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# Analytical data on marble sculptures' polychrome traces (Palatine hill, Rome).

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***Abstract* – Polychromy in ancient statues is raising interest both from an archaeological and archaeometrical point of view. In this study we show analytical data obtained both non-invasively *in situ* and on micro-fragments in the laboratory. A complementary approach based on portable X-ray fluorescence and vibrational spectroscopies (Diffuse Reflectance Infrared Fourier Transform and Raman spectroscopies) was used for studying polychromy traces of two marble sculptures from excavations on the Palatine hill.**
**This combined approach allowed the characterization of both pigments and organic media, highlighting the use of pigments such as ochres, Egyptian blue, lead-based compounds, malachite, and of gold.**

## I. INTRODUCTION

The interest of archaeologists and conservation scientists in the polychromy of ancient marble sculptures is growing. The exhibition 'ClassiColor – the colour of ancient sculpture', held at the Ny Carlsberg Glyptotek, Copenhagen in 2004 gave rise to The Copenhagen Polychromy Network (CPN) and to the project 'Tracking Colour', that testifies the importance of the awareness around polychromy even for a wide audience, and collects case studies of different sorts and epochs ([1] and www.trackingcolour.com).
Many of these researches involved archaeometry [1-14], more and more evolving towards non-destructive, non-invasive and *in situ* investigations, due to the preciousness of such feeble traces of ancient color. The most widespread colours are red, blue, pink, yellow and white, usually obtained with ochres, Pb-based pigments, Egyptian blue, calcite [4-7, 9, 11, 13-14]; organic colorants are also reported, mainly lakes for red and pink tones [3, 6, 9, 12-14].
Focusing on Roman sculpture, in the last decade, the most employed technique has been Raman spectroscopy [4-7, 9], due to its peculiar suitability in the detection of pigments and to its non-invasive nature. It is sometimes coupled with complementary techniques to fully characterize the paint layer, as for example X-ray Fluorescence [6, 13], infrared spectroscopy [4, 9], separation techniques such as liquid [6, 9] and gas-chromatography [9], the latter three appropriate for the identification of organic substances. Also, optical [4, 5, 9, 14] and electron [4, 9, 14] microscopy observation of fragments can be performed. Moreover, imaging techniques [3, 12] and 3D reconstructions [5] are being implemented.
In the present work, two sculptures found on the Palatine hill in Rome were considered: a male statue with mantle and a *cista* (basket): the former shows pink, blue and red traces, while the latter must have been gilded and coloured in red, yellow and green. With a mainly non-invasive approach including portable X-ray Fluorescence (pXRF) and portable Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS), integrated with laboratory micro-Raman analysis of few micrograms of pigmented powder, this study aims at shedding light on the employed raw materials, to widen the knowledge on Roman sculptures polychromy and place the objects of the study within the frame of the state of the art.

## II. MATERIALS AND METHODS

### A. Materials

The male statue with mantle (Inv. 536548), kept at Museo Palatino (Rome) was found in 2008 on the Palatine hill, in the context of the excavations of the *Domus Tiberiana* [15]. It was lying horizontally in a renaissance age dump in the area of the central *cryptoportico*. The headless Paros marble statue was sculpted in the Augustan-Giulio-Claudian epoch with the technique of piecing. It is 170 cm tall and is composed of 16 pieces held together by iron hinges and gypsum containing plaster [16]. It has been interpreted as the representation of a remarkable member of the imperial family, the emperor himself, or one of his relatives. The sculpture surface has been enriched with polychromy applied directly on the marble without a preparatory layer: except for the skin, evident pigmented traces are found on the base, on the prop in the form of a tree trunk, as well as on the mantle. The formers still show much of the original reddish-brown shade, while the folds of the mantle show a bright pink band, approximately 5 cm wide, and a 1 cm blue line overlapping to the pink.


