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PIGMENTS MAPPING ON TWO MURAL PAINTINGS OF THE "HOUSE OF GARDEN" IN POMPEII (CAMPANIA, ITALY)

Domenico Miriello[1], Raffaella De Luca[1*], Andrea Bloise[1], Giancarlo Niceforo[1], J. Daniel Martin-Ramos[2], Alberta Martellone[3], Bruno De Nigris[3], Massimo Osanna[4] and Giacomo Chiari[5]

[1]Department of Biology, Ecology and Earth Sciences (DiBEST), University of Calabria, via P. Bucci, 87036 Rende (CS), Italy
[2]Department of Mineralogy and Petrology, Campus of Fuentenueva, s/n, University of Granada, 18017 Granada, Spain
[3]Applied Research Laboratory of Archaeological Park of Pompeii, via Plinio 4, 80045 Pompeii (NA), Italy
[4]General Director of Archaeological Park of Pompeii, via Plinio 4, 80045 Pompeii (NA), Italy
[5]Getty Conservation Institute (Retired), Getty Center Drive, Los Angeles, USA

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**Corresponding author: Raffaella De Luca (raffaella.deluca@unical.it)*

ABSTRACT

Two mural paintings located in the "House of Garden", recently excavated in the Regio V of the archaeological site of Pompeii (Campania, Southern Italy), were studied.
The mural paintings are in room 3 of the house. The first is a large-scale scene representing Venus with a male figure (possibly Adonis or Paris since he has a bow) and Eros, while the second one is a fine female portrait, perhaps depicting the *domina* of the house.
All analyses were carried out *in situ*, using a new non-destructive methodology based on the acquisition of good-resolution visible images and the chemical information obtained by a portable hand-held X-ray fluorescence device. All data were statistically combined using a computer program, named SmART_scan, obtaining maps of the distribution of the elements (or compounds) on the painting. Visible induced luminescence (VIL) was used to confirm the presence of Egyptian Blue.
The study performed on the two mural paintings allowed us to identify the various pigments used and to determine the presence of degradation products, such as soluble salts and a violet-black discoloration that, in the first painting, has modified some of the original colours, producing substantial changes in the interpretation of the figures.
The results of the work show that the SmART_scan methodology, coupled with an X-ray fluorescence device and a good-resolution visible image, is a valid tool for obtaining the spacial distribution of each element and often of the pigments as combination of them, on large surfaces in a short time and at low cost.

KEYWORDS: mural paintings; pigments; SmART_scan; elemental maps; Egyptian blue; manganese; soluble salts; efflorescence

1. INTRODUCTION

The archaeological site of Pompeii, located in the southern slope of Mount Vesuvius, in Southern Italy (Fig. 1a), is a testimony of a Roman town of the 1st century C.E. in all its urban, architectural, and decorative aspects, exceptionally preserved due to the layers of ash and lapilli that covered them during the volcanic eruption of 79 C.E. The city, inhabited since Neolithic times, was subjected to the Etruscan, Greek and Samnite domination until the 4th century B.C.E., when it was conquered by the Romans (Panebianco, 1979). Around the 2nd century B.C.E., named "golden century of Pompeii", the city had a significant growth, reaching its magnificence just before its total destruction. It was heavily reconstructed after the 62 C.E. earthquake and repair works were still in progress when the volcanic eruption of 79 C.E. completely buried the city, hiding it to the point that even its location was forgotten. At the beginning of the 16th century, during remediation works in the Sarno Valley, the first inscriptions of the ancient city were discovered (De Vos and De Vos, 1982; Richardson, 1988; Santini, 2004; Varone, 2005).

The archaeometric approach applied to cultural heritage is fundamental to obtain information on materials, production techniques and history of ancient people (Bratitsi et al. 2019; Liritzis et al. 2020); in particular, the multidisciplinary approach allows to solve archaeometric problems that concern mural and other surface paintings (Vázquez de Ágredos-Pascual et al. 2019; Acri et al. 2020; Mona Ali and Marian Youssef 2020a; Mona Ali et al. 2020b; Mona Ali and Mahmoud Elkawy 2021).

Starting a long time ago (Chapal, 1809), many studies have been carried out to identify the pigments employed in Pompeii (Augusti, 1967; Zanella et al., 2000; Cotte et al., 2006; Welcomme et al., 2006; Aliatis et al., 2009; Duran et al., 2010; Piovesan et al., 2011; Miriello et al., 2018; Marcaida et al., 2018; Angelini et al. 2019) using destructive and/or, more recently, non-destructive methods.

The present work aims to provide a further contribution to the knowledge of the materials and execution techniques used in Roman mural paintings. It is part of the collaboration agreement, signed in 2018, between the Department of Biology, Ecology and Earth Science (DiBEST) of the University of Calabria and the Archaeological Park of Pompeii (PAP). This project, taking advantage of the Applied Research Laboratory, aims to become a 'hub' for Pompeian research and studies aimed at the conservation of the site. The goal of our study is to clarify the pigments composition and their distribution on two mural paintings located in the "House of Garden" discovered, during the last excavations of 2017-2018, in the Regio V of Pompeii.

The excavations of Regio V, between the 2nd and the 3rd insula, carried out under the Great Pompeii Project to secure 2.6 km of the slopes of the unexcavated plateaus, have brought to light several previously unknown sectors of the ancient city. A previous excavation in this area took place at the beginning of the 20th century, at the time of the excavation of the famous "House of the Silver Wedding", close to the new sector.

The "House of Garden" was discovered during the last phase of the 2017-2018 excavation. Its name is due to the presence of a large open space, probably a "*hortus*" based on archaeobotanical studies, with several rooms overlooking it (Fig. 1b): one of these is the "room of the skeletons", where the archaeologists found at least nine corpses – men, women and children – who were looking for escaping during the eruptive event. The house had its main access from the "Vicolo dei Balconi", connected with the decumanus of "Via Nola". The entrance led to an atrium (room 5) communicating with a portico (room 10) which opens into the garden where, at the time of discovery, some amphorae were found *in situ*. The portico is separated from the garden by two masonry columns (Fig. 1c), placed on a plinth decorated with flowering plants painted over a black background (Fig. 1d). The house has preserved most of the decorative apparatus. The portico, and the rooms that face it, show a decoration belonging to the 4th Pompeian style, with architectural motifs and red and yellow panels adorned with idyllic-sacral images (Osanna, 2019).

The mural paintings studied are in the room 3 of the house. The first one (Fig. 1e), on the east wall, is a large-scale scene that shows Venus with a male figure (perhaps Paris since a bow is showing next to his sitting, or Adonis) and Eros. For simplicity, hereafter we will indicate the male figure as "Paris" and the entire mural painting as "Venus's mural". The second mural painting (Fig. 1f) is located at the end of north wall and is a refined female portrait, perhaps depicting the *domina* of the house.

The study of these two mural paintings was performed *in situ* using a non-destructive methodology proposed by Martin-Ramos and Chiari (2019) based on the combination of good-resolution visible images with chemical compositional measurements obtained by portable X-ray fluorescence.

Figure 1. (a) Location of Pompeii in Southern Italy with detail of the bay of Naples. (b) Plan of the "House of Garden" in Regio V. (c) Portico (room 10) with the two columns. (d) Plinth on which the two columns of the portico are located, decorated with flowering plants on a black background. (e) Venus's mural. (f) The female portrait.

2. MATERIALS AND METHODS

In the Venus's mural the three figures are painted in light colours on a red background (Fig. 1e). One can notice a darker tone concerning Paris hair, the Eros wings, a small triangle at Venus's feet (point 33 in Fig. 2a) and, to a lesser extent, Venus's dress. Fig. 2a documents the location of the 35 XRF points measured, selecting the most representative colours.

The female portrait (Fig. 1f) is better preserved, showing warm tones varying from red to yellow, except for the woman dress, in which a grey-bluish colour dominates. For this smaller mural, which appears to be more homogeneous, 21 representative points were analysed (Fig. 2b).

Figure 2. Location of the points analysed by portable XRF fluorescence. (a) Venus's mural. (b) Female portrait.

