Heritage Science

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The Roman villa at the Castle of Baia (Naples, Italy): investigations on the polychromy of frescoed surfaces by using non-destructive spectroscopic techniques

Piergiulio Cappelletti[1,2], Alberto De Bonis[1,2], Diego Di Martire[1], Renata Esposito[3], Chiara Germinario[4], Sossio Fabio Graziano[2,5], Celestino Grifa[2,4], Francesco Izzo[1,2], Giovanna Montesano[1], Vincenzo Morra[1], Concetta Rispoli[1,2*] and Maria Verde[6]

Abstract

During the Roman age, the southern promontory of the gulf of *Baia* was the perfect location for the construction of *villae maritimae* for the Roman *élite* that decided to spend their summer residences by the sea.

One of these residences is now located in the military fortress of the *Castello Aragonese di Baia*, built in 1495 CE during the *Aragonese* period (15th century). Here, during restoration works, the ruins of the residential sector of the *villa,* which historical sources ascribe to Caesar, were unearthed. The most representative evidence of this is the outstanding in situ remain of mosaics, decorated plasters and finely frescoed surfaces decorated according to the repertoire of the II style. This research aims to investigate the polychromy of a wall decoration representing a perspective depiction of architectural scenes *en trompe l'oeil* analysed by means of a multi-analytical, non-destructive approach performed in situ. The combined use of spectroscopic techniques (portable X-ray fluorescence, Raman and Fourier Transform Infrared Spectroscopy) points out the use of a characteristic Roman palette, quantitatively assessed by colorimetric measurements. It consists of red and yellow ochre, calcite, hematite, organic black pigments, precious materials such as cinnabar and Egyptian blue, green copper compounds. Fourier Transform Infrared Spectroscopy also revealed the presence of synthetic resins, likely used for the conservation of mural paintings. These are, however, damaged by atmospheric humidity, as detected by Infrared Thermography. Gypsum has been identified as the main weathering product.

Keywords Non-destructive techniques, Roman frescoes, Pigments, Baia, Phlegraean Fields

*Correspondence:
Concetta Rispoli
concetta.rispoli@unina.it
Full list of author information is available at the end of the article

Introduction

The Phlegraean Fields were one of the favourite places of the Romans. *Baia*, in particular, was often mentioned in literary sources, both for the beauty of the landscape and for the wealth of natural resources and thermal waters, as well as for its characteristics (Liv., XLI, 16; Pliny the elder N.H., IX, 168). Several names of many illustrious personalities who, starting from the first century BCE, owned a villa in the Gulf of Naples, particularly in the area of *Baia*, are well known: M. Antonio, Licinio Crasso, Q. Cecilio, Metello Celere and his wife Clodia, P. Cornelio Dolabella, Q. Ortensio Ortalo, C. Mario, C. Giulio Cesare, L. Licinio Lucullo, Cn. Pompeo Magno, L. Calpurnio Pisone [1, 2].

Most of these residences were *villae maritimae*, built to enjoy *otium* and *balnea*, but at the same time to earn a living by fish farming, through the breeding and cultivation of fish and oysters. In these residences, frescoed surfaces are commonly found. Previous studies focused on the use of spectroscopic techniques for the study of frescoed surfaces [3] used high-resolution visible- and raking- light imaging, XRF and SEM–EDX analyses to examine wall paintings of a tomb in Macedonia (Greece), highlighting the application of elaborate painting techniques with a varied and rich chromatic "palette"; [4] established a multi-analytical protocol including Transmitted and Reflected- Light Optical Microscopy, SEM–EDS, XRPD and μ-Raman analyses to reconstruct wall paintings and other paint-plastered fragments of a roman villa in Verona (Italy); [5] used XRD and SEM–EDS methods to analyse mosaic paving and wall paintings in a hall of a roman sanctuary in the Capitolium area (Brescia, Italy) to recognize the making techniques, the pigments and the decay products; [6] focused on pigments of the frigidarium in the Sarno Baths of Pompeii (Italy) by using a multi-analytical approach comprising laser scanning confocal microscopy (LSCM), optical microscopy (OM), μ-Raman, SEM–EDS, p-XRF and XRPD analyses to identify the composition of pigments and the techniques used, as well as decay products.

This study focuses on one of these villas, in particular the one that stood on the promontory, where the *Castello Aragonese di Baia* now stands. The aim of this research is to analyse the Roman wall painting made during the first building phase of the late Republican villa. The peculiarities of the stratification and conservation of the fresco still in situ are an added value, since many frescoes in this area have disappeared irremediably, found in fragments or decontextualised.

The wall painting decoration here characterized, unlike the more famous frescoes in the Vesuvian area, is one of the very few testimonies of decorative apparatus of the late Republican age present in the Phlegraean Fields, because of the transformation of the landscape, the historical stratification of the sites, the bradyseism and, unfortunately, unauthorized building activities.

Archaeological context

Perched on a steep cliff, the *Castello Aragonese di Baia* (Fig. 1) is a military fortress hosting the Archaeological Museum of the Phlegraean Fields. It was built during the *Aragonese* period in the late fifteenth century CE, on the ruins of an ancient Roman *villa*, discovered in 1999 during some restoration works inside the fortress and incorporated in the castle keep known as "*Padiglione Cavaliere*". The ruins belong to the residential sector of a Roman *villa*, which historical sources identify as the summer residence of Julius Caesar. This villa can be considered as one of the famous residences identified as *villae maritimae*, built between the second-first century

