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## Multi-technique investigation of Roman decorated plasters from Villa dei Quintili (Rome, Italy)



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### ABSTRACT

In the present study, we investigated by the joint use of portable instrumentations, namely a handheld X-ray fluorescence (XRF) analyser and a portable Raman spectrometer, the painted surface of plasters withdrawn from different areas of an important Roman monumental complex, known as *Villa dei Quintili* (Rome, Italy), dated back to the first half of the 2nd century a.C. XRF and Raman measurements contributed to the identification of the pigments through the elemental and molecular composition, respectively. In particular, the multi-technique non-invasive approach proved to be crucial for distinguishing two different reddish pigments. In order to confirm and integrate XRF and Raman results, two micro-destructive laboratory methods, namely optical microscopy (OM) and scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS), were also employed on the same samples. All the experimental results shed light on the material characterizing the painted surface layer and the painting methodologies, providing in principle useful information for proper restoration processes. It is worth underlining that this experimental investigation takes part of a recent multidisciplinary study performed on this impressive archaeological site, aimed to characterize for the first time the monumental complex from an archaeometric point of view.

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### 1. Introduction

As is well established, the archaeometric research in cultural heritage is a multidisciplinary work. Therefore, a complete and correct investigation needs to join different points of view and several qualified expertise, ranging from chemistry to physics, from geology to biology. The archaeological considerations are important to classify the aesthetic style of an artwork and hypothesize the possible historical and geographical context in which it has to be framed. This approach helps to understand the meaning and the sense of the

object in the artist's mind, in order to point out the problem we are requested to solve. Nevertheless, the scientific investigation allows to unambiguously characterize the materials and provides information about the manufacture techniques, the production site, the historical age of the artefact.

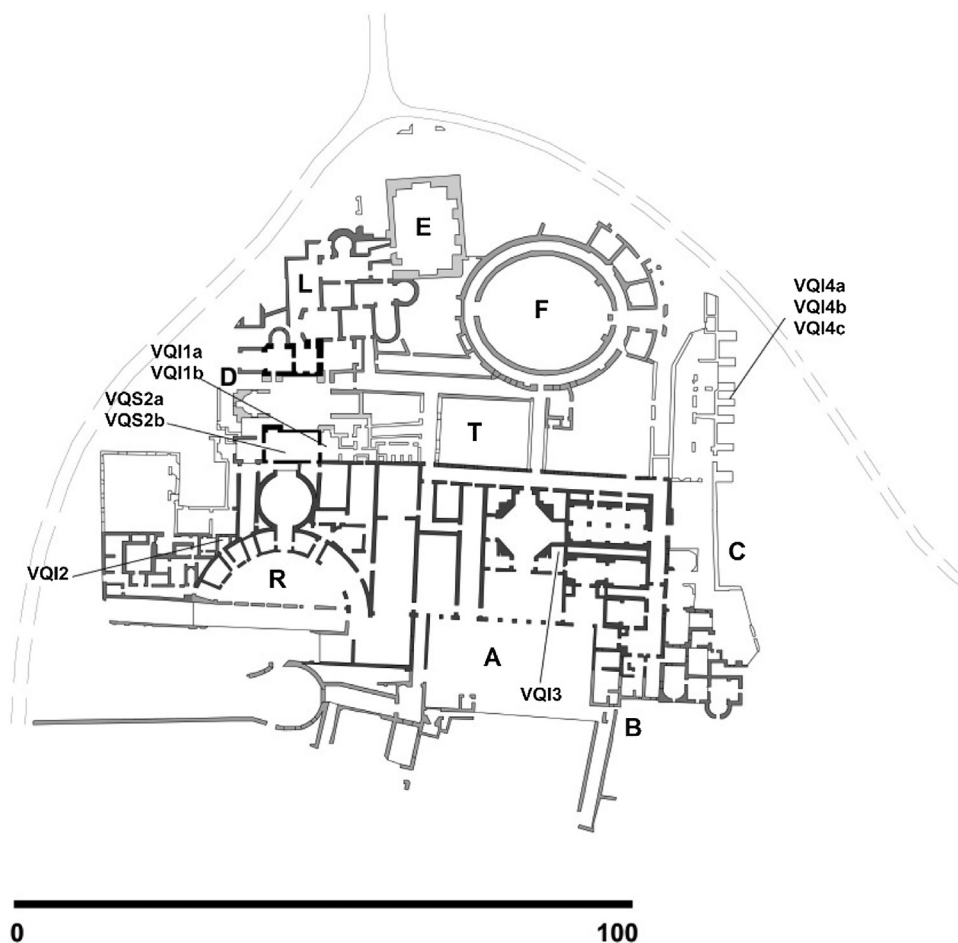
Again, the artwork can exhibit different types of decorations with various colours, as artistic and cultural expressions. The characterization of materials and methods used for the preparation of colouring substances is mandatory to carry out a correct classification of artworks, since pigments composition and production techniques reflect both art and technology development available to the craftsmen and peculiar of a population, settled in a geographical region and located in a particular historical age.