The study of the two mural paintings was carried out *in situ*. Chemical analyses were performed using a Bruker Tracer IV SD portable spectrometer, equipped with a Rhodium (Rh) tube, coupled with a vacuum pump (conditions: 40 kV, 35 µA, 35 s acquisition time, with a vacuum < 17 Torr, no filters, spot size approximately 5 mm in diameter). Spectra interpretation was performed by the "Bruker AXS MA Artax 7.4" software.

The XRF results (counts/sec) and the net counts are shown in the Supplementary Materials (Table S1 for the Venus's mural and Table S2 for the female portrait).

The visible images were captured using a Nikon d750 camera, with a 24-120 f4 lens.

The combination of the good-resolution visible images (Figs. 2a and 2b) and the chemical data was performed using the programme SmART_scan that statistically combines the colour (RGB) gained by the program from the visible image, the chemical elemental information obtained by XRF and the relative position of the observed and unknown points in the maps. The minimization, throughout the whole painting, of the Euclidean distance between the measured and unknown points in the multi-dimensional space allows for the making of the maps. These false-colour maps show, under request, the distribution of the various elements. To identify pigments that contain discriminating elements (e.g., mercury for cinnabar) it is simple. More complex is the situation for pigments whose formula contains several elements. However, it is possible to combine the elements that are part of complex formulas, by using Boolean operators such as <AND>, <OR>, <NOT> (e.g., joint presence of calcium and sulphur to obtain calcium sulphate, of which the most common is gypsum - $CaSO_4 \cdot 2H_2O$, or Ca,Cu,Si to get Egyptian Blue – $CaCuSi_4O_{10}$).

We quote here for a more in-depth comprehension of the method, the mathematical description given by the Martin-Ramos and Chiari (2019). "The method requires that the composition of n points Po(n), with n possibly large [20-40 depending on the dimension of the object], together with their precise position, are measured (XRF, XRD, Raman, FTIR, FORS) and that at least a good quality visible image is available. Each known Po(n) is characterized by 6 values: the composition Co(n), the position on the object (Xo(n), Yo(n)), and the colour coordinates of the visible image (Ro(n), Go(n), Bo(n)). For other images that may add further information (UV, IR multispectral if available), coordinates equivalent to those of the visible colour cube can be defined (R1(n), G1(n), B1(n), … Rj(n), Gj(n), Bj(n)). For any point P of unknown composition CP, we can write: P = (CP, Xp, Yp, R1p, G1p, B1p, … Rjp, Gjp, Bjp) where CP is the only unknown, since all other variables can be deduced by SmART_scan for each position Xp, Yp, from the various images inserted in the procedure. In the colour hyper-cube, we can calculate the Euclidean distance between the point P in exam and all the n known points P0(n): E(P-P0(n)) = [(XP-X0(n)^ 2 + (YP-Y0(n))^ 2 + (RP-R0(n))^ 2 + (GP-G0(n))^ 2 + (BP-B0(n))^ 2]^ ½. The composition of the point Po having the smaller Euclidean distance (EMIN) is assigned to the generic point P, located at any (XP,YP) coordinates. The composition C(Px,y) so calculated can now be shown in a false colour map for each Xp,Yp point of the object. A very high-quality image (up to 50 Mb large) can be obtained with more computation time when a high-resolution main image is used".

Another methodology used in our study is the Visible Induced Luminescence (VIL) that is the most powerful method for visualizing the presence of Egyptian Blue (EB) (Pozza et al., 2000; Verri, 2009; Rainer et al., 2017; Chiari, 2018; Nicola et. al. 2018). The visible light, particularly the red component, since EB reflects the blue light, excites EB that emits the absorbed energy in the near infrared [peak at 910 nanometres, Pozza et al., 2000]. To capture the luminescence, one can use a regular digital camera, provided that the IR filter in front of the sensor is removed. However, the camera detector is sensitive to visible light as well, which, unless one is in totally dark conditions, is overwhelming the IR signal. In our case, operating in daytime, there was no possibility to obtain dark conditions. Therefore, our procedure consists of illuminating the painting using a flashlight modified by adding a short pass filter [750 nanometres] to remove the IR component coming from the flashlight and reflected by the object, simulating a luminescence that does not exist. A long pass filter [850 nanometres] cutting the visible light and letting through the IR signal was used in front of the sensor. The use of the filtered flash is necessary to obtain a strong visible illumination increasing the VIL signal, since the abundant ambient light contains a large IR component.

3. RESULTS AND DISCUSSION

3.1. *Venus's mural*

3.1.1. Calcium and Iron

Calcium and iron are obviously the elements present in greater amounts. Using the program SmART_scan (Martin-Ramos and Chiari, 2019), the false-colour maps for calcium and iron, shown in Fig. 3, were obtained. In all the maps shown hereafter, white colour represents higher concentration of the elements, while dark colour indicates lower levels, as shown by the scale bar at the bottom of each image. The number next to the scale is the maximum XRF count for that element in the whole painting. Next to it there is the name of the element in question or sometimes the combination of more than one of them. For example, Fig. 3c shows in white only those points for which Ca and Fe are simultaneously present. The maps can show the distribution of the elements over the entire mural or in selected details.

Calcium is ubiquitous in the mural (Fig. 3a) since it is part of the underlying plaster. However, calcium is also part of pigments such as gypsum, calcite and EB. Therefore, it is not surprising that it is found in the whitish parts of the background and in some, but not all, the figures.

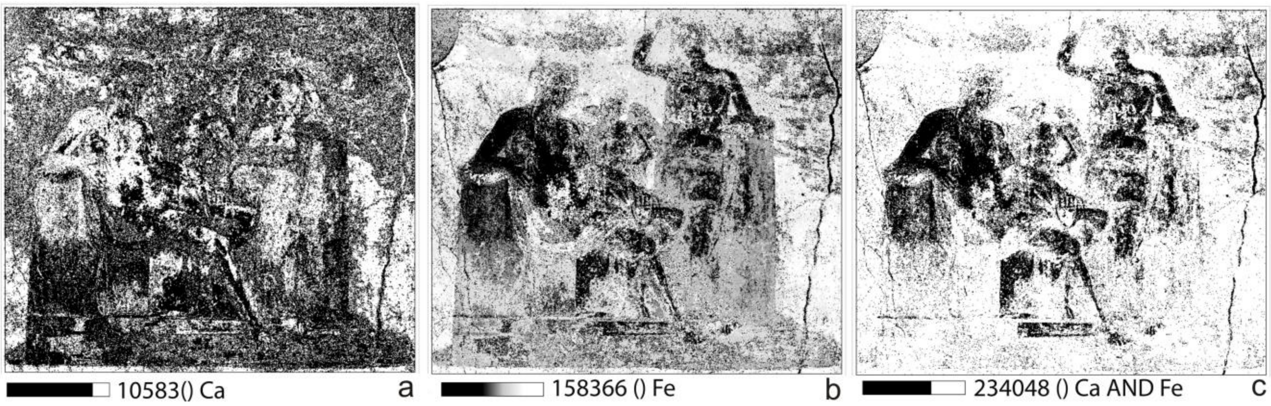

Figure 3. Venus's mural. (a) Mapping of calcium (Ca). (b) Mapping of iron (Fe). (c) Map of the regions in which Ca and Fe are simultaneously present.

The maps of Ca and Fe present similarities as well as differences. This may be because both elements are part of the substrate: calcium in the plaster and iron in the red background layer, as shown by the point analysis 1-6 taken on the red substrate only. The Ca and Fe content is much lower where the surface pigments of the figures adsorb the fluorescence signal coming from the back. For Ca we must also consider the absorption by the overlying Fe red preparation layer. The high amount of iron (Fig. 3b) is likely due to hematite, the most common red pigment used by the Romans. The other, more expensive red pigment, cinnabar (HgS), can be excluded given the absence of Hg in the XRF data. The three figures were painted on the smooth red fresco layer, using thick pigments in tempera, evidenced in UV images. However, the Fe distribution is not uniform. This may be due to a different thickness of the background layer, to the possible mixing of the red pigment to change the hue of some parts of the figures, thus adding to the signal, or to the fact that the X-rays fluorescence emitted by underlying elements is absorbed by the pigments that cover them. Therefore, the iron appears in lesser quantity where the painted surface reduces the intensity of its emission from the wall. This corresponds to the presence of heavier atoms in the figures. However, iron reaches its maximum intensity in the drapery lying on Paris leg and in parts of Paris's figure and his seat (Fig. 3b). This apparent contradiction with what was just stated can be explained by the fact that in these areas there may be the addition of the signal deriving from surface pigments. In these regions, the painted layer [light yellow] is likely made of yellow ochre (goethite) and therefore its iron signal is added to the one coming from the background.

