. verdigris, cinnabar), the complexity of some recipes and the use of technical expedients in the painting creation (such as the use of *verdaccio* for figure skin), denote high level artistic ability and then the presence of rich clients and art workshops in the region.

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