A multi-analytical approach for the study of the pigments used in the wall paintings from a building complex on the Caelian Hill (Rome)

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Abstract In the present study, shards from Roman wall paintings (from the end of the first century to the fourth century A.D.) decorating the domus below the Basilica of SS. John and Paul on the Caelian Hill (Rome), were analyzed in order to identify the pigments used. The analytical techniques employed for the characterization of the pigments were the scanning electron microscope coupled with an energy dispersive spectrometer (SEM-EDS) and infrared spectroscopy (ATR and micro ATR). While SEM-EDS allowed to perform a qualitative analysis of the material, by FT-IR chemical species have been identified. The pigments identified were those mentioned in the literature for the Imperial Roman fresco painting: different types of ochre (yellow and red), mixtures containing lead, green earths and precious pigments such as cinnabar and Egyptian blue. They were often used as mixtures and the use of the most valuable pigments (cinnabar and Egyptian blue) were found in the most ancient rooms.

1 Introduction

The determination of the nature of the pigments used for the realization of ancient wall paintings is one of the most important issues in the field of the characterization of painting techniques by means of archaeometrical methodologies.

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M. de Vos · M. Andreoli Dipartimento di Lettere e Filosofia, Università degli Studi di Trento, via Tommaso Gar, 14, Trento, Italy Chemical analyses contribute from one hand to define the palette of pigments available locally, and from the other hand to understand and define the techniques used for the realization of the paintings.

The use of pigments in works of art dates back to prehistoric times. Since the oldest times, pigments in fact have been used by man for the decoration of tools, for the realization of paints, and for personal use (for example, in the formulation of cosmetics). The colored earths, such as yellow, red and brown ochre, and calcite, were abundant everywhere in sedimentary deposits; the black color (as soot or coal) could easily be found in fireplaces. Less available were the ores containing heavy metals (malachite, azurite, lapis lazuli, and cinnabar): These pigments were considered precious or semi-precious and their use was limited only to certain regions. Finally, there were the artificial pigments: An example is represented by the Egyptian blue, a silicate of copper and calcium already produced in 3000 B.C. [1].

In regard to the use of pigments in Roman times, ancient works such as *De Architectura* by Vitruvius (before the Augustan age) and Pliny's *Naturalis Historia* (first century A.D.) provide an invaluable contribution to the knowledge of the pigments used in Roman paintings. A rather complete discussion on the nature of the pigments used at Roman times is reported in the scientific literature [2–4] and this subject is always of great interest as evidenced by the most recent literature [5–7].

The samples analyzed in the present work belong to wall paintings from the archaeological area conserved under the Basilica of SS. John and Paul Giovanni e Paolo, on the West slope of the Caelian Hill at Rome. The earliest archaeological traces were found in 1658 in the garden next to the church, but the discovery of the first painted environments dates back to 1887, when Father Germano S. Stanislaus, rector of the Basilica, descending from an opening, dug in the floor of the church in search of the tomb of the martyrs, and found these vast underground vaults. Between 1913 and 1914, Father Lambert performed the excavation of the socalled *Confessio*, in which it was thought might be the remains of two martyrs. The investigation resumed, between 1948 and 1951, in the area under the left nave of the Basilica. Here, during the excavations, a large painting of Flavian time was discovered.

The area preserves remains of walls belonging to different building phases. The stratigraphy includes a late Flavian wall painting (end of the first century A.D.), a painting of the middle of the second century A.D., remains of a balneum of the second century A.D., a whole commercial insula of Severan period (192–235 A.D.), modified between third and fourth century A.D. in a private domus, further the transformation of the house into church and the erection of the Basilica in the fifth centrury. The studied samples belong therefore to six building phases from different rooms of the "Case Romane" on the Caelian Hill.

The samples in this study come from different rooms of the Roman *domus* on the Caelian Hill, and date back to different historical phases. In order to identify the pigments palette used by the ancient artisans, two techniques were employed in a synergic way: scanning electron microscope coupled with an energy dispersive spectrometer (SEM-EDS) and infrared spectroscopy (FT-IR) in both ATR and micromode.