It is rather difficult to establish a general methodological approach for the identification of the pigmenting agents on ancient

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**Fig. 1.** Plan of the Villa dei Quintili and details of the sampled areas. Notes: A = representation area; B = private residences; C = Basis Villae; D = Frigidarium; E = Calidarium; F = Ludus-Viridarium; L = Tepidarium; R = Hippodrome; T = Arcades.

artefacts, so often the choice of the analytical techniques depends on the substrate on which the pigments are laid. In the last decade, various multi-technique studies [1–7], based on a combination of information from non-destructive and micro-destructive investigations were devoted to the analysis of pigmenting agents on different artworks, including paintings, pottery, plasters and manuscripts. Recently, a number of portable and handheld instrumentations have become commercially available, enabling in situ measurements, in a museum or in archaeological excavations, as examples. So, the use of these kinds of equipment in the study of archaeological findings is increasing more and more [8–10].

In the present work, we report a spectroscopic study performed on painted surfaces of ancient Roman plasters and stucco fragments collected from a relevant archaeological site known as Villa dei Quintili, in Rome (Italy), dated back to the first half of the 2nd century a.D. [11]. Actually, few archaeometric studies have been carried out on this renowned site. Recently, a multi-analytical approach, including polarized optical microscopy, scanning electron microscopy coupled with energy-dispersive system and laser ablation inductively coupled plasma mass spectrometry, was used to analyze the pozzolanic material used for the preparation of mortars collected from several buildings into the complex. The results of such a multidisciplinary approach allowed to recognize the use of three different pozzolan types for the aggregate fraction of examined mortars, namely “Pozzolana rossa”, “Pozzolana Nera” and “Pozzolanelle”, widely used by Roman builders during the Imperial age and all of which erupted from the Alban Hills volcanic district [12].

Here, for the first time an analytical approach is employed in order to study the painted surface of plasters from this monumental site. The focus of the study is to determine the elemental and structural composition of the painted layer, in order to identify the pigments and the materials used for the wall decorations. We used two totally non-destructive spectroscopic techniques: X-Ray Fluorescence (XRF), using a handheld energy-dispersive XRF analyser, and Raman spectroscopy, using a portable spectrometer. The portable designs of the used instruments permitted to collect easy and quick data on the investigated fragments. In particular, XRF measurements allowed us to individuate elemental major and minor constituents of the painted surface of the samples, while Raman analysis provided the molecular nature of the used pigments. In addition, in the present work the obtained data were integrated and supported by measurements through two micro-destructive laboratory techniques, including optical (OM) and scanning electron microscopy, this latter coupled with energy-dispersive X-ray spectrometry (SEM-EDS). Microscopic observations by OM were performed in order to define the textural characteristics of the samples substrate, while morphological observation and elemental characterization of the superficial layers have been carried out on thin-sections by SEM-EDS.

## 2. Experimental details

### 2.1. Materials and sampling

Villa dei Quintili, located in the south-eastern part of Rome, represents one of the greatest evidence of the Roman architecture. The

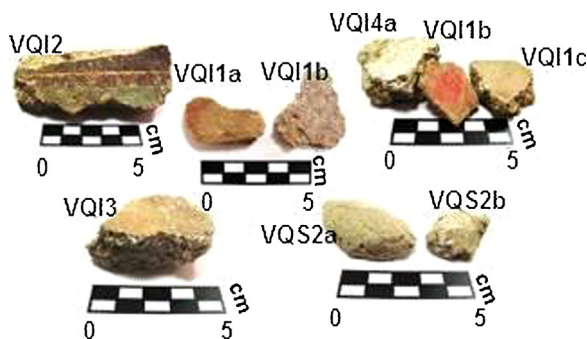


Fig. 2. Photographs of analyzed archaeological fragments.

monumental complex dates back to the first half of the 2nd century a.D. and was owned by the Quintili brothers, Sesto Quintilio Condiano and Sesto Quintilio Valerio Massimo. The villa was the imperial residence of several emperors and was in use until the 6th century a.D.; only in 1985, it became a state-owned property [13].

The main structures of the villa, displayed in Fig. 1, include: (a) the residential area, which represents the main nucleus of the villa, divided into public and private zones; (b) the thermal environments, comprising three different areas: Calidarium, Frigidarium and Tepidarium; (c) the service sector of the villa, namely the basis villae, consisting of several rooms used by the servants; (d) the Ludus/Viridarium, a structure firstly used as a small amphitheatre for gladiatorial games and later changed to a panoramic garden; (e) the Hippodrome, a second garden with statues, fountains and sculptures, of about 400 m length and between 90 and 115 m wide, whose name derived from the typical shaped hippodrome; (f) the Arcades, porticoes gardens with baths and fountains decorated with painted plaster and connected by several corridors and ramps; (g) the Nymphaeum, a monumental fountain which probably represented the original entrance to the villa from Appia Antica road. A straight portico (Xystus) connected the residential sector to the Nymphaeum [14].

