

# Archeometric investigation on wall paintings from the most ancient Hellenistic hypogeum found in Sicily (C.da Apaforte-Licata (AG))

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**Abstract** In the present work, an analytical study of paintings from an ancient hypogeum, dated back to 4th–3rd cent B.C. and located in Licata (Sicily, Southern Italy) has been carried out. A selection of representative red, yellow and white wall colored plasters have been sampled and analyzed in non-destructive and micro-destructive way to identify the pigmenting agents, preparation layers and study the deterioration processes. In particular, the quantitative analysis of the chemical composition of the different layers (pigments, preparation layers, deteriorated parts) has been obtained through scanning electron microscopy coupled with energy-dispersive spectrometry (SEM–EDS), while micro-Raman spectroscopy have been performed to investigate the molecular nature of the coloring agents used in the pigment layer. Finally, preliminary macroscopic and thin section analyses (OM) have been carried out with the aim to characterize plaster features and degradation processes. The obtained results, together with previous data on Hellenistic art in Sicily, may be helpful to create a database about the evolution of mural painting in Sicily as well as identify raw materials, pigment agents and painting techniques used in local plasters manufacture.

**Keywords** Hellenistic paintings · Pigments · Spectroscopic analysis · Sicily

## 1 Introduction

Wall paintings represent a relevant archeological element in the definition of Hellenistic and Roman culture (Kakoulli 2002). Among the information that can be obtained from the study of the ancient wall colors remains, the knowledge about pigmenting agents and manufacture process is a current issue in the archeometric literature (Mazzocchin et al. 2003; Moretto et al. 2011; Cheilakou et al. 2014; Syta et al. 2014). In recent years, the use of non-destructive spectroscopic analyses has become a routine in the study of archeological and art works (Vandenabeele 2004), especially in the investigation of pigments; in particular, Raman spectroscopy has been widely applied in the study of pigments (Smith and Barbet 1999; Daniilia et al. 2000; Bersani et al. 2003, 2004). For aforementioned, a large number of database on ancient and modern pigments are available (Bell et al. 1997; Vandenabeele et al. 2000; Burgio and Clark 2001). In addition, the use of scanning electron microscopy with energy-dispersive systems (SEM–EDS) represents a useful tool in highlighting interesting aspects on both pigments and preparation layers (Galli et al. 2004).

In the framework of the studies on Sicilian painting production during Hellenistic Age, the plasters found near a hypogeum situated in C.da Apaforte-Licata (Sicily) are of relevant interest in view of the importance of the archeological site (La Torre 2011). The tomb, in fact, represents the most ancient Hellenistic hypogeum found in Sicily. The archeological significance of the site has led to a scientific project finalized to study the technological features of the colored plasters. Therefore, some representative specimens

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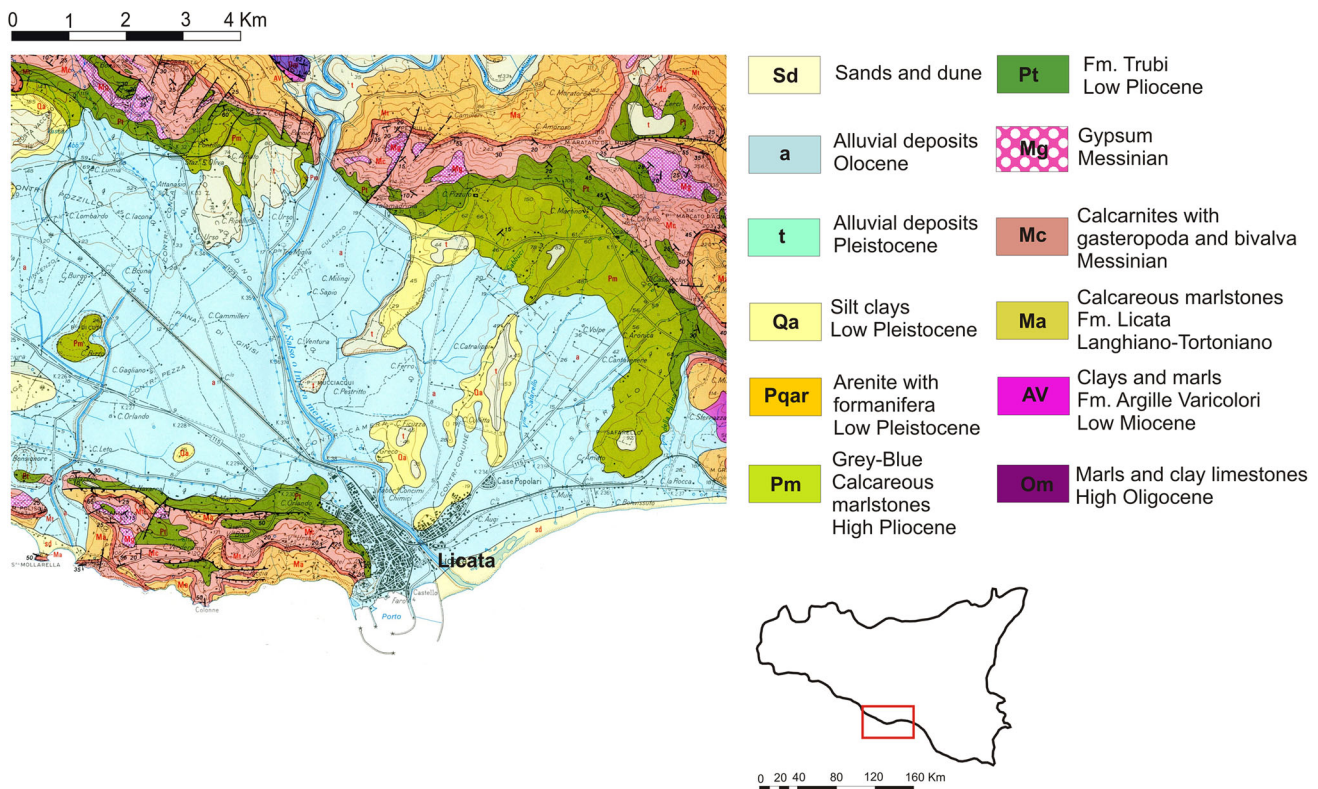
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**Fig. 1** Geological map of the area from Grasso et al. (1997)

