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Pigments through the ages: examples from archaeological contexts of *Campania* region (southern Italy)

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Abstract – **The technological skills in the selection, combination and use of pigments from the ancient painters were investigated through the study of mural paintings of five archaeological contexts of *Campania* region, dated back from the 5th century BCE to the 1st century CE. The pigments were analysed by means of in-situ spectroscopic techniques and micro-destructive laboratory analyses. The multi-analytical approach revealed the use of pure (natural and synthetic) pigments and admixtures, created by the ancient painters to obtain different colour shades.**

I. INTRODUCTION

The study of mural paintings is relevant to deepen the technological skills of the ancient painters over time. The analysed paintings belong to five archaeological sites located in *Campania* region (southern Italy) and they are distinguished in residential and funerary contexts.

The oldest one is the well-known funerary context of Tomb of the Diver (5th century BCE,) a chest tomb that takes its name from the note pictorial representation placed on the covering slab and located 2 km south of *Paestum* (Fig. 1a). Along with this, other tombs recovered in the *Paestum* site and belonging to different chronological phases were analysed [1,2].

Another investigated funerary context is the *Tomba del Banchetto per l'Eternità* in the ancient city of *Cumae* (fist decades of the 1st century BCE), an extraordinary hypogeum chamber tomb entirely decorated with a figurative representation on the upper part of the walls, which makes it exceptional in the contemporary *Campania* panorama (Fig. 1b) [3,4].

The other investigated wall paintings refer to Roman residential contexts: i) the *domus* attributed to *Marcus Vipsanius Primigenius*, identified in the site of *Abellinum* (1st century CE; Fig. 1c) decorated in 3rd and 4th Pompeian style [5]; ii) the *domus* of *Octavius Quartius* in *Pompeii* (Fig. 1d) , located in the Insula 2 of the *Regio II* and decorated by frescoes in 4th Pompeian style, built after the earthquake of 62 CE [6,7]; iii) the *domus* with thermal baths in the city of *Pollena Trocchia* (near Naples; Fig. 1e) in the place of *Masseria de Carolis*, located on the northern slopes of the volcanic complex of *Somma-Vesuvius* [8,9].

The wall paintings from these contexts were analysed in order to identify the type of pigments adopted by the ancient painters, the way of applying and mixing them to obtain different colour shades, as well as evaluate their diachronic use in the *Campania* region in a time span ranging from the 5th century BCE to the 1st century CE.

II. EXPERIMENTAL

Materials

The present study is based on data obtained by a multi-analytical approach used to analysed both pictorial surfaces directly in-situ by spectroscopic analyses (*Paestum, Pompeii*) and representative samples by lab-techniques using with micro-destructive methods (*Cumae, Abellinum, Pollena Trocchia*).