The analysis of the elemental composition of samples belonging to historical artifacts (from fresco to ceramics) can be performed by both quantitative (such as ICP-OES or ICP-MS) or qualitative/semiquantitative techniques (such as SEM-EDS) [8–11]. Quantitative analysis allows sometimes to discriminate the raw material provenance [7, 11] or to dif-

Fig. 1 Sala dei Geni (Ambiente 7), *domus* on the Caelian Hill (Rome), East wall, and South lunette (Photo from Archivio SAR) [2] ferentiate quite similar minerals (such as, for example, glauconite and celadonite [7]). Nevertheless, the main drawback is represented by the fact that these methods are destructive. On the contrary, the advantage in the microchemical analysis of decorated surfaces of EDS [12], or of other more sensitive techniques (such as PIXE), [13] is that they leave the sample intact, a fundamental aspect in the case one wants to perform other analyses or if the material is precious. In regard to the shards studied in this work, only a qualitative analysis by SEM-EDS was possible, mainly because of the very low sample quantities available. In this way, the sample has been preserved for FT-IR measurements. The information acquired by EDS and FT-IR have allowed in most cases to define the chemical nature of the pigment.

The rich palette identified is that typical of the Imperial Roman period and includes both single pigments and mixtures of two or more substances to obtain certain particular shades.

2 Experimental

2.1 The samples

The samples examined in this study refer to different colors (formed by the surface pigment and sometimes the underlying plaster), always of small sizes (average few mm but in some case even smaller) collected from the frescoes under the *domus* below the Basilica of SS. John and Paul on the Caelian Hill in Rome (see Fig. 1). These rooms were attributed to successive historical phases: Domitianic period (81–96 A.D.), Hadrian's time (117–138 A.D.), the Severan dynasty (192–235 A.D.), end the Flavian Age (69–96 A.D.),



Age of Hadrian (117–138 A.D.), Age of the Severi (192–235 A.D.), end of the third, beginning of the fourth century, second half of the fourth century.

Altogether 18 painted rooms were examined for a total of approximately 90 samples of pigments analyzed and characterizing the entire chromatic range employed. In Fig. 1, an image of the *Sala dei Geni* is shown.

2.2 The analytical techniques

The chemical composition of the samples was investigated using an electron microscopy coupled to an energy dispersive system spectrometer (SEM-EDS). The instrument used is a microscope Stereoscan 420 Leica (Cambridge). The spectra were acquired on both fragments covered by a graphite layer in order to make the surface conductive and on polished cross sections obtained incorporating the samples in epoxy resin. On these sections, it has been possible also to acquire X-ray fluorescence maps to study the elements distribution.

The infrared spectra were collected with a spectrophotometer Nicolet 380 (Thermo Electron Corporation) equipped with ATR accessory Smart Orbit and interfaced with a microscope FT-IR Nicolet Centaurus. The ATR accessory is equipped with a crystal diamond while on the microscope it is possible to mount an accessory with a silicon crystal (μ ATR). The ATR technique was used to analyze small amounts of dust drawn from samples surfaces using a scalpel.

3 Results and discussion

The area of the Roman domus on the Caelian Hill has long been the focus of much interest and controversial discussions, especially for the Christian meaning attributed to some preserved paintings. In recent years, the Superintendence of Archaeological Heritage of Rome has worked a lot for the restoration and comprehensive study of the complex [14]. These Roman *domus* certainly cannot be considered a complex of easy reading. As said in the introduction, the conserved building belong to a long historical period (from the first to the fifth centuries A.D.) A total of about 90 shards representative of the entire range of colors used during the centuries has been examined (a more detailed descriptions of the samples collected in each different environment is reported in [14]). Some preliminary results have been already published by these authors [15]. In the present paper a larger number of samples has been considered and numerous examples are discussed. The pigments palette used for the decoration of the wall paintings present in the different rooms is formed by a rich variety of colors (red, yellow, blue, green, etc.) present in different shades obtained by diluting with white pigments or by mixtures. In Table 1, an overview of the most representative pigments identified by the synergic use of SEM-EDS and FT-IR is shown.