have been sampled and analyzed. In view of the uniqueness of the archeological site the sampling has been allowed only for a limited number of specimens, representative of the different colors identified in the hypogeum wall painting.

In detail, micro-Raman and SEM–EDS measurements have been performed to investigate the pigments and obtain chemical composition of pigments and preparation layers, respectively. Moreover, preliminary macroscopic and thin section analyses by optical microscopy (OM) have been performed with the aim at characterizing plaster features and degradation processes. Finally, a comparison with data on more recent Hellenistic plasters coming from Licata (Barone et al. 2011; Aquilia et al. 2012) and Gela (Aquilia et al. 2011) have been carried out to obtain information on the changes in manufacturing process in Sicily.

## 2 Archeological and geological settings

In the 1970–1980 of the last century, during a survey carried out by the Archeological Association of Licata a hypogeum grave with a chamber tomb has been identified (La Torre 2011). The hypogeum, built in squared stone blocks, consists of a rectangular room with painted walls and a narrow access corridor with steps carved on the rocks. The archeological relevance of the hypogeum is highlighted by the artifacts

found near the entrance, represented mainly by potteries dated back to late IV–III B. C.

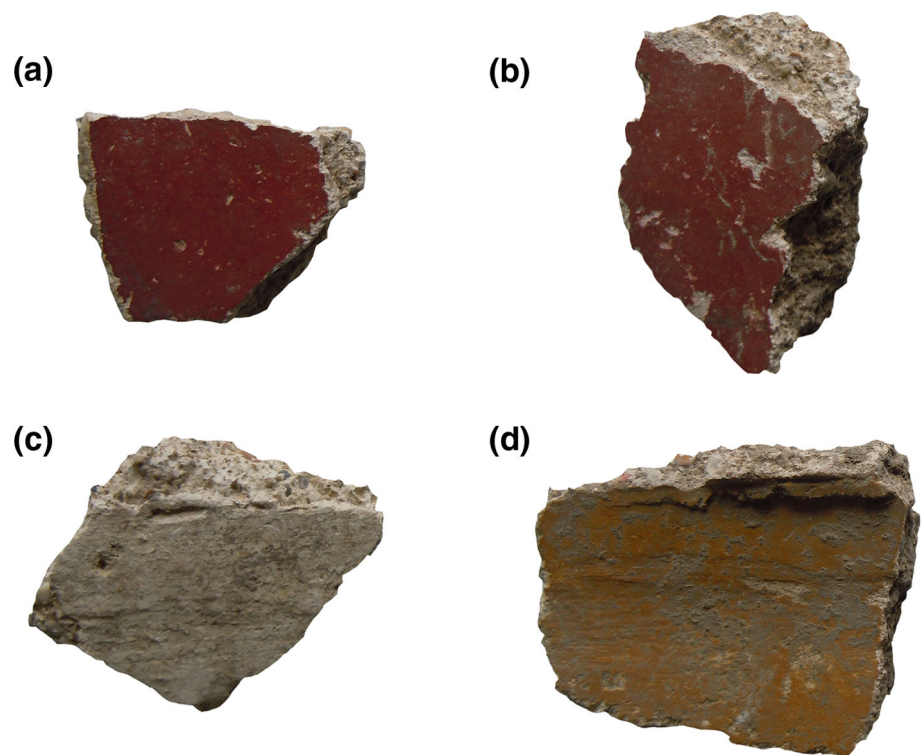
According to the artifacts found in the site and the architectural characteristics of the hypogeum, it can be considered the oldest example of funerary hypogeum in Sicily. Therefore, the plasters founded with are the oldest specimens of Hellenistic wall painting from funerary context in Sicily.