When mapping Ca and Fe together (Fig. 3c) one can see that only the figures do not show the combined presence of both elements.

3.1.2. Lead

Other elements such as lead (Pb), copper (Cu) and manganese (Mn) were found in correspondence of the body and dresses of the three figures.

In the Eros wings (Fig. 4a), the Paris's hair (Fig. 4a), in a small part of his drapery (Fig. 4b) and in the small spot near Venus's feet (Fig. 4c) one can notice a dark-purple colour that does not match the harmony of the surrounding painting. This may be hardly due to an intentional intervention of the painter and may be interpreted more as a discoloration due to the alteration of a pigment. The black pigments commonly used by the Roman are carbon black, MnO_2 (pyrolusite) and rarely antimony (Sb). Carbon is not detected by XRF, and antimony was proved to be absent. Mn was absent in the dark spots mentioned above. SmART_scan maps of Fig. 4 suggest that, given the presence of Pb, one can suppose that plattnerite (PbO_2) may be the reason for the dark colour, although no experimental evidence supports this hypothesis. This is a well-known alteration of which the most famous example occurs in the Cimabue's frescoes in Assisi (Giovannoni et al., 1990; Nevin, 2018; Vagnini et al., 2018). The alteration of lead white to plattnerite is known to be erratic, taking place in one spot and not in an adjacent one, thus perhaps justifying the fact that the darkening is found in these spots only and not in other parts where Pb is present.

In Fig. 4 the coloured images show the details as seen in visible light, while the black and white ones show the same details mapped by SmART_scan for Pb.

Obviously Pb containing pigments, of which the most used by the Romans is lead white (cerussite and hydrocerussite mixed), may extend well outside of the dark spots as shown by the maps.

If this interpretation is correct, in those details the original colour of the mural was quite different from the present one, with a sharp change from bright yellow to dark purple. What now are dark spots, disturbing the harmony of the ensemble, originally could have been yellow areas perfectly inserted in the context. Paris's hair may have been originally blond, while now it is dark purple.

Unfortunately, we did hot have at disposal a non-invasive portable diffractometer, to confirm by XRD the mineral composition, nor it was possible to remove even the smallest sample to confirm or discard by laboratory analyses the above hypotheses.

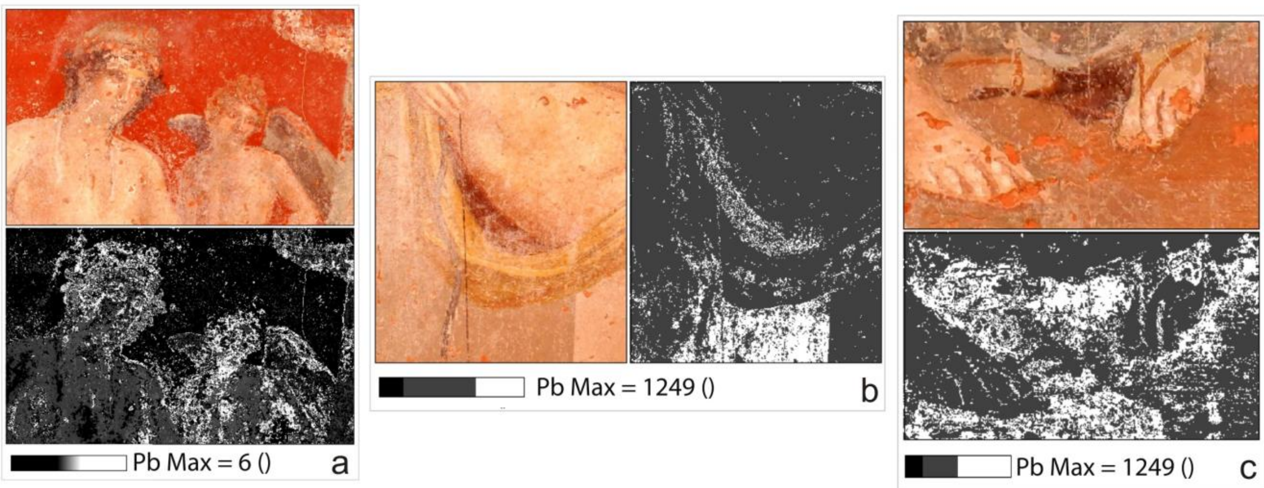

Figure 4. Visible light images (in colour) and SmART_scan Pb maps done on the same details. (a) Paris and Eros; (b) Arc shaped region between Paris's drapery and his body; (c) Dark spot near Venus's feet.

3.1.3. Manganese

A bow, symbol of the hero, is located next to Paris's seat. Its colour is similar to the dark spots above described but, in this case, XRF showed the presence of manganese (Mn) rather than lead. Fig. 5a shows the distribution of Mn in the whole painting, while Fig. 5b shows the map of Pb for comparison. Fig. 5c is a detail of the Paris's bow, showing Mn presence. Manganese is not part of the dark spots and instead it is clearly visible on the bow, including the string. It may have been used purposely to paint the dark bow and its string and to darken details of Venus's vest and other parts of the figures (Fig. 5a). It may be in the form of pyrolusite (MnO_2) mixed with a light pigment, or raw umber (Mn_3O_4) mixed with Fe rich ochre.

Raw umber does not have a definite colour, but a range of different colours, from medium to dark, from yellowish to reddish to greyish. The colour of the natural earth depends upon the amount of iron oxide and manganese in the clay. Umber earth pigments contain between five to twenty percent manganese oxide, which accounts for their being a darker colour than yellow ochre or sienna.

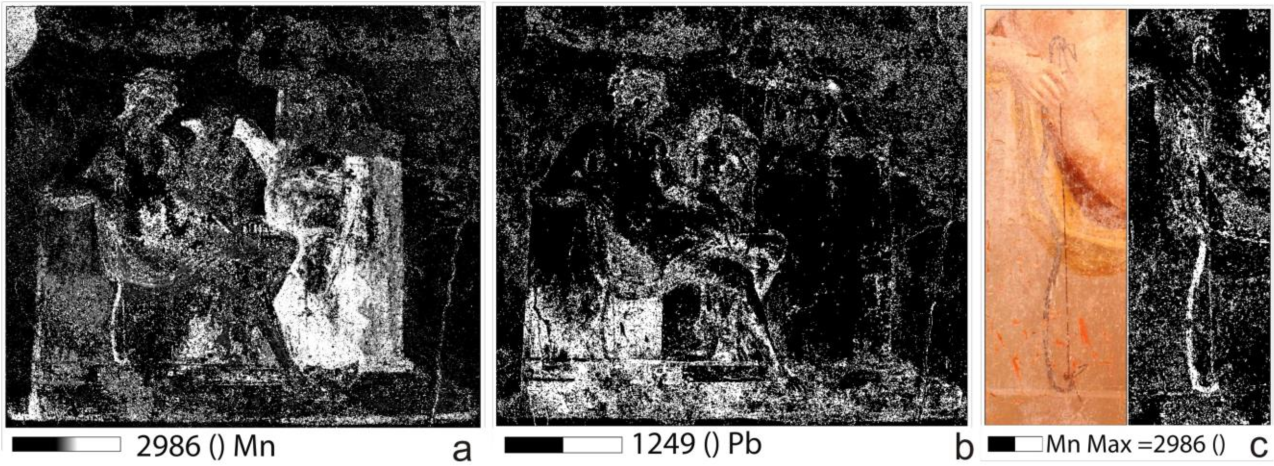

Figure 5. Manganese and lead mapping of the Venus's mural. (a) Mn distribution over the whole painting; (b) Map of Pb; (c) Detail of Paris's bow showing the string as well.