Nine construction phases, characterized by different building techniques, have been identified by archaeologists within the monumental complex, ranging in a wide time period starting from 98–138 A.D. (Trajan–Hadrian) up to Middle and Modern Ages [15]. The archaeological importance of the villa is mainly related to the high quality of the building and decorative materials, particularly fine marble from around the world. The ornamental elements of the floors generally consist of opus sectile and polychrome mosaics, whereas marble, frescoes and mosaics were used for the walls.

We investigated nine fragments of plasters and stucco (Fig. 2), collected from different decorative elements of the monumental complex of Villa dei Quintili. The sampling phase was carried out, according to the NORMAL 3/80 [16] with the support of archaeologists from the Archaeological Superintendence of Rome. The list of the samples is given in Table 1.

## 2.2. Non-destructive techniques: XRF and Raman scattering

XRF measurements were carried out by the handheld XRF spectrometer 'Alpha 4000' (Innov-X System), equipped with an X-ray tube with Ta anode and a high-resolution Si PIN diode detector (FWHM < 220 eV at 5.95 keV for Mn K $\alpha$  line). Two sequential tests were performed on each sample. In particular, the operating conditions were 40 kV and 7  $\mu$ A for the first run and 15 kV and 5  $\mu$ A for the second one. Fluorescence signal was collected for a time of 60 s for each test. By the analysis of the XRF spectra, elements from P to Pb were detected.

Raman spectra were collected by the portable 'MiniRamTM' (B&W TEK, USA) spectrometer using an excitation wavelength

Table 1

List of investigated fragments, together with their macroscopic features and the indication of provenance area.

Sample	Description	Provenance area
VQI1a	Fragment of plaster with reddish finishing layer	R54
VQI1b	Fragment of plaster with reddish finishing layer	R54
VQI2	Fragment of plaster with 3 finishing layers: reddish-brown, green and light yellow	R6
VQI3	Fragment of plaster with two reddish-brown finishing layers	A5-A6
VQI4a	Fragment of plaster with whitish finishing layer	Basis Villae
VQI4b	Fragment of plaster with reddish finishing layer	Basis Villae
VQI4c	Fragment of plaster with reddish finishing layer	Basis Villae
VQS2a	Fragment of stucco with whitish finishing layer	R53
VQS2b	Fragment of stucco with whitish finishing layer	R53

of 785 nm (diode laser), ~280 mW maximum laser power at excitation port, and Charge Coupled Device (CCD) detector (Thermoelectric Cooled, TE). The system is equipped with a fibre optic interface for convenient sampling. All the spectra were registered in the wavenumber range from 60 to 3150  $\text{cm}^{-1}$ , accumulating several scans for each spectrum to improve the signal-to-noise ratio. The experimental spectra were compared with those from various database [17–20].

## 2.3. Micro-destructive techniques: OM and SEM-EDS

The microscopic observations were carried out through polarized optical microscopy (OM), performed with a Zeiss Axiolab microscope (equipped with a digital camera to capture images), on polished thin sections. In addition, morphological analysis and elemental composition of the superficial layers have been performed on thin-sections by using a FEI Quanta 200F (Philips) SEM-EDS. Operating conditions were set at 20 kV accelerating voltage, 0.2 nA beam current, 100 s acquisition time and 30–35% dead time. All the measurements were collected under high vacuum conditions ( $10^{-8}$  mbar pressure), working in energy-dispersive spectrometry, with an ultra-thin Be window to ensure lower detection limits (of the order of 0.1%) for all analyzed elements.

## 3. Results and discussion

Firstly, we will discuss the results obtained from the extensive surface investigation performed through the joint use of non-destructive methods by portable instrumentations, i.e. XRF and Raman analyzers. Afterwards, in order to provide a full characterization of the samples, we will integrate these results with those furnished by micro-destructive investigation using OM and SEM-EDS analyses.

### 3.1. XRF analysis

As first step, portable XRF measurements were performed in order to achieve the qualitative chemical composition of all the investigated samples. As is well known, XRF is an elemental non-destructive technique, widely employed in archaeometry in order to obtain an indirect identification of pigment mixtures through the evidence of key elements. In this work, the XRF data were collected on various painted areas of the surface of each sample. The

**Table 2**

Elements detected by XRF analysis. The minor or trace elements are presented between brackets. The main key-element for pigment identification is marked in bold.

