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Published Version:
Alberghina M. F., Milazzo G., Schiavone S., Randazzo L., Ricca M., Rovella N., et al. (2020). The Contribution of Microchemical Analyses and Diagnostic Imaging to the Conservation and Identification of the Degraded Surfaces of Hellenistic-Roman Wall Paintings from Solunto (Sicily). STUDIES IN CONSERVATION, 66(6), 342-356 [10.1080/00393630.2020.1805252].

Availability:
This version is available at: https://hdl.handle.net/11585/916620 since: 2023-02-21

Published:
DOI: http://doi.org/10.1080/00393630.2020.1805252

(Article begins on next page)

Alberghina M. F.; Milazzo G.; Schiavone S.; Randazzo L.; Ricca M.; Rovella N.; Spatafora F.; Fiorenza E.; La Russa M. F.: *The Contribution of Microchemical Analyses and Diagnostic Imaging to the Conservation and Identification of the Degraded Surfaces of Hellenistic-Roman Wall Paintings from Solunto (Sicily)*

STUDIES IN CONSERVATION VOL. 66 ISSN 0039-3630

DOI: 10.1080/00393630.2020.1805252

The contribution of the microchemical analyses and diagnostic imaging for conservation and identification of degraded surface of Hellenistic-Roman wall paintings from Solunto (Sicily)

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ABSTRACT

The Archaeological Museum of Palermo (Sicily) has recently presented the results of the restoration of three wall paintings coming from the House of the Masks of Solunto archaeological site. These precious paintings, dating back to the first century BC, are the most considerable examples of Pompeian style discovered in Sicily until today. The whole unearthed cycle of frescoes is the better preserved and complete example of wall painting dated to Republican Roman period in Sicily.

This house was a luxurious private residence built on two floors and articulated around a peristyle. These frescoes cycle embellished the walls of a banquet room (*oecus*) discovered during an archaeological excavation carried out by Giovanni Patricolo in 1869. The definition House of the Masks was suggested by Salemi Pace in 1872 when he published the discovery of those frescoes with colourful garlands and theatrical masks. In 1874, only five panels were detached from the walls and moved to the National Museum of Palermo for conservative purposes. The recent careful cleaning of the pictorial surfaces and the new archaeological and archaeometric researches revealed unusual details on the pictorial technique and newly painted subjects. The scientific investigation has been preliminary based on a non-destructive approach, performed *in situ* by portable equipment and subsequently, a further deepening on a micro fragment by the micro-destructive investigation. In particular, X-Ray fluorescence analyses have been carried out to identify the original pictorial palette and Electron Microprobe analyses coupled with Energy-Dispersive Spectrometry allowed to define the chromatic alteration products. Finally, the infrared imaging technique provided new data about the pictorial technique and iconography readability. The new archaeometric evidences light on these

rare examples of Roman wall painting of the Sicilian Roman province until today not systematically studied from the point of view of materials and execution techniques, confirming the dating and the connection with contemporary workshops active in other Roman provinces.

KEYWORDS: mural painting; Solunto; Pompeian style; Egyptian Blue; cinnabar blackening; Roman pigments; conservation

1. INTRODUCTION

Solunto is one of the most relevant archaeological sites of the northern coast of Sicily. It is not often mentioned by ancient writers, but according to Thucydides it was one of the three Phoenicians settlements, with Mothia and Panormo, established between VIII and VII century BC [1]. Furthermore, Diodorus Siculus refers to the destruction of the oldest settlement of Solunto, among several towns of Carthaginian eparchy, by Dionysius I of Syracuse in 397 BC [2,3,4]. After that, the town was rebuilt on the Monte Catalfano in the IV century BC [4,5,6]. During the first Punic war, Solunto fell under the rule of the Romans in 254 BC as Diodorus describes [7]; it later became one of the *civitates decumanae* of Sicily until the III century AD, when the Hellenistic-Roman town was intentionally and gradually abandoned [4,8,9].