Methods

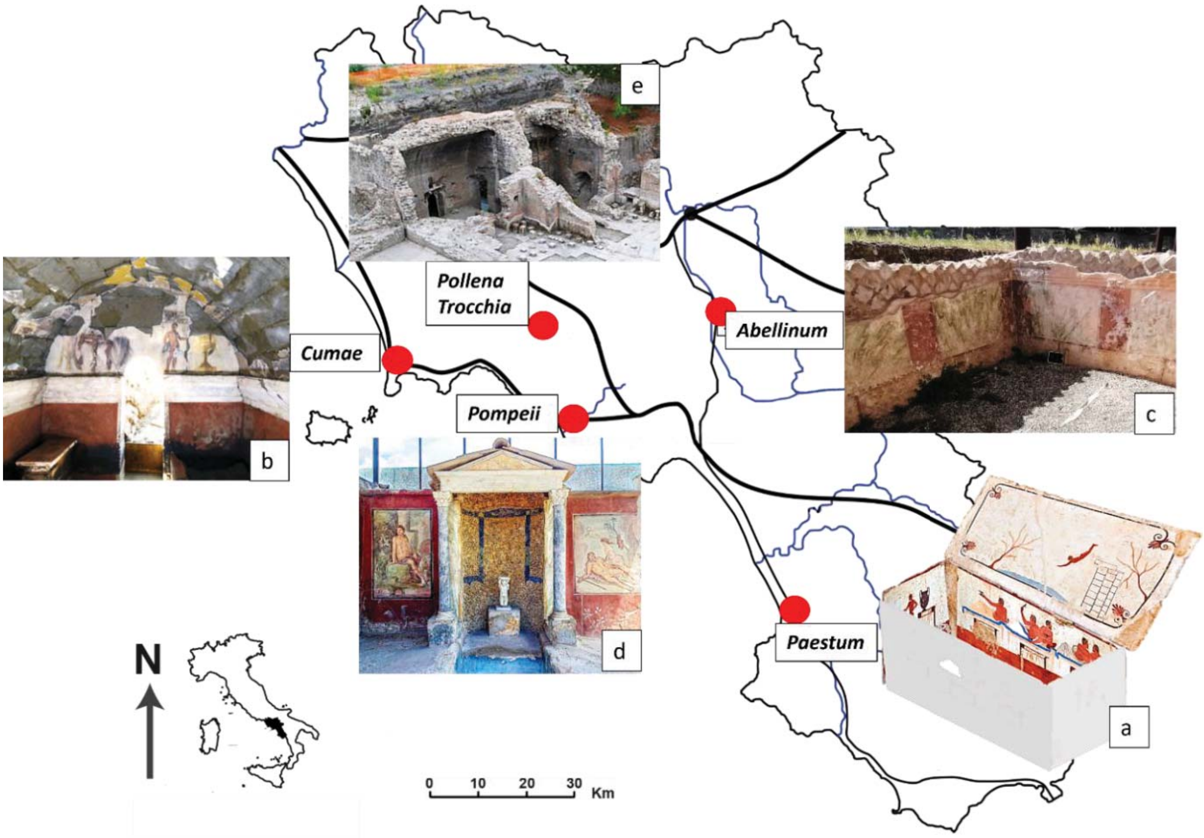

Figure 1. Archaelogical sites studied in *Campania* region (southern Italy): a) funerary box at *Paestum*; b) funerary chamber in *Cumae*; c) *domus* of *M. Vipsanius Primigenius* at *Abellinum*; d) *domus* of *Octavio Quartio* at *Pompeii*; e) *domus* at *Pollena Trocchia*.

At first, painted surfaces (from *Cumae*, *Abellinum* and *Pollena*, in Fig. 2) were observed with Dino-Lite digital microscopes (magnification range 400x - 470x), built-in coaxial illumination and Flexible LED Control (FLC), equipped 5.0-megapixel colour CMOS sensor. DinoCapture2.0 software was adopted for the acquisition of the images.
The chemical composition of pigments was detected by a SKYRAY LTD Genius 9000 X-ray fluorescence porTab. spectrometer (40 kV/100 µA power supply, Ag transmission target, 25 mm^2 Be-window, silicon drift SSD detector), and a BRUKER Tracer 5G X-ray fluorescence spectrometer, featuring at 30 kV/10 µA power supply, a rhodium (Rh) transmission target, acquisition time of 10 seconds and spot size of 8 mm. XRF spectra have been processed by the software Bruker ARTAX Spectra 8.0.
FTIR spectra were collected with a portable BRUKER Alpha FTIR spectrometer using front-reflection and attenuated total reflectance modules, covering a spectral range between 4000 and 400 cm^{-1} at the resolution 4 cm^{-1}.