3.1.4. Calcium, Copper and Silicon

Venus's mantle and part of Paris's seat are characterized (XRF) by the simultaneous presence of calcium, copper and silicon. The average content of copper on Venus's robe [points 20-24 in Fig. 2a] is 9570 counts. On Paris's seat [points 8-9] it is 550 and on the rest of the mural, excluding the above points, is 308 counts. Of course, calcium is mainly influenced by the underlying wall, but silicon shows the following values: 4565 for Venus vest, 2250 for the seat and 2950 for the remaining points. Therefore, one can notice a strong concentration of Cu and Si on the vest, and a smaller one on the seat. Supposing that these three elements are part of the same pigment, one can conclude that it is EB ($CaCuSi_4O_{10}$), abundantly used in Pompeii and in neighbouring towns in the first century. The colour in the visible image of the vest is greyish blue, supporting this hypothesis. Given the availability and low cost of this pigment it is not surprizing that the robe of Venus was painted using EB, at times mixed with other light pigments.

Fig. 6a shows the joint presence of Ca, Si and Cu, obtained by SmART_scan on Venus's robe detail, by imposing the simultaneous presence of Ca, Cu, Si. To confirm this distribution of EB we applied the technique known as Visible Induced Luminescence [VIL] that allows detecting EB only. The result is shown in Fig. 6b.

The images so obtained show abundant EB on Venus's robe, as expected given the greyish-blue colour of the vest. Obviously, the VIL technique is optimal in evidencing EB and our maps are not competitive with it.

The smaller amount of the same pigment found in Paris's seat and other parts, which appear yellowish, needs more discussion. EB is also part of Paris bow, indicating how often the pigments were mixed to obtain the desired hue. It may seem odd to find EB in parts of lighter tone, but this occurrence has been observed in many murals, both Egyptian (such as in Tutankhamun tomb) and in several examples in Herculaneum (Chiari, personal communication). A small amount of EB was added to other colours, especially to white, to make them more brilliant. There is no surprise that in those areas, SmART_scan maps also show the presence of EB, although is lesser amount.

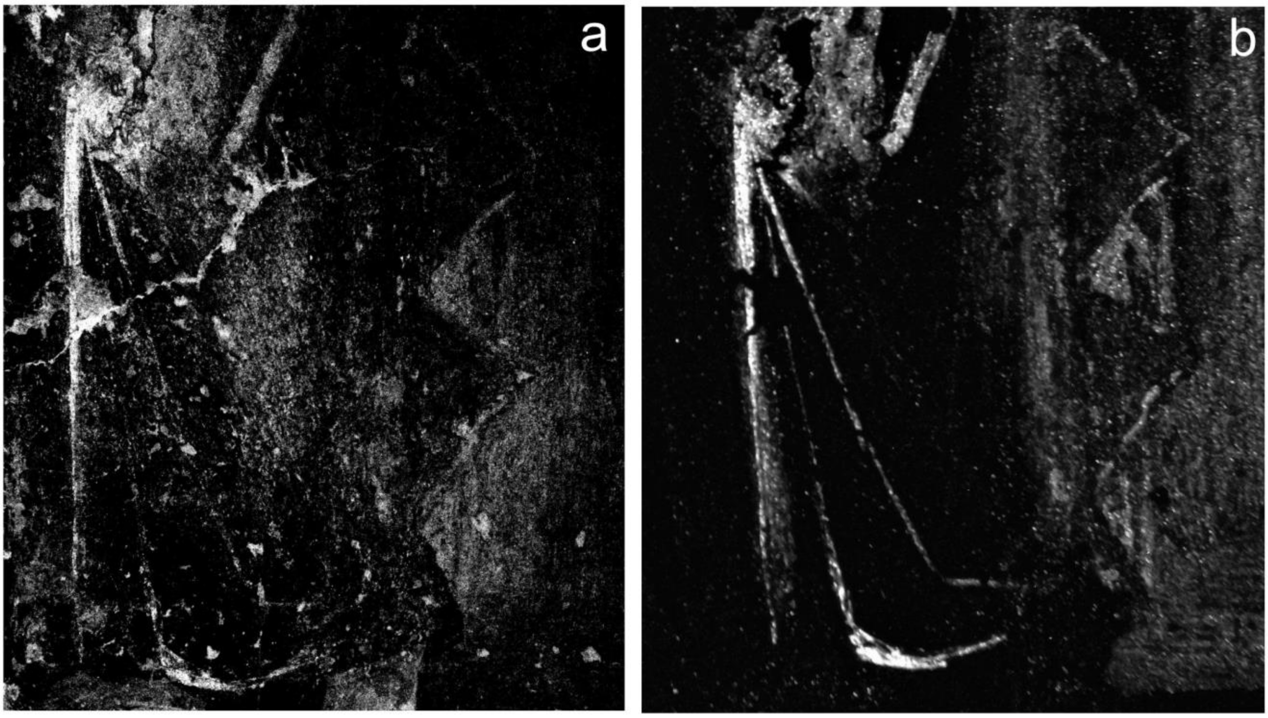

Figure 6. Detail of Venus's vest comparing SmART_scan to VIL maps. (a) SmART_scan showing the simultaneous presence of Ca, Cu, Si. (b) Visible Induced Luminescence (VIL) map of the same detail.

3.1.5. Calcium, Potassium and Sulphur

The Venus's mural painting is in rather good condition. However, by visual examination, one can see a whitish veneer, especially in the top right corner and at the bottom. This may be due to white efflorescence of soluble salts, particularly evident in the small pores that allowed for the movement of water from the interior, loaded with salts contained in the wall. This phenomenon may happen very quickly, being driven by capillarity and evaporation, and it is not surprising that it took place in the relatively short time after the excavation.

This white patina is clearly visible in the maps of Fig. 7 and corresponds to calcium sulphate (likely gypsum since bassanite would have turned into gypsum during the almost 2000 years of the mural life, and anhydrite is much less soluble) (Fig. 7a) and to a less defined potassium sulphate (Fig. 7b). Since sodium is not detectable by our XRF instrument, one cannot identify for sure the composition of the K containing salt. If is correct to suppose the presence of Na in the white patina, since sodium is abundant in the wall, one could suggest the presence of aphthitalite, $(K,Na)_3Na(SO_4)_2$. This is one of the most common salts in Pompeii and Herculaneum environment (Marcaida et al., 2018; Prieto-Taboada et al., 2018), and it can be distinguished from gypsum, which can also be present in the same white efflorescence, thanks to the presence of K.

The water, likely due to condensation since no rain can hit the mural, after penetrating the wall, can surface again loaded with sulphates that crystallize as efflorescence. This is more evident in small cracks and, using a portable microscope, it was possible to reveal a large amount of extremely small round craters, with white crystals protruding from them. The tuff inside the wall is responsible for the presence of the sulphates.

Despite the small amount of K detected, its distribution is somehow like to the one of [Ca AND S], appearing particularly where the white efflorescence is visible, indicating that the two soluble salts used the same capillaries to effloresce to the surface. It can also be noticed that the salts tend not to be present on Paris's body and seat, on Venus's robe and on the regions of the red preparation layer that appear sounder. In fact, the dense layer of paint does not have capillary fissures. Details of the efflorescence are shown in Fig. 8.