The ancient ruins of Solunto were already known by antiquarians and voyagers since XVI century [10] (Fig. 1a). Systematic archaeological excavations took place in 1827 with the Commission for Antiquities and Fine Arts of Sicily, led by the Duke of Serradifalco [11,12]. The activities of the Commission allowed to excavate a wide well-preserved area of the ancient town, uncovering houses, statues, furniture, frescoes and artefacts of ancient people; for this reason, Solunto earned the name of “Sicilian Pompeii” [13]. The most relevant house, among those found in Solunto in XIX century, was unearthed by Giuseppe Patricolo [4], between 1868 and 1869, in the highest part of the *insula* XI near the western walls. On the eastern terrace of this luxurious private residence [9,14], a banqueting room (*oecus*) (Fig. 1b) was excavated unearthing a cycle of frescoes with false marble, garlands and theatrical masks. The subject of these decorations suggested the name of House of the Masks. In 1872 G. Salemi Pace mapped a plant of the house and he made an accurate coloured drawing of the paintings, reproducing the central panels with a black background [15]. In 1874, for preserving them from degradation [16] only five frescoes panels were detached and moved to the National Museum of Palermo (today Archaeological Museum of Palermo “Antonino Salinas”) and catalogued in the museum inventory as I.n. 2297, 2298, 2299, 2300 and 2301. The detachment was assigned on 7 May 1874 to Fortunato Tamburini, a restorer who already made working experiences moving Pompeian mosaics and wall paintings at the Museum of Naples [17]. Tamburini succeeded in the *distacco* process (the detachment of the paint layer with its support of plaster) of five panels transferring them to new support made of gypsum and iron bars, as described in an expense report that lists several materials bought by Tamburini useful for the detachment processes like: gypsum, canvas, glue, brushes, paper, etc [16]. Then, the five panels were displayed in the great “hall of mosaics and wall paintings” at the ground level of the National Museum of Palermo, until the II World War. During the bombing of Palermo of 1943, a bomb affected lightly a wing of the National Museum. After it was chosen to renovate the museum layout and the “hall of mosaics and wall paintings” was moved to the second level, like today. It is likely that during the rearrangement, the five panels from Solunto may have been restored as happened to the mosaics in the same hall. Actually, there is no archival data available about the restorations before 2005, when a conservation treatment was performed only on two panels (I.n. 2298 and 2300) and it was suggested a hypothetical reconstruction with a yellow background [18].

1.1 The wall paintings from oecus of the House of the Masks

The five panels of wall painting from Solunto, now exhibited at the Archaeological Museum of Palermo, were part of the Second Style decoration of the *oecus* in the House of the Masks (room n.8, Fig. 1b), where large parts of wall painting cycle are still present. The panels imitate an illusionistic architecture and masonry, achieved purely by pictorial means, as an alternative to a costly covering with real marbles. The paratactic system was divided into three horizontal zones consisting of a central zone with orthostats and pillars in imitation of breccias, veined marbles and coloured alabasters, except the north-western wall and the first pair of orthostats of the adjacent ones (SW and NE). In these walls, the decoration alluded to an illusionistic architecture, like a portico. In particular, the wall paintings reproduced, high square orthostats containing figurative, outlined by green frames, separated by narrow veined marbles pillars. A coloured fillet also lined them simulating the profile of embossing. Furthermore, the figurative of the north-western panels depicted opulent garlands of fruits and leaves suspended between the two pillars, on which are hanged two embroidered strips and a theatrical mask by red cords. From this wall have detached the panels with young mask (I.n. 2299; Fig. 2b), Silenus mask (I.n. 2298), old man mask (I.n. 2300). Instead, the side panels had to represent a simpler garland composed of two pines branches laden with cones and from the centre of which are suspended with red cords musical instruments. A couple of panels taken from the south-western wall have figurative of an unknown representation (I.n. 2297) (Fig. 2a) and a yellow *tympanum* (tambourine drum) with a figurine depicted on its field (I.n. 2301; Fig. 2c) [19]. The decoration of the upper zone is unknown because of was already lost when the room was unearthed; on the contrary, the well-preserved lower zone has a decoration divided in a high socle over a podium. The socle depicts a green moulded frame above which a single course of headers and stretchers in alternate colours (purple outlined with yellow frame and yellow with red frame) is painted on a black background. Instead, the podium is decorated to simulate panels of wide black orthostats with narrow blocks to the imitation of breccias marbles (Fig. 2d-f). At last, the stylistic and iconographic scheme of the decorations was compared to the contemporary decorative system found both in the cities of the Vesuvius area, like in the Villa of *P. Fannius Synistor* in Boscoreale and the *Casa delle Nozze d'Argento* in Pompeii, and in Rome. Recent studies also propose dating for the cycle at the beginnings of I century BC (with the "Phase Ia" of Beyen), also for the white mosaic floor bordered by a black frame that reflects current roman-italic trends [14, 19, 20, 21, 22].