From the geological point of view (Fig. 1), the area is characterized by the Gela Nappe, a structural element of the Gela-Catania foredeep, mainly filled by Miocenic-Quaternary deposits coming from the Appenninic-Magrebide chain (Grasso et al. 1997). The stratigraphy is dominated by submarine marls and clays, evaporitic and clastic deposits (mainly product of the Messinian low stand), Pliocene chalks and marls, Plio-Pleistocene sandstones, Holocene alluvial deposits and Pleistocene marine and alluvial deposits.

## 3 Materials and methods

Representative samples of the different pigment color recognized in the decorated walls of the archeological site (i.e., red, yellow and white) have been selected for archeometric analysis (LIC 17, LIC 18, LIC 19 and LIC 20; Fig. 2). The selection criteria is related to the correspondence of color and texture of selected samples with several fragments of

**Fig. 2** Pictures of analyzed samples. **a** LIC 17, **b** LIC 18, **c** LIC 19 and **d** LIC 20



Hellenistic wall paintings from Via S. Maria and Monte S. Angelo in Licata previously studied (Barone et al. 2011; Toscano Raffa and Limoncelli 2011).

To obtain a preliminary characterization of samples, macroscopic description and color determination through Munsell soil color chart (Munsell index = MI) (Munsell and Color 2000) have been performed.

Macroscopic observations highlight the presence of two different layers under the pigment strata; the first one is homogeneous and without aggregates, while the second one exhibits a light gray color and coarse grain aggregates in the binder. On the whole, the degree of adhesion between the layers is good. Referring to conservation state, all the studied samples exhibit a good degree of cohesion and preservation. Only samples LIC 19 and LIC 20 exhibit a slight chromatic alteration. Description on sampling and macroscopic features of each sample is summarized in Table 1.

All samples have been studied by petrographic, chemical and spectroscopic analyses.

In detail, thin section analysis has been carried out by optical microscopy (OM) using a polarized transmitted light microscope Nikon Eclipse E400POL.

With the aim to obtain semi-quantitative analysis on the chemical composition of pigments and preparation layers, scanning electron microscopy (SEM) measurements have been performed using a Tescan Vega LMU scanning electron microscope equipped with an EDAX Neptune XM4-60 micro-analyzer, characterized by an ultra-thin Be

window. Data have been collected using spot mode analysis on polished thin section and attached to an aluminum stub with double-sided tape and coated in carbon, with 20 kV accelerating voltage and 0.2 mA beam current.

Finally, with the goal of determining the pigmenting agents, spectroscopic analyses have been carried out. In detail, micro-Raman spectra have been acquired on samples with a Raman Jasco NRS-3100 apparatus, equipped with a microscope with 10×, 20× and 100× objectives and two laser excitation source at 532 and 785 nm; laser power has been controlled by means of a series of density filters, to avoid heating effects; depth resolution was set to few micrometers by means of a confocal hole. The system has been calibrated using the  $520.7\text{ cm}^{-1}$  Raman band of silicon before each experimental session.

## 4 Results

### 4.1 Petrographic analysis

Observation in thin section allows to obtain detailed information about the different layer recognized macroscopically and binder-aggregates features (see Table 2).