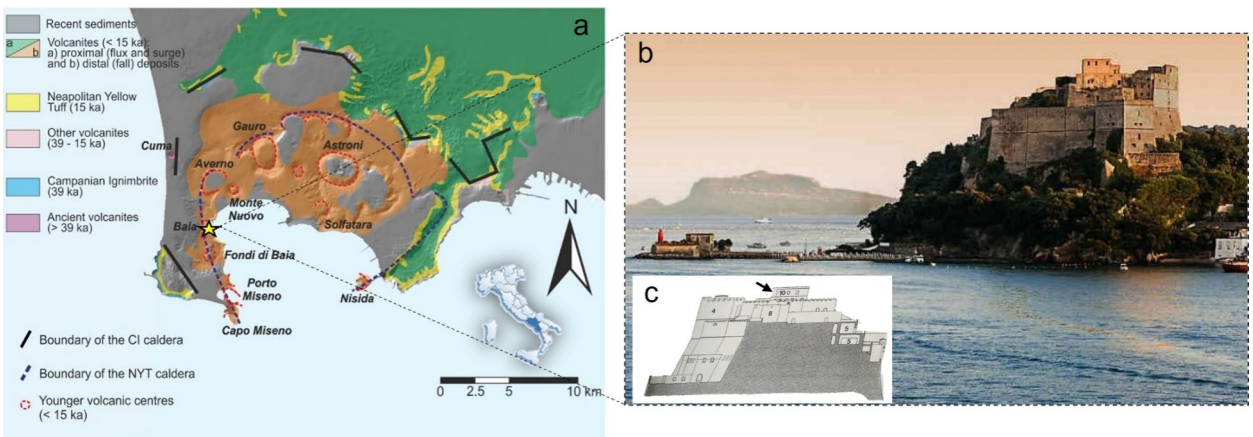

Fig. 1 **a** Geological sketch map of the Phlegraean Fields caldera (mod. after [8]); **b** location of the *Castello Aragonese di Baia* (yellow star in a); **c** sketch map of Baia Castle [9]; the black arrow points to the "*Padiglione Cavaliere*"

BCE by a late Republican Roman political elite, who also established their residences in *Baia* [7].

During the Roman period, the southern promontory of the gulf of *Baia* was the ideal place to build *villae*, whose prestige was also evidenced by the topographical position, which made them visible at a great distance from the sea and, at the same time, allowed their owners to enjoy a wide panoramic view.

The recovery has provided information about the site plant, the building phases and the decoration techniques. The *villa,* built on terraces sloping down to the sea, has undergone two building phases, chronologically ranging from the late Roman age (250 – 450 BCE) to the first Imperial era (27 BCE—68 CE).

The oldest structure, relative to the first building phase, dates back to the late Republican age and is divided into three levels with different intended uses: the upper level hosted the *atrium* and terraces, while the lower level, which formed the supporting substructure, housed the service areas. A third underlying level consisted of two tunnels with the function of water pipes. The second building phase, dating back to the Julian-Claudian age, involved the extension and the transformation of the *villa* into a large residence linked to the lower seaside neighbourhood [7].

The most representative evidence of the *villa* here discovered are the remains in situ of mosaics, decorated plasters and frescoed surfaces [7]. An outstanding discovery from the ruins is a painted wall reporting a perspective depiction of architectural scenes relating to the first building phase of the *villa*, which is the focus of the present research (Fig. 2). The frescoes are a part of a back

Fig. 2 3D recontruction of wall in *opus quasi reticulatum* (from [10]) preserving, in its upper part, the perspective depiction of architectural scenes *en trompe l'oeil,* decorated according the II style repertoire, and details of the areas where non-invasive analyses have been performed

wall in *opus quasi reticulatum* pertaining to a wall of an unidentifiable space decorated according to the II style repertoire. The surface is cut by an apse built in the late Julio-Claudian phase, which preserved the upper part of the painted wall, obliterating, at the same time, the remaining lower part (Fig. 2). Unfortunately, only the upper part of the decoration is preserved [7]. The decorative scheme testifies to the originality and the high quality of *Baia*'s painting. The decoration represents a perspective depiction of architectural scenes *en trompe l'oeil* and is divided into three areas: i) the central part of the scene is occupied by a round arch unveiled by a red coloured drape framing a *tholos*, a circular temple with twelve columns; ii) in the foreground is a porch with ionic columns; iii) behind the *tholos*, shades of green were used for painting the sky. The lateral decorations are mirrored and represent the top of an angular ionic colonnade (Fig. 2) [7].

Although the remaining part of the painted wall has not been preserved, the perspective architectures here represented are related to the II style formal repertoire (60–50 BCE) [7].

Methods

Non-invasive techniques were performed in situ to obtain minero-petrographic and chemical information on the polychromy of wall paintings (Supplementary Table 1).

A total of 62-point analyses were performed through Digital-Microscopy (DM) via portable MIC-FI colour digital microscope with Wi-Fi transmission (smartphone/tablet-connected), white/UV/IR light and magnification 5x-200x. Chromatic coordinates of the painted areas were obtained using a Minolta CM700d portable spectrophotometer, which allowed spectral reflectance to be measured in the visible wavelength range (400–700 nm). A pulsed xenon lamp with UV cut filter illuminated the surfaces, with a spot size of 3 mm in diameter. A silicon photodiode array detected and measured both incident and reflected light. Colour space coordinates CIE L*a*b*with an illuminant C, simultaing daylight with a colour temperature of 6774 K were determined (8° view angle, 10° observer) [11]. Portable X-ray Fluorescence (pXRF) analyses for qualitative to semi-quantitative chemical compositions were carried out on 62-point analyses by means of a Bruker TRACER 5G portable spectrometer (Rh target X-ray source, silicon drift detector, 3 mm collimator) operating with a 30 kV voltage, 10 μA current and 15 s acquisition time. The spectra were processed by the software ARTAX Spectra 8.0.0.476 (Bruker AXS Handheld, Inc.). Raman spectra were collected with a BRAVO Handheld Raman Spectrometer by Duo LASER, using patented technology (SSE™, Sequentially Shifted Excitation, patent number US8570507B1) to mitigate fluorescence phenomena. The spectrometer is equipped with two excitation lasers with wavelengths (DuoLaser™) centered at 785 and 853 nm. Different integration times were used to collect the spectra in the 178–3200 cm^{-1} range. Data acquisition and processing (smoothing, baseline correction) were performed using Opus 7.8 software [12]. Evidence of alteration and restoration products was obtained by Fourier Transform Infrared Spectroscopy (FTIR) by using a Bruker Optics Alpha-R portable FTIR spectrometer with an External Reflectance (ER) head for contactless and non-destructive analyses equipped with a ROCKSOLID™ interferometer and a ZnSe/KBr beam splitter with a DTGS detector (room temperature). Circular areas of about 3 mm of diameter have been analysed. The spectra were collected in the spectral range between 7500 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 128 scans for each acquisition (2 min). Data acquisition and processing have been carried out with Opus 7.0 software [13]. Infrared Termography (IT) allows the detection of anomalies in energy emission and therefore, with the same emissivity, thermal anomalies. Thermography is one of the non-destructive methods used in the diagnosis of pathologies in cultural heritage [14]. In fact, although properly made, works are subject to degradation due to aging of materials and possible lack of maintenance.