Raman spectrometry was performed on the wall painting using a BRUKER BRAVO Handheld Raman spectrometer, using a Duo Laser excitation and a Sequentially Shifted Excitation (SSETM) technique for the fluorescence mitigation, equipped with a charge-coupled device detector (CCD). The Raman spectra were recorded in a spectral range between 3200 and 178 cm^{-1}. OPUS 7.2 software was adopted for the acquisition of spectra and for data processing for both FTIR and Raman analyses.
For the identification of the organic pink pigment and to check some pigments (e.g. to confirm iron oxides/hydroxides-based pigments from *Paestum* and for the EB from *Abellinum* and *Paestum*) punctual analyses were performed by Fiber Optics Reflectance Spectroscopy (FORS) in the spectral range 380-1050 nm by using a tungsten lamp (BeWTek, Inc. BPS101 Tungsten Halogen Light Source with a spectral output of 350 to> 2600nm) as source and the grating Qmini Broadcom as detector. The measuring head geometry was 45°/0°; the B&WTek inc. white plate (99%) was used as a reference.

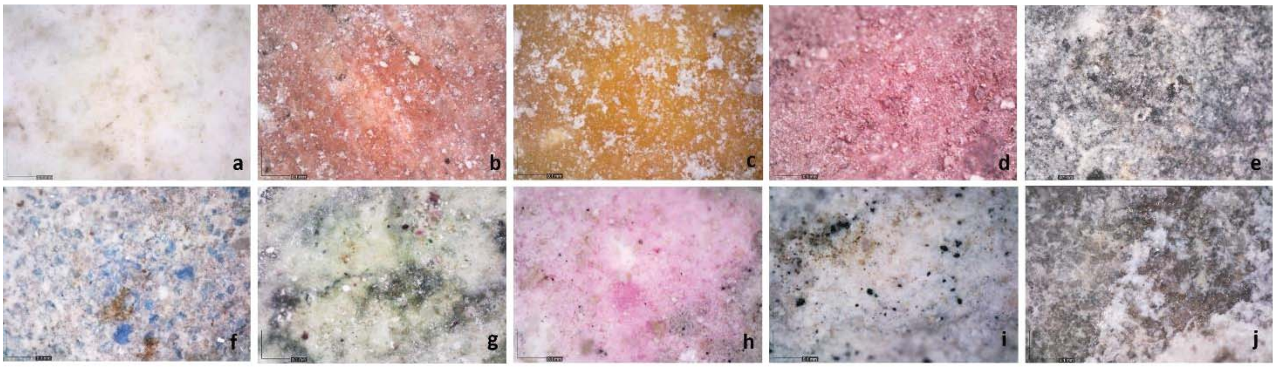

Figure 2. Representative images of pictorial layers obtained by Digital Microscopy: a) white paint from *Abellinum*; b) red paint from *Cumae*; c) yellow paint from *Cumae*; d) violet paint from *Cumae*; e) black paint from *Pollena*; f) blue paint from *Abellinum*; g) green paint from *Pollena*; h) pink paint from *Cumae*; i) grey paint from *Cumae*; j) brown paint from *Cumae*.

III. RESULTS AND DISCUSSION

A. White

Chemical analyses of white decorations (Fig. 2a) showed the ubiquitous presence of calcium (Tab. 1), as well as the infrared and Raman bands of calcium carbonate (Tab. 2,3), which suggested the diachronic use of calcite or aragonite as white pigment. Occasionally, it was also observed aragonite associated to precious coloured pigments (e.g. with the Egyptian blue on the *Abellinum* samples) [10,11].

B. Red

The red paint (Fig. 2b) is the most common colour in the analysed wall paintings, observed in different shades corresponding to compositional differences.

Dark red shades are featured by the presence of iron and calcium (Tab. 1), the latter attributed to the underlying plaster and/or the *medium* in which the pigment was dispersed. Infrared bands (Tab. 2) between 600-400 cm^{-1}, along with the peak of silicates between 1200 and 900 cm^{-1} allowed us to associate this pigment to red ochre, a natural red earth containing iron oxides, identified by Raman spectra as hematite (Fe_2O_3) (Tab. 3). Red ochre was used in almost all contexts and the FORS data confirmed the use of an earth-based pigment; in the tombs of *Paestum* the presence of lead (Tab. 1) suggested the addition of *minium* (Pb_3O_4).