Sample	Description of analyzed sample	Detected elements
VQ11a	Reddish finishing layer	Ca, Fe, Sr, <b>Hg</b> (S, K, Ti, Cr, Mn, Zn, Se, Rb, Zr, Ba, Pb)
VQ11a	Back of fragment	Ca, Fe, Sr (K, Ti, Cr, Mn, Zn, Rb, Zr, Ba, Pb)
VQ11b	Reddish finishing layer	Ca, <b>Fe</b> , Sr (K, Ti, Cr, Mn, Cu, Zn, As, Rb, Zr, Ba, Pb)
VQ11b	Back of fragment	Ca, Fe, Sr (K, Ti, Cr, Mn, Cu, Rb, Zr, Ba, Pb)
VQ12	Reddish-brown finishing layer	Ca, <b>Fe</b> , Sr (K, Ti, Cr, Mn, Cu, Zn, As, Rb, Zr, Pb)
VQ12	Greenish and light yellowish finishing layers	Ca, <b>Fe</b> , Sr (K, Ti, Cr, Mn, Cu, Zn, As, Rb, Zr, Ba, Pb)
VQ12	Back of fragment	Ca, Fe, Sr (K, Ti, Mn, Cu, Zn, Rb, Zr, Ba, Pb)
VQ13	Reddish-brown finishing layers	Ca, <b>Fe</b> , Sr (K, Ti, Cr, Mn, Cu, Zn, As, Rb, Pb)
VQ13	Back of fragment	Ca, Fe, Sr (K, Ti, Mn, Cu, Zn, Rb, Zr, Ba, Pb)
VQ14a	Whitish finishing layer	<b>Ca</b> , Fe, Sr (S, K, Mn, Zn, As, Ba, Pb)
VQ14a	Back of fragment	Ca, Fe, Sr (K, Ti, Mn, Co, Cu, Zn, Rb, Zr, Ba, Pb)
VQ14b	Reddish finishing layer	Ca, Fe, Sr, <b>Hg</b> (S, K, Ti, Mn, Zn, Se, Rb, Zr, Ba)
VQ14b	Back of fragment	Ca, Fe, Sr (K, Ti, Mn, Zn, Rb, Zr, Ba)
VQ14c	Reddish finishing layer	Ca, Fe, Sr, <b>Hg</b> (S, K, Ti, Cr, Mn, Cu, Zn, As, Se, Rb, Zr, Ba, Pb)
VQ14c	Back of fragment	Ca, Fe, Sr (K, Ti, Cr, Mn, Cu, Zn, Rb, Zr, Ba, Pb)
VQS2a	Whitish finishing layer	<b>Ca</b> , Fe, Sr (K, Cr, Mn, Cu, Zn, As, Ba, Hg, Pb)
VQS2a	Back of fragment	Ca, Fe, Sr (K, Ti, Mn, Cu, Zn, As, Rb, Zr, I, Ba, Hg, Pb)
VQS2b	Whitish finishing layer	<b>Ca</b> , Fe, Sr (K, Mn, Cu, Zn, Zr, Pb)
VQS2b	Back of fragment	Ca, Fe, Sr (K, Ti, Cr, Mn, Zn, Rb, Zr, Ba, Hg, Pb)

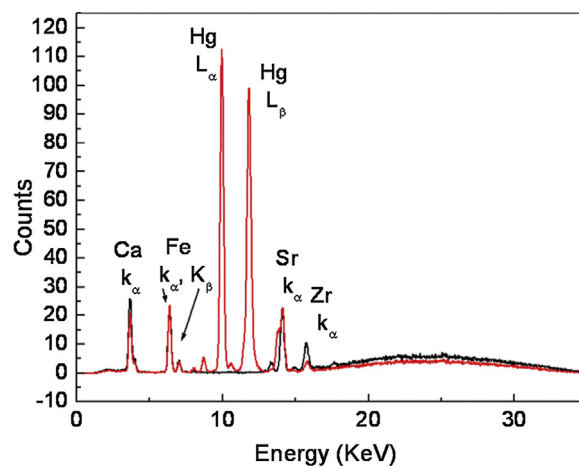
elemental composition, as obtained by the spectra analysis, is summarized in Table 2.

As is well established, since the penetration depth of X-ray source is of the order of few micrometres, the XRF response reflects not only the contribution coming from the pigmented layer, but also from the preparation substrate.

This latter is principally constituted by calcite and contributes to the high fluorescence lines of Ca and Sr.

All the other elements revealed by XRF analysis are indicative of the pigments and/or other substances added to the pigments with the aim to improve the aspect of the plasters. In order to be sure on the detected key-element responsible for the pigmentation agents, the measurements were also performed on the back of the fragments. Indeed, for each fragment, by comparing the measurements collected on the decorated surface and on the back, respectively, we were able to unambiguously distinguish the contribution due to the decorated surface from that of the preparation layer. Fig. 3 displays, as an example, the XRF spectra collected on the reddish finishing layer of the surface and on the back of VQ14c sample. As can be seen, from a first inspection of the figure, the XRF profile of the coloured surface clearly shows the presence of Hg ascribable to the reddish pigment.