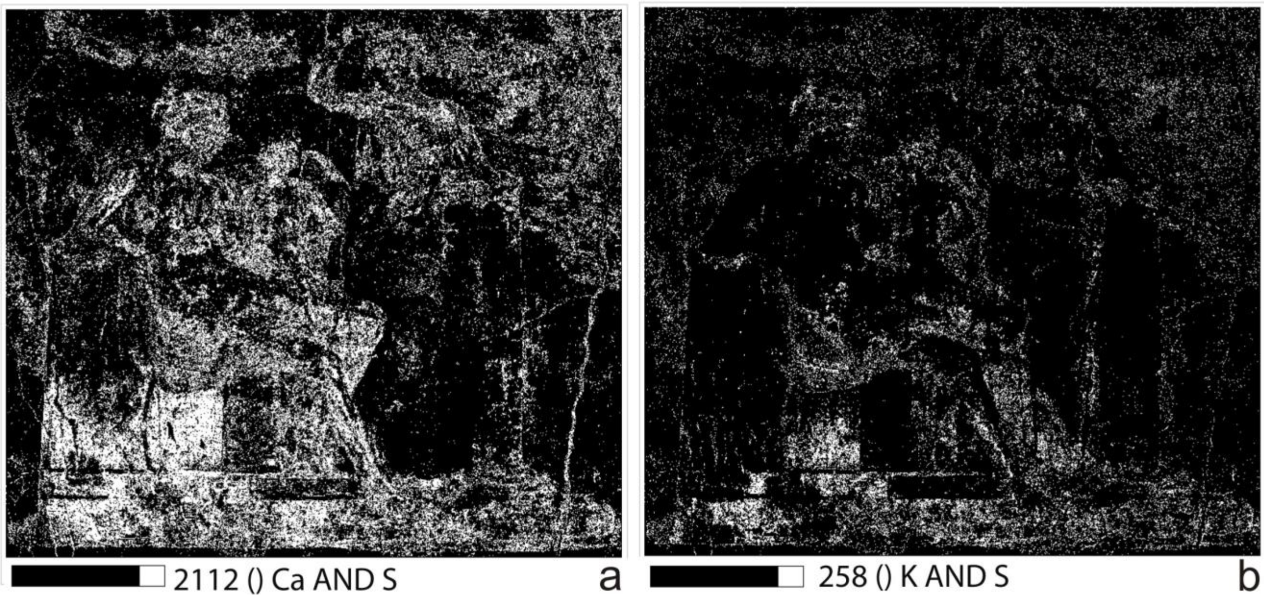

Figure 7. SmARTscan maps of [Ca and S], possibly gypsum (a) and [K and S] possibly aphthitalite (b). Notice that the amount of K is much lower that Ca.

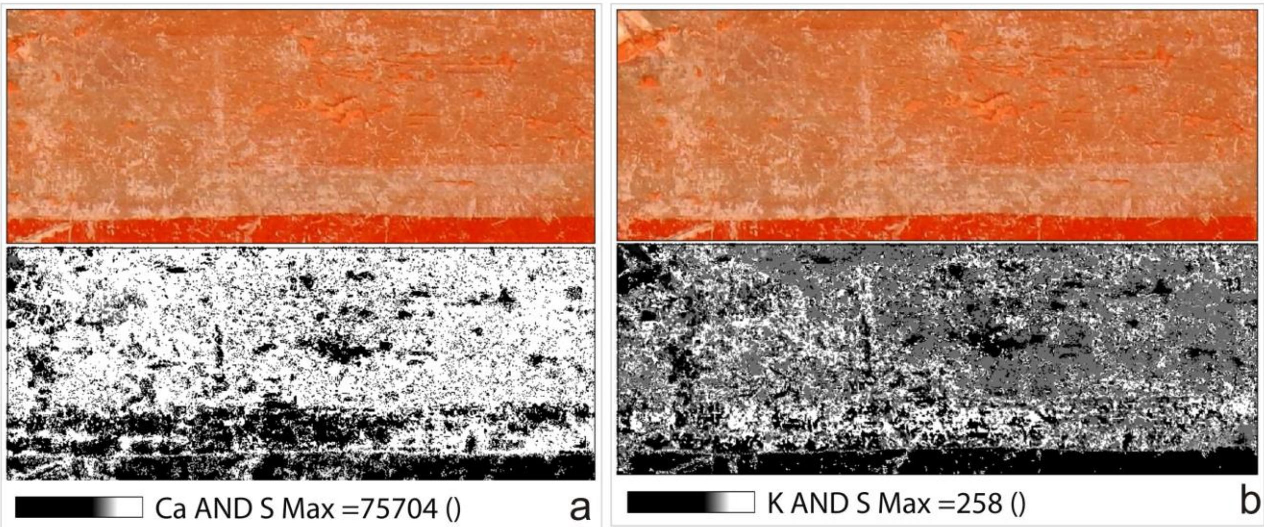

Figure 8. Detail maps of the alteration of the Venus's mural. (a) Calcium and sulphur (b) K and sulphur. Both maps show a good coincidence with the visible image. The black spots correspond to lacunae in which the red background can be seen. Notice that the amount of K is is much smaller than Ca, which is abundant in the substrate as well.

3.1.6. Visual observation and small lacunae

Venus's mural, whose colours are in general well preserved except for the alteration in the dark spots already discussed, is affected by some painting losses, evinced by the raking light images of Fig.9.

In raking light one can appreciate how thick the painted layer is. This feature is coherent with a thick tempera application rather that a fresco technique. In the top of Fig. 9a the white veneer instead appears to be flat, coherently with the hypothesis of salt efflorescence.

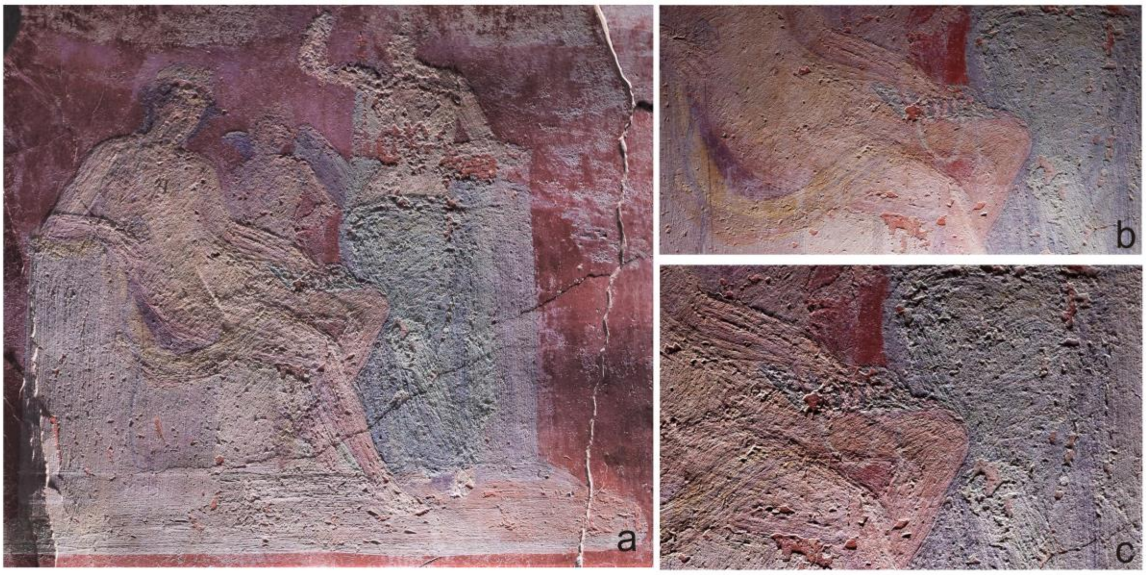

Figure 9. Raking light images of the Venus's mural. (a) Whole painting; (b) and (c) Details with different angles of the incoming light.

In Fig. 9 one can appreciate the thickness of the tempera layers and the extent of losses through which the red background wall is visible. Here the whitish patina, clearly visible to naked eye, is more noticeably flatter. To document the small losses of paint one can recur to the map of iron. In fact, even a very small lacuna in the paint allows for the red colour, and the XRF signal from the underlying preparation, to come out. This signal usually is absorbed by the overlying thick preparation layer. Fig. 10 shows this effect. It may also be observed that the central part of Paris's body and his drapery contain more iron than parts of the red background itself. Given the yellow colour of that area, one can suppose that the additional signal comes from an overpaint of Fe containing yellow ochre. For the preparation layer, Fig. 10b shows that the large region in the lower right and small details, such as near Paris neck among others, there is the larger concentration of Fe. These regions correspond to the most dense and pristine part of the red layer (see Figs. 1 and 2).

Looking at Fig. 10b one sees that some regions with higher Fe content correspond to the parts showing the dark purple colour previously interpreted as suspected plattnerite. If the presence of Fe in these areas can be attributed in part to goethite, this find supports the idea that those details were originally a bright yellow, being the mix of lead white and yellow ochre. This interpretation needs to be proved by other techniques not available during this study. The documentations of the lacunae and efflorescence in such a minute detail (Fig. 10a) may help, in the future, to keep track of the evolution of the micro-cracks.