Before every acquisition, the following parameters were checked by using a thermo-hygrometer: (i) ambient temperature at 10 °C; (ii) humidity at 65%; (iii) distance of 2 m; (iv) emissivity at 0.93. The parameters were evaluated with FLIR T1030sc, Thermal sensitivity of < 20 mK, Resolution of 1024 × 768 pixel, Accuracy of ± 1% or ± 1 °C of measurements, Flir Tools + software for image analysis, recording, video file, and enhanced report generation.

Results and discussion

Binding substrate

The spectroscopic analyses of wall paintings revealed the type of binding substrate used to decorate the surfaces. The results indicated that only calcium carbonate was used. This assumption was confirmed by all the spectroscopic data. As described below, the ubiquitous presence of Ca, with subordinate Sr was detected by pXRF (Table 1), and Raman Spectroscopy always showed a strong band at ca. 1086 cm^{-1}, along with other weaker peaks at ca. 712 and 280 cm^{-1}, assigned to calcite (Table 1) [15, 16].

Moreover, ER-FTIR spectra acquired on representative areas mainly for investigating conservation products (see Sect. "Alteration and conservation products"), also show the bands at ca. 2510 cm^{-1}, with a shoulder at ca. 2590 cm^{-1} (undistorted $\nu_1 + \nu_3$ combination band of $(CO_3)^{2-}$ group), 1794 cm^{-1} ($\nu_1 + \nu_4$ mode), Reststrahlen

Table 1 Results of non-invasive analyses

	ID point	Colorimetry			pXRF	Raman (cm^{-1})	Pigment
		Average L*	Average a*	Average b*			
White	CB10, CB45, CB49, CB50	59.28	11.4	11.93	**Ca**, Fe*, S*, Si^{tr}, K^{tr}	ca. 280, 712, 1086	Calcite
Bright red	CB6, CB7, CB14, CB26, CB62, CB63, CB64	41.19	19.03	15.13	Ca, **Hg**, **S**, Si*, Fe*, Al*, K^{tr}, Ti^{tr}, Pb^{tr}	ca. 251, 283, 340	Cinnabar
Dark red	CB8, CB9, CB17, CB18, CB25, CB51, CB56, CB57	45.48	10.49	10.64	Ca, **Fe**, S*, Hg*, K*, Si*, Sr*, **Al***, Ti*, Pb*, Cu^{tr}	ca. 225, 290, 413, 498, 616	Red ochre
Purple	CB1, CB5, CB24, CB27, CB31, CB32, CB42	46.04	10.09	8.38	Ca, **Fe**, S*, Sr*, Si*, K*	ca. 225, 290, 413, 498, 617	Hematite
Pink	CB19, CB33, CB34, CB35, CB43, CB44, CB55	62.57	9.94	15.16	**Ca**, S, **Fe**, Sr*, Si*, K*	ca. 247, 304, 361, 426, 509, 955, 1012, 1116, 1184, 1241, 1288, 1324, 1334, 1430, 1482, 1511, 1533,1616	Calcite + Red ochre/ hematite + organic pigment
Yellow	CB4, CB15, CB21, CB39, CB40, CB41, CB60, CB61	60.51	11.04	31.98	Ca, **Fe**, S*, K*, Si*, Ti*, **Al***	ca. 245, 298, 386, 553	Yellow ochre
Black	CB2, CB3, CB16, CB20, CB28, CB36, CB37, CB59	36.71	5.06	4.78	Ca, Fe*, S*, Ti*, Si*, K*, Al*, P^{tr}, Pb^{tr}	ca. 1380, 1620	Carbon black
Green	CB11, CB12, CB13, CB29, CB30, CB38, CB53, CB54, CB58	51.54	-9.97	5.80	**Ca**, S, **Cu, Fe**, Cr, K*, **Si***	-	Green earth + Egyptian blue
Blue	CB46, CB47M CB48, CB65	66.50	-3.50	-2.50	**Ca, Cu**, S, Cr, Fe*, Ti*, Si*, K*	-	Egyptian blue

* Subordinate elements and compounds

tr = present in traces. pXRF elements are in order of decreasing abundance

In bold, elements corresponding to the pigments

effect at ca. 1410 cm^{-1} (asymmetric stretching band of CO_3) and derivative effects at ca. 873 and 713 cm^{-1}, due to the "out-of-plane" and "in-plane" bending vibration of the $(CO_3)^{2-}$. All these spectral evidences are typical of calcium carbonate [17]. This can suggest possible application of pigment with a fresco technique, based on the mixing of the pigments with slaked lime and water and application on a thin layer of lime-based plaster, while this was still moist, to form a very stable coloured surface [18].

Pigments

Below is the description of each colour hue, visible in Fig. 3.

White

White was used to decorate the columns framing the central element depicting the *tholos* (CB45), with their relative capitals and the overlying entablature (CB10, CB49, CB50) (Fig. 2). As can be seen, the Raman spectrum (Fig. 4) shows the peaks of calcite, indicating that the white pigment was obtained from lime [19]. However, pXRF also shows the presence of S, Si, Fe, and K (Fig. 5; Table 1), suggesting the addition of a Fe-based pigment to create the grooved columns. Digital microscopy supports this conclusions, as reddish-brown spots are visible in the whitish areas (Fig. 3). On the other hand, the presence of S could be due alteration products (*i.e.*, gypsum) (see Sect. "Alteration and conservation products").