As already aforementioned, the samples under study are characterized by various coloured finishing layers (see Table 1), hence in the following, the results will be discussed accordingly to the different analyzed colours.



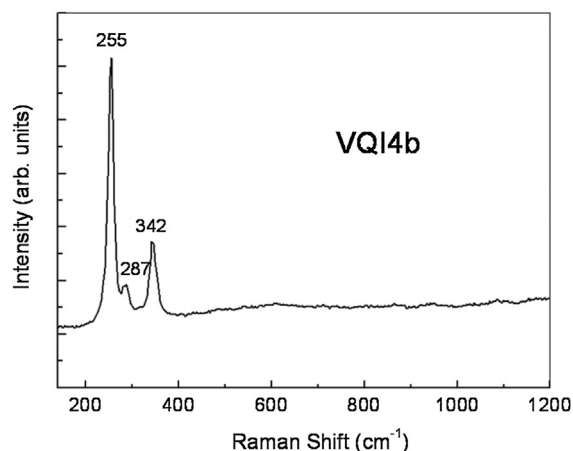
**Fig. 3.** XRF spectra collected on VQ14c sample measured with the X-ray tube operating at 40 kV. Red line: measurement on reddish finishing layer. Black line: measurement on the back of the fragment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Regarding the fragments of plasters with reddish finishing layer, it is worth remembering that red colour was really common in the roman wall paints [21] and was obtained by different red pigments. As examples, we can mention pigments based on iron oxides such as red ochre and Pompeian red, and again cinnabar/vermillion containing HgS, red lead containing Pb<sub>3</sub>O<sub>4</sub>.

Looking at Table 2, the simultaneous presence of Hg and S, detected in the fragments labelled as VQ11a, VQ14b and VQ14c, unambiguously indicates the use of the red pigment known as cinnabar (HgS), as it is also clear from an inspection of Fig. 3, as an example.

Going on, the red area of VQ11b surface does not displays Hg and S lines, but it is richer of Fe with respect to that from the back, suggesting the presence of larger amount of iron oxides, allowing us to hypothesize the use of an inorganic iron-based red pigment known as red ochre, widely used in Roman mural paintings [21]. It is worth noting that VQ14b and VQ14c are two fragments of plasters from basis villae and their chemical composition is comparable indicating the use of the same pigment; while, although VQ11a and VQ11b are fragments of stucco both collected from the R54 area, different key elements are revealed. This latter result could be indicative of a different manufacturing technique, probably connected to the occurrence that the monumental complex of Villa dei Quintili was the imperial residence of emperors belonging to different periods of time.

Concerning VQ12 sample, a fragment of plaster with three finishing layers (reddish-brown, green and light yellow), the chemical composition provided by XRF measurements is quite homogeneous. The XRF spectra collected on the surface of this sample show a higher Fe line respect to the measurement performed on the back, this occurrence could again indicate the presence of iron-based pigments, as red ochre/umber. Also in the case of VQ13, a fragment of plaster with two reddish-brown finishing layers, the only key element seems to be iron. In the samples, VQ14a, VQS2a and VQS2b, whitish finishing layers can be observed. The measurements do not indicate the presence of different elements from the surface and the back, only the peak associated to the Ca K $\alpha$  line is higher in the measurements performed on the white area. This experimental evidence suggests the use of a Ca-based white pigment, such as CaCO<sub>3</sub> powder. In fact as is also reported [22], at Romans' time one of the most common white pigment was produced by the same lime used from the plaster substrate. In particular, in the case of fresco as painting methodology, in order to brighten the painted surface, a small quantity of marble was mixed with the calcite.



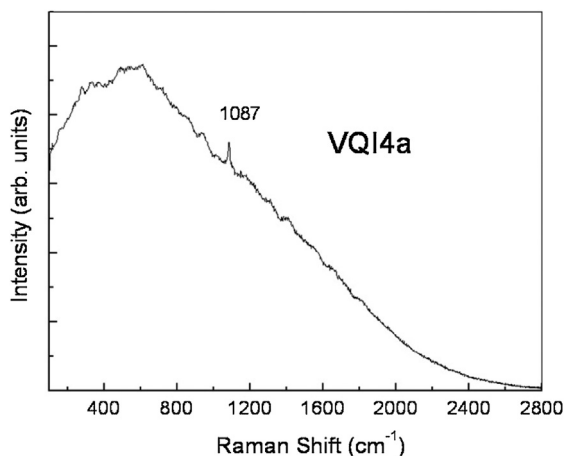
**Fig. 4.** Raman spectrum of VQI4b, fragment of plaster with reddish finishing layer. The clear peaks are associated to cinnabar (HgS).