Petrographically, samples LIC 17 (Fig. 3a) and LIC 18 exhibit the same petrographic features. In detail, three different layers can be distinguished: a thinner red colored one, without aggregates; an intermediate bedding layer one

**Table 1** Macroscopic features of analyzed samples

ID sample	Description	Color	MI	Conservation state
LIC 17	Wall painted plaster and mortar	Red	10R 4/4	Good cohesion and degree of preservation
LIC 18	Wall painted plaster and mortar	Red	10R 4/4	Good cohesion and degree of preservation
LIC 19	Wall painted plaster and mortar	White	2.5YR 8/1	Good cohesion and chromatic alteration
LIC 20	Wall painted plaster and mortar	Yellow	10YR 6/8	Good cohesion and chromatic alteration

MI Munsell index (Munsell and Color 2000)

**Table 2** Petrographic features of studied materials

	LIC 17	LIC 18	LIC 19	LIC 20
<b>Aggregates</b>				
Composition	Sedimentary (80 %) and metamorphic (15 %) rock fragments	Sedimentary (80 %) and metamorphic (15 %) rock fragments	Sedimentary (55 %) and metamorphic (35 %) rock fragments	Sedimentary (80 %) and metamorphic (15 %) rock fragments
Morphology	Quartz (5 %) Rounded-spherical (sed.) Sub-angular (met.) Sub-rounded (Qz)	Quartz (5 %) Rounded-spherical (sed.) Sub-angular (met.) Sub-rounded (Qz)	Quartz (10 %) Rounded-spherical (sed.) Sub-angular (met.) Sub-rounded (Qz)	Quartz (5 %) Rounded-spherical (sed.) Sub-angular (met., Qz)
Grain size distribution	Medium: 1.25 mm Min: 0.5 mm Max: 2.5 mm	Medium: 1.25 mm Min: 0.5 mm Max: 2.5 mm	Medium: 1.5 mm Min: 0.3 mm Max: 3.5 mm	Medium: 1.25 mm Min: 0.5 mm Max: 3.75 mm
Sorting	Moderate	Moderate	Moderate	Good
Aggregate:binder ratio	45:55	40:60	45:55	40:60
Distribution clasts	Homogeneous	Homogeneous	Homogeneous	Homogeneous
<b>Binder</b>				
Color	Grayish brown	Grayish-brow	Grayish-brow	Grayish-brow
Lumps	Scarce; absent in the 3rd layer	Present	Present	Rare
Porosity	Globally 15 %	Globally 15 %	Globally 20–30 %	Globally 10–15 %

Aggregate:binder ratio and porosity have been determined on the basis of the chart for estimating proportion of mottles and coarse fragments in Munsell soil color chart (Munsell and Color 2000)

poor in aggregates (represented by calcite fragments) and with lumps (Fig. 3b) and, finally, a thicker nucleus layer rich in aggregates, mainly represented by rounded-spherical sedimentary rock fragments (80 %—sandstones, oolitic carbonate rock fragments and bioclasts, mainly represented by bivalve fragments), sub-angular metamorphic (15 %) rock fragments and scarcely sub-rounded quartz (5 %). The aggregate shows medium–high aggregate:binder ratio (40–50 %), an homogeneous distribution and a moderate sorting, measuring about 1.25 mm in diameter. The binder shows scarce lumps, a grayish brown color and about 15 % of porosity.

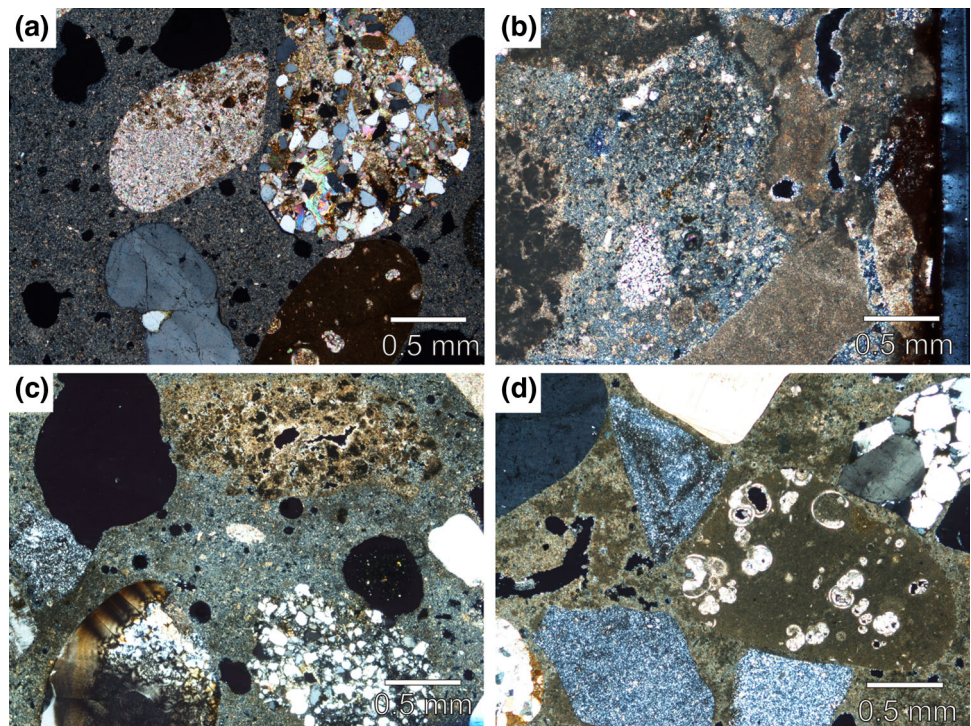
Thin section observation of sample LIC 19 (Fig. 3c) highlights four different layers: a cream white-colored layer; a thinner one, without aggregates; an intermediate bedding grayish layer rich in lumps and without aggregates and a thicker nucleus layer rich in lumps and aggregates,

the latter mainly represented by rounded-spherical sedimentary (55 %—sandstones, carbonate stones with globigerinae and oolites and bioclast, mainly represented by bivalve and oolites), sub-angular metamorphic (35 %) rock fragments and scarcely sub-rounded quartz (10 %). The aggregate shows medium–high aggregate:binder ratio (40–50 %), an homogeneous distribution and a moderate sorting, measuring about 1.5 mm in diameter. The binder shows common lumps, a grayish brown color and about 20–30 % of porosity mainly represented by bubbles.

Finally, also sample LIC 20 is characterized by four layers: a pigment yellow-colored layer, a thinner one poor in aggregates; an intermediate bedding layer one poorly in aggregates (represented by calcite fragments) and with lumps and a thicker nucleus layer rich in aggregates, mainly represented by rounded-spherical sedimentary (70 %—sandstones, carbonate stone with globigerinae and bioclast



**Fig. 3** Microphotographs of analyzed samples. **a** LIC17; **b** LIC18; **c** LIC19 and **d** LIC20



fragments, mainly represented by brachiopod, bivalve and gastropods), sub-angular metamorphic (20 %) rock fragments and scarcely sub-angular quartz (10 %) (Fig. 3d). The aggregate shows medium aggregate:binder ratio (40 %), an homogeneous distribution and a good sorting, measuring about 1.25 mm in diameter. The binder shows rare lumps, a grayish brown color and about 10–15 % of porosity.

#### 4.2 Chemical analysis

To obtain information on pigments agents and plaster features, SEM–EDS analysis has been performed using spot mode analysis on polished thin sections.

According to petrographic observations, almost three different layers can be identified; a pigment layer about 0.1–0.2 mm in thickness, a bedding layer from 1.5 to 4 mm in depth and, finally, a nucleus layer (Fig. 4). It is worth of noting the presence of well-evident carbonation layer immediately underneath the painted layer and between bedding and nucleus layers.

Referring to pigment layers, grains are quite regular distributed in a thin and homogeneous carbonate layer, the latter one exhibiting a chemical composition enriched in FeO level in both red (LIC 17, LIC 18) and yellow (LIC 20) fragments and with SrO in the white sample LIC 19 (Table 3). Note worthy is the presence of trace amount of chlorides and sulfates, probably attributable to alteration processes.

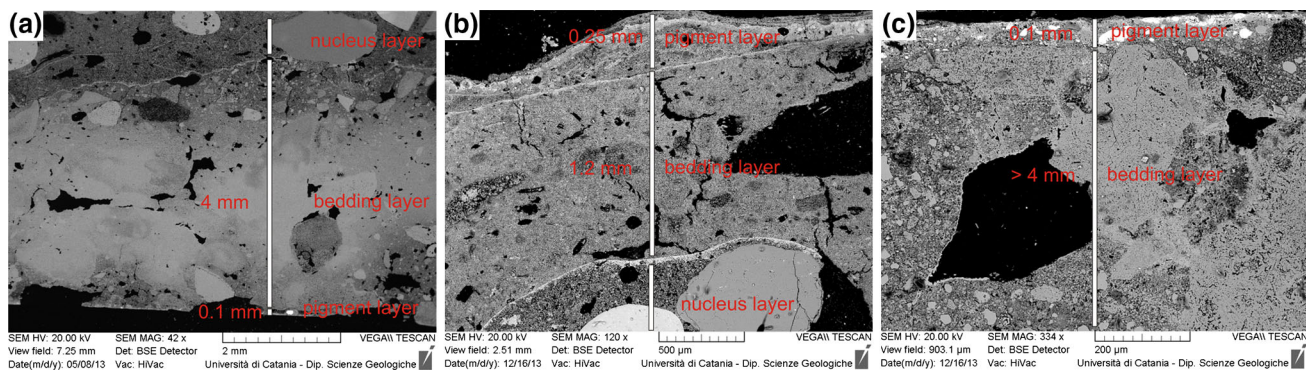
The mineral composition of pigment grains consists mainly in FeO (see Table 3), both in yellow and red plasters; referring to microtextural features, note worthy is that in red samples the pigment grains dispersed in the carbonate layer are finer than in the yellow one (Fig. 5).