The two techniques employed have allowed to obtain results that often are complementary. Not always FT-IR data are shown in the table because for different reasons. In fact, some species such as cinnabar or minium, do not absorb in this region while, for example, ochre shows signals (at about 470 cm⁻¹) that overlap with absorption peaks of other species (furthermore, in the case of μ ATR, there is a limit due to the specific detector at 650 cm⁻¹.) Finally, in some cases, the sample quantity was not enough.

The pigments employed in almost all cases were those mentioned in the two ancient treatises Vitruvius' *De Architectura* and Pliny's *Naturalis Historia* (first century A.D.) and identified by modern analytical techniques [2–4].

The pigments of the classical age were of two types: natural colors or artificial colors and are mainly consisting of oxides, carbonates, and various minerals.

3.1 Red, yellow, orange, and brown pigments

For yellow and red colors, an extensive use of ochre has been found. They are naturally occurring pigments whose color is given by the different degree of hydration of the iron oxide contained therein: Usually red ochre is composed of pure hematite (Fe_2O_3), while the yellow is obtained by limonite and goethite (oxides of iron hydrates, Fe₂O₃·H₂O and α -FeO (OH)). By SEM-EDS, these pigments can be identified by the presence of iron, although with these analyses it is not be possible to discern the crystalline phases or the degrees of hydration. The name "earth" is attributed when the red pigment has some clay impurities, i.e., when you are not in the presence of pure oxide. Minium (Pb_3O_4) was also employed to obtain red, sometimes mixed with red ochre to obtain a pigment named sandix or syricum (see Cella Vinaria, Table 1) [3]. In some environments (In Abside, Menadi, and Orante, Table 1), the red color has been obtained by using a precious pigments such as cinnabar (HgS). In the oldest of these three rooms (In Abside of the Hadrian era, half of the second century), three different red (sandix/syricum, cinnabar, and red ocher mixed with cinnabar) are present to indicate a careful choice in the use of color.

In the red sample M1 (*Menadi*, Table 1), a pigment applied in recent times is present: It has been identified as cadmium red, a color made up of artificial cadmium sulphose-lenide (CdS (Se)), used only since the twentieth century [16] and applied during a repainting.

The yellows were obtained using yellow ochre probably obtained by using the mineral limonite, $Fe_2O_3 \cdot nH_2O$. Also, in this case, mixtures were also applied: for example, in *Menadi*, an orange has been identified as ochre plus Table 1Some examples of
pigments identified in the
Roman building complex on
Caelian Hill and describing the
entire palette used; for each
environment the results of both
SEM-EDS and FT-IR analysis
are reported together with the
pigment identified and the
sample name

Room	SEM-EDS	FT-IR
Affianco Geni	<i>Glauconite</i> (AG2, light blue) Na, Mg, Al, Si, low: Ca, Fe, P, S, K, Ti	
Arieti	<i>Calcite</i> (A4, white) Ca, low: Al, Si, S	Calcite
Cella Vinaria	Green earth + Egyptian blue (CV3, blue) Al, Si, K, Ca, Fe, Mg, Cu Red ochre + minium (CV4, red) Al, Si, Ca, Fe, Pb, low: Mg, K Egyptian blue + cinnabar (CV6, violet) Si, Ca, Cu, S, Hg	
Confessio	Calcite (C1, white) Al, Si, Ca, Iow: Fe, K, S, P Celadonite (C3, green) Mg, Al, Si, Ca, Fe, Iow: K, Ti Azurite and malachite (C5, light blue)	Calcite
Corridoio	Al, Si, Mg, Ca, Fe, Iow: 11, Cr <i>Green earth</i> + <i>ochre</i> (CO2, blue) Na, Al, Si, S, Ca, Fe, Iow: P, K, Pb, Cr <i>Red ochre</i> (CO5, red) Mg, S, Al, K e Si, Ca, Iow: Na, Ti, Fe, Mn <i>Yellow ochre</i> (CO6, yellow)	Copper carbonate Green earth + gypsium + caolinite
	Al-Si, Ca, Fe, low K, traces: Sr	Calcite + silicates (quartz)
Geni	Brown earth + red earth (G5, blue) Mg, Al, Si, K, Ca, Fe, Pb, Hg S, low Ti Glauconite (G3, green) Na, Mg, Al, Si, K, Ca, Fe Cinnabar + Egyptian blue (G4, red) Si, Ca, Cu, S, Hg	Glauconite
Menadi	<i>Cadmium red</i> (M1, red) S, Se, Cd, Fe, Ca, Si, Al <i>Yellow ochre</i> + <i>cinnabar</i> (M2, red) Ca, Si, Al, Fe, Hg, S <i>Calcite</i> (M3, white) Ca, Si, Al, Ba, S, low: K, Fe <i>Yellow ochre</i> (M4, yellow) Ca-Si-Al, S, low: Fe, Mg e K <i>Glauconite</i> (M5, green) Na, Mg, Al, Si, Ca, P, S, K, low: Ti, Mn, Fe	
In Abside	<i>Red ochre</i> + <i>minium</i> (IA3, red) Al-Si, S, Ca, Fe, Pb, K <i>Red ochre</i> + <i>cinnabar</i> + <i>Egyptian blue</i> (IA4, Al-Si, P, S, Ca, Hg, K, Fe, low: Mg, Cu <i>Cinnabar</i> (IA2, red) Hg, S, Ca	Silicate + animal glue; sulphatation blue on a red layer) Egyptian blue