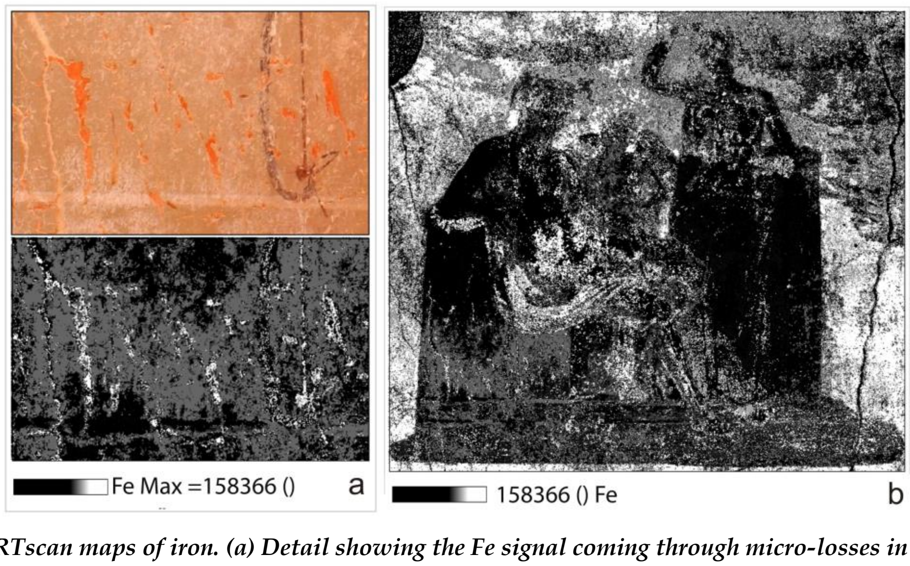

Figure 10. SmARTscan maps of iron. (a) Detail showing the Fe signal coming through micro-losses in Paris's seat. (b) Whole image showing a higher content of Fe on yellow painted regions, possibly due to goethite, and in some small part in which the red preparation looks sounder.

3.2. *Mural painting with the female portrait*

3.2.1. Painting technique - Calcium and Iron

In the mural painting depicting the female portrait (Fig. 11) a totally different technique was used. The smooth supporting wall was painted in fresco, using yellow ochre over the entire surface. On this, a circle was drawn using a compass (a small hole was found in the centre of the circle where the compass point was positioned) and a uniform red background was accurately laid inside of it in tempera after the yellow layer was dry. In fact, there is no mixing of the two colours. This red area was then confined with a dark frame, on top of which small brush strokes of lighter colour were applied as a decoration. The figure was painted using a thick pigment paste, covering the two preparation layers.

The XRF data (Table S2 in Supplementary Materials) show that iron and calcium are the dominant elements. The iron signal (Fig. 11a) can be linked to the presence of hematite. The maximum intensity of iron corresponds to the background and to part of the female dress. In these areas, there may be the contribution to the XRF signal from elements of the painted layer. Conversely, in the lower right part of the vest, there is some missing paint, letting the signal from behind to come through.

The calcium signal (Fig. 11b) seems to come from the underlying plaster, and it is reduced by the absorption from the painted figure and in part from the red background. However, the black round frame contains much more calcium than the rest. This can be explained by supposing that a mixture of black carbon powder, that does not give XRF signal, for the colour, and lime wash as a binder were used for the frame.

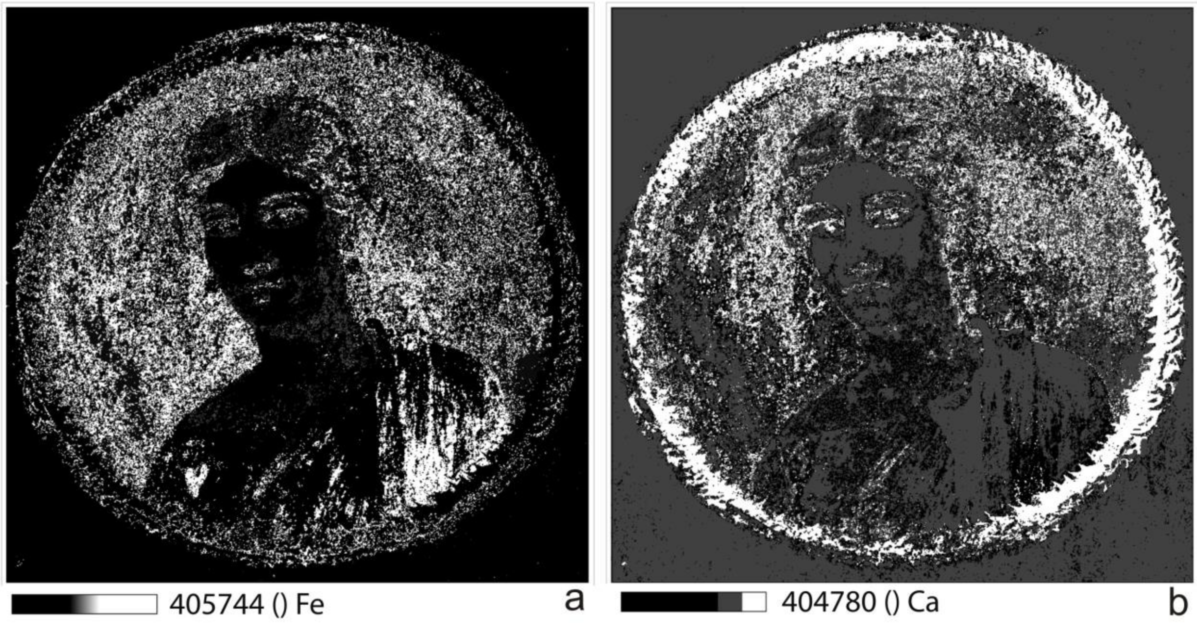

Figure 5. Mural painting with the female portrait. (a) Mapping of iron (Fe); (b) Mapping of calcium (Ca).

3.2.2. Manganese

Pigments commonly used by the Romans containing manganese are the black oxide pyrolusite (MnO_2) and the pinkish-brown raw umber (Mn_3O_4) iron containing as part of the ochre, as already pointed out. To investigate their possible presence in the tondo, the map of manganese (Mn) is shown (Figs. 12a and b). From these maps the presence of Mn in the dark part of the frame, where it was expected to be, can be excluded. On the contrary, Mn was found in the brush strokes in the shape of a comma, laid on the black frame (Fig. 12b). These strokes show a much lighter colour, not matching pyrolusite. One can propose two alternative explanations for the matching of Mn with the two different colours: a) the black pyrolusite was mixed with lighter pigments to obtain the desired hue or b) raw umber of lighter colour was used instead. XRF does not provide enough data for deciding whether one of these possibilities is correct or both. In Fig. 12c the map of the same detail is shown for Fe that is found in smaller quantity in the same brush strokes. Lacking a confirmation by a compound detecting technique (e.g., XRD) one can guess that either some pyrolusite was mixed with yellow ochre to darken the tone, or that umber was directly used, since it contains a small amount of Fe. The same features can be found on the left part of the woman's torso, in the shading of her face and in her hair. In all these instances the colour is close to a pink orange and does not correspond to the violet-black pyrolusite, while it may correspond to raw umber.