1.2 Pictorial technique and state of preservation

A closer observation of the wall painting surface allowed to make preliminary considerations about the executive technique of the painter and its workshop.

The wall painting substrate is made of two plaster layers: the *intonaco* and *tonachino*. The first is composed of a grey fine lime plaster (containing a fine mixture of sand and crushed marble) with a thickness of 4-5 mm; the second, above the first, is a white very thin plaster with an average thickness of 2 mm, made of lime and marble dust to give a translucent finish. Moreover, the visual analysis of *in situ oecus'* wall paintings has shown a lime coarser plaster layer (*arriccio*) applied directly over the stone wall behind the *intonaco*. It is likely that *arriccio* was removed for reducing the thickness and the weight of the panels after the detachment process in 1874.

The brilliant and smooth surface of paintings demonstrates the expertise of painter about the polishing process (*expolitiones*), mentioned for *fresco* technique by Vitruvius [23]. Furthermore, it is a remarkable feature essential for the illusionistic effect in the Second style of Roman wall paintings.

The use of fresco technique is also shown by traces of preparatory marks quite commons in the roman decorations, as the string impressed into the damp plaster, guidelines incised by using pointed tools and a red painting used for tracing preparatory lines under the frames. It is not found traces of the *giornate* or *pontate*, likely masked in correspondence of borders between the central and lower zone. In addition, traces of nails print and fingerprints demonstrate that the plaster was still damp or not completely dry when was painted. We can deduce that first thin paint layer of the background colours was laid out using the *fresco* technique (yellow, purple, red ochre, green earth and black and white pigments). *Mezzo-fresco* or *secco* techniques were used instead for shadows, lighting, veined marble and figures, on a plaster nearly dry or dry with successive thin paint layers, often overlapped. This exquisite technique, proper of the roman frescos, needed of specialized craftsmen, certainly influenced by Hellenistic-Roman culture despite the Punic substratum. The accurate comparison of the painting technique of panels, from the north-western and south-western wall, shows differences that lead to suppose the presence of two or three painters; one or more (*pictor parietarius*) whom laid the backgrounds and the master (*pictor imaginarius*) that added details and figures, like festoons, masks and musical instruments [24, 25]. There seems to be an exception for the purple orthostats of the socle in the north-western wall that are executed more realistic than in the rest of the room. It is probably that this wall was all painted by the master.

The close observation of the three of wall paintings panels (I.n. 2299, 2301 and 2297), involved in the 2017 restoration works, aided by using a magnifying lens and direct and ranking light, allowed to check their state of preservation. The panel paintings showed cracks of the plaster, especially the two ones of the south-eastern wall in which a fine network of fissures had created some misalignments between each plaster pieces. It is likely that some cracks may have been caused during the detachment in 1874, especially considering their great size and considerable weight. The paint layers were altered showing flaking of green layer, loss of colour layers (particularly those made with *secco* technique), abrasions from mechanical damages, concretions and altered deposits of glue, used for cloth facing the surface during the detachment [16]. Fillings *lacunae* were made in the 1950s, as shown by the comparison with a picture made previous to that time in which the wall painting had no fillings. Two different filling techniques has been observed, stucco coloured according to the colour of paint layers for the cracks and little lacunae, grey-yellowish stucco (as neutral) for the large *lacunae* placed on the panel's border. Some little filled *lacunae*, near to the figurative subject, had retouching made by using oil colours. Furthermore, the chromatic alterations of the colours suggested the evidence of aged coatings treatments, that caused a glossy appearance and a turning of the colours to yellow-brownish. The use of organic oil varnishes was an efficacious treatment for mitigating the quick whitening of ancient paintings after discovery, improving their readability during the XIX century. The yellow thin organic layer, easily visible on white paint, showed the presence of a varnish. These remedies were of great help to enhance the damaged appearance of paintings in particular after the detachment. Also, there was a second layer made of a synthetic wax. Wax-based coatings were widely used for the protection of ancient wall paintings *in situ* or in museums from the second half of XIX century. These coatings laid out in several layers, hot or cold, depending on the recipe, were used to enhance the brightness of paintings, given them an aspect like *encausto* [26]. Unfortunately, the ageing of wax coatings often caused an opacification of the surface due to adsorption of dust.

