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ORIGINAL PAPER

Archaeometric study of wall rock paintings from the *Sant'Angelo in Criptis cave*, Santeramo in Colle, Bari: insights on the rupestrian decorative art in Apulia (Southern Italy)

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Abstract
The paper deals with the archaeometric investigation of wall paintings in the Sant'Angelo in Criptis karst cave in Santeramo in Colle (Southern Italy) dedicated to St. Michel the Archangel. The investigated wall paintings portray the Virgin with Child, the Christ Pantocrator and Descent of the Holy Spirit, both consisting of two overlapped pictorial cycles, and St. Michael the Archangel slaying the dragon, containing a single painting. Archaeometric research focuses on the characterisation of 56 samples of mortars and pictorial layers in terms of raw materials, pigment mixtures and painting techniques and aims to provide a meaningful contribute to the historical and chronological knowledge of the site. The analytical approach involved microstratigraphic observation under reflected-light optical microscope and compositional characterisation through micro-Raman spectroscopy and scanning electron microscope-energy dispersive X-ray spectroscopy. Results indicated a colour palette involving shades of red, yellow and black, obtained using common pigments such as red and yellow ochres and carbon black frequently mixed to each other, or with lime, to produce secondary hues and most precious pigment, as cinnabar. Mortar analysis provided information on technological aspects and helped to validate chronological hypotheses. The most relevant aspect emerging from results was the custom and the ability of the workers to mix few pigments to obtain several shades and chromatic nuances and the competence in the overlapping of different coloured layers to produce specific chromatic effects. Such considerations suggested the modus operandi of the artists who worked in the Apulia region in the Middle Ages and helped to define technical procedures and material features of the Apulian rupestrian paintings.

Keywords Pigments · Mortars · Rupestrian paintings · Apulia

Introduction

The rupestrian civilisation is a historical phenomenon of remarkable importance in several countries in the Mediterranean area, and it is remarkable also in various regions of Southern Italy. The Apulian territory discloses numerous natural karst cavities, which were in the past object of continuous human presence (Venturo 2007) and that represent a very meaningful cultural and historical heritage. Most of these caves were used, in addition to housing purposes, as places of worship, the reason why they frequently included typical decorative and architectonic components, valuable paintings, religious elements and signs (Manghisi 1995; Tunzi 1999; Manghisi et al. 2003; Lorusso and Manghisi 2007; Castelfranchi 2016; De Giorgi 2016; Ortese 2016; Mignozzi 2018). However, in contrast to a widespread literature about historical and artistic aspects of these important historical contexts in the Apulia peninsula, archaeometric studies focusing to the characterisation of raw materials and identification of pictorial techniques of wall paintings and to their conservation state are rather scarce (Cavallo and Van der Werf 2001; Capitanio et al. 2005; Grassi et al. 2006).

Among these Apulian caves, extremely noteworthy and interesting are those dedicated to St. Michael the Archangel, which where intensely frequented in the past by worshippers and pilgrims (Otranto and Carletti 1990; Manghisi 1993; Lorusso and Larocca 2002; Trotta and Renzulli 2004; Mignozzi 2019).

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In the valuable context of the wall paintings of the Apulian karst caves, the present work focussed on the archaeometric investigation of wall paintings of the Sant'Angelo in Criptis cave (DSM coordinates from Google Earth: 40°49′29″N 16°42′13″E) with the aim of characterising materials and painting techniques, to contribute to the historical reconstruction of the site, through the correlation among the different paintings and their overlapped pictorial cycles, as well as to contribute further to the knowledge of Apulian rupestrian settlements.

Sant'Angelo in Criptis cave

State of art

Sant'Angelo in Criptis cave is located in Santeramo in Colle countryside and belongs to a larger site, locally known as Iazzo Sant'Angelo. Today, the cave appears like a natural karst cave space markedly modified by humans, rich in stalactites, stalagmites and other typical forms of the karst landscape, which outline a well-defined physical path. On the walls of the cave are visible religious signs, writings and three wall paintings, not always easily readable due to their very bad state of conservation.

The cave was discovered for the first time in the 1970s of the twentieth century (Tangorra 1969) and, in the following years, explored and studied by local scholars (Fraccalvieri 1975; Fiorentino 2005), who highlighted the attendance of the site since the fourth century BC, as space dedicated to the "cult of water", which consisted in collecting the dripping waters of the cave and using them as a means of spiritual purification (Catino 2009). From the fifth to eighth century up to the sixteenth century, when the site was converted into a farm and then progressively abandoned, the cave turned into a church entitled to St. Michael the Archangel. During this long period, the cave of Sant'Angelo became very dear to pilgrims, who visited it to travel a path of spiritual atonement, and in the eleventh to twelfth century, its attendance was so dense that it was necessary to build a hospitality shelter.

In 1939, Authority for the Archival heritage for Apulia declared the considerable historical interest of the site and then subjected it to protection actions.

Recently, the cave was object of a multidisciplinary project, to which this study belongs, conducted by researchers of the University of Bari, who carried out a complete study based on the historic, archaeological, archaeometric and geomechanics approach of the cave and its digital 3D survey.

Wall paintings

The Sant'Angelo cave boasts the presence of three wall paintings, which portray the Descent of the Holy Spirit and Christ Pantocrator, the Virgin with Child flanked by St. John the Baptist and the St. Michael the Archangel and finally the St. Michael the Archangel slaying the dragon (in this paper, for practical reason, named respectively Christ Pantocrator, Virgin with Child and St. Michael the Archangel). A detailed description of the paintings in terms of iconographic analysis and chronological dating was carried out by Caragnano (2008, 2013) and most recently by Calò (2016). In the first painting, the figure of Christ Pantocrator sits on the throne, above which a dove represents the Holy Spirit, and at his side twelve Apostles are arranged on the right and on the left. The Christ head is surrounded by a yellow and cruciferous halo. He wears open sandals, blue mantle on the left shoulder and a decorated purple tunic. The losses of the Pantocrator face and other large part of pictorial layer disclosed an older painting layer, depicting larger head, where halo, eyes, eyebrows, lip and beard are still discernible. Palaeographic fonts of Latin writing of the open book in the Christ hand, visible in the two chronological painting levels, allowed dating the oldest painting in the late twelfth and early thirteenth century and the most recent one, between the thirteenth and fourteenth century (Caragnano 2008). The latter was painted respecting the representation of the older one, which probably had been deteriorated especially for the high pilgrim flow.

In the Virgin with Child painting, a red frame surrounds the scene; however, picture is vague since it is not well preserved because of a clumsy restoration. The Virgin sits on a throne and wears blue tunic, red *maphorion* and red shoes. The blessing Child wears a red tunic and sits on the left arm of his Mother; he holds a parchment roll in his left hand. On the right, the Baptist is characterised by a yellow halo and wears a red tunic and a blue mantle; the right foot fits a Roman-type sandal. The left hand holds an unreadable open scroll. The Archangel stands on the left and holds the chains of a censer with which incenses toward the Virgin. In some limited and scattered areas of the painting, the pictorial losses brought to light an underlying painting (first pictorial cycle) which, however, is not sufficiently visible and therefore could not be dated. Conversely, the second painting cycle, although appears darken by the decay effects and covered by soot and black smoke from candles, could be dated at the second half of the thirteenth century thanks to its iconographic features (Calò 2016). The last painting, St. Michael the Archangel, dedicated to St. Michael, is included in a little recess; it seems to be definitively lost; however, traces of a drawing

are still recognisable. The subject is ascribable to the Archangel with red open wings, who holds a lance killing the dragon in his right hand and the globe in the other hand. This iconography model, typical of St. Michael worship in Medieval rocky churches in Apulia, suggests dating the painting between the eleventh and fourteenth century (Caragnano 2008).

Currently, all the walls of the cave including the three wall paintings are affected by the deposition of consolidated and dark crusts, formed by the continuous percolation of calcium carbonate-rich water, as a consequence of the natural karst activity and by the deposition of carbon black particles from candle smokes during the past frequentations of the cave. Such process determined a darkening of the painted surfaces, hiding the brilliance and hue of the original colours. Even, in the St. Michael the Archangel painting, traces of plants, fungi and moulds were observed with naked eyes. Moreover, the state of conservation of the artistic evidence appeared considerably compromised by several large losses of pictorial layer portions and effects of vandalism acts.

Sampling

The sampling involved all the three wall paintings in the cave, i.e. the Christ Pantocrator, the Virgin with Child and the St. Michael the Archangel paintings. Most of the sampled painting fragments included mortar, intonaco (if present) and pictorial layers, and, in the case of paintings showing more than one pictorial cycle, fragments containing the full painting stratigraphy were also picked up. A total of 56 samples were taken from different scenes and figures of paintings showing yellow, red, pink, black, grey and blue colours in different shades.