The elements in traces, revealed in each measurement, indicate impurities in the ores used for the production of pigments as well as for the preparation layers.

### 3.2. Raman analysis

Raman spectra were collected on different spots of the coloured finishing layer of the analyzed fragments. In particular, the measurements performed on the reddish finishing layer of VQI1a, VQI4b and VQI4c samples of plasters showed clear peaks at  $\sim 255\text{ cm}^{-1}$ ,  $287\text{ cm}^{-1}$ ,  $342\text{ cm}^{-1}$ , typical of cinnabar (HgS) [17–20], in full agreement with the above mentioned XRF results. The Raman spectrum collected on VQI4b is reported in Fig. 4, as an example.

Furthermore, the Raman profile of VQI4a, a fragment of plaster with whitish finishing layer, displays a rather high background, due to unwanted luminescence contribution, where a peak centred at  $\sim 1087\text{ cm}^{-1}$  is detected (see Fig. 5) [17–20]. This band can be associated to the strongest Raman contribution of calcium carbonate ( $\text{CaCO}_3$ ). Once again, this latter result confirms the hypothesis suggested by the XRF analysis, i.e. the presence of a Ca-based white pigment. In the case of other fragments the high contribution of luminescence covered most of the entire corresponding spectra, preventing the identification of other pigments present on the previously investigated samples.



**Fig. 5.** Raman spectrum of VQI4a, fragment of plaster with whitish finishing layer. The peak is associated to calcite ( $\text{CaCO}_3$ ).

### 3.3. Petrographic analysis by OM

As OM measurements are concerned, the samples were separated into three different groups according to similarities in the mineralogical-petrographic features; in particular, they have been characterized on the basis of the type/sorting of the aggregate and on the main features of the binder present in each fragment, as can be seen from an inspection of Table 3. The first group includes VQI1a and VQI1b samples. They show a quite homogeneous and compact micritic binder, with a light brown colour in the whole section. The aggregate fraction is mostly constituted by volcanic fragments with a porphyric texture, cocciopesto and single crystals of pyroxene, biotite, quartz and Fe-oxides which ranging in size from 0.1 mm to 2.0 mm and vary in shape from angular to strongly angular. The overall particle size distribution is poorly sorted and the percentage of the aggregate is approximately of 30 vol%. This latter is been evaluated by a semi-quantitative visual estimation. Regarding the porosity, it ranges from about 0 to 20 vol% and it consists of both primary and secondary pores with size ranging from 1 mm to 5 mm. In addition, abundant areas of recrystallization of the binder were observed in voids. Finally, no preferred orientations of volcanic fragments and crystals were observed.

The second group includes VQI2 and VQI4a samples. They both display a micritic binder with a beige and homogeneous colour in almost all the section. Regarding the aggregate fraction, it is mainly composed by volcanic, carbonatic and metamorphic fragments and cocciopesto; in addition single crystals of pyroxene, biotite, quartz, micas and Fe-oxides were detected. The particle size distribution is moderately sorted and the percentage of the aggregate is approximately of 40 vol%. Particles ranging in size from 0.2 mm to 2.7 mm and vary in shape from angular to sub-rounded. No preferred orientations were observed. The porosity, both primary and secondary, ranges from about 0 to 20 vol% and consists in pores from 0.6 mm to 2.5 mm.

The third group includes the remaining samples, namely VQI3, VQI4b, VQI4c, VQS2a and VQS2b. Samples belonging to this group are characterized by a micritic and compact binder with a colour from light to dark brown. The aggregate fraction is mostly constituted by carbonatic fragments, cocciopesto and rare crystals of pyroxene, Fe-oxides and quartz. In addition, marble fragments were recognized. The particle size distribution is moderately sorted and the percentage of the aggregate ranging approximately from 30 to 40 vol%. Particles ranging in size from 0.1 mm to 4.0 mm and vary in shape from sub-angular to sub-rounded without a preferred distribution. The porosity ranges from about 0 to 20 vol% and consists in primary and secondary pores with size ranging from 0.7 mm to 3.5 mm.