Bright red

The red colour predominates in the wall painting, both in bright and dark shades (Fig. 3) and, interestingly, spectroscopic data revealed that the different colours were obtained by using different pigments.

Bright red, with a very homogeneous microscopic appearance (Fig. 3), was used for the red drape framing the *tholos* in the central decoration and for the monochrome background of the lower part of the lateral depictions, framing painted, pink marble slabs. It was obtained by using cinnabar, the mineral form of mercury (II) sulphide α-HgS, which is one of the most valuable pigments [20, 21]. pXRF spectra are indeed characterised by the Hg peaks (Fig. 5; Table 1). As reported in the literature, the occurrence of cinnabar in its pure form is very rare ([21] and references therein). However, although the Raman

Fig. 3 Images of each colour hue acquired in situ on the frescoed surfaces via digital microscopy

spectra show only the typical peaks of mercury (II) sulphide (251, 283 and 340 cm^{-1}; Fig. 4), the presence of Fe and occasionally of Pb (Supplementary Table 2) could suggests that cinnabar was mixed with other pigments [19, 22, 23]. In fact, cinnabar was an expensive pigment often used as an admixture with the cheaper and more readily available haematite or red lead, presumably both to extend it and to brighten the other red pigments (*e.g.*, [21, 24, 25]). It is worth noting that on the right sight of the lateral depiction, in correspondence of the bright red band below the entablature (Fig. 2), the colour appears darker, as confirmed by colorimetric coordinates that show significantly lower values in CB7 ($L^*=31.78$; $a^*=4.31$; $b^*=6.33$) compared to CB14 ($L^*=39.48$; $a^*=17.69$; $b^*=14.15$) (Fig. 6; Supplementary Table 3). In the central depiction, where the colour is well-preserved, L^* (lightness) values are clearly higher (Fig. 6; Supplementary Table 3). The lowering of colorimetric coordinates can be attributed to a darkening of the cinnabar. The Romans recognised this colour change and used the pigment for interior painting away from direct sunlight. The process is mainly due to the exposure to direct sunlight (or even moonlight; [26]), but it is also controlled by several other factors (*i.e.,* atmospheric agents and associated pollutants, relative humidity, soluble salts and organic compounds) that can accelerate the blackening effect, determining the phase transition to black meta-cinnabarite, by oxidation of the sulphur, or other chemical reactions, mainly achieved by the presence of certain components (*e.g.,* chlorine or other halogens; [24, 27–31]).

Dark red

The dark red colour was used to frame both lateral and central depictions with dark red stripes (Fig. 3). With respect to the bright red colour, the pigment appears less compact (Fig. 3), darker (average $L^*=45.48$; average $a^*=10.49$; average $b^*=10.64$; Table 1), and compositionally different (higher Fe counts; Fig. 5). Spectroscopic data revealed that it was obtained by using a different pigment, composed of iron oxide compounds. The narrow doublet at ca. 225 and 290 cm^{-1} and the peaks at ca. 413, 498 and 616 cm^{-1} (Table 1) [19, 23], in fact, feature hematite, the iron oxide representing the principal colouring component of red ochres, a pigment mainly used for red decorations in the Roman period (*e.g.,* [21, 25, 32, 33]. In the parts of the wall painting where dark red decoration overlying the bright red ones, a* and b* values appear higher (Fig. 6; Supplementary Table 3) and pXRF detected Hg (Table 1). This is due to the presence of the underlying cinnabar, as confirmed by the diagnostic peaks on Raman spectra at ca. ca. 251, 283 and 340 cm^{-1} (Fig. 4). In CB57, on the other hand, copper was observed in the XRF data (Table 1; Fig. 5), likely because dark red details, as observed with DM, were later drawn where a green decoration had been carried out.

Purple

The stripes framing the *tholos* and the details decorating the lateral parts of the wall painting were purple (Fig. 3). As observed for the dark red, the purple pigment was also characterised by the presence of predominant Fe with Ca, along with lesser S, Sr, Si and K