Indeed, concerning the background of the great slab in the main zone, its colour was not clearly understood due to also conservation state. Earlier publications tried to define it, like G. Salemi Pace, as described above, proposed a black colour, B. Pace suggested a Pompeian red (cinnabar) altered in black in 1934 [27] and, another proposal was drawn up after the conservation of the two panels in 2005, by suggesting a yellow-orange background (Fig. 3). The diversity of proposals had doubts concerning the technique and the original appearance of the panels, becoming one of the main topics of this study.

1.3 Research aims

The aim of the diagnostic campaign was to provide new insight into the technical and iconographic features of these wall paintings for assisting the recent conservation treatment carried out on the three I.n. 2299, 2301 and 2297 panels and to improve the knowledge about this rare Sicilian works of art. In particular, following an interdisciplinary and multi-analytical approach the research activity has been focused on: *i)* to increase the identification of the pigment palettes for comparing the scientific data obtained on two frescoed panels studied during the 2005 restoration works; *ii)* to confirm the current knowledge on the original executive technique and to support the dating of the cycle of frescoes today provided only from a stylistic point of view; *iii)* to guide the cleaning treatments providing better readability of the iconographic altered subject and, finally, *iv)* to shed light on the real colour pictorial background for a univocal and definite interpretation, resolving definitely this archaeological controversy.

2. MATERIALS AND METHODS

2.1 Conservation Treatment

The new conservation treatment was carried out on three panels (I.n. 2299, I.n. 2297, I.n. 2301) not previously restored, in order to complete the conservation of the wall painting cycle. The main aim of the conservation treatment was to remove extraneous substances from the painted surface to enhance their appreciation. Different cleaning methodologies was undertaken depending on extraneous substances nature, their thickness and the state of preservation of painting layers. A consolidating treatment of the flakes of colour was provided using an acrylic resin (10% in distilled water). Then, the removal of the thick coating of wax was performed with a thermal treatment by using water vapour, under pressure and temperature controlled, useful to emulsify the hydrophobic layer avoiding the widespread inside the porosity of the substrate. This treatment was more efficient than organic solvents cleaning, that they were not so performing for removing thick layers of wax and also the solvents solubilizing wax may spread it inside the substrate. Glue residues and organic varnished were removed with compress (1:1 cellulose powder and sepiolite) of alkaline solution applied with cellulose paper for an hour on Japanese paper. Then, the removal of swelled organic substances was made by using cotton tampons, scalpel and probes. After the cleaning, the colour showed their proper brightness and original appearance. The oil retouching was still removed during the cleaning treatment, revealing also the presence of black retouching on fillings in the slab of background, imitating the black alteration. Hard concretions, that hidden painting details, were removed with a mixture of ion exchange resins (in a ratio of 70 anionic and 30 cationic) applied over Japanese paper for 40 minutes. After concretions became weaker and were gradually thinned with scalpel. A revision of the previous fillings was performed using white stucco, retouching them with the technique of “chromatic selection” (executed as pointillism) in accordance to the modern theory of the restoration [28, 29, 30].

2.2 Instrumentation

The following non-destructive and micro-invasive scientific methodologies were involved in the present project: Infrared imaging, Visible-induced infrared luminescence (VIL); X-Ray Fluorescence analysis (XRF); Optical Microscopy (OM); Electron Microprobe Analysis coupled with Energy Dispersive Spectroscopy (EMPA-EDS).