*Fig.1. The male statue with mantle (a) and details of the polychrome decoration (b, c); the 'cista' (d) and a painted and gilded detail (e).*

Three marble fragments belonging to a *cista* (basket, Inv. 537364a-b-c), kept at Museo Nazionale Romano (Rome), were recovered from the same excavation context. The marble is fine grained, likely of Greek origin. It has been dated between the Giulio-Claudian and the Flavian period. It is most likely an element pertaining to a sculptural group of Dionysian context. Two fragments match and correspond to the cover of a wicker basket, while the third shows the truncated cone shape of the woven wicker basket. The basket was partially covered by a piece of leather with fringes (apparently yellow colored), and branches of ivy and corymbs in bright green. The wicker basket shows both a reddish-brown pigment and gold traces.

### *B. Analytical techniques*

Portable X-Ray Fluorescence (pXRF) analyses were performed in air with a battery-operated Bruker Tracer IV-SD system equipped with a Rh target X-ray tube with Pd slits and a Silicon Drift Detector. The tube was operated at 40kV and 17μA for trace element analyses (K, Ca, Ti, Fe, Cu, As, Sr, Sn, Au, Pb). 60s live time accumulations were collected. Qualitative data were obtained by means of the S1PXRF software, while the abundances of trace elements in ppm by means of PyMCA software [17], which is based on fundamental parameters adapted to the measurement setup. Finite thickness of the pigmented layer, the presence of surface deposits, and the irregular surface of the paint affect the quantitative analysis, but as these errors are common to all the spectra, the results can be compared.

DRIFT spectra were acquired with an Agilent Cary 630® modified by Madatec srl with an accessory for Non-Contact Measures (MadaIR). Thanks to its small size (16x31x13 cm) and weight (4.8 Kg), the instrument is handy and easily mounted on a tripod with xyz translators. It employs a Michelson Interferometer, covers the spectral range 650-5500 $cm^{-1}$ and reaches a spectral resolution of 4 $cm^{-1}$. The software Agilent MicroLab PC was used to control the system. 360 scans (about 3 minutes) were averaged. The intensity unity in the spectra is defined as absorbance A' (A'= log(1/R)).

The micro-Raman laboratory investigations were performed by means of a Jasco NRS3100 spectrometer. It is furnished with a microscope with 50× LWD and 100× objectives, a Notch filter, a Peltier-cooled (-55 °C) 1024x128 CCD detector and two solid state lasers (532 and 785 nm). In order to avoid heating effects, the power of illumination can be modulated with neutral optical density filters. The spectral resolution reaches 1 $cm^{-1}$ with the1800gr/mm grating; the minimum lateral and depth resolutions can be as good as 1 μm. The system calibration was performed using the 520.7 $cm^{-1}$ Raman band of silicon. The employed parameters, adjusted for each sample considering its color and the arising fluorescence, were set as follows: power values between 0.3 and 2.5 mW, time of acquisition between 10 and 60 seconds and accumulations between 3 and 100.

## III. RESULTS

### *A. The male statue with mantle*

The pXRF results (Fig.2) show the signals of Ca, Fe and Sr from the marble. Moreover, in the pigmented areas, they highlight a significant lead content in all the coloured areas. This can be explained by the variety of Pb-based pigments available to Romans, such as red lead and lead white, which could be used alone or in mixtures [11]. The reddish-brown base and prop show high iron as well. Copper is revealed in the blue areas, as well as in a pink spot, probably indicating feeble traces of the original layering (blue stripe on top of pink band).

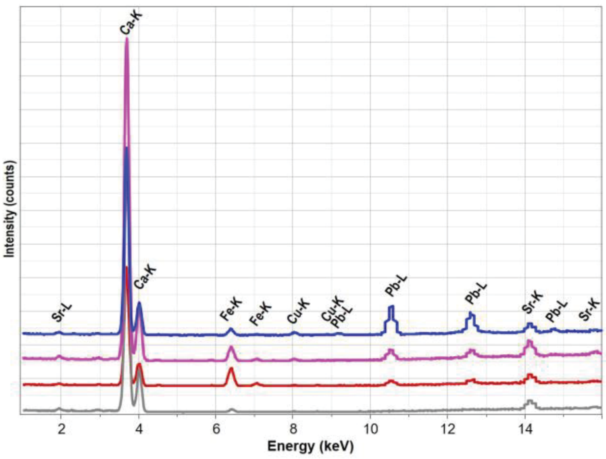


*Fig.2. pXRF spectra acquired on the male statue with mantle. From bottom to top: marble (torso), reddish-brown base, pink, blue.*