In the contexts from the Vesuvian environment, instead, more brilliant red shades were obtained by cinnabar (HgS) a mineral used as pigment in the relevant Pompeian style paintings during the Roman period, as proved by the additional presence of Hg and the peculiar Raman shifts at 344 cm^{-1} (Tab. 3).

C. Yellow

Chemical analyses of yellow paints (Fig. 2c) revealed high concentrations of iron (Tab. 1) as well as the infrared bands of silicates and iron oxides/hydroxides (Tab. 2). Raman bands defined the presence of goethite ($Fe^{+3}O(OH)$), an iron hydroxide showed characteristic peaks at 385 and 568 cm^{-1} (Tab. 3). This mineralogical phase represents the main constituent of yellow ochre, used in all archaeological context analysed.

D. Violet

Violet pigment was identified in two archaeological sites, namely a residential (*domus* at *Pollena Trocchia*) and a funerary context (*Cumae* tomb; Fig. 2d) However, it was prepared by using different recipes.

Although there is also evidence in the Roman world to attest the organic origin of the violet pigment [12], the aforementioned studied sites do not fall into this typology. In the wall painting covered the rooms of the *domus* in *Pollena Trocchia* XRF spectra revealed the presence of high concentration of copper, iron and calcium (Tab. 1). Hematite, showed by molecular analyses (Tab. 3), seems to be one of the components of the mixture. On the other hand, the presence of copper was justified by the digital microscope images (Fig. 2) that highlighted the presence of (Egyptian) blue particles in the mixture, as it was commonly carried out for the preparation of the violet colour [13]. In the decorated tomb of *Cumae*, instead, the pictorial layer revealed only the presence of iron and calcium (Tab. 1); Raman spectra identified the hematite (Tab. 3). therefore, the violet colour was obtained by heat-treating red iron oxide in an oxidizing environment, using a technique equally common in the Roman world. In this pigment typology, the darker colour hue is due to the α-Fe_2O_3

Colour	PAESTUM	CUMAE	ABELLINUM	POMPEII	POLLENA
White	Ca, Al, Si, Fe*, Sr*	Ca, Sr*	Ca, Sr*	Ca, Fe*, Sr*	Ca
Red	Al, Si, S, K, Ca, Mn, Fe, Zn, Pb, As*	Ca, Fe, Si, Al*, K*, Mn*, Sr*	Ca, Fe, Sr*	Ca, Fe*, Sr*/ Ca, Hg, S, Fe*, Sr*	Ca, Fe, Hg, Sr* / Ca, Fe, Pb*, Sr*
Yellow	Ca, Fe, Al, Si, S, K, Mn, Sr*, Pb*	Ca, Fe, Si*, Al*, K*, S*	Ca, Fe	Ca, Fe, Sr*	Ca, Fe, Al*, K*, Sr*
Violet	—	Ca, Fe, Si*, Al*, K*	—	—	Cu, Fe, Ca
Black	Al, Si, S, K, Ca, Fe, Ti*, Cr*, Sr*	—	—	Ca, Fe*, Sr*	Ca, Fe, Sr*
Blue	Cu, Ca, Fe, Al, Si, S, Sr*	Cu, Ca, Fe, Si* Al*	Cu, Ca, Fe, Sr*	Ca, Cu, Fe, Sr*	Cu, Ca, Fe
Green	Al, Si, S, K, Ca, Ti, Fe, Cu*, Sr*	—	—	Ca, Fe, Cu, Sr*	Ca, Fe, Cu*, Sr*
Pink	—	Ca, Fe, Si, Al, K, Cu, S*, Sr*	Ca, Fe	Ca, Fe	—
Grey	—	Ca, Fe, Si, Cu, Al, S, K, Ti*, Sr*	—	—	—
Brown	—	Ca, Fe, Si*	—	—	—

Table 1. XRF results on painted fragments from the studied archaeological sites (the asterisk indicates trace elements; the slash indicates the presence of two shades of the same colour).