Infrared diagnostic imaging (IR) has been carried out by means of a scientific digital CCD camera, CHROMA C4-DSP series, C250ME model of DTA srl, with KAF8300ME sensor, equipped with an internal 8-position interference filter wheel (8 spectral bands). The following are the technical specifications of the employed digital scientific camera: CCD cooled, 6 Mpixel (3326 × 2504 points) effective (pixels with a side of 5.4 μm); Full Well Capacity: 25.5 ke-; Dark Current: 3.5 e-/pixelsec (at -5 ° C): Quantum Efficiency at 450, 550, 650 nm: 45, 57, 48; Fill Factor: 100%; Peltier cooling with $\Delta T = 30°C$; Acquisition filter 1000 nm (± 50 nm).

The IR images, thanks to the transparency of some materials at the IR wavelengths (centred to 1000 nm with 100 nm bandwidth) and to different spectral behaviour of constituting materials, allowed to study the executive technique, *pentimenti* or variations made by the artist and to improve the legibility of iconographic details no longer appreciable with the naked eye due to ageing phenomena of the pictorial layer and the presence of patinas, so as to support the recently completed cleaning work.

Visible-induced infrared luminescence (VIL), an imaging technique that highlights the typical characteristics of some pigments luminescent in the infrared region when excited with visible light, was used for identification and localisation of Egyptian Blue pigment. For VIL acquisitions, the surfaces were irradiated with visible green light by using; the infrared emission was collected with an 850 nm infrared filter to cut all stray radiation from the visible spectrum and thus collecting only infrared luminescence emission. The VIL acquisitions were made with a CCD photographic sensor, the MADATEC multispectral system consisting of Samsung 500, 28.2 MP, BSI (Back-Side Illuminated) CMOS multispectral back-thinned camera.

The employed portable spectrometer for X-Ray Fluorescence analysis consists of a miniature X-ray tube system, which includes the X-ray tube (max voltage of 40 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics and the USB communication for remote control; a Silicon Drift Detector (SDD) with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line Energy Resolution (depends on peaking time and temperature); 1 keV to 40 keV Detection range of energy; the max rate of counts to 5.6×10^5 cps; software for acquiring and processing the XRF spectra. Primary beam and detector axis form an angle of 0 and 40 degrees respectively with the perpendicular to the sample surface. Measurement parameters were as follows: tube voltage 35 kV; current 80 μA, acquisition time 60 s; no filter was applied between the X-Ray tube and the sample; distance between sample and detector around 1 cm. The setup parameters were selected to have a good spectral signal and to optimize the signal to noise ratio (SNR). Measurement areas were selected according to the results of IR imaging technique, in an attempt to avoid the restoration areas. XRF analyses were performed on 16 sample areas for the identification of the pigments used in the original pictorial layers not affected by earlier treatments (Fig. 4), allowed to identify the typical colour palette and to provide information about the stratigraphic sequence of pictorial layers. Moreover, information has been obtained on the blackening alteration of red background layers by using an Electron MicroProbe Analyses coupled with Energy-Dispersive Spectrometry (EMPA EDS) JEOL JXA 8230 instrument on micro sample of wall painting including red and black layer portions in order to establish the composition of a degradation product (Fig. 4). The technical characteristics of the JEOL JXA 8230 instrument are Source: W/LaB6; 5 Spectrometers WDS with LDE, TAP, PETJ, LiF, crystals; Proportional Counter Detector, Xe-Filled Detector; 5th spectrometers with large crystals: PETL and LIFL for trace element analysis; 1 Spectrometer EDS – JEOL EX-94310FaL1Q - Silicon drift type (Resolution: 129 eV; Window: Ultra-Thin Window (UTW); Detection area: $10mm^2$). The EMPA images were acquired according to the following instrumental parameters: HV: 15 KeV; probe current: 10 nA; working distance: 11mm; Image: BSE – SE signal; detector image: Solid State detector (SSD), Everhart Thornley detector (SE); Image size: 2560 x 1920 pixel. Moreover, the EDS analyses were carried out according to the following measurement parameters: 15 keV HV; 266 10 nA probe current; 11mm working distance; 40° take off; and 30 seconds live time. The measurements were performed after coating the sample with a thin and highly conductive film (graphite).