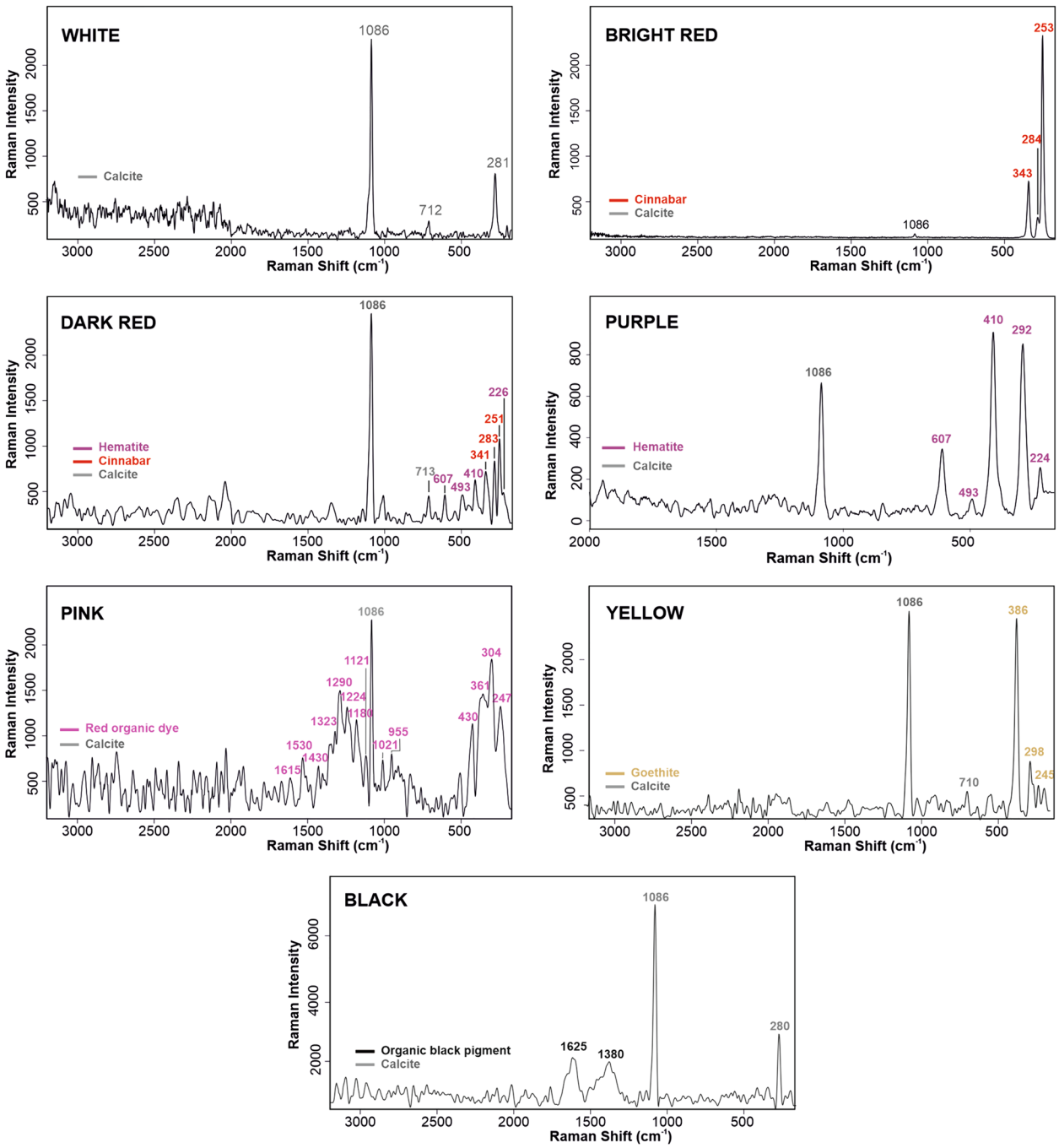

Fig. 4 Representative XRF spectra of each colour hue analysed on the wall painting

(Table 1). Raman spectroscopy identifies hematite as the main component of the pigment (ca. 225, 290, 413, 498, 617 cm^{-1}) [34] (Fig. 4), proving the use of such an iron oxide for the purple decoration. Although Roman sources mention the shellfish-derived Tyrian Purple as the main purple dye [21], recent research revealed that purples was made using both organic (mixing of madder and indigo; [35]) and inorganic compounds. In this regard, it was proved that a common practice in the Roman world was the heat treatment of red iron oxide, with an α-Fe_2O_3 particle size effect (larger crystals give a purple/violet colour as well as the mixing of hematite (red) with Egyptian Blue [36–38]).

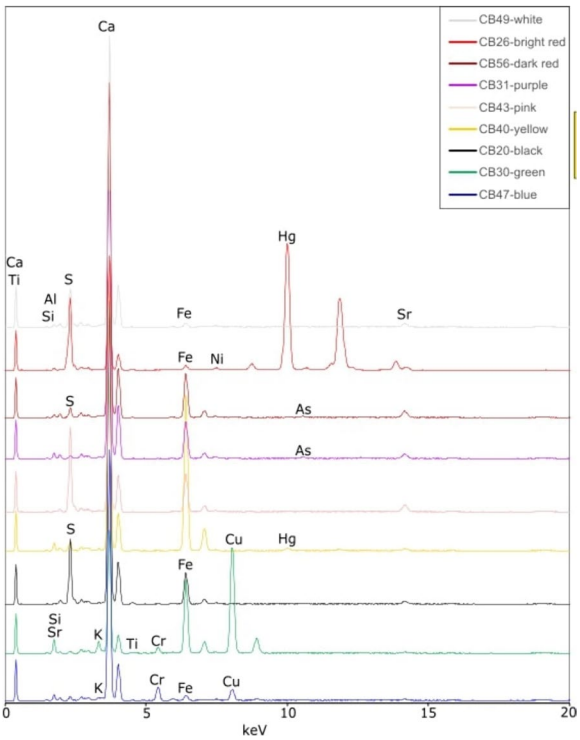

Fig. 5 Representative Raman spectra of analysed pigments

Pink

Pink colour was used to reproduce the *tholos* (CB33, CB34, CB35), the marble slabs on the lateral decorations (CB19, CB55), and those framing the central figure (CB43, CB44) (Fig. 2). For this hue, colorimetric data are almost homogeneous (average L*=62.57; average a*=9.94; average b*=15.16; Fig. 6; Table 1). XRF data always showed the presence of Fe (and minor Si), along with Ca and S due to the alteration phenomena (Table 1; see next section), likely indicative of the use of an iron-based red pigment to obtain the pink shades, namely a red ochre. ER-FTIR spectroscopy showed a sharply shaped band at ca. 3695, 3653 and 3622 cm^{-1} (O–H stretching), usually exhibited by clay minerals, the mineralogical phases present in ochres [39], but also used as extender to obtain precisely this colour [37]. The ER-FTIR spectra also revealed the presence of two derivative bands at 1615 and 1555 cm^{-1} (Fig. 7a). This evidence, together with the Raman peaks at ca. 247, 304, 361, 426, 509, 955, 1012, 1116, 1184, 1241, 1288, 1324, 1334, 1430, 1482, 1511, 1533 and 1616 cm^{-1} (Fig. 4), could suggest the addition of a red organic dye [40–43] possibly in mixture with inorganic materials (e.g., calcite)to obtain the desired pink hue.