Colour	PAESTUM	CUMAE	ABELLINUM	POMPEII	POLLENA
White	2510, 1794, 1410, 873, 713	1412, 871, 709	2510, 1795, 1410, 873, 713	2590, 2510, 1794, 1420, 875, 713	1415, 873, 729, 711
Red		545, 448	1795, 1640, 1409, 1034, 873, 712, 692, 532, 460	1100-900; 600-400	533, 462
Yellow	1200-900; 600-400	3400, 1640, 890, 800	3359, 2517, 1795, 1646, 1407, 1029, 872, 712, 526, 471	1112, 1030, 1005, 910, 460, 430	3694, 3617, 1029, 912, 795, 531, 467, 426
Violet	—	536, 463	—	—	543, 466
Blue	1150-1000	—	1795, 1649, 1414, 1160, 1048, 1010, 874, 712, 664, 519, 477	1159, 1049, 1004	1158,1047, 1004, 792, 755, 663, 593, 517, 467
Green	3600-3400; 1200-900	—	—	3700-3500	3555, 3530, 968, 3694, 3617, 1029, 912, 795, 531, 467, 426
Pink	—	3692, 3620, 3482, 1028, 913, 793, 751, 535, 462, 425	—	2510, 1793, 1410, 872, 713, 545, 470	—
Grey	—	3690, 3620, 1200, 1029, 912, 794, 752, 597, 535, 466, 428	—	—	—
Brown	—	Ca. 3400, 2900-2800, 1413, 873, 711	—	—	—

Table 2. Infrared bands (in cm^{-1}) of analysed colour hues. Data are obtained from ATR-FTIR for pigments studied in *Cumae*, *Abellinum*, *Pollena* sites, and from ER-FTIR for *Pompeii* and *Paestum*.

particle size effect, bigger than the hematite constituting the red pigment [14].

E. Black

Spectroscopic analyses and in particular the Raman bands at ca. 1600 and 1320 cm^{-1} (Tab. 3) carried out on the painted wall surfaces of the *domus* in *Pompeii* and *Pollena Trocchia* (Fig. 2e) as well as on the painted tombs from *Paestum* revealed that black decorations were obtained by using the black carbon, a pigment derived from the combustion of organic material (coal, wood, oil) able to produce soot [15,16]. Unfortunately, it is not possible to have comparisons from all contexts either due to the lack of black painting or to restoration work that do not allow the identification of the underlying original pigment.

F. Blue

Chemical analysis on blue paints (Fig. 2f) identified the ubiquitous use of a copper-based pigment (Tab. 1). Infrared spectroscopy and reflectance curves related to electronic transitions attributable to Cu^{2+} ions confirmed the use of Egyptian blue (Tab. 2), a synthetic pigment prepared by mixing a sand containing quartz, feldspar, and carbonates with copper colouring compounds and alkaline flux to form a synthetic frit containing cuprorivaite ($CaCuSi_4O_{10}$) [17]. The use of the unique Egyptian blue pigment in *Campania* is not surprising, considering that between the 1st century BCE and the 2nd century CE factories of Egyptian blue were born in the Phlegrean territory and then widely used in regional and

Colour	PAESTUM	CUMAE	POMPEII	POLLENA
White	1086, 712	1086, 710, 280	1086, 713	1097, 1087
Red	612, 498, 410	614, 498, 410, 291, 224	610, 410, 496/344	343, 283, 253
Yellow	388	553, 386, 298	547, 488, 388	568, 385
Violet	—	611, 495, 408, 291, 223	—	417, 298, 226
Black	1596, 1320	—	2880, 2846, 1598, 1325	1615, 1390
Pink	—	—	1086, 608, 412	—
Grey	—	1086, 711, 281, 209	—	—
Brown	—	1625, 1310, 1085, 705, 553, 386, 298, 282, 207	—	—