3. RESULTS AND DISCUSSION

3.1 Improvement in the iconographic understanding

The IR imaging diagnostic investigation has provided clearer legibility of the figurative details no longer appreciable to the naked eye, highlighting the skilful use of *chiaroscuro* and chromatic effects sought for the volumetric rendering of the subjects. It confirms the sophisticated quality of the technique of execution to paint garlands and the details like fruits, leaves and embroidered strings. In particular, it was possible to retrace better the outline of figurine depicted in the centre of the *tympanum* suggesting that it may be a female subject, with decoration with green leaves and purple fruits that surround her (Fig. 5). Furthermore, IR images of the mask (Fig. 6) showed the complexity of painting details suggesting its upsizing and new iconographic details like the two little horns on the front [31]. The IR images suggest that the painter mastering the fresco technique, working quickly to add also many details to the surface before the plaster dried fully. Moreover, the IR images provide that the overlapped thin brush works used for modelling the volume of the embroidered bandages, fruits, leaves and masks may be executed with *secco* technique (Fig. 6). An important iconographic discovery was done during the cleaning of the square fields of the panel I. n. 2301. A musical instrument, identified as *tibia* (two crossed flutes), was found suspended from the centre of the garland. But its details were not clear readable because of many losses of paint layers. The IR images improved the readability of the musical instrument, showing also the two cords on which, the flutes are hanged (Fig. 7).

3.2 Palette identification

The XRF investigation, carried out on 16 pictorial areas for identifying the original inorganic material and for understanding the background pictorial stratigraphy, has showed a homogeneous result on the three panels here studied and on two panels previously analysed, except for a blue pigment not reported in previous studies [18].

In all investigated painted areas, high values of the intensity of the calcium emission lines were found, attributed to the lime binder matrix, according to the minero-petrographic analysis performed on the other two panels and previously undergoing restoration [18]. Moreover, the calcium XRF signal is attributable also to the preparation layers. Indeed, the previous cross-section analyses of mortar layers confirmed the use a calcite matrix characterized by rhombohedral calcite crystals (calcareous alabaster), according to the typical technique of the imperial period in Rome [18].

The XRF analyses identified pigments typically ascribed to the Roman palette of the first century BC [32]. Table 1 summarizes the pictorial pigments identified by XRF for each of the investigated colour layer. The results suggested the use of calcite for white decoration layers, carbon-black for black decoration elements, and confirmed the presence of yellow and red iron-based pigments, cinnabar and green earth as previously identified on the other two panel in 2005 investigation. In particular, yellow iron-based pigments have been used for background pictorial layer and decoration subject; red iron-based pigments have been mixed in flesh tone and dark-red figurative elements or frame decorations, and, finally green earth pigments (natural pigments composed by hydrated Fe-rich silicates, e.g. glauconite, celadonite, chlorite) have been found on green frame decorations. Moreover, in correspondence of these green layers, optical microscopic observation revealed for the first time the presence of blue pigment grains spread in the matrix of the green earth pigment, never mentioned to date for this cycle of frescoes.

The low XRF intensity values of copper at 8.04 keV and 8.90 keV, simultaneously high in silicon and calcium, detected in correspondence of iron-based green pictorial layers suggested the use of Egyptian blue pigment (Fig. 8). The pigment identification also was confirmed thanks to VIL image acquisition that detected in corresponding of blue grains a luminescence typical of Egyptian blue. It is therefore clear that the Egyptian blue pigment was added in low content to the green earth mixtures to make more brilliance and darker the green pictorial layer [33].

Egyptian blue is a synthetic pigment, consisting of a mixture of cuprorivaite blue crystals [$CaCuSi_4O_{10}$ or $CaOCuO\ (SiO_2)_4$ - calcium copper tetrasilicate], continuously used since the fourth dynasty in Egypt until the end of the Roman period in Europe [34]. The use of an artificial mixture of Egyptian blue and green earth to create different greens shades, it was a practice quite common for Roman painters and it was found in the wall paintings of many Roman sites [32, 35].