About binder and lumps recognized both in bedding and nucleus layers (Fig. 6) no relevant differences have been detected between them. The average composition of the binder and of the lumps are summarized in Table 4.

On the whole, all samples show Ca-rich binder with low hydraulic index close to those measured on lumps. In some analyses, low amount of sulfates and chlorides (evidenced by the presence of SO<sub>3</sub> and Cl<sub>2</sub>O) have been detected and can be attributable to slight degradation processes affecting the plasters. Note worthy is that in samples LIC 18 and LIC 19 a significant amount of SrO is present.

#### 4.3 Spectroscopic analyses

Micro-Raman spectra have been collected on the colored surface of plasters with the aim at characterizing the chemical composition of pigments. In detail, spectra collected on red plasters LIC 17 (Fig. 7a) and LIC 18 exhibit the typical Raman modes of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (226, 292, 411, 497 and 612 cm<sup>-1</sup> corresponding to A<sub>1g</sub>, E<sub>g</sub>, E<sub>g</sub>, A<sub>1g</sub> and E<sub>g</sub> modes, respectively) (RRUFF Project 2014), while

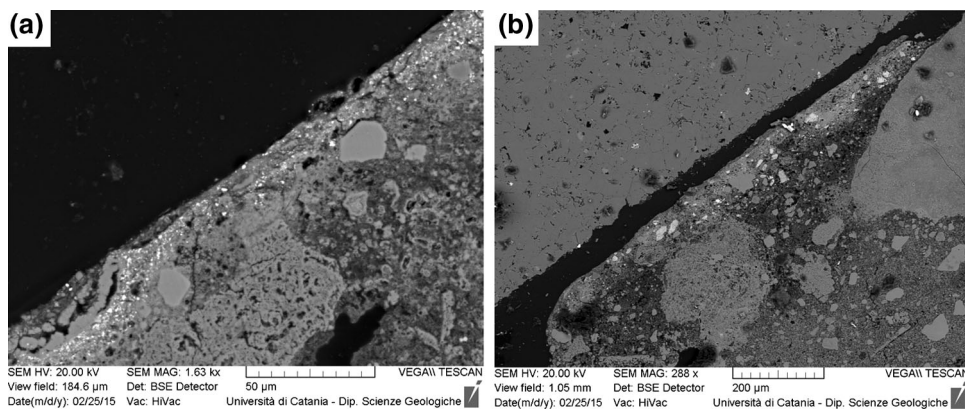


**Fig. 4** SEM images and thickness of the different layers of studied samples. **a** LIC 17; **b** LIC 19; **c** LIC 20

**Table 3** Semi-quantitative average chemical composition (wt%) of pigment layers and pigments grains in analysed samples obtained by EDS analyses

	Pigment layers				Pigment grains	
	LIC 17	LIC 18	LIC 19	LIC 20	Red (LIC 17)	Yellow (LIC 20)
SiO <sub>2</sub>	10 ± 2	12 ± 3	3	7 ± 1	3 ± 1	4 ± 1
TiO <sub>2</sub>	–	1	–	–	–	–
Al <sub>2</sub> O <sub>3</sub>	5 ± 2	6 ± 4	2	4 ± 2	2	3 ± 1
FeO	28 ± 6	29 ± 14	2	30 ± 11	87 ± 9	92 ± 3
MgO	3 ± 1	3 ± 1	3	2	1	1
CaO	50 ± 8	46 ± 13	84 ± 2	53 ± 6	7 ± 2	1
SrO	–	–	5 ± 2	–	–	–
Na <sub>2</sub> O	2	1	2	1	–	–
K <sub>2</sub> O	1	1	–	–	–	–
P <sub>2</sub> O <sub>5</sub>	–	1	3	1	–	–
SO <sub>3</sub>	1	2	2	2	–	–
Cl <sub>2</sub> O	–	–	2	1	–	–