The DRIFT spectra obtained *in situ* on the blue and the pink areas are reported in Fig.3. The spectrum of blue (Fig.2a) is characterized by the presence of signals typical of organic substances: 4265 and 4410 cm$^{-1}$ ($\nu + \delta$(C-H)), and, in detail, lipids (derivative 1740 cm$^{-1}$ ($\nu$(C=O)) [16], and proteins (1590 (Amide I), 1654 (Amide II) and 2900 ($\nu$ (C-H)) cm$^{-1}$) [19, 20]. Actually, the signals in the region between 2800 and 3000 cm$^{-1}$ could also be attributed to calcite [21]. Indeed, the features of carbonatic phases are well visible: probably hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) peaks (1740, 4300 cm$^{-1}$) are summed to calcite ($CaCO_3$) ones (2515, 2595 cm$^{-1}$), due to the marble substrate [22]. The features of a blue pigment are difficult to be spotted: the inverted band at 1050 cm$^{-1}$ may lead to think to Egyptian blue ($CaCuSi_4O_{10}$) presence, but the other characteristic peak at about 1005 cm$^{-1}$ is missing [22, 23]. The spectrum acquired on the pink area, even if noisy, (Fig.3b), clearly shows a broad band centered at 3650 cm$^{-1}$, which may account for the doublet 3618, 3695 cm$^{-1}$, as well as the band at about 4530 cm$^{-1}$, characteristic of kaolin [20]. The signature in the low wavenumber region is less clear. The bands in the region of silicates may support the attribution either to earths or to a mineral support for an organic lake, or to burial deposits.

The Raman analyses carried out on the powder of pink material at the laboratory reveal a spectrum characteristic of hematite (Fig.4, $\alpha$-$Fe_2O_3$), principal constituent of red ochres (230, 294, 412, 496 cm$^{-1}$) [24, 25]. Seen the colour of the sample, it appears that other materials have to be present, either white or pink [2], but they were not identified so far.

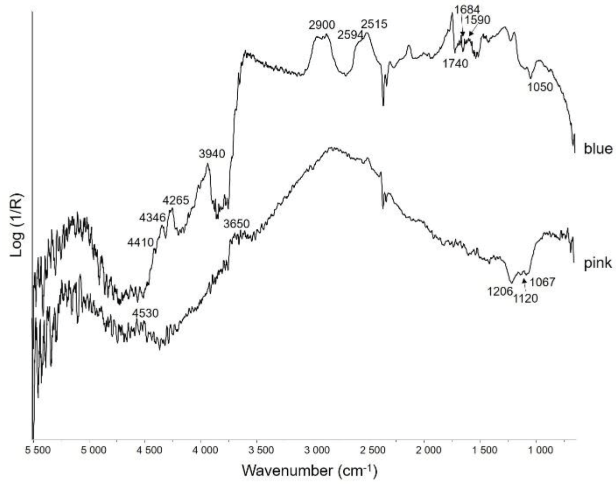


*Fig.3. DRIFT spectra of the blue and the pink areas on the male statue with mantle.*

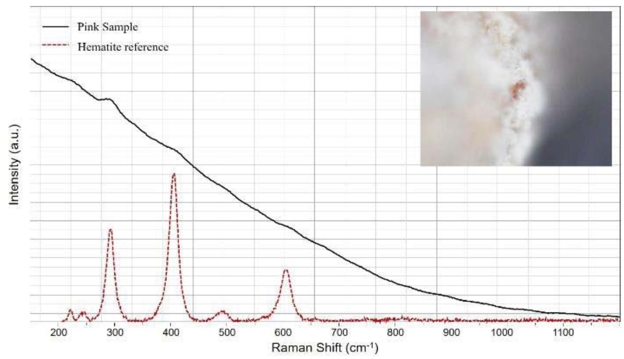


*Fig.4. Raman spectrum acquired on the pink powder and reference spectrum of hematite.*