Egyptian blue grains mixed with green earth pigment were recently identified on older archaeological finds coming from Lucanian necropolis in Campania. The green decorations depicting the leaves of the painted T110 and T21 tombs displayed at the Archaeological Park of Paestum (Salerno, Italy), dating back V century BC and IV century BC respectively [36] are characterized by the presence of copper along with calcium and iron and by the high luminescence in VIL investigation.

Moreover, regarding the archaeological question about the up, today misunderstood original colour of the background, the XRF results had a crucial role to confirm the pictorial stratigraphy thank to the chemical identification of the yellow pigments in correspondence of *lacunae* or overlapped with the light red layers. Indeed, the XRF analysis definitively verified that a thin cinnabar bright red layer was laid out over a thin undercoat yellow iron-based pigment layer, homogeneously on the whole pictorial surface of panels. In figure 9, the comparison of the spectra acquired on the panel (I.n. 2301) shows as the yellow iron-based pigment of tambourine drum was given over this double pictorial stratigraphy. The technical use of undercoating is confirmed in other provincial sites such as York (United Kingdom), Dietikon (Switzerland) and Aix-en-Provence and Narbonne (France) [37, 38, 39]. It is possible to assume that there are practical reasons for the presence of yellow undercoat. This yellow layer may be applied to save the expensive red pigment in order to use a thin application of cinnabar without losing the intensity of colour [37]. Furthermore, the undercoat was also a barrier to neutralize the caustic lime in consideration that cinnabar was one of the pigments that may altered if used by the *fresco* technique.

The preliminary conservation state observation confirmed that a typical alteration has occurred that has led to the red pigment blackness, when this light red background is not covered by other pictorial layers (Fig. 10) or protective finishing but has been in contact with the external environmental condition or with the restoration materials over time. The phenomenology of typical cinnabar degradation was known to the Romans, indeed Vitruvius [40-41] mentioned the need of a protective varnish based on Punic wax and to avoid the direct contact between the pigment and the lime preparation layer in order to prevent cinnabar from blackening.

Useful information has been provided from the comparison between the red background layer of the *tibia* panel and the one acquired at the areas affected by pigment blackening. It should be noted that this blackened portion is not due to residues of the deposited layer of deposits and protective elements already removed prior to the execution of the XRF analyzes. As shown from the comparison in figure 11, no differences were found in terms of the presence of chemical elements constituting the pictorial layers, supporting the hypothesis that it is an alteration of the cinnabar pigment and this is not a superimposed layer to be remove during the cleaning treatment.

The most common alteration of natural or synthetic cinnabar is due to the change of the typical red pigment colour in black or grey-silver hues. This phenomenon is not systematic and its origin is not yet fully understood [41-45]. In the process of photochemical alteration, a key role is probably played by chlorine, an element presents as an impurity in cinnabar or deriving from the atmospheric pollution.

Under the action of light, mercury sulfide can partly dissociate from elemental mercury and sulfur ($HgS \Rightarrow Hg_{(0)} + S_{(0)}$). The metallic mercury nanoparticles, deposited on the surface, make the colour turn from red to black. In this process the ion Cl^- acts as a catalyst, i.e. it increases the reaction rate. Furthermore, it causes the probable formation of corderoite ($Hg_3S_2Cl_2$) from which, by the effect of light, calomelane (Hg_2Cl_2, white), sulfur and metacinnabar (HgS with a cubic crystalline structure, black) or amorphous mercury sulfide (black) are produced according to the following reaction ($Hg_3S_2Cl_2$) $\Rightarrow$ $Hg_2Cl_2 + S + HgS$.

The chemical characterization of degradation products is made more difficult both by the micrometric size of the multilayer structure of the paint layers and by the presence of minor or trace elements that can cause the alteration. Consequently, in order to identify any compositional difference between the thin superficial blackened layer and the below unaltered red layer, electron microprobe analyses coupled with energy-dispersive spectrometry were further performed along the cross-section of sample S1. Once again, the presence of the same chemical composition concerning the two red and black portions is confirmed, verifying the absence of Chlorine-based degradation products (Fig. 12). The micro-destructive analyses confirmed that the blackening colour portions are not a deposit of material but are likely due to the photochemical alteration of the cinnabar pigment, supporting unambiguously the choices conservative and cleaning procedures.