Yellow

Yellow colour was used to paint both entablatures of the lateral decorations and the shelves on which the base of the round arch framing the *tholos* of the central scene stands (Fig. 3). The yellow pigments were obtained from yellow ochre, widely used in Roman times for wall decoration (*e.g.,* [18, 33, 36, 44, 45]). Both XRF and Raman spectroscopy confirmed the use of yellow ochre: XRF shows the predominance of Fe and Ca (Table 1), while Raman spectroscopy displays the presence of goethite. In fact, Raman spectra (Table 1; Fig. 4), along with the

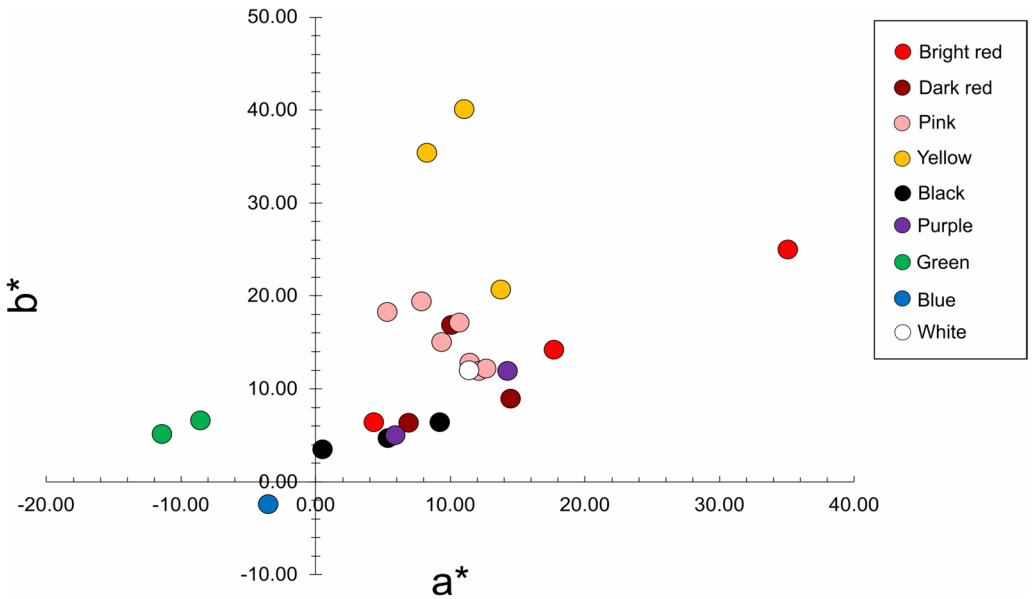

Fig. 6 Plot of colorimetric coordinates (**a***, **b***) obtained on each colour hue by portable colorimetry

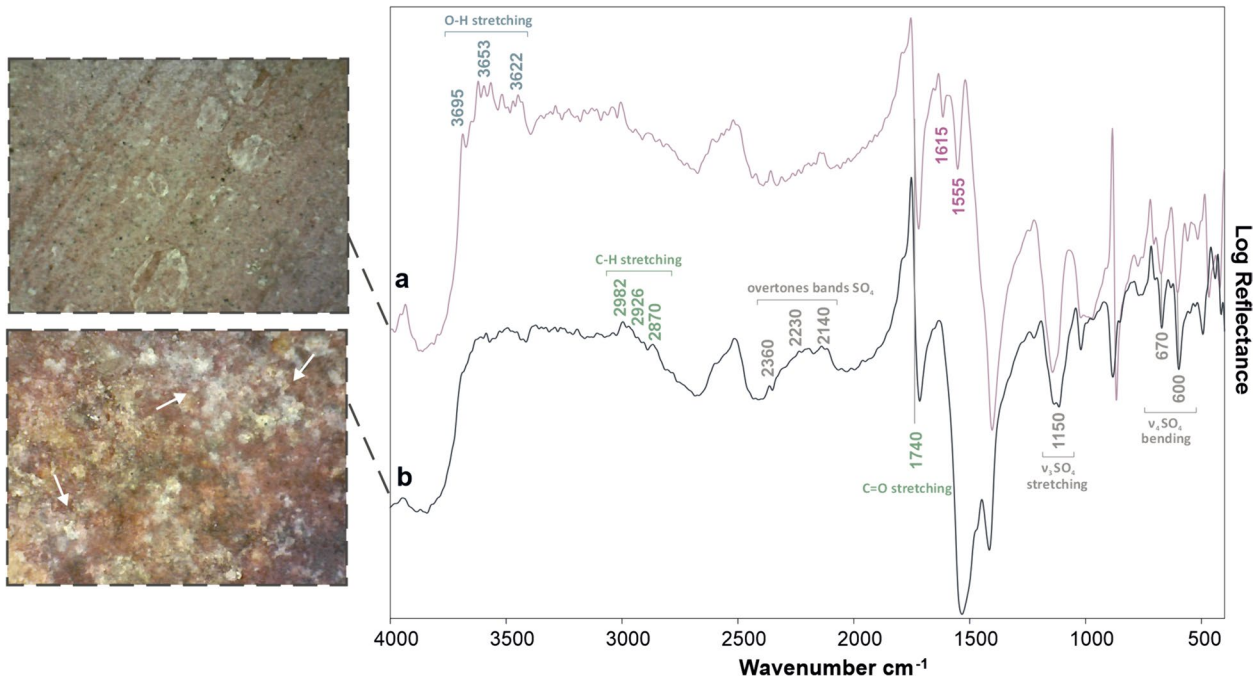

Fig. 7 ER-FTIR spectra of a pink (**a**) and red area (**b**) showing spectral evidence of alteration and restoration products (white arrows on image of red area indicate visible efflorescence phenomena)

bands of calcite at ca. 1086 and 710 cm^{-1}, displays peaks at ca. 245, 298 and 386 cm^{-1}, which are typical of goethite, the iron hydroxide constituting yellow ochre, which is the earth pigment containing not only iron hydroxide but also clay impurities and other silicates as accessory phases. Such a derived information about mineralogical composition also justifies the presence of Si, Al, K, and Ti detected by pXRF (Table 1).

Although pXRF and Raman spectroscopy provide univocal information, differences in colorimetric coordinates were observed (Fig. 6). The point with the lowest b* value (CB15; Supplementary Table 3) corresponds to darker shades drawn along the yellow entablature (Fig. 3).