Table 3. Raman results (cm^{-1}) on painted fragments from the studied archaeological sites. Raman spectroscopy was not carried out on the *Abellinum* fragments and the restored surfaces did not allow for the pigment identification at *Paestum*. Raman spectra for the blue and green pigments are not available, as the high fluorescence obscured their diagnostic bands.

extra-regional construction sites [18,19]. Due to the high florescence of the pigment, no Raman spectra were acquired on the blue paintings [6].

G. Green

Three contexts (*Paestum*, *Pompeii* and *Pollena Trocchia*) offered the possibility of analysing green pigments (Fig. 2g). The results revealed the use of two different typologies of pigment used for the green decorations. Chemical composition (Tab. 1) of these colour, in fact, showed the presence of aluminium, silicon, iron, calcium and potassium referred to the use of green earths [20]. This hypothesis was confirmed by FTIR analyses, which revealed diagnostic bands at 3700-3500 cm^{-1}.

Chemical analyses, however, also highlighted the presence of copper in lighted shades, confirmed by FTIR spectra that recorded the infrared bands of Egyptian blue (Tab. 2), suggesting the use of a mixture, made by the addition of Egyptian blue pigment to the green earths, a recipe widely used in the ancient world [21]. As the blue pigment, also for the green one the high florescence does not allow us to acquire Raman spectra.

H. Pink

Chemical and mineralogical analyses revealed that pink colour was obtained using two different "recipes".

Skin tones come from the depiction of *domus* in *Pompeii* were obtained by mixing inorganic red pigment (red ochre) with calcium carbonate, to lighten the red colour [6].

On the bright pink decorations found at *Cumae* (Fig. 2h), on the other hand, ATR-FTIR highlighted the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) (Tab. 2) which suggests the use of a white (kaolinite-bearing) clay as an extender, in which other materials were mixed. In fact, the presence of copper and iron (Tab. 1) suggests the addition of hematite and Egyptian blue, likely to give more brilliance to the colour shade, as observed also via DM (Fig. 2h) [22]. Nevertheless, FORS revealed the characteristic pattern of the organic (madder) pigments in the visible region, with the strong absorption band between 500 and 600 nm divided two main sub-bands, occurring at 510-515 nm and 540-545 nm [3]. This type of shade already was known by the ancient author: it was obtained by mixing of a white kaolinite-rich clay to a violet madder and other inorganic compounds [23].

I. Grey

An interesting pigment mixture was detected for the grey decorations in the *Cumae* tomb (Fig. 2i). Chemical analysis showed high concentration of copper, iron, silicon, aluminium, potassium (Tab. 1), whereas ATR-FTIR detected the infrared bands of kaolinite (Tab. 2). Again, it suggests the use of a white clay as an extender, in which blue and black particles composed of Egyptian blue and iron oxides, respectively, were mixed, as confirmed by the presence of copper and iron [3].

J. Brown

Brown pictorial layer evaluated in the present study come from the archaeological context of *Cumae* (Fig. 2j). The analyses revealed that brown shades were obtained by mixing yellow ochre and black pigment of organic origin [3]. Goethite and carbon black, in fact, were detected by molecular analyses (bands in Tab. 2, 3). Brown paint, thus, was obtained mixing in different proportions yellow and black pigment, depending on the darkness of brown shade to obtain.

IV. CONCLUSIONS

The analysis and comparison of the pigments used in *Campania* region in both funerary and residential contexts emphasized the similarity in the technological choices made by the ancient master over five centuries of the Roman world. The chemical-mineralogical analyses allowed the identification of natural and synthetic pigments useful to evaluate the technological skills of the ancient painters and the used recipes mixing various typologies of pigments to obtain different colour shades.

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