As regards the painting of the Christ Pantocrator (Fig. 1), 14 fragments were sampled from the oldest pictorial cycle in correspondence to areas where the second (most recent) pictorial cycle was loss and 8 fragments were taken from the second (most recent) pictorial cycle, whereas 3 samples including the whole stratigraphy of the two cycles were considered. The sampling on the St. Michael painting (Fig. 2b) was quite difficult since the pictorial layer was heavily thinned causing the loss of details and figures; nevertheless, 13 fragments were sampled from the single pictorial cycle present. As regards the painting of the Virgin with Child (Fig. 2c), 5 samples were selected from the few visible areas of the first (oldest) pictorial cycle, 8 samples from the second (most recent) pictorial cycle and 5 samples were composed by the full stratigraphy of both cycles.

A detailed summary of sampling data is reported in Table 1.

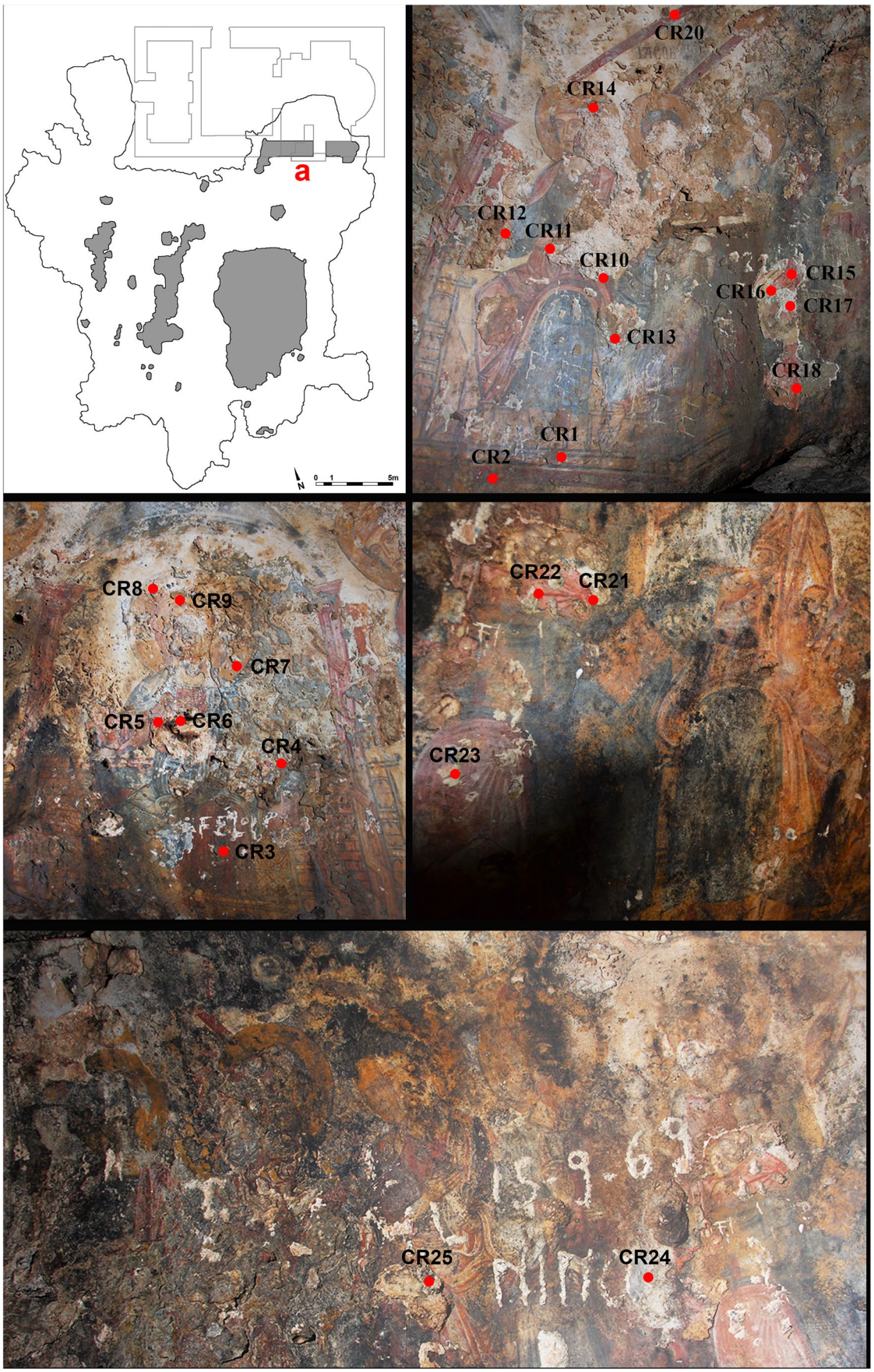
Analytical methods

Preliminarily, sampled fragments were observed by a stereomicroscope and detailed description and photographic documentation were recorded. Afterward, the cross sections of samples were observed under a Nikon Eclipse80i reflected-light microscope equipped by a camera for digital image acquisition in order to observe the main features of different painting layers, i.e. stratigraphy, number and thickness of painting layers, type and abundance of pigments. Based on the microscopic features and in virtue of their affinity, in terms of texture, presence/absence of aggregate, type of aggregate and colour of binder, 10 representative samples of preparatory mortars were selected for the mineralogical and petrographic observation of thin sections under a Zeiss Axioskop 40 optical microscope, following classification method proposed by Pecchioni et al. (2018). The chemical analysis of aggregate, binder, pigments and deposit crust layers was performed by 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 were 15 kV accelerating potential, 500 pA probe current and 8.5-mm working distance). Compositional data analysis on pigments was completed by micro-Raman Xplora spectrometer equipped with YAG laser source with wavelength of excitation equal 532 and 638 nm, a diode laser emitting at 785 nm, a triple grating (800, 1200 and 1800 l/mm), an optical microscope provided with four objectives (5×, 20×, 50× and 100×) and a charge-couple device detector (CCD) cooled to -65° C with a Peltier cooling system; sample irradiation was accomplished using the 50× and 100× microscope objectives of an Olympus BX41 microscope; the exposure time, beam power and accumulations were selected to get sufficiently informative spectra; the laser spot size was adjusted between 1 and 3 µm; the wavelength scale was calibrated using Si(111) standard (520.5 cm^{-1}).

Results

Preparatory mortars

The analysis under optical microscope of the 10 selected samples of preparatory mortars revealed in all cases a mortar generally characterised by a micritic binder and containing few fragments of cocciopesto. However, significant peculiar markers (in particular, abundance, type, shape and size of aggregate particles) allowed to classify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CR3
CR22
CR21
CR23
CR25
CR24

◂**Fig. 1** Map of the cave and detailed areas of sampling points of the Christ Pantocrator painting

the analysed samples in 4 groups, each related to 4 different types of preparatory mortar (Fig. 3). A summary is reported in Table 2, while a detailed description is in the following.

Type CA (Carbonate Aggregate) includes samples from the first (oldest) cycle of the Christ Pantocrator painting (CR25 and CR14a). The petrographic observation highlighted a lean mortar containing about 35–40% of aggregate composed of large and rounded carbonate fragments (about 2500 µm) and very rare sand grains (about 80 µm) of quartz and K-feldspar. Rare and rather rounded fragments of cocciopesto (900 µm) were observed. The micritic binder includes scattered and rare iron oxides. Evidence of bioclasts were not recorded. Porosity consists of small and sparse angular voids (10%).

Type ACA (Angular Carbonate Aggregate) includes samples M1a, M5 and M10a taken from the first (oldest) cycle of the Virgin with Child paintings. Apparently, this type seemed to be very similar to the previous one; however, the microscope observation revealed the presence of aggregate (35–40%) containing, both rounded fragments (about 400 µm) and very angular carbonate rock fragments (about 250 µm). Some fragments of cocciopesto were observed. The binder presents some lime lumps and rare and small underburnt relicts. Rare are iron oxides. Porosity is about 10% and consists of straighten pores and fractures.

Type FA (Fossiliferous Aggregate) was recognised in the second (most recent) cycle of the Christ Pantocrator painting, namely, in samples CR1, CR8, CR14b and CR25b and in the second (most recent) cycle of the Virgin with Child (M1b, M10b, M7, M14). The mortar is characterised by a high content of aggregate (45–50%) composed of fossiliferous sand (about 400 µm), rounded in shape and rich of foraminifera and bryozoan. Rare fragments of cocciopesto (about 600 µm) are present. The binder is micritic and homogeneous and contains few and small iron aggregates. Lime lumps are absent, and underburnt relict are rare. Porosity is lower than 5% and consists of fine and angular pores.