### 3.4. SEM-EDS analysis

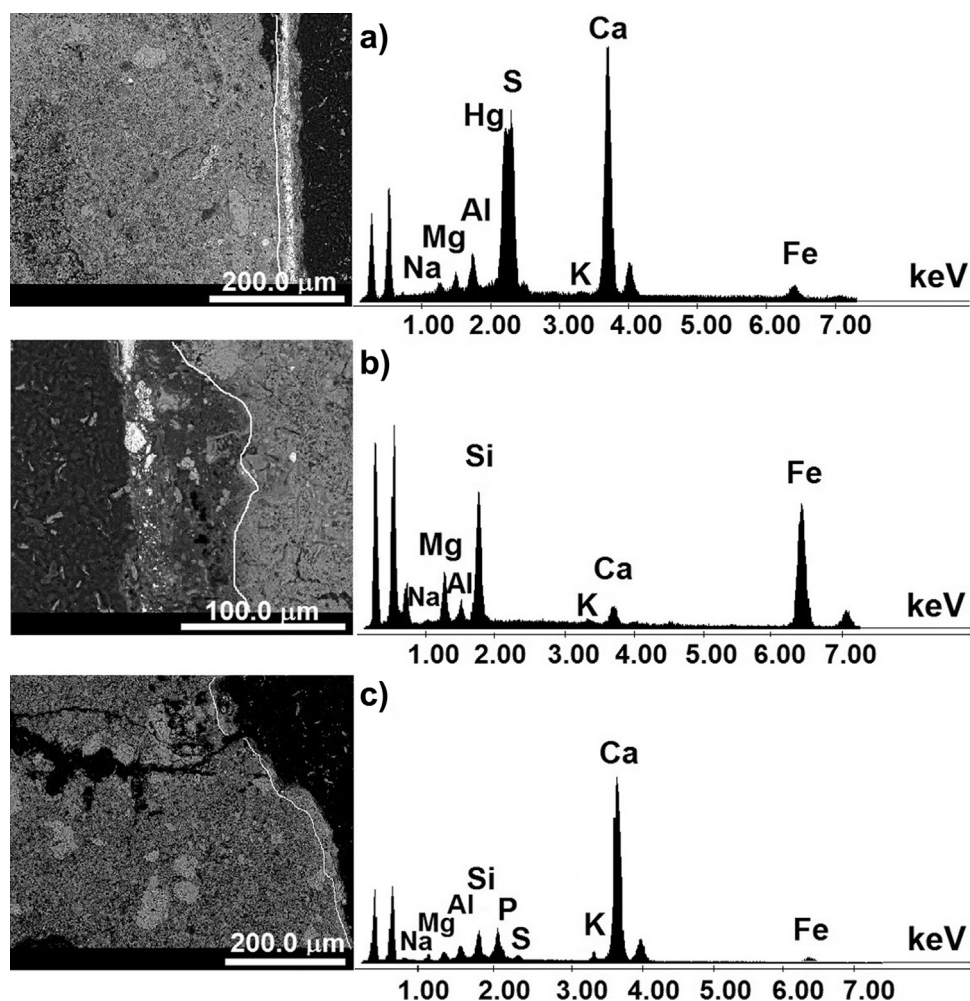
All the samples, investigated by SEM analysis, revealed the presence of two layers (Fig. 6), one is identified as the preparation layer and the other as the painted layer. The thickness of preparation layer shows a range from 0.5 cm to 1.5 cm for all the analyzed fragments, while we measured a thickness of painted layer ranging from 20  $\mu\text{m}$  to 100  $\mu\text{m}$  for all the plasters and from 150  $\mu\text{m}$  to 200  $\mu\mathbf{m}$  for the two fragments of stucco. In Fig. 6, SEM images are reported, as example, for the following three samples: VQI1a (red plaster), VQI1b (red plaster) and VQS2a (white stucco).

Elemental analyses have been performed on painted layers and results are summarized in Table 4. Although EDS analyses have a semi-quantitative nature, they can provide information about pigments by the identification of the key-element responsible for the colour, as in the case of XRF investigation. In Table 4, for all the studied samples, the main key-element is marked in bold. The red pigments used for the pictorial layers are quite different among

**Table 3**

Summary of mineralogical and petrographic features of the examined samples. Bt: biotite, Fe-ox: Fe-oxides, Px: pyroxene, Qtz: quartz, xxx: abundant, xx: moderate; x: scarce; /: absent.

Sample	Binder	Size of aggregate (mm)	Type of aggregate (rock fragments)	Type of aggregate (mineralogical phases)	Cocciopesto	Sorting of aggregate
VQI1a	Micritic with light brown colour	0.1–2.0	Volcanic fragments	Qtz, Bt, Px, Fe-ox	+++	Poorly sorted
VQI1b	Micritic with light brown colour	0.1–1.0	Volcanic fragment	Qtz, Bt, Px, Fe-ox	++	Poorly sorted
VQI2	Micritic with beige colour	0.2–2.7	Volcanic, carbonatic and metamorphic	Qtz, Bt, Px, Fe-ox	+	Moderately sorted
VQI3	Micritic with dark brown colour	0.1–3.5	Carbonatic and metamorphic	Qtz, Bt, Px, Fe-ox	/	Moderately sorted
VQI4a	Micritic with beige colour	0.2–2.0	Volcanic, carbonatic and metamorphic	Qtz, Bt, Px, Fe-ox	+	Moderately sorted
VQI4b	Micritic with light brown colour	0.1–4.0	Carbonatic and metamorphic	Qtz, Px, Fe-ox	/	Moderately sorted
VQI4c	Micritic with light brown colour	0.1–3.6	Carbonatic and metamorphic	Qtz, Px, Fe-ox	/	Moderately sorted
VQS2a	Micritic with dark brown colour	0.1–1.7	Carbonatic and metamorphic	Qtz, Bt, Px, Fe-ox	/	Moderately sorted
VQS2b	Micritic with light brown colour	0.1–2.2	Carbonatic and metamorphic	Qtz, Px, Fe-ox	/	Moderately sorted



**Fig. 6.** Representative SEM-EDS Images: (a) sample VQI1a (cinnabar); (b) sample VQI1b (red ochre) and (c) sample VQS2a (bone white).