*B. The 'cista'*

The elemental analyses carried out *in situ* by means of pXRF (Fig.5) allowed to highlight the presence of Ca, Fe and Sr from the marble. Strong signals of lead, and the overlapping arsenic signal can suggest the presence of the mineral mimetite ($Pb_5(AsO_4)_3Cl$), common in lead-ore deposits or ochres [11]. On the green areas, instead, the copper concentration was remarkable, together with some lead (possibly a white or yellow lead-compound). Furthermore, one of the pink spots clearly showed, together with iron, the L lines of gold. The pink material, composed of Fe-rich ochres, can be interpreted as the coloured layer (*bole*) on top of which gold leaf was applied. Such gilding technique was widespread during classical times [13, 14, 26, 27].

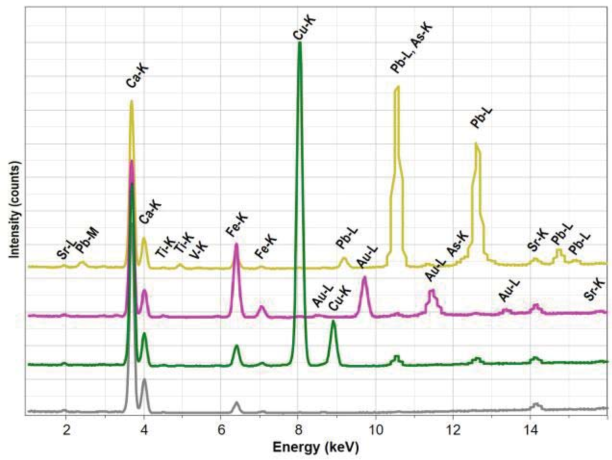


*Fig.5. pXRF spectra acquired on the 'cista'. From bottom to top: marble, green, pink, yellow.*

The laboratory Raman analyses (Fig.6) gave interesting spectra for what concerns the green powder: they exhibit signals attributed to yellow ochres (398 and 695 $cm^{-1}$) and to malachite ($Cu_2CO_3(OH)_2$) (180, 218, 271, 353, 431, 535, 718, 1056-1094, 1495, 3305, 3375 $cm^{-1}$), the latter being a rare and precious green pigment [24, 25, 28]. The punctual micro-Raman analyses on the minute yellow sample did not allow to confirm the nature of the Pb-containing pigment.

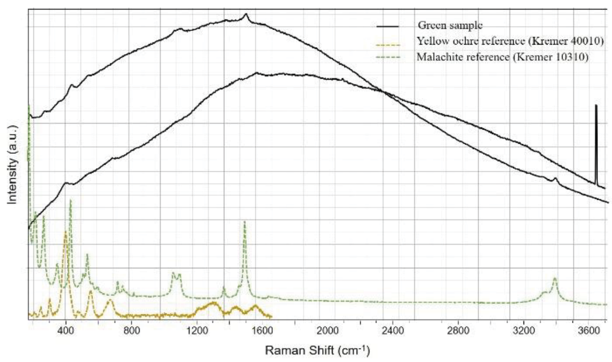


*Fig.6. Raman spectra acquired on the green powder and reference spectra of yellow ochre and malachite.*

## IV. CONCLUSIONS

The employed approach proved successful for the identification of the pigments constituting the coloured traces of the two marble sculptures.

The male statue with mantle revealed the use of Egyptian blue in the blue stripe, and red ochres with the addition of Pb-rich pigments, respectively white in the pink and red lead in the reddish brown base; unfortunately, the identification of an organic lake in the pink, whose presence has been proposed, could not be achieved neither *in situ* nor in the laboratory. For the blue areas, traces of an organic binder can be hypothesized by *in situ* non-invasive analyses.

The *cista* was decorated with red ochres and malachite with the addition of yellow ochres. Moreover, hints to the presence of mimetite in the yellow areas were also found. The presence of malachite to give the green colour, instead of green earths, marks this object as particularly precious. Finally, *in situ* non-invasive analyses allowed to put forward hypothesis on the gilding technique employed, which was likely based on the application of gold foil on top of a reddish coloured Fe-rich layer.

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