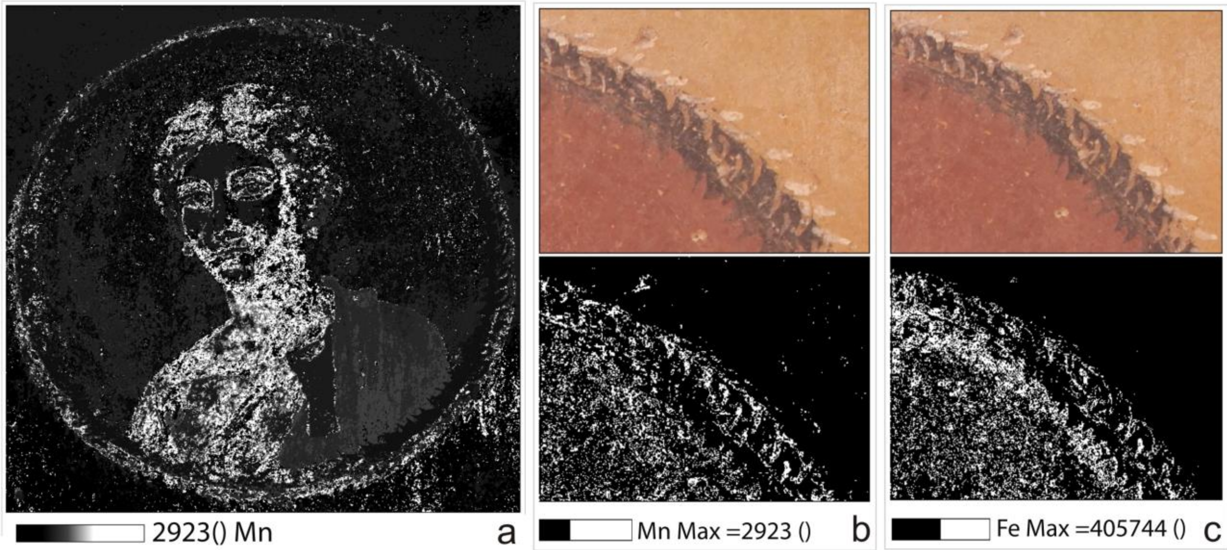

Figure 6. Mural with the female portrait. (a) Map of manganese (Mn); (b) Detail of the right top corner of the frame, showing the presence of Mn in the brush strokes of light colour, on top of the dark frame. (c) Map of the same detail for iron (Fe). It may be guessed that some Mn oxide was added to yellow ochre to darken the tone.

3.2.3. Sulphate efflorescence

The portrait of the woman shows brilliant colours, perfectly preserved. As the conservation of the painting is concerned, it is possible to visualize the presence of Ca sulphates (gypsum?) (Fig. 13a). It appears more abundant on the background where, as for the Venus's mural, it is possible to observe, with high magnification, although for lesser extent, small pores facilitating the release of soluble salts (essentially sulphates and chlorides from the tuff). On the female figure, this phenomenon is less marked due to the presence of the thick layer of uncracked paint.

The same phenomenon is visible in Fig. 13b, showing the distribution of chlorine (Cl), which is quite extended but not uniform since its concentration on the figure is much lower. This suggests that chlorides are coming from the masonry rather than from marine aerosol, since in this case, it would be uniformly distributed over the whole mural. K in lacking in the tondo. This discrepancy may be due to the different orientation of the supporting walls. Venus's painting is standing on a wall facing the room on both sides, while the woman's medallion wall is separating the room from a narrow corridor, possibly the original access to the latrine, which is exposed to the environment and may cause the extraction of different salts.

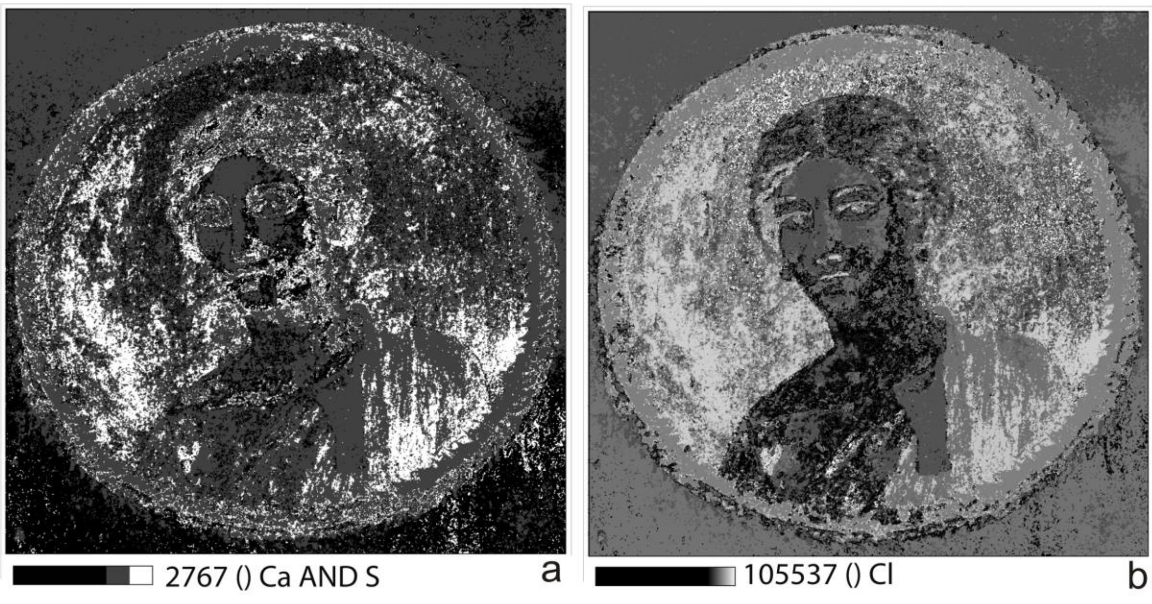

Figure 7. Mural painting with the female portrait. (a) Mapping of Calcium (Ca) and Sulphur (S) [likely Gypsum]; (b) Mapping of chlorine (Cl), likely sodium chloride from the tuff of the wall.

4. CONCLUSION

The application of the SmART_scan methodology, proposed by Martin-Ramos and Chiari (2019) to the study of the two mural paintings located in the "House of Garden", into the Regio V of the archaeological site of Pompeii, allowed for the elucidation of most of the palette used, and of the alterations present. The method is based on a limited number of carefully selected hand-held XRF measurements and a good-resolution visible image to which, if available, other images, such as UV, IR or Multi-spectral can be added. The computer program, user friendly and rapid, generates maps of elements or of compounds when imposing the simultaneous presence of more than one element, thus producing valuable information in a non-destructive way. Data concerning the pigments composition and their special distribution on the two mural paintings, studied for the first time, were obtained. The type and location of the soluble salts present on the surface in uneven way contribute to understand the state of conservation of the murals.

For the Venus's mural painting it is possible to summarise the following finds:

- The background is likely composed of hematite alone.
- Three other pigments were applied: lead white, possibly combined with yellow ochre in the light-yellow regions; Egyptian blue (confirmed by VIL) in Venus's vest and in minor quantities in Paris's seat; manganese oxide particularly on the bow and string of Paris arc and to darken details of the figures.
- In a few spots, lead white is possibly altered to plattnerite, a black lead oxide. If so, originally the Paris hair were blond and other minor details were bright yellow, while now they show a dark purple colour possibly due to this alteration, substantially changing the appearance of the painting.
- Calcium and potassium sulphates (possibly gypsum and aphthitalite, a sodium-potassium sulphate) form the white efflorescence, particularly in correspondence of micro-cracks and fine pores.

For the tondo with the female portrait the main findings are:

- The background uniformly painted on the entire wall is made of a bright yellow ochre.
- On this layer, a circular region was delimited using a compass and accurately painted with red hematite.
- Manganese oxide was used for the shading of the woman torso and face but not for the black round frame of the medallion, which, given the high content of Ca, was likely obtained using a mixture of black carbon powder and lime wash.

The sulphates and chlorides coming from the tuff constitute a micro-efflorescence, mainly presents on the background of the medallion. This feature is much less pronounced than for Venus's mural, to the point that they are hardy visible to naked eye and were shown by the elemental maps and by portable microscope observations only. Among the soluble salts coming from the masonry, chlorides were detected, not present in Venus's mural. Our findings, besides increasing the knowledge of Roman mural paintings techniques, may provide a base to evaluate future alteration of these magnificent paintings.

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REFERENCES

Acri, G., Testagrossa, B., Faenza, P. and Caridi, F. (2020) Spectroscopic analysis of pigments of the antonello gagini annunciation's sculptural marble group, church of st. Theodore martyr (bagaladi, reggio calabria, italy): case study, *Mediterranean Archaeology and Archaeometry*, Vol. 20, pp. 1-5.