Black

Black colour was used for the horizontal drape hiding the top of the colonnade depicted in the lateral sides, as well as for three drapes that allowed the sky to filter through (Fig. 3).

The pXRF results indicate that Ca was the dominant element, followed by Si and other trace elements probably present in surface impurities. Therefore, the black pigment was likely derived from carbon. The Raman spectra for black provided useful information, showing two broad bands around 1380 and 1620 cm^{-1} along with Raman peaks of calcite (Fig. 4). These spectral features represent a highly disordered graphitic structure in which the peak at ca. 1380 cm^{-1} is due to D band (or "Defect" bands, *i.e.,* graphitic lattice vibration mode with A_{1g} symmetry), and the peak at ca. 1620 cm^{-1} is relative to the G ("Graphite") first-order band (*i.e.,* ideal graphitic lattice vibration mode with E_{2g} symmetry). This band likely includes also the D2 band (*i.e.,* disordered graphitic lattice mode with E_{2g} symmetry), as observed in the solid product of incomplete combustion or pyrolysis of organic materials and fossil fuels, such as soot [46–48]. Thus, the use of a carbon-based pigment is confirmed. The presence of copper in CB16 (lateral decoration) and CB28 (central decoration; Supplementary Table 2) is likely due to the presence of the underlying green decoration (Fig. 2).

Green

The sky was depicted using a unique shade of green, with an average L* value of 51.54, an average a* value of −9.97 and an average b* value of 5.80 (Fig. 6; Supplementary Table 3).

The identification has been carried out by pXRF, which shows the presence of Cu, Fe, Cr along with Ca, S, K and Si (Table 1). The presence of copper suggests the use of Cu-based pigment. According to Pliny, the most commonly used green pigments were malachite (Cu_2 (CO_3) $(OH)_2$) and green earths, as well as verdigris and other pigments derived from the corrosion of copper in an acidic environment [32, 49]. However, Roman wall painters commonly obtained the green colour by mixing green

pigments with synthetic blue (Egyptian blue) and natural yellow (ochre) pigments, as well as Egyptian blue with green earths to have more brilliant colours [32, 49–55]. In our case, we cannot exclude this eventuality, which could justify the presence of both Cu and Fe in such a brilliant green. Another clue supporting this hypothesis could be the occurrence of Cr, which was found in wall paintings decorated using Cr-bearing green earths in Campania (Oplonti, Naples) and surrounding regions (i.e. from *Vigna Barberini*, *Domus Aurea*, *Ostia Antica*, Rome) [56–59].

Blue

The microscopically compact blue decoration was observed in the uppermost part of the painted wall, above the main white entablature (Fig. 3). The chemical nature of this pigment was supposed through pXRF data. Cu was found to be prevalent along with Ca, while other elements such as S, Fe, Ti, Si and K were also observed, albeit in negligible amounts (Table 1). Cr was also detected (Fig. 5). Although unusual, this element was detected in other Roman blue-coloured paints, such as those used in the *Domus Aurea* in Rome [57], as well as in other ancient purple or green pigments [56, 59, 60]. It can be inferred that the blue pigment was obtained from a copper compound. Definitely, the blue pigment could be identified as Egyptian blue [61], a pigment unequivocally detected by means of imaging techniques [62]. This was the first synthetic pigment in history, widely used across the Mediterranean ancient world, and obtained by firing a mixture of quartz-rich sand, feldspar, carbonates and copper colouring compounds at high temperature and alkaline flux. This process resulted in the formation of a Cu-bearing polycrystalline sintered material (synthetic frit) containing cuprorivaite ($CaCuSi_4O_{10}$) ([63] and references therein). The use of this pigment in the Campania region dates back to before the Roman period [12, 18, 33, 36, 45, 64–66] and is most likely linked to the presence of workshops in *Puteoli*, *Cuma* and *Liternum* specialized in producing blue (and green) frits according to the instruction reported by Vitruvius, exploiting the high-quality raw materials available in surrounding areas [22, 51–55, 67].

Alteration and conservation products

Spectroscopic analyses performed on decorated surfaces revealed the presence of mineralogical phases due to the alteration phenomena affecting them, mainly consisting in sulphation. Most of pXRF spectra (Fig. 5), in fact, detected S (Table 1) and digital microscopic images occasionally revealed the presence of efflorescence (related to salt crystallization) (white arrows in Fig. 7), which affected the frescoed surfaces, compromising their aesthetic value.

ER-FTIR highlighted the presence of gypsum, featured by the inverted peaks at ca. 1150 (ν_3 antisymmetric SO_4 stretching vibration modes), 670 and 600 cm^{-1} (ν_4 antisymmetric SO_4 bending vibration modes) and by the broad bands at ca. 2230 ($2\nu_3$ SO_4; $\nu_2+\nu_L$ H_2O) and 2140 cm^{-1} ($\nu_1+\nu_3$ SO_4) (Fig. 7b) [45]. Raman Spectroscopy confirmed this evidence, showing in some spectra the typical Raman shifts at ca. 1008 cm^{-1} [7]. Moreover, ER-FTIR detected products likely used during previous restoration works; actually, characteristic signatures of acrylic resin at ca. 2982, 2953, 2926, 2870 (C-H stretching vibration) and 1740 cm^{-1} (C=O stretching vibration) [58] have been observed (Fig. 7b).