Pittura Flavia

Si-Al, S, Ca, Fe

Si, Ca, Cu

Egyptian blue (PF2, light blue)

 Table 1 (Continued)

Room	SEM-EDS	FT-IR	
Lato Abside	<i>Red ochre</i> (LA2, red) Al-Si, K, Ca, Fe <i>Yellow ochre</i> (LA3, yellow) Si, Al, Ca, Fe, low: K		
Scala	Celadonite + Naple yellow (SC1, green) Al, Si, Ca, Mg, K, S, Fe, Mn, Ti, Zn, Pb, Sb Naple yellow (SC5, yellow) Pb, Sb, low: Al, Si, Cl Fe, K		
Ninfeo	<i>Egyptian blue</i> (N1, dark blue) Ca, Si, Cu, low S, Al, K <i>Calcite</i> (N2, white) Al, Si, Ca, low: Fe, S	Egyptian blue; sulphatation Clay mineral (montmorrilonite) + animal glue	
	<i>Yellow ochre</i> + <i>minium</i> (N3, yellow) Al, Si, Ca, Fe, Pb, low: Mg, P, K e Ti	C.	
Orante	Red ochre (AO3, red) Al, Si, Ca, Fe <i>Yellow ochre</i> + <i>Cinnabar</i> (AO4, red) Ca, Si, Al, S, Fe, Hg	Iron silicate	
Sala Pannelli	<i>Minium</i> + <i>red earth</i> (SP1, red) Na, Mg, Al, Fe, Si, S, K, Ca, low: Ba, Cr, Pb <i>Yellow ochre</i> (SP2, yellow) Al, Si, S, K, Ca, Fe, low Mg		
Stanzetta Stretta	Green earth + brown earth (SS3, dark brown/green)		
	Al, Si, S, K, Ca, Fe, low Mg	Silicates (caolinite)	
Pelte	Red ochre (P2, red)		

cinnabar while in Nymphaeum orange was obtained from ochre and minium. As already discussed [15], an interesting case is represented by the Scala where Naples yellow, a lead antimonate $(Pb_2Sb_2O_7)$, was used. The brown tones were realized through the use of brown earth (alumino-silicates ferrous) sometimes containing manganese. The white pigments generally have been obtained by calcium carbonate, (CaCO₃) [15]; this pigment was often used as lightening to obtain particular shades.

3.2 Blue pigments

The blues have been obtained mainly using the precious pigment Egyptian blue, an artificial polycrystalline compound whose main component, responsible for the color, is a tetra silicate of calcium and copper, CaCuSi₄O₁₀ often identified as cuprorivate [17]. The production technique of Egyptian blue was described in the first century A.D. by Vitruvius: his writings tell in detail how the pigment (coeruleum) is formed as a result of a firing in a furnace ("due to the vehement heat") of small parts consisting of copper, fine sand, and nitro, previously ground and moistened. It has been identified as pure pigments in: (1) the oldest painted wall of the archaeological complex, dating probably to 81-96 A.D. (Emperor Domitian); (2) paintings of the Nymphaeum (late third or beginning of the fourth centuries A.D.), realized during the transformation of a commercial insula into a private house (in this case the use of this pigment attests the social status of the owner); (3) In Abside dating to the Hadrian's era (mid second century) and within one of the most ancient frescoes of the complex. In Fig. 2a, an image of a polished cross section obtained on sample PF2 (Pit-