Aliatis, I., Bersani, D., Campani, E., Casoli, A., Lottici, P.P., Mantovan, S., Marino, I.G. and Ospitali, F. (2009) Green pigments of the Pompeian artists' palette, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol 73, 532-538.

Angelini, I., Asscher, Y., Secco, M., Parisatto, M. and Artioli, G. (2019) The pigments of the frigidarium in the Sarno Baths, Pompeii: Identification, stratigraphy and weathering, *Journal of Cultural Heritage,* Vol. 40, 309-316.

Augusti, S. (1967) *I Colori Pompeiani, Studi e Documentazioni I. Ministero della Pubblica Istruzione, Direzione Generale delle Antichità e Belle Arti*. Roma: De Luca Editori.

Bratitsi, M., Liritzis, I., Alexopoulou, A. and Makris, D. (2019) Visualising underpainted layers via spectroscopic techniques: a brief review of case studies, *Scientific Culture*, Vol. 5, pp. 55-68.

Chapal, J. A. (1809) Notice sur quelques couleurs trouvées à Pompéia, *Annales de Chimie*, Vol. 70, pp. 22-31.

Chiari, G. (2018). Photoluminescence of Egyptian Blue. In *The Encyclopedia of Archaeological Sciences*. L. Sandra López Varela (Ed.), Hoboken, Wiley Blackwell.

Cotte, M., Susini, J., Metrich, N., Moscato, A., Gratziu, C., Bertagnini, A. and Pagano, M. (2006) Blackening of Pompeian cinnabar paintings: X-ray microspectroscopy analysis, *Analytical Chemistry*, Vol. 78, 7484–7492.

De Vos, A. and De Vos, M. (1982) *Pompei, Ercolano e Stabia. Guide Archeologiche*. Bari: Laterza.

Duran, A., Jimenez De Haro, M.C., Perez-Rodriguez, J.L., Franquelo, M.L., Herrera, L.K. and Justo, A. (2010) Determination of pigments and binders in Pompeian wall paintings using synchrotron radiation–high-resolution X-ray powder diffraction and conventional spectroscopy–chromatography, *Archaeometry*, Vol. 52, 286-307.

Giovannoni, S., Matteini, M. and Moles, A. (1990) Studies and developments concerning the problem of altered lead pigments in wall painting, *Studies in Conservation*, Vol. 35, 21-25.

Liritzis, I., Laskaris, N., Vafiadou, A., Karapanagiotis, I., Volonakis, P., Papageorgopoulou, C. and Bratitsi, M. (2020) Archaeometry: an overview. *Scientific Culture*, Vol. 6, pp. 49-98.

Marcaida, I., Maguregui, M., Morillas, H., Prieto-Taboada, N., de Vallejuelo, S.F.O., Veneranda, M., Madariaga, J.M., Martellone, A., De Nigris, B. and Osanna, M. (2018) In situ non-invasive characterization of the composition of Pompeian pigments preserved in their original bowls, *Microchemical Journal*, Vol. 139, 458-466.

Martin-Ramos, J.D. and Chiari, G. (2019) SmART_scan: A method to produce composition maps using any elemental, molecular and image data, *Journal of Cultural Heritage*, Vol. 39, 260-269.

Miriello, D., Bloise, A., Crisci, G.M., De Luca, R., De Nigris, B., Martellone, A., Osanna, M., Pace, R., Pecci, A. and Ruggieri, N. (2018) Non-Destructive Multi-Analytical Approach to Study the Pigments of Wall Painting Fragments Reused in Mortars from the Archaeological Site of Pompeii (Italy), *Minerals*, 8(4).

Mona Ali, F. and Marian Youssef, M. (2020a) An analytical study of a mural with colorful geometric decoration, coptic museum, cairo, Egypt: a case study, *Scientific Culture*, Vol. 6, pp. 37-52.

Mona Ali, F., Sawsan Darwish, S., Ahmed El Sheikha, M. (2020b) Multispectral analysis and investigation of overlapping layer cartonnage fragments from Egyptian museum, Cairo, *Scientific Culture*, Vol. 6, pp. 25-36.

Mona Ali, F. and Mahmoud Elkawy, H. (2021) physical analysis and treatment of disintegrated islamic mural paintings from the 15th century taqi aldin albistami hospice. *Scientific Culture*, Vol. 7, pp. 45-56.

Nevin, A. (2018). Pigment Alteration. In *The Encyclopedia of Archaeological Sciences*. L. Sandra López Varela (Ed.), Hobken, Wiley Blackwell.

Nicola, M., Aceto, M., Gheroldi, V., Gobetto, R. and Chiari, G. (2018) Egyptian blue in the Castelseprio mural painting cycle. Imaging and evidence of a non-traditional manufacture, *Journal of Archaeological Science: Reports*, Vol. 19, pp. 465-475.

Osanna, M. (2019) *Pompei. Il tempo ritrovato. Le Nuove Scoperte*. Milano: Rizzoli.

Panebianco, V. (1982) Le origini storiche di Pompei. *In proceedings Convegno internazionale la regione sotterrata dal Vesuvio, studi e prospettive 11–15 Novembre 1979*; Napoli: Università degli studi di Napoli, pp. 229–239.

Piovesan, R., Siddall, R., Mazzoli, C. and Nodari, L. (2011) The Temple of Venus (Pompeii): a study of the pigments and painting techniques, *Journal of Archaeological Science*, 2011, Vol. 38, 2633-2643.

Pozza, G., Ajo', D., Chiari, G., De Zuane, F. and Favaro, M.L. (2000). Photoluminescence of inorganic pigments Egyptian Blue, Han Blue and Han Purple, *Journal of Cultural Heritage*, Vol. 1, 393-398.

Prieto-Taboada, N., De Vallejuelo, S.F.O., Veneranda, M., Marcaida, I., Morillas, H., Maguregui, M., Castro K., De Carolis E., Osanna M. and Madariaga J.M. (2018) Study of the soluble salts formation in a recently restored house of Pompeii by in-situ Raman spectroscopy, *Scientific Reports*, Vol. 8, 1-8.

Rainer, L., Kiernan, G, Maekawa, S., Gittins, M. and Pique, F. (2017) *Conservation of the architectural surfaces in the Tablinum of the House of the Bicentenary. Herculaneum Phase I*. Los Angeles: Getty Conservation Institute.

Richardson, L.J.R. (1988) *Pompeii: An Architectural History*. Baltimore: Johns Hopkins University Press.

Santini, L. (2004) *Pompeii*. Sesto Fiorentino: Plurigraf.

Vagnini, M., Vivani, R., Viscuso, E., Favazza, M., Brunetti, B.G., Sgamellotti, A. and Miliani, C. (2018) Investigation on the process of lead white blackening by Raman spectroscopy, XRD and other methods: Study of Cimabue's paintings in Assisi, *Vibrational Spectroscopy*, Vol. 98, 41-49.

Varone, A. (2005) *Pompeii. I Misteri di una Città Sepolta-Storia e Segreti di un Luogo in Cui la Vita si è Fermata Duemila Anni fa*. Roma: Newton Compton Editori.

Vázquez de Ágredos-Pascual, M.L., Zapata-Meza, M., Sanz-Rincón, R., Garza Díaz Barriga, A., Expósito De Vicente, C., Rojo-Iranzo, L., Herreras Sala, S. (2019) physicochemical and cultural study of coloring materials from 1st c. ad magdala, lower galilee, *Mediterranean Archaeology and Archaeometry*, Vol. 19, pp. 173-188.

Verri, G. (2009) The spatially resolved characterization of Egyptian blue, Han blue and Han purple by photo-induced luminescence digital imaging, *Analytical and Bioanalytical Chemistry*, Vol. 394, 1011-1021.

Welcomme, E., Walter, P., Van Elslande, E. and Tsoucaris, G. (2006) Investigation of white pigments used as make-up during the Greco-Roman period, *Applied Physics A,* Vol. 83, 551–556.

Zanella, E., Gurioli, L., Chiari, G., Ciarallo, A., Cioni, R., De Carolis, E. and Lanza, R. (2000) Archaeomagnetic results from mural paintings and pyroclastic rocks in Pompeii and Herculaneum, *Physics of the Earth and Planetary Interiors,* Vol. 118, 227–240.