4. CONCLUSIONS

Among the studies on Roman wall paintings, this study provides new data on this rare example of wall decorations in the Roman Sicilian province, coming from House of the Masks in Solunto and not yet investigated systematically. The Solunto's palette indeed includes rich and precious pigments like cinnabar and Egyptian blue. In particular, it is relevant to confirm the use of Egyptian blue for the green colour in Solunto's frescoes paintings, relating them to a practice already attested in Rome, Pompeii and other Roman provincial sites.

Furthermore, the insight of the pictorial technique and the cinnabar background layers, previously misunderstood, offers further considerations into the prestige of the building, the workers engaged and the client involved. In fact, cinnabar is known to have been one of the most expensive pigments, generally used only in luxurious decorations scheme. Another house in Solunto (VI *insula*, House of the Mosaic Circle, room h) shows a double painting layer, made of yellow and red, in a decoration scheme affine to panels of House of the Masks. Moreover, cinnabar is attested in provincial sites until the middle of first century BC when it was gradually substituted by red ochre [37].

These aspects of the production technique and of the materials used to allow to confirm the dating of this Sicilian cycles performed previously only through an archaeological and stylistic comparison.

The pictorial details, obtained by IR images, shows the high quality of painting technique in which *chiaroscuro* effects are used for achieving subjects and decorations. IR imaging allowed to support the reading of some depicted details, hidden until now. The chronological and technical analogies with other Roman wall paintings confirm the presence of a sophisticated painter's workshop in Solunto [46]. This study also contributes to enriching the iconographic analogies with the wall decorations from Villa of *P. Fannius Synistor* in Boscoreale among those already known (panel I .n. 2301 is comparable with a wall painting from the east wall of room L in Musée Picardie of Amiens; while the subject of masks suspended from opulent garlands is also present in tablinum L decorations in Metropolitan Museum of New York). The panel with the *tibia* (I.n. 2297) finds a comparison with a painting in Louvre Museum (I.n. P100), from the room D of this Boscoreale's villa [47]. These analogies can corroborate the presence of itinerant painters in Solunto, who carried pattern books showing the current fashionable designs from Rome or Venusian area [33, 48, 49], providing even more perception about the *status* of the owner and how his taste was influenced by knowledge of trends in main Roman towns.

Acknowledges

The authors would like to thank Dr. Lorella Pellegrino, Senior Conservator at the Centro Regionale per la Progettazione e il Restauro of the Sicilian Region, and Samira D'Agostino, Francesca Onorato, Chiara Tuccio e Tatiana Fastampa of the Graduation Course in *Conservazione e Restauro dei Beni Culturali* University of Palermo, for supporting the final phase of conservation work of three wall paintings. The Authors acknowledge, concerning the VIL imaging investigation, the Project PON03PE_00214_2 "Sviluppo e Applicazioni di Materiali e Processi Innovativi per la Diagnostica e il Restauro di Beni Culturali (DELIAS)" provided by the National Ministry of Education and Research (MIUR).

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TABLE CAPTION

Table. 1. XRF results for different chromatic pictorial layers analysed on three mural painting panels (A) and comparison with the previous chemical results (B). For each XRF measurement, any Hg contribution from the underlying layers is indicated, when cinnabar is not related to the pictorial mixture of the observed layer on the surface.

FIGURES CAPTIONS

Figure. 1. a) Solunto (Sicily) archaeological site and b) localization of the House of the Masks. The red line indicates the original location of the five detached panel and displayed at the Archaeological Museum of Palermo “Antonino Salinas”.

Figure 2 Three panels of roman mural paintings (I century BC) found in Solunto (Sicily) archaeological site: I.n. 2301 (a, d); I.n. 2299 (b, e); I.n. 2297 (c, f). The shown conservation state in a), b) and c) is to be referred to the surface conditions before the restoration; in d), e) and f) it is to be referred to after the conservative treatments carried out in 2017.

Figure. 3 Archaeological hypotheses proposed for the interpretation of the background colour for the Old Man Mask (I.n. 2