**Table 4**  
SEM-EDS chemical data (wt%) of the examined samples. The main key-element for pigment identification is marked in bold.

Sample	Colour	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>2</sub>	Cl <sub>2</sub> O	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	FeO	HgO	P <sub>2</sub> O <sub>5</sub>	Pigment
QI1a	Red	0.5	1.0	1.5	2.5	<b>7.8</b>		0.1	36.3		4.3	<b>46.0</b>		Cinnabar
VQI1b	Red	1.5	10.3	3.8	20.8			0.6	3.0		<b>60.0</b>			Red ochre
VQI3	Red-brownish	0.5	2.3	6.6	14.9	0.9	1.0	1.4	58.9		<b>13.5</b>			Red ochre
VQI4a	White	1.0	2.2	0.8	1.8	2.0			<b>92.2</b>					Calcite
VQI4b	Red			7.6	0.4	<b>10.1</b>			3.0			<b>78.9</b>		Cinnabar
VQI4c	Red		2.1	13.3	32.9	<b>2.5</b>		1.6	31.1		9.5	<b>7.0</b>		Cinnabar
VQS2a	White	0.96	2.45	3.38	7.17	0.71		0.49	<b>70.51</b>		5.3		<b>9.03</b>	Bone white
VQS2b	White	5.0	2.6	10.6	31.2	1.0	2.0	3.3	<b>30.0</b>	0.9	2.5		<b>10.9</b>	Bone white

the paintings. Indeed, in VQI1a, VQI4b and VQI4c samples, the co-presence of Hg and S oxides confirms the use of the red pigment constituted by cinnabar; VQI1b and VQI3 fragment show an high amount of iron oxide together with aluminium and silicon oxides, this occurrence could suggest that the red ochre pigment revealed by XRF measurements could be constituted by hematite. According to the elements found in the sample VQI4a, calcite has been used as white colour, since calcium content exceeds 90%. Furthermore, in the samples VQS2a and VQS2b the presence of phosphorus in the white layer, together with calcium, is compatible with the use of bone white as pigment, already known at Romans' time.

Finally, it is worth noting that all the fragments present calcium in the pictorial layer, this evidence can be explained taking into account the technique used for realizing Roman fresco. In fact the pigments were usually applied on a dry plaster on which they were absorbed and permanently fixed due to the process of carbonation of the lime during which the calcium hydroxide reacts with the CO<sub>2</sub> of the atmosphere to produce calcium carbonate in the top layer. At the end, a mixture of water-lime was used for tuning the right nuances.

As it is evident, the overall SEM-EDS results confirm the non-destructive XRF investigation.

#### 4. Conclusions

In this paper, we investigated different painted plasters and stucco, withdrawn from Villa dei Quintili, a Roman archaeological site, located in the south-eastern part of Rome (Italy), with the aim of identifying the pigments. The study was performed by the joint use of portable instrumentations, such as a handheld X-Ray Fluorescence (XRF) analyzer and a portable Raman spectrometer. The measurements from these non-destructive portable methodologies were also integrated with those obtained by two micro-destructive laboratory techniques, namely OM and SEM-EDS. Microscopic observations by OM allowed us to define the textural characteristics of the samples substrate, while SEM-EDS investigation furnished a semi-quantitative analysis on the chemical composition of the pigments, including also the oxides of light elements (such as Al and Si), not revealed by the XRF apparatus.

As the red painted plasters are concerned, we mainly supposed the use of two different inorganic pigments largely used since the antiquity, namely cinnabar and red ochre, this latter probably constituted by hematite. Furthermore, the analyses of white painted fragments revealed a Ca-based pigment essentially constituted by calcite, probably originated by the same lime from the substrate plaster. Another typical white pigment called bone white, already known at Romans time, was also detected.

We would like to underline that the present study represents the first archaeometric characterization of pigments used in the wall

paintings of this archaeological site. This investigation represents a first step to plan an extensive non-destructive in situ investigation without removing or causing damage to any part of this important and charming monumental complex. Finally, all the experimental results shed light on the material characterizing the painted surface layer, providing in principle useful information for eventual proper restoration processes.

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