Regarding the thermal anomalies detected on the rear fresco, the thermogram overlapping the optical image that highlights the features of the fresco (Fig. 8) showed

Fig. 8 Thermogram and optical images of the rear fresco

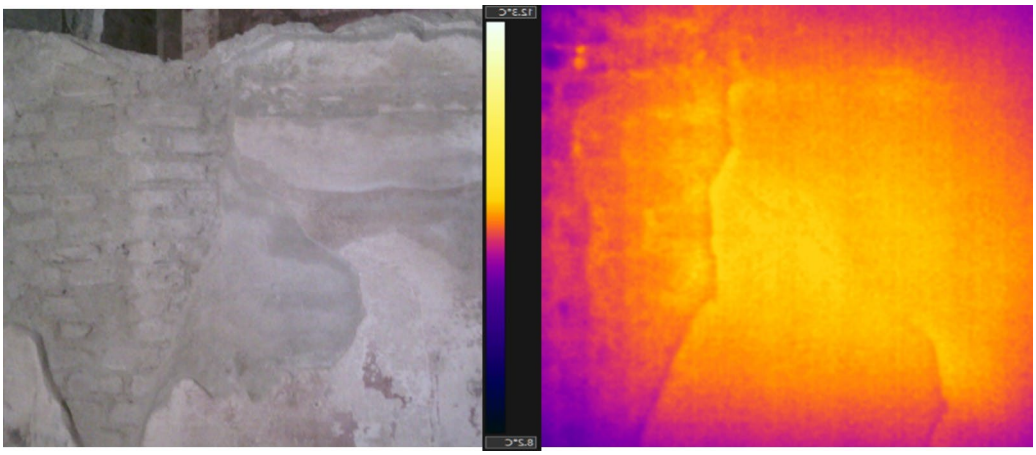

Fig. 9 Thermogram and optical images of the front fresco

lower temperatures at the boundaries of the fresco, about 9°, highlighting possible phenomena of water accumulation. The condition of the front fresco is different (Fig. 9), where the thermogram does not show any significant thermal anomalies, but at the same time there are evident traces of humidity in the masonry behind (about 10°), which could be a con-cause of the significant alteration of the fresco and its detachment.

Conclusions

This comprehensive research uses a multi-analytical and non-invasive approach, combining spectroscopic techniques (pXRF, Raman and ER-FTIR) performed in situ, to provide a complete characterization of the polychromy of frescoed surfaces of the Roman Villa at the Castle of Baia (Naples, Italy), which represent depictions of architectural scenes *en trompe l'oeil.* This multi-analytical approach allowed us to point out the use of a characteristic Roman palette composed of different groups of colour consisting of different ochres, organic pigments and precious materials:

(i) bright red, attributed to the use of cinnabar mixed with other pigments;
(ii) dark red and pink, derived mainly from the use of red ochres and, in the case of pink, also from red organic dye mixed with inorganic materials;
(iii) purple, attributed to the use of hematite;
(iv) yellow, derived from yellow ochre;
(v) green, a Cu-based pigment;
(vi) blue pigment can be identified on Cu-based pigment, most likely Egyptian blue;
(vii) black, a carbon-based pigment.

It is worth noting the use of cinnabar and Egyptian blue, which were rich and precious pigments. The use of these pigments for the Roman *villa* offers insights about the prestige of the building. In fact, they were the most expensive among pigments [(*e.g.*, cinnabar had a pigments legally fixed price of 70 sesterces per pound vs 6 dinars for minium (Cerussa Usta) or 2 dinars for hematite (sinopia) [22]. This is the reason why painters used to mix cinnabar with other, less expensive, pigments as red ochre [62].

Regarding green pigment, it is a Cu-based pigment probably mixed with Egyptian blue and natural earth pigments to have more brilliant colours. This has been confirmed by the presence of both Cu and Fe in this green. Moreover, ER-FTIR showed the possible presence of synthetic resins, likely used for the conservation of mural paintings, but damaged by atmospheric humidity as detected by thermography. The main weathering product is gypsum. This study may represent a valuable reference for future restoration projects of the investigated fresco. Future developments should regard a deeper investigation involving the recovery of samples to perform laboratory analysis (e.g., X-Ray powder diffraction, cross sections, chemical analysis) or other non-invasive analyses such as multispectral imaging.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-024-01436-6.

Supplementary materials 1: Supplementary Table 1 Synoptic table of the analytical techniques performed on the wall painting.

Supplementary materials 2: Supplementary Table 2 Results of all pXRF measurements carried out on the painted surfaces.

Supplementary materials 3: Supplementary Table 3 Colorimetric data obtained for each colour.

Acknowledgements
The Authors extend special thanks to Pierfrancesco Talamo (Parco Archeologico dei Campi Flegrei—Museo Archeologico dei Campi Flegrei nel Castello di Baia – Bacoli) for assistance and authorization.

Author contributions
Conceptualization, C.R.,Ch.G. and P.C; methodology, C.R., Ch.G., M.V and G.M.; validation, C.R., P.C. and V.M.; formal analysis, C.R., Ch.G., M.V., G.M., and A.C.; investigation, C.R., Ch.G., A.D.B., Ce. G., P.C, R.E., resources, P.C. and V.M.; data curation, C.R., Ch.G., G.M., P.C. and M.V.; writing—original draft preparation, C.R., Ch. G., M.V.; writing—review and editing, C.R., G.M., M.V., Ch. G, P.C., A.D.B,.; visualization, C.R.; supervision, P.C. and M.V. All authors have read and agreed to the published version of the manuscript.

Funding
This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. This research received no external funding.

Availability of data and materials
No datasets were generated or analysed during the current study.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
All authors have read and agreed to the published version of the manuscript.

Competing interests
The authors declare no competing interests.

Author details
[1]Dipartimento Scienze della Terra, Dell'Ambiente e delle Risorse, Università di Napoli Federico II, Complesso Universitario Monte Sant'Angelo, Ed. 10, Via Cintia 26, 80126 Naples, Italy. [2]CRACS, Center for Research On Archaeometry and Conservation Science, Complesso Universitario Monte Sant'Angelo, Ed. 10, Via Cintia 26, 80126 Naples, Italy. [3]Naples, Italy. [4]Dipartimento di Scienze e Tecnologie, Università Degli Studi del Sannio, Via Dei Mulini 59/a, 82100 Benevento, Italy. [5]Dipartimento di Farmacia, Università di Napoli Federico II, Via D. Montesano 49, 80131 Naples, Italy. [6]Dipartimento di Architettura, Università di Napoli Federico II, Complesso Dello Spirito Santo, Via Toledo, 402, 80134 Naples, Italy.

Received: 6 May 2024 Accepted: 30 August 2024
Published online: 13 September 2024

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