Type FM (fat mortar) is the mortar of sample SM6 from the St. Michael the Archangel painting. It is a very fat mortar, with about 5% of aggregate, consisting of some fine quartz and K-feldspar sand particles (about 80 µm), rounded carbonate fragments (about 500 µm) and rare cocciopesto (about 200 µm). The micritic binder shows a fractured texture and is marked by several iron oxides, lime lumps and underburnt relicts. Porosity is lower than 5% in volume and is due to fine pores, both rounded and angular.

Pictorial layers

Microscopic observation revealed the presence of one or more overlapped pictorial thin layers (about 10–60 µm), even if in a few samples they are thicker (up to 250 µm). Generally, the interfaces between the ground layer and the first pictorial layer appear irregular and rough.

Furthermore, microscopic observations and compositional analysis obtained by SEM–EDS and micro-Raman spectroscopy on representative samples (Table 3) allowed the identification of different pigments and their mixtures (Table 4). The analyses showed that paintings were generally executed using a limited number of natural pigments, but the results highlighted a considerable variability of the mixtures and a mindful overlapping of different coloured layers in order to create specific chromatic effects and shades.

Red

Concerning red pictorial layers, the investigation highlighted the use of four mixtures, three based on red ochre and one based on the cinnabar. The common red pigment is red ochre. It appeared both translucent and opaque under the reflected-light optical microscope, depending on its sizes and purity (Fig. 4a). SEM–EDS spectrum of ochre pigment particles revealed chemical composition generally based on iron, titanium and manganese oxygen mixed to silicon, aluminium, magnesium and calcium which suggested the use of a natural red ochre (Fig. 4d). Raman analysis confirmed the use of red ochre as the typical bands of this pigment were observed, as for example reported in Fig. 4c, at 605, 402 and 286 cm^{-1} (Bell et al. 1997).

In the first colour (R1), the red ochre was used without other pigments and was detected in several samples from all the three paintings. In detail, it was recognised in the following: the frames and background, St. John's halo and St. Andrea's mantle in the first cycle and in the frames and in St. John's mantle and halo in the second cycle of the Christ Pantocrator painting; in the frames and background in the first cycle and St. John's mantle, St. Michael's tunic and foot in the second cycle of the Virgin with Child painting; and the calcite crust and the St. Michael's mantle in the St. Michael the Archangel painting. In colour R2, red ochre was mixed with carbon black pigment to obtain dark red colour. This mixture was recognised: in the second cycle of the Christ Pantocrator painting, as chromatic preparation layer under the R1 coloured final layer in St. John's halo; in the rhombus decoration, in the Virgin's mantle and St. Michael's tunic in the first cycle and the St. Michael's tunic, Virgin hand and St. Michael wing in the second cycle of the Virgin with Child painting; and finally in the St. Michael the Archangel painting, from the mantle of the saint and in the strips on dragon. The colour R3, where small amount of lime

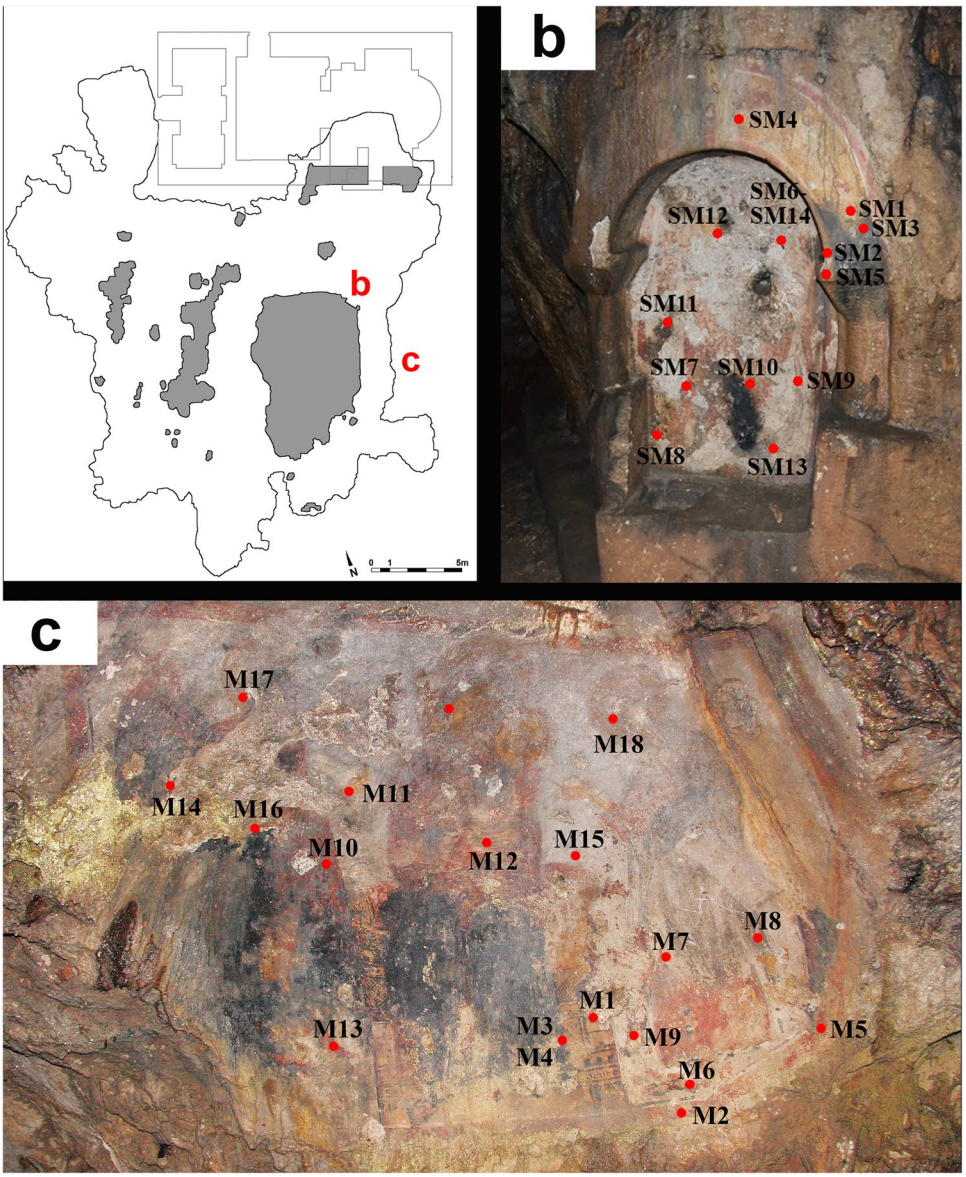

Fig. 2 Map of the cave and sampling points of the St. Michael the Archangel (**b**) and the Virgin with Child (**c**) paintings

was added to the red ochre (naturally including yellow ochre particles) to obtain an orange-red colour, was recognised only in some coloured preparation layers from both cycles of the Christ Pantocrator painting, specifically for the Christ's tunic for both the pictorial cycles, in the hand skin of the first cycle and in the St. John's mantle for the second one.

In colour R4, the presence of cinnabar was first indicated by SEM–EDS analyses showing pigment particles (Fig. 4b) composed by sulphur and mercury (Fig. 4e) and subsequently confirmed by Raman spectrum reported in Fig. 3f, showing characteristic bands of this pigment at 343, 282 and 252 cm^{-1} (Bell et al. 1997). The cinnabar-based colour was applied in a very thin layer (20 µm) above a red–orange layer (colour R3) on the oldest cycle in the Christ Pantocrator painting, exclusively in correspondence of the mantle of Christ.

Very pale red-pink colour was reached by adding small amount of red ochre to lime (R5) and employed to paint: the hand and St. Andrea's mantle in the first cycle and St. John's mantle in the second cycle of the Christ Pantocrator painting; St. John's mantle for the first and the background for the second cycle of the Virgin with Child painting; and St. Michael's mantle and in the background for the St. Michael the Archangel painting. In this case, under the microscope, red ochre appeared to have a different hue of red, slightly more intense, due probably to the higher content of titanium oxides showed out by SEM–EDS analysis, which suggest the use of a different variety of red ochre with respect to the other mixtures.

Table 1 Sampling table, reporting for each sample, the visible colour and the sampling area (painting and pictorial cycle)

Painting	Pictorial cycle	Sample	Sampling point	Visible colours
Descent of the Holy Spirit	I (late twelfth to early thirteenth century)	CR3	Bottom of the frame around Christ	Red
		CR5	Christ's tunic	Red
		CR7	Christ's halo	Yellow
		CR13	St. John's tunic	Yellow
		CR15	Background near hand	Pink
		CR16	Hand skin	Pink, yellow
		CR17	Finger profile	Pink, red
		CR18	Area under the hand	Yellow, red, black
		CR19	Area near the dove	Red
		CR21	St. Andrea's mantle	Red
		CR22	St. Andrea's background	Red
		CR23	St. Andrea's mantle	Red
		CR24	Background	Yellow, grey
		CR25	St. Andrea's mantle	Red
	II (thirteenth to fourteenth century)	CR1	Border of the frame of St. John	Yellow, black
		CR2	Border of the frame of St. John	Red
		CR6	Christ's tunic	Red, black
		CR8	Christ's halo	Yellow
		CR9	Christ's hair	Yellow
		CR10	St. John's mantle	Red
		CR12	St. John's tunic	Blue
		CR20	Red zone near IACOB writing	Red
	I–II	CR4	Area near Christ title block	Dark grey
		CR11	St. John's mantle	Red, black
		CR14	St. John's halo	Yellow, red, black
Virgin with Child	I (undated)	M2	Red frame near the Archangel	Red
		M5	Area under red frame	Red
		M6	Red frame	Red
		M9	Red and pink area between Virgin and St. John	Red
		M16	Area between St. Michael wings and mantle	Yellow, black
	II (undated)	M7	St. John's mantle	Red
		M8	St. John's mantle	Dark grey
		M11	St. Michael's tunic	Yellow
		M12	Virgin hand	Yellow, red
		M13	St. Michael foot	Red
		M14	St. Michael wing	Dark grey
		M18	St. John's halo	Yellow, black
		M19	Virgin face	Yellow
	I–II	M1	Rhombus decoration	Yellow, black
		M3	Virgin's mantle	Blue-grey
		M4	Virgin's mantle	Blue-grey
		M10	St. Michael's tunic	Red, yellow
		M15	Background between Virgin and St. John	Black

Table 1 (continued)

Painting	Pictorial cycle	Sample	Sampling point	Visible colours
St. Michael the Archangel	-	SM1	Yellow external frame	Yellow
		SM2	Outside frame	Red
		SM3	Decoration on outside frame	Yellowish grey
		SM4	Outside yellow frame	Yellow
		SM5	Carbonatic crust	-
		SM6	Inside recess	Dark and pale red, black
		SM7	St. Michael's mantle	Red
		SM8	Strips on dragon	Yellow, black
		SM9	Dragon tail	Red, dark grey
		SM10	St. Michael's mantle	Yellow
		SM11	Black strip	Yellow, black
		SM12	St. Michael's halo	Yellow
		SM13	Dragon tail	Grey

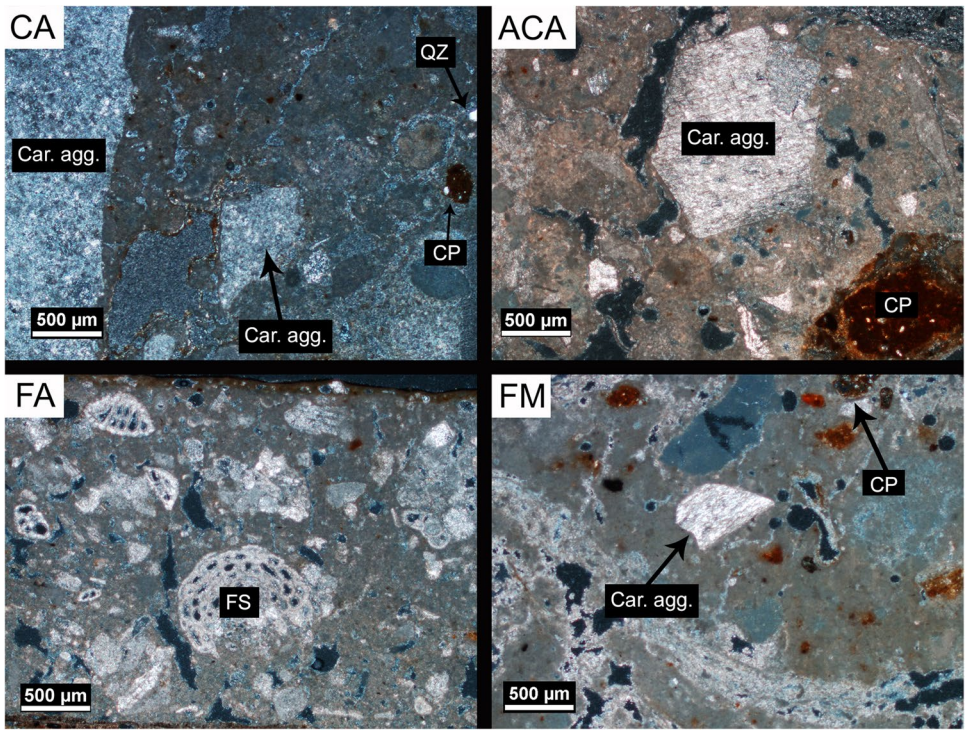

Fig. 3 Microphotographs of representative samples in thin section for mortar types. The CA mortar figure shows, on the left, a large fragment of aggregate; the ACA mortar shows an example of angular fragment of aggregate and in the right bottom, a fragment of cocciopesto; the FA type displays its peculiar fossiliferous content as aggregate; in FM mortar figure, the binder rich in binder nodules is evident. Abbreviations: Car.agg. = carbonate aggregate, CP = cocciopesto, FS = fossils

Yellow–brown

All the mixtures of pigments considered to decorate yellow–brown areas in the Sant'Angelo cave paintings were mainly based on the yellow ochre (Fig. 5a). SEM–EDS analyses which showed pigment particles rich in iron (Fig. 5b), which based on the Raman spectroscopy (Fig. 5c), were referred to the yellow ochre pigment. In the reported example, the bands centred at 552, 396 and 296 cm^{-1} identified the occurrence of goethite, the main mineral of the yellow ochre (Edwards et al. 2000). Coloured areas realised by pure yellow ochre (Y1) were recognised: in the Christ's halo, the hand skin and St. Andrea's mantle of the first cycle and for the border of the frame of St. John, the Christ's halo and hair and St. John's halo of the second cycle of the Christ Pantocrator painting; in

Table 2 Petrographic characterisation of mortar types

Mortar type	Binder			Aggregate				Other characteristics	Samples				
	Structure	**Texture**	**Porosity**	**Volume**	**Size (mode)**	**Composition**			**The Christ Pantocrator**		**The Virgin with Child**		**St. Michael the Archangel**
						Minerals	**Other**		**I cycle**	**II cycle**	**I cycle**	**II cycle**	
CA	Non-hom., nodular	Micritic	Angular, fine (10%)	35–40%	80 µm	mQtz, K-feld		-	CR25a, CR14a	-	-	-	-
					2500 µm		Rounded carbonate fragments						
					900 µm		Cocciopesto						
ACA	Non-hom. (nodular-fractured)	Micritic	Straighten (10%)	35–40%	400 µm		Rounded carbonate fragments	Lime lumps	-	-	M1a, M5, M10a	-	-
					250 µm		Very angular carbonate fragments	Underburnt relicts					
					600 µm		Cocciopesto						
FA	Hom	Micritic	Angular, fine (5%)	45–50%	400 µm		Fossiliferous sand	Few small iron oxides	-	CR1, CR8, CR25b, CR14b	-	M1b, M10b, M7, M14	-
					600 µm		Cocciopesto						
FM	Non-hom. (nodular-fractured)	Micritic	Rounded, fine; angular, fine (<5%)	5%	90 µm	mQtz, K-feld		Iron oxides	-	-	-	-	SM6
					500 µm		Rounded carbonate fragments	Lime lumps					
					200 µm		Cocciopesto	Underburnt relicts					

Abbreviations: *Hom.* homogeneous, *non-hom.* heterogeneous, *mQtz* monocrystalline quartz, *K-feld* K-feldspar

Table 3 Chemical elements, identified by SEM–EDS, and Raman bands of the investigated samples

Colour	Sample	Chemical composition (SEM–EDS)	Raman bands	Pigment
Red (R1)	CR2 (II)	Fe, Si, Al, Ca, Mg, K		Red ochre
	CR11 (I)	Fe, Si, Al, Ca, Mg, K		Red ochre
	CR11 (II)	Fe, Si, Al, Ca, Mg, K		Red ochre
	CR21 (I)	Fe, Si, Al, Mg, Ca, K	605, 407, 292 cm^{-1}	Red ochre
	M9 (I)	Fe, Si, Al, Ca, Mg, K		Red ochre
	SM7	Fe, Si, Al, Mg, Ca, K	605, 408, 290 cm^{-1}	Red ochre
Dark red (R2)	M3 (I)	Fe, Si, Al, Ca, Mg, K	607, 405, 293 cm^{-1}	Red ochre
	M3 (I)		1598, 1312 cm^{-1}	Carbon black
Orange red (R3)	CR5 (I)	Al, Si, Fe, Ca, Mg, K	605, 402, 286 cm^{-1}	Red ochre
	CR11 (I)	Fe, Ti, Si, Al, Mg, Ca, K		Red ochre
	CR6 (II)	Fe, Si, Al, Mg, Ca, Ti, K		Red ochre
Red (R4)	CR5 (I)	S, Hg	343, 282, 252 cm^{-1}	Cinnabar
Pink (R5)	CR15 (I)		613, 413, 295 cm^{-1}	Red ochre
	CR22 (I)	Fe, Si, Al, Ca, Mg, K		Red ochre
	M7 (II)	Fe, Si, Al, Ca, Mg, K	611, 413, 293 cm^{-1}	Red ochre
	SM2	Fe, Si, Al, Ca, Mg, K	618, 411, 296 cm^{-1}	Red ochre
Yellow (Y1)	CR2 (II)	Ca, Fe, Si, Mg		Yellow ochre
	CR7 (I)			Yellow ochre
	M3 (I)	Fe, Si, Ca, Mg, Al	552, 396, 296 cm^{-1}	Yellow ochre
	M11 (II)	Si, Al, K, Fe, Mg, Ca, Ti, Na		Yellow ochre
Dark yellow (Y2)	CR24 (I)	Ti, Fe, Si, Ca, Al, Mg		Yellow ochre
	M19 (II)	Ti, Fe, Si, Ca, Mg, Al		Yellow ochre
	M19 (II)		1590, 1322 cm^{-1}	Carbon black
Brown (Y3)	M7 (II)	Fe, Si, Mg, Al, Ca, K		Yellow ochre
Black (B1)	CR6 (II)		1590, 1310 cm^{-1}	Carbon black
Blue-grey (B2)	CR12 (II)		1581, 1318 cm^{-1}	Carbon black
	M3 (I)		1585, 1312 cm^{-1}	Carbon black
	M3 (I)	Fe, Si, Al, Ca, Mg, K		Red ochre
	M3 (II)	Fe, Si, Al, Ca, Mg, K		Red ochre
	M4 (II)	Fe, Si, Al, Ca, Mg, K		Red ochre
	M3 (I)	Ca, Fe, Si, Mg		Yellow ochre
	M4 (II)	Ca, Fe, Si, Mg		Yellow ochre
Pale grey (B4)	M4 (I)		1581, 1326 cm^{-1}	Carbon black

the rhombus decoration, the Virgin's mantle, St. Michael's tunic and the area between St. Michael wings and mantle of the first cycle and for St. Michael's tunic, the Virgin hand and the St. John's halo in the second cycle of the Virgin with Child painting; and in the frames, St. Michael's mantle and halo in the St. Michael the Archangel painting.

Instead, a mixture of yellow ochre and carbon black in different percentage to obtain dark yellow (Y2) and brown (Y3) colour was also identified in the samples. In detail, the mixture corresponding to Y2 was used to realise the skin of the Virgin face, the mantle of St. John and some background areas in the second cycle of the Virgin with Child painting; the dark yellow–brown mixture (Y3) was recognised in the second cycles of the Christ Pantocrator and in the Virgin with Child paintings, in both cases as preparation beneath a red layer surface.

Black, grey, blue

All black, grey and apparently blue (to the naked eye) coloured areas (Fig. 6a) for all the cave paintings were mainly composed of a black pigment, pure or occasionally mixed with lime or natural earth (Fig. 6b). For black layers, carbon black was recognised by Raman spectroscopy as main pigment (1584 and 1330 cm^{-1} in Fig. 6c). Considering both the wavenumbers of the two bands detected and their relative ratio, it is possible to advance the hypothesis that the black was obtained from grape soot (Coccato et al. 2015). The use of carbon black was clearly revealed as main pigment to

Table 4 Colours and mixtures/pigments recognised in samples. Asterisks on the most representative sample names indicate the analytical technique used for the pigment characterisation (*SEM–EDS; **micro-Raman spectroscopy, ***both techniques)

				Paintings				
		Identified pigment		***The Christ Pantocrator***		***The Virgin with Child***		***St. Michael the Archangel***
Colour		**Major component**	**Minor component**	***I cycle***	***II cycle***	***I cycle***	***II cycle***	
Red	R1	Red ochre	-	CR3, CR11*, CR18, CR19, CR21***	CR2*, CR10, CR11*, CR14, CR20	M2, M5, M6, M9*, M15	M7, M10, M13	SM5, SM7***
Dark red	R2	Red ochre	Carbon black	-	CR14	M1, M3***, M10	M10, M12, M14	SM8, SM10
Orange red	R3	Red ochre	Lime	CR5***, CR11*, CR16	CR6*	-	-	-
Red	R4	Cinnabar	-	CR5*	-	-	-	-
Pink	R5	Lime	Red ochre	CR15**, CR17, CR21, CR22**, CR23, CR25	CR10	M15	M7*	SM2***, SM6
Yellow	Y1	Yellow ochre	-	CR7**, CR16, CR25	CR1, CR2*, CR8, CR9, CR14	M1, M3***, M10, M16	M1, M10, M11*, M12, M18	SM1, SM3, SM4, SM6, SM8, SM10, SM12
Dark yellow	Y2	Yellow ochre	Carbon black (+)	CR24*	-	-	M8, M19*	-
Brown	Y3	Carbon black	Yellow ochre	-	CR14	-	M7*	-
Black	B1	Carbon black	-	CR14, CR18, CR25	CR1, CR4, CR6**, CR11*	-	M1, M13, M18	SM1, SM6, SM7
Blue-grey	B2	Carbon black	Red ochre (-), yellow ochre (-)	-	CR12**	M1, M3**	M3**, M4**	-
Dark grey	B3	Carbon black	Lime	CR4	CR4	-	-	-
Pale grey	B4	Lime	Carbon black	CR4, CR24	-	M4*	-	SM9, SM11, SM13
Grey-beige	B5	Lime	Carbon black, yellow ochre	-	-	-	-	SM3

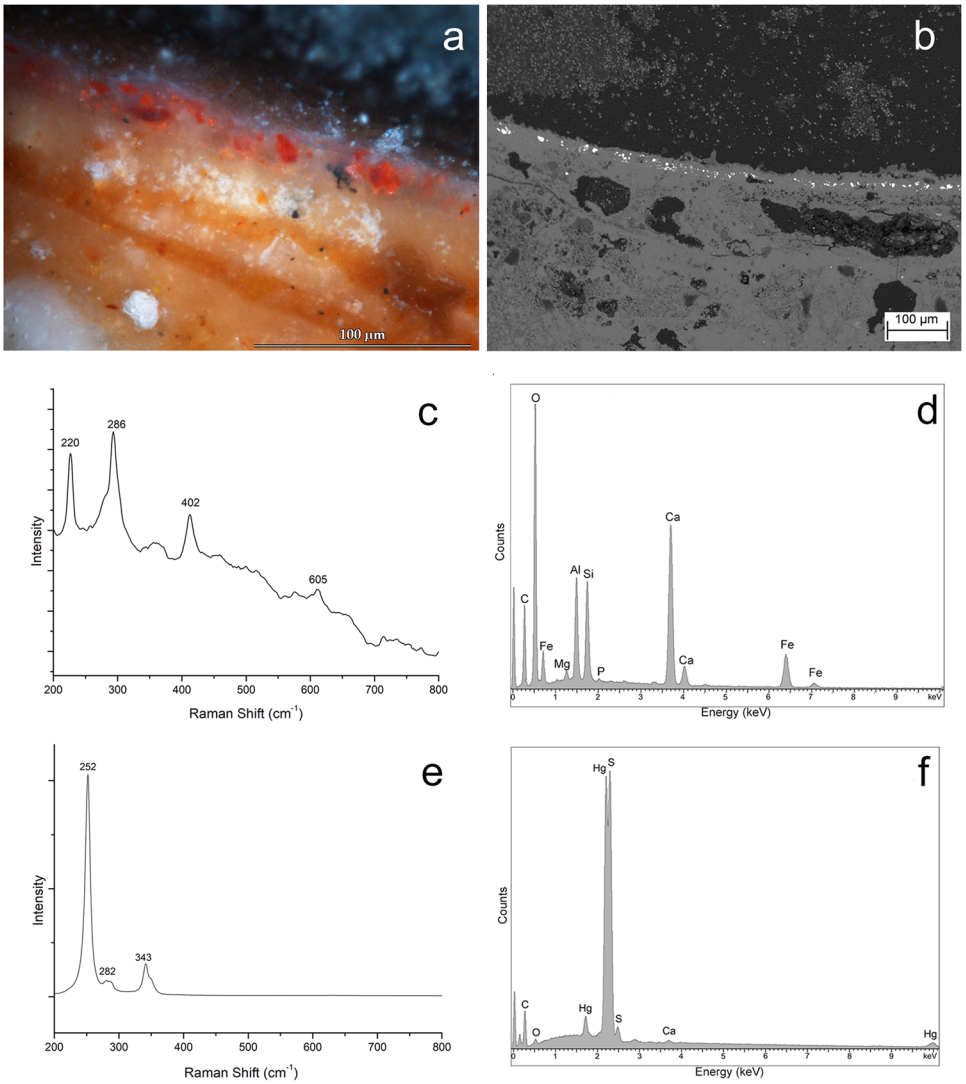

Fig. 4 Microphotograph showing the red layers in the sample CR5 (first cycle of the Christ Pantocrator painting), namely the orange-red ochre (colour R3) layers and on the top the layer of cinnabar (colour R4) (**a**); BSE-SEM image of the same sample, showing, on the surface, the cinnabar (HgS) pigment particle, which appear very lucent (**b**); micro-Raman spectrum of red ochre (**c**) (λ0 = 638 nm, 5 mW, 1-s exposure time, 20 accumulations) and cinnabar (**e**), both identified in the CR5 sample (λ0 = 638 nm, 5 mW, 1-s exposure time, 20 accumulations); SEM–EDS spectra of red ochre (**d**) and cinnabar (**f**), showing their typical compositions

obtain black, different hues and shades of grey and even to produce blue-grey shades.

Colour B1 was characterised by the sole presence of carbon black and was clearly recognised in the Christ Pantocrator painting, in correspondence with outlines of St. Andrea's mantle and St. John's halo and in some background areas of the first cycle and the Christ's tunic and St. John's mantle of the second cycle. Furthermore, it was recognised in the second cycle of the Virgin with Child painting, specifically on St. Michael foot, St. John's halo and the rhombus decoration and, finally, in frames and St. Michael's mantle of the St. Michael the Archangel paintings.

Very low amount of natural red and yellow ochres was mixed with carbon black (colour B2) to create a shade of grey turning to blue, which was identifiable in the second cycle of the Christ Pantocrator painting in correspondence of the St. John's mantle and for both the first and second cycles of the Virgin with Child painting (in the latter on the Virgin's tunic). In these cases, since the black colour displays typical shades of blue, the employed pigment could be the vine black, a variety of carbon black obtained from burning of vine wood (Matteini and Moles 2007). Only on the Christ Pantocrator painting, both in the first and in the second cycle in the area near Christ title block, was used a mixture (B3) based on small adding of lime to carbon black to paint some dark grey areas, whereas for pale grey decorations in the same area and in the background of the first cycle of the Christ Pantocrator, in the Virgin face of the first cycle of the Virgin with Child and in the dragon tail and strip in the St. Michael the Archangel paintings was used carbon black pigment lighten by lime (colour B4). Finally, in a sample from a grey-beige frame decoration of the St. Michael the Archangel painting, a colour (B5) obtained by mixing of carbon black, lime and yellow ochre was identified.

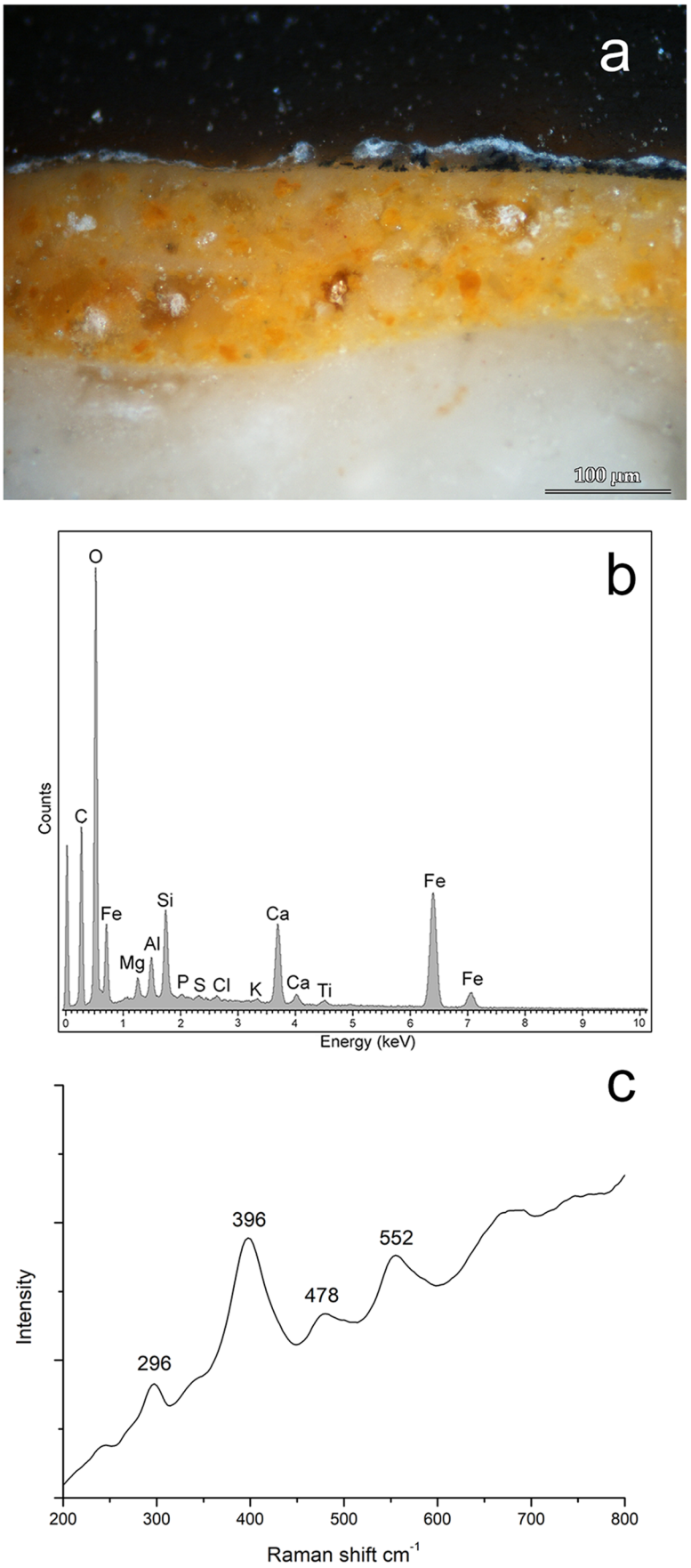

Fig. 5 Microphotograph of the yellow layer (colour Y1) in sample M10 from the second cycle of the Virgin with Child layer (**a**); SEM–EDS (**b**) and micro-Raman spectrum of goethite identified in the CR5 sample (**c**) (λ0 = 638 nm, 5 mW, 1-s exposure time, 20 accumulations)

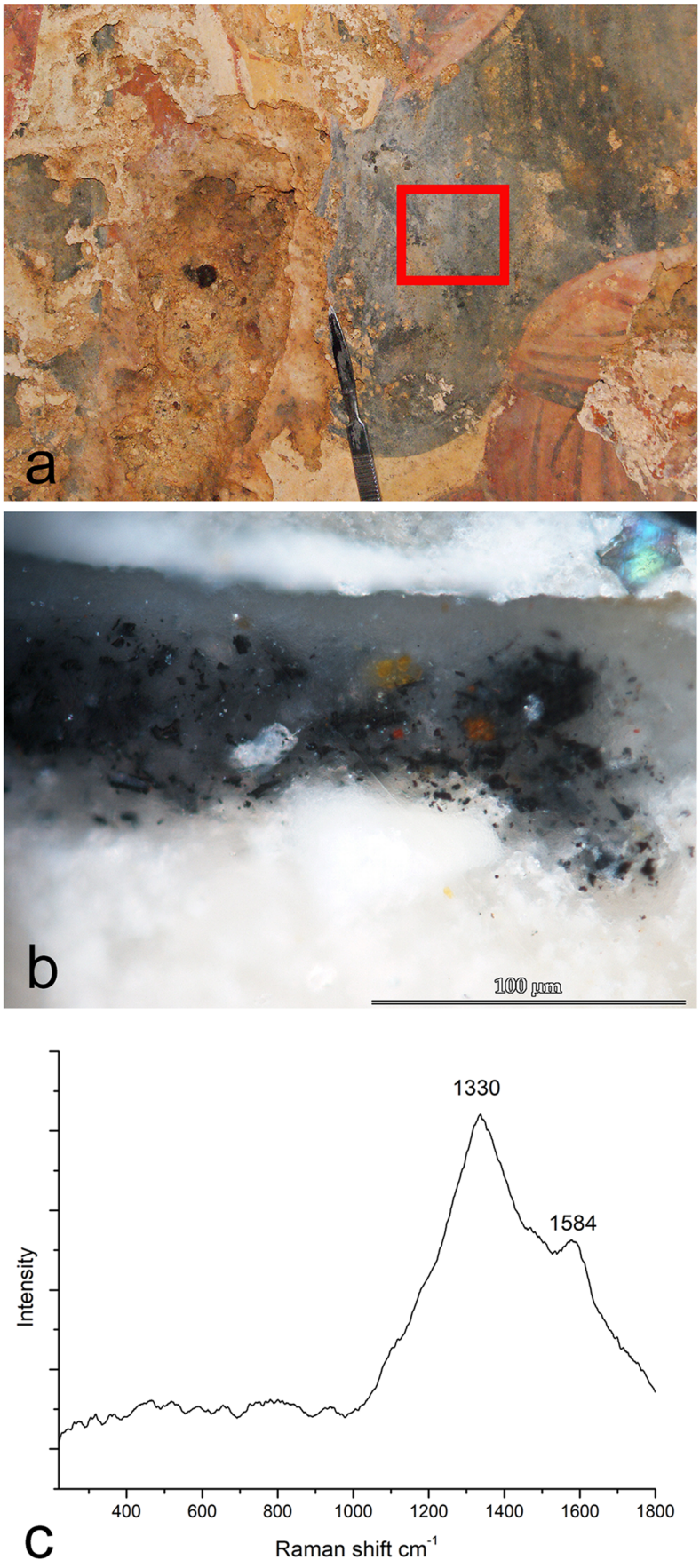

Fig. 6 Macrophotograph (**a**) of sample CR14 (second cycle of the Christ Pantocrator) and the microphotograph in reflection mode (**b**) showing the overlapping of brown colour (Y3) used as background to darken final effect due to the red layer (colour R1)

Discussion

The results obtained from the archaeometric investigation on the pictorial samples of the Sant'Angelo in Criptis cave proved to be extremely significant and encouraged the discussion of some important aspects concerning raw materials and pictorial techniques, allowing at the same time to advance hypotheses about the relative dating of paintings through the long history of the site. First, it should be emphasised that the microstratigraphic observations of painting fragments confirmed the historic-artistic hypotheses that attributed two pictorial cycles to the Christ Pantocrator and the Virgin with Child paintings and only one pictorial cycle to the St. Michael the Archangel painting, so definitely excluding here the presence of further older and not visible pictorial layers.

Materials and painting technique

The archaeometric investigation revealed 4 types of preparatory mortars, generally constituting of the same lime binder but with different kind of aggregate. Interestingly, both the second cycle of the Virgin with Child and the Christ Pantocrator paintings showed the same kind of mortar (type FA), whereas different mortar type were used for the first cycle of the Christ Pantocrator painting (type CA) and the first cycle of the Virgin with Child painting (type ACA).

Even the mortar of the St. Michael the Archangel painting (type FM) did not fit with the others.

The cocciopesto fragments were found in every mortar types denoting its intentional adding to promote hydraulic properties of the mortars (Sabbioni et al. 2001, 2002; Zendri et al. 2004; Farci et al. 2005), regardless of whether or not the type of cocciopesto used was suitable for conferring hydraulicity to the mortar. Moreover, in the mortar of the first cycle of the Christ Pantocrator painting, the roundness of cocciopesto fragments would suggest the likely intention to modify them, by means of a smoothing process, even if it seems to have not a specific technological function.

In the mortar of the first cycle of the Christ Pantocrator painting and the second cycles of the paintings of Christ Pantocrator and Virgin with Child, the absence of underburnt relics and lime lumps is an indication of care in controlling firing temperature, time and blending of mixtures during lime preparation, contrary to mortars from both the first cycle of the Virgin with Child (type ACA) and the St. Michael the Archangel (type FM) paintings, showing higher number of nodules and relicts of calcination.

In all the mortar samples, remains of underburnt relicts showing texture and structures of the raw material used for the calcination are lacking; however, the geolithological setting suggests the use of a white and variable fossiliferous limestone belonging to the Calcare di Altamura Formation (Ricchetti et al. 1988), largely outcropping in the surrounding area. Moreover, the nearest sand outcrops, possibly employed as aggregate in the mortar production, correspond to the yellow calcareous-quartz sand of the Monte Marano Formation (Azzaroli et al., 1968).

The chemical investigations carried out on the pictorial layers of the entire set of samples highlighted the prevalent use of few natural pigments, namely red ochre, yellow ochre and carbon black, which represent the same inorganic pigments used also for the decoration of walls in other sites of the region, i.e. churches or rupestrian settlements (Laviano et al. 2004; Capitanio et al. 2005; Pinto et al. 2008; Pinto 2011; De Benedetto et al. 2013; Fico et al. 2015).

Despite the scarcity of the pigments used, the final rendering of the wall paintings appears much richer, and the hues and shades produced to paint scenes and figures seem to show a wider chromatic variability. Such aspect was highlighted by means of stratigraphic investigation, which revealed that, in most cases, the mixtures created are

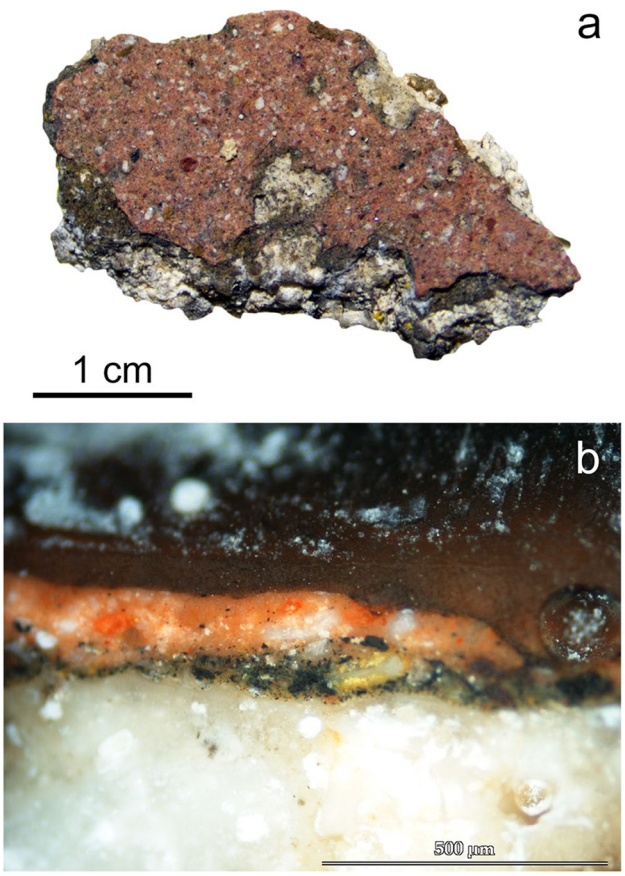

Fig. 7 Sampling point (**a**) and microphotograph (**b**) of the St. John's halo (sample CR14, second cycle of the Christ Pantocrator painting) where the gold effect was obtained by the overlapping of brown (Y3), red (R1) and yellow (Y1) layers

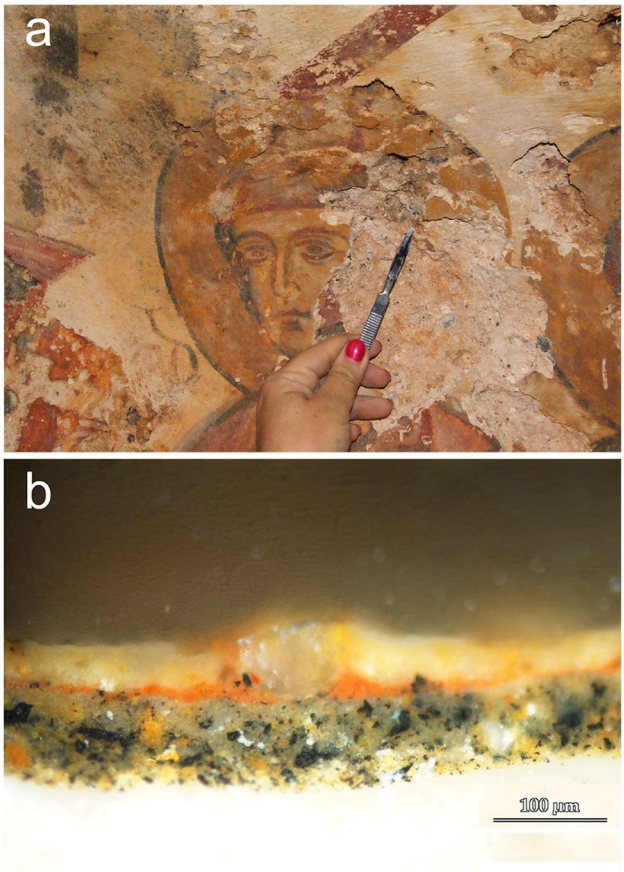

Fig. 8 Sampling point (**a**) and microphotograph (**b**) of the St. John's tunic (sample CR12, second cycle of the Christ Pantocrator painting), showing the grey-blue colour (B2) obtained by carbon black, red and yellow ochres

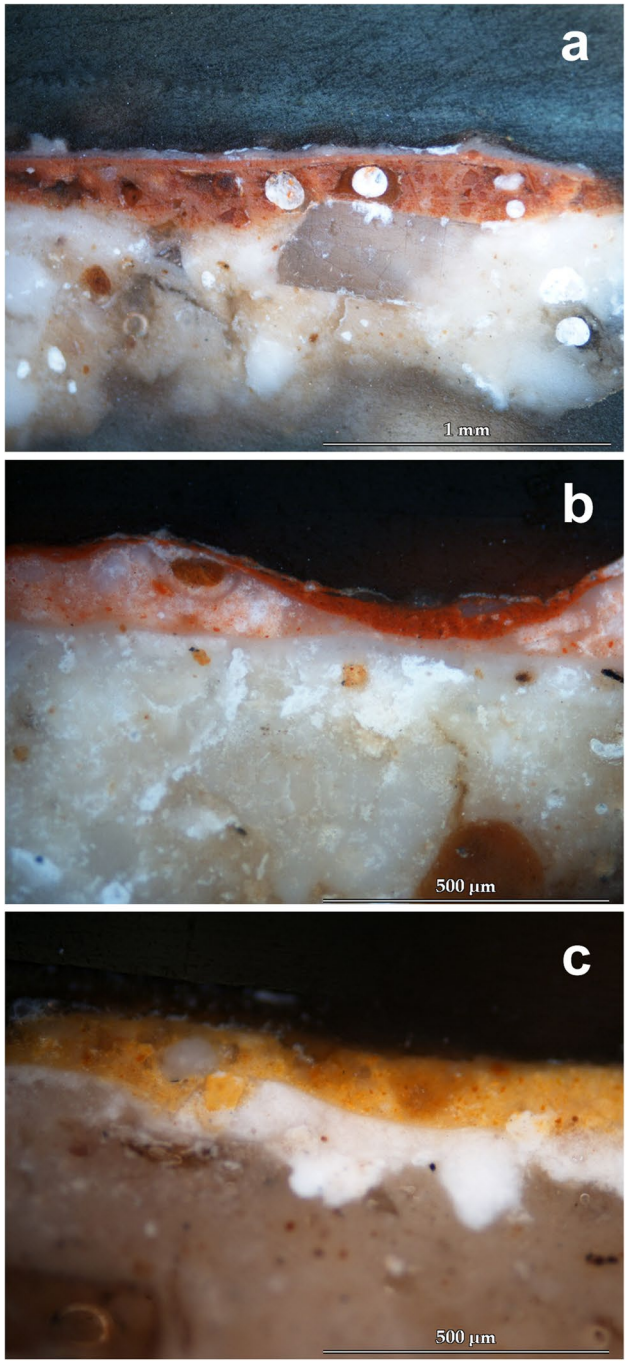

Fig. 9 Microphotographs showing the absence of the plaster layer in the Christ Pantocrator (**a**) and Virgin with Child (**b**) paintings and the presence of a white, thin and not continuous layer in the St. Michael painting (**c**), probably correlated to the presence of intonaco

composed by two or more pigments, wisely proportioned in different amounts, in order to obtain several hues and shades. The only case of use of a more precious pigment was found in the first cycle of the Christ Pantocrator painting, where the pure cinnabar (colour R4) was applied in a very thin layer above a red ochre layer exclusively for the decoration Christ's mantle, in order to give emphasis to the main subject of the scene in a period of prosperity of the site. The use of this precious pigment has been documented in byzantine paintings (Poulia et al. 2001; Franquelo et al. 2009; Sotiropoulou et al. 2008; Sawczak et al. 2009, Fioretti et al. 2020), although generally admixed with other red pigments, i.e. red ochre and minium.

In contrast to a very poor number of used pigments, at least 13 different mixtures were highlighted from this study, showing that the chromatic variability of the paintings were wisely obtained by mixing few simple pigments in order to obtain specific colours and shades; furthermore, the stratigraphic analysis highlighted the overlap of different layers of colour in order to obtain specific chromatic effects, i.e. the use of two or three layers of red ochre under the cinnabar layer (CR5) in correspondence to the Christ's mantle (first cycle) to enhance the pigment intensity and the final effect; the use of brown (Y3) as background to darken the overlying red in some areas of the second cycle of the Christ Pantocrator and Virgin with Child paintings (Fig. 7); and finally,

the overlapping of three layers (brown, red and yellow) to simulate the gold effect in the St. John's halo in the Christ Pantocrator painting (Fig. 8).

Even the light blue colour, presumably obtained using vine black with very small amounts of red and yellow ochres, added probably to correct and lighten the colour, denotes a remarkable skill of the artists (Fig. 6).

As for the painting technique, the irregularity, the roughness, the absence of discontinuity and the high cohesion of the interface between the plaster and the pictorial layer, the thickness of this last, and the absence of a carbonate-rich surface on the top of the plaster, as observed by SEM, suggest the use of *fresco* technique, according to Piovesan (2009).

Moreover, in some pictorial layers, the adding of lime to the pigment mixture was discovered; however, it does not proof the *mezzofresco* (lime) painting technique, but its use with the aim of lightening the colours due to natural ochre and carbon, to obtain orange, pink and grey colours.

The cinnabar layer in the Christ Pantocrator painting could represent an exception, and it should be applied by the a secco technique since, as known, the use of the pigment was discouraged in wall paintings because of its darkening when it reacts with lime (Cennini 1821). Such hypothesis should be confirmed by the absence of the carbonatation layer in the cinnabar layer, which however could be missing for the bad conservation state of the painting surfaces (i.e. abrasions, losses of pictorial film, crusts). Also, the thickness (about 25 μm) of the cinnabar layer and the presence of a carbonate matrix around the pigment particles, together with the absence of the carbonatation layer in the underlying ochre layer (Fig. 4b), testifying the application of cinnabar on a still wet surface, could prove that the cinnabar was unusually applied by the fresco (or possibly *mezzofresco*) technique.

Generally, in all the investigated samples the pictorial film is overlapped to a single mortar layer without any interposed fine intonaco (Fig. 9a,b). Only in a sample (SM4) from the St. Michael the Archangel painting, a thin not continuous layer of fine intonaco was observed (Fig. 9c).

Chronologic hypothesis

The differences outlined in the used materials and preparation technique of mortars from the first cycles of the Christ Pantocrator and the Virgin with Child paintings and the painting of St. Michael the Archangel suggest that they were not executed simultaneously, but probably in different times and/or by different artworks. Conversely, a correlation has been observed between the mortars used for the second cycle in the Christ Pantocrator painting, dated between the thirteenth and fourteenth century based on the palaeographic analysis of the cartouche of Christ (Caragnano 2008), and those used in the second cycle of the Virgin with Child painting, dated presumably at the second half of the thirteenth century (Calò 2016). Such aspect could suggest a contemporary execution of them.

On the basis of the present archaeometric results and taking into account the dating hypotheses based on iconography (Caragnano 2008; Calò 2016), it is possible to suggest that the second pictorial cycle of the two paintings Christ Pantocrator and Virgin with Child can probably be contemporary or even made by the same workers in the same decorative time. Therefore, both the pictorial cycles could be dated in the second half of the thirteenth century, when the cult site was still living its prosperous period. Furthermore, considering that during the two previous centuries, the site was the destination of intense pilgrimages (Fiorentino 2005) which could have worn the surfaces of the paintings and that, in the Christ Pantocrator painting, the two cycles depict the same subject, it is plausible that the repainting was a restoration work.

Finally, the application of cinnabar on the Christ's mantle is consistent with the historic hypotheses that dated the first cycle of the Christ Pantocrator painting to the twelfth to thirteenth century, during the celebrity and devotion climax of the cave.

Conversely, the absence of cinnabar in the samples corresponding to the Christ's mantle in the second pictorial cycle should indicate a decrease in the economic possibilities of the monastery in the thirteenth to fourteenth century.

Conclusion

The archaeometric results allowed to discuss hypothesis on chronological assumptions, raw materials and painting technique. The correspondence to the mortar of second pictorial cycles of the Christ Pantocrator and the Virgin with Child paintings, in well agreement with iconographic and historical evidence, attributed the former between the thirteenth and fourteenth century and the latter to the second half of the thirteenth century. However, the astonishing findings were the variability of colours due to different mixings and proportions of pigments and the overlapping of different chromatic layers, to obtain a large chromatic palette.

Furthermore, the exception in the use of pure cinnabar applied to the tunic of Christ Pantocrator of the first pictorial cycle suggested an acquired prestige and richness of the site in the period of execution of the artwork (twelfth to thirteenth century). Finally, the conducted study revealed the overlapping of the pictorial layers directly on a single layer of mortar, without other preparation layers, which is a rather spread evidence in the region, namely in the rupestrian settlement.

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