Calcite + iron aluminium silicates



Fig. 2 Image of a polished cross-section of blue sample PF2 ($15 \times$) (**a**); EDS spectrum acquired on the *blue* grains (**b**); an area of the polished cross-section at higher magnification ($95 \times$) (**c**); BSE image of the same area (**d**)

tura Flavia, Table 1) is shown together with a magnification (Fig. 2b) where the pigment blue grains, whose composition is shown in Fig. 2c, are mixed with calcium carbonate. The presence of the grains are evidenced also by the BSE (back scattered electrons) image (Fig. 2d) where they appear lighter.

In the case of sample IA4 (*In Abside*, Table 1), formed by a blue layer superimposed to a red one (identified by EDS as cinnabar), the identification of Egyptian blue was carried out by means of μ ATR on the polished cross-section (Fig. 3).

In the IR spectrum, the peaks at 1003, 1080, and 1160 cm⁻¹, and the shoulder at 950 cm⁻¹ are due to Si– O–Si linkages characteristic of Egyptian blue. The absorptions due to calcite and aragonite are also present. These two species both show a wide peak at 1416 cm⁻¹ but can be distinguished thanks to the diagnostic peaks at 872 and 712 cm⁻¹ for calcite and at 853 and 699 cm⁻¹ for aragonite. The latter is the most valuable being extracted from shells of marine origin [18]. In accordance with what reported by other authors [18], this pigment has been used to dilute Egyptian blue to obtain a lighter tone.

Finally, in regard to the blue colors only in one case (*Confessio*, Table 1) it has been obtained using azurite, a basic copper carbonate. This pigment, identified by FT-IR as

shown in our previous work, has partly transformed into malachite [15].

Egyptian blue has been in some cases mixed with a red ochre as in the case of the red sample G4 (*Geni*, Table 1). As it is evident from the image obtained on the polished cross section (Fig. 4a), blue grains are mixed with a red pigment identified as ochre (Fig. 4b). The X-ray fluorescence map has allowed to put in evidence the distribution of iron (Fig. 4c), copper (concentrated in some grains in Fig. 4d and which appear as black spots in Fig. 4c) and silicon (Fig. 4e), whose distribution exactly corresponds to that of copper. EDS spectrum acquired where Cu and Si are both present confirms the presence of Egyptian blue (Fig. 4f).

To obtain a violet nuance a higher quantity of Egyptian blue (with respect to the case of sample G4 previously described where only few grains were present), has been mixed with cinnabar, as in the case of sample CV6 (*Cella Vinaria*, Table 1, Fig. 5). The use of this particular mixture is also attested in the Pompei's frescos [4].

An alternative solution adopted to obtain a blue nuance, as in the case of sample G5 (*Geni*, Table 1, Fig. 6a), is mixing earths of different colors. From the image of the sample cross section (Fig. 6b), the presence of two or more compounds is evident. In fact, brown earth (whose marker is

Fig. 3 IR spectrum acquired on blue sample IA4 showing the signals due to Egyptian blue



manganese, Fig. 6c) and red ochre (Fig. 6d) have been identified by SEM-EDS.