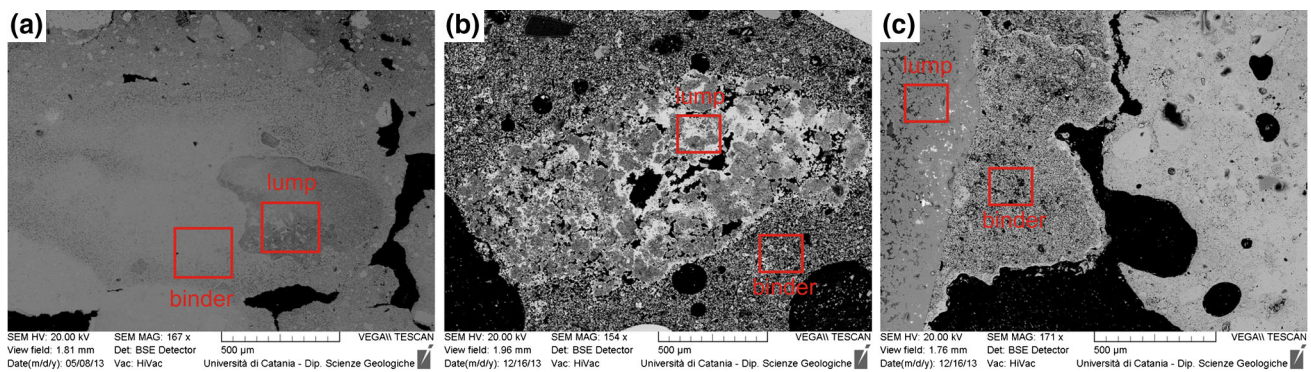
**Fig. 5** SEM images of samples (a) LIC 17 and (b) LIC 20 as example of red and yellow pigment grains, respectively



in the yellow plaster the Raman spectra of goethite ( $\alpha$ -FeOOH) (RRUFF Project 2014) can be identified (Fig. 7b), suggesting the use of ochre containing hematite and goethite as chromophore (Froment et al. 2008). Finally, Raman analysis performed on the white plaster highlights

the presence of calcite ( $282$  and  $1087$   $\text{cm}^{-1}$ ). It is worth of note that the peak at  $1085$   $\text{cm}^{-1}$  related to calcite has been revealed in the spectra acquired also on red and yellow samples, due to the carbonate nature of the preparation layer.





**Fig. 6** SEM images of analyzed lumps and binder of studied samples. **a** LIC 17; **b** LIC 19; **c** LIC 20

**Table 4** Semi-quantitative EDS analysis of lumps and binder in the studied samples

	LIC 17		LIC 18		LIC 19				LIC 20			
	Bedding layer		Bedding layer		Bedding layer		Nucleus layer		Bedding layer		Nucleus layer	
	Binder	Lump	Binder	Lump	Binder	Lump	Binder	Lump	Binder	Lump	Binder	Lump
SiO <sub>2</sub>	3	3	2	1	3	2	3 ± 1	3 ± 1	2	4 ± 1	3	2
Al <sub>2</sub> O <sub>3</sub>	2	1	0	1	1		1	1	1	2	1	1
FeO	0	0										
MgO	8	22 ± 5	5	30	3 ± 2	2	91 ± 2	1	4 ± 3	2	2	26 ± 4
CaO	85 ± 1	72 ± 4	89	68	88 ± 2	91 ± 1	3 ± 1	84 ± 2	86 ± 3	87 ± 1	89 ± 1	70 ± 3
SrO				1				2 ± 1		1		
Na <sub>2</sub> O	1	0		1				1			1	
K <sub>2</sub> O	0	0						1				
P <sub>2</sub> O <sub>5</sub>			1		1	1	1	2		1	2	1
SO <sub>3</sub>	2	1	1		3 ± 1	1		4			2	
Cl <sub>2</sub> O	1	3	1		1	1		1	1		1	
HI	0.05	0.05	0.03	0.02	0.03	0.03	0.04	0.05	0.03	0.04	0.04	0.03

HI hydraulic index ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3/\text{CaO} + \text{MgO}$ )

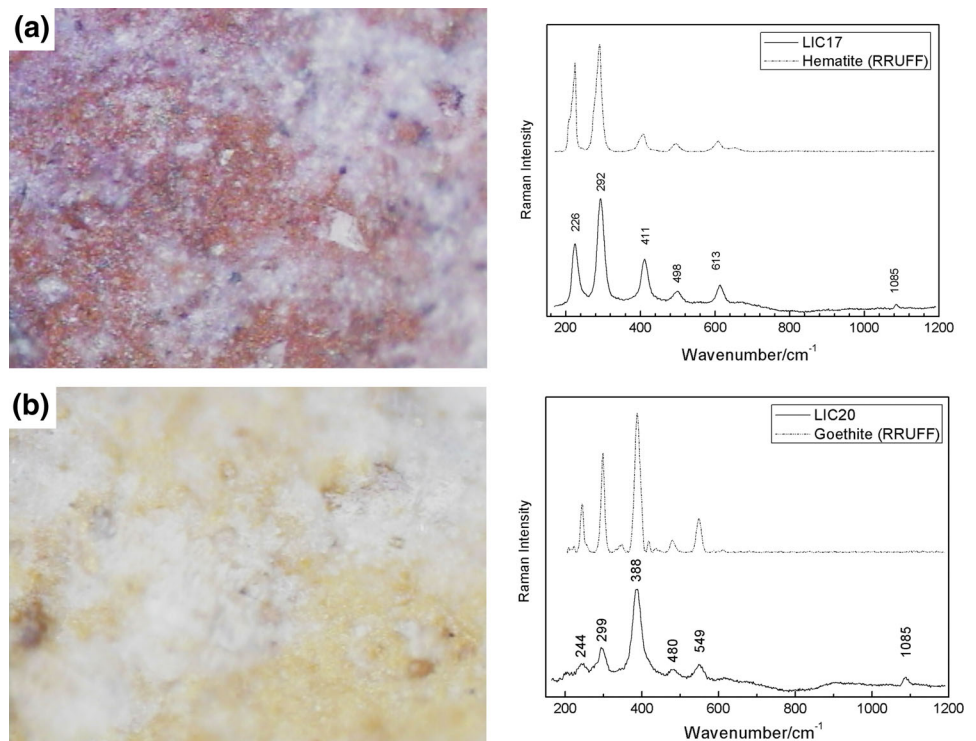
## 5 Discussions and conclusions

In the framework of the studies of wall paintings, information on raw materials and painting techniques are fundamental to support the archeological interpretation of ancient artifacts (Ajo et al. 2004; Mugnaini et al. 2006). In the present studies, the combined use of OM and SEM–EDS methods allow to light up both of these aspects. Referring to raw materials, on the basis of composition of aggregates identified in thin section, the presence of both sedimentary and metamorphic sub-rounded rock fragments, especially sandstone and bioclastic fragments, suggest a local supplying of raw materials, according to the geological formation outcropping in the area. In particular, a level compatible with observed aggregates through thin section analysis could be identified in the recent alluvial deposits widely

outcropping in the area (Olocene and Pleistocene Alluvial Fm.). About the binder composition, the average chemical composition and the low hydraulic index calculated suggest the use of a quite pure limestone as raw material. Finally, the presence of small amount of chlorides and sulfates both on the surface and in the preparation layers probably is imputable to degradation processes. About pigmenting agents, both chemical and spectroscopic analyses performed on colored surfaces suggest the use of red and yellow ochre (i.e., hematite and goethite, respectively, mixed with quartz sand and clay) for the red and yellow pigments, while the white one show a prevalently carbonate composition (e.g., S. Giovanni white pigment).

Considering the recent attempt finalized to supply objective criteria for distinguish among the most known painting techniques (Piovesan et al. 2012), OM and

**Fig. 7** Macrophotographs and Raman spectra collected on *red* (a) and *yellow* (b) plasters (color figure online)



SEM–EDS results have been used to obtain information on technological manufacture aspects. In particular, the presence of thin, homogeneous, well-defined pigment layers with quite regular dispersed pigment grains and the evidence of carbonation layers at painted-bedding and bedding-nucleus interfaces characterized by sharp boundaries at the contact (see Fig. 4), allow to identify in lime paint, the technique applied in the manufacturing of the colored wall painting analyzed.

In light of the previously, with the aim at highlighting the technological evolution of mural painting in south Sicily during the Hellenistic Age, a comparison between the obtained data and the archeometric information about other and less ancient painted fragments from Gela (Aquila et al. 2011) and different building in Licata (Aquila et al. 2012) have been also performed.

In detail, the common petrographic features in terms of aggregate and binder characteristic suggest a continuous use of the same raw materials over the time. Regarding the use of pigmenting agents, analytic data reveal the use of common calcite-based pigments both in Gela and Licata. However, even if the use of yellow and red ochre have been testified in all sites, differences can be observed in the yellow plasters from Gela and in the red ones from Licata; in fact, the presence of massicot and cinnabar have been also identified, respectively. These differences could be related to the most ancient production of plaster samples in the Apaforte hypogeum, in which only ochre pigments have been used (both yellow and red).

In conclusion, in the lack of literature about Hellenistic Sicilian painting, the present work contribute to the knowledge of the wall paintings production, supplying an overview on the production and manufacturing technique used by the craftsmen in south Sicily over the time.

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