3.3 Green pigments

The green colors were often obtained by green earths, which are formed by the two minerals celadonite and glauconite [19–21], having a quite similar composition and for this reason hardly distinguishable. In fact, often in the literature no distinction is made between the two phases, and they are indicated generically as green earths. These pigments were well known at Romans time and Pliny refers to them as *creta virdis*. The most valuable pigment was formed almost exclusively by celadonite and came from Monte Baldo, near Verona (Northern Italy). Celadonite (or earth of Verona) has the mean chemical formula $K(Mg, Fe^{2+})(Fe^{3+}, Al)(Si_4O_{10})(OH)_2$ and is characterized by a blue nuance; glauconite has the mean chemical formula (K, Na)(Fe³⁺, Al, Mg)₂(Si, Al)₄O₁₀(OH)₂ and shows a more yellowish tone. Depending on the quarry, the color, and hence the composition could vary. In particular, it can vary from bluish (higher ratio FeII/FeIII) to more yellowish (lower ratio FeII/FeIII). Also, other clay minerals such as montmorillonite ((Na, Ca)_{0.3}(Al, Mg)₂Si₄O₁₀ $(OH)_2 \cdot n(H_2O)$, chlorite ((Fe, Mg, Al)₆(Si, Al)₄O₁₀(OH)₈) or kaolinite $(Al_2Si_2O_5(OH)_4)$ can be included in the group of green earths. Therefore, a green earth could be formed by a single phase (celadonite or glauconite), a mixture of the two or a more complex mixture containing also others minerals. The identification of the minerals present is hardly performed; however, taking into account both elemental composition and features of IR spectra, it is sometimes possible to distinguish the two phases [7, 22].

Regarding the green samples coming from the *domus*, we have identified in three cases glauconite, in two cases celadonite, and in some other cases generically green earths formed by a mixtures of two or more phases (Table 1).

In Fig. 7a, it is shown the EDS spectrum acquired on sample M5 identified as glauconite, following [22], because of the low ratio Mg/Al and the presence of Na. Sample C3, whose spectrum is shown in Fig. 7b and having a high Mg/Al ratio, corresponds to celadonite.

Nevertheless, in most of the cases, it is not possible to identify the pigment only on the basis of EDS analysis. Looking at FT-IR spectra, celadonite shows two main peaks at 1018 and 979 cm^{-1} (stretching of the silicate) while glauconite is characterized by a broad band centered at 1030–1000 cm^{-1} [7]. Analyzing a sample of green earth from Monte Baldo, we have identified mainly celadonite even if glauconite could not be excluded [15]. Nevertheless, other authors analyzing a green earth coming from the same quarry have only identified celadonite [7]. So, simply depending on the point where the sample is taken in the quarry, its composition can slightly vary. In the case of sample G3 (Fig. 8) the pigment has been identified by the IR spectrum as glauconite due to the wide absorption at about 1030 cm^{-1} (on the base of the relative peaks intensity in the EDS spectrum, it was not possible to do any certain assumption). In another case (sample SS3), a generic green earth has been employed since in the IR spectrum, in addition to the signals of calcite, it has been identified the presence of caolinite (or a mineral phase quite similar). In one case, a mixture green earth/Egyptian blue has been found (sample CV3).



5



e

p



Fig. 5 EDS spectra acquired on violet sample CV6, a mixture of Egyptian blue (a) and cinnabar (b)



Fig. 6 Image of the blue sample G5 (15×) (a); a polished cross-section (95×) (b); EDS spectra acquired on a brown area (c) an on a red area (d)



Fig. 7 EDS spectrum acquired on green sample M5 identified as glauconite (a), and on green sample C3 identified as celadonite (b)

Fig. 8 IR spectrum acquired on green sample G3 showing the signals due glauconite



4 Conclusions

An investigation on pigments from different buildings on the Caelian Hill (Rome) has been carried out in order to identify the chromatic palette employed during the different phases through the centuries. In fact, this area is characterized by a complex stratigraphy dating from Domitianic era (81–96 A.D.) to the early fifth century A.D. Eighteen different painted walls were considered for a total of about 90 samples. The basic pigments identified were 10: red ochre, yellow ochre, calcite, aragonite, Egyptian blue, azurite, brown earth, cinnabar, minium, and green earth. In Fig. 9, the frequency with which the five more abundant basic colors are present (on the total of the examined pigments) is reported.



Fig. 9 Frequency with which the 5 more abundant basic pigments have been employed in the building complex on the Caelian Hill

The most precious pigments (cinnabar and Egyptian blue) have been employed only in a few cases and mainly during the most ancient periods. The identification of these valuable materials made it possible to date back some rooms: materials confirmed for example the antiquity of the Cella Vinaria where both cinnabar and Egyptian blue have been detected (Hadrian's time). In addition to the basic pigments, 13 more shades were obtained mixing them. The wide variety of colors that has been employed attests the interesting pigment assortment of these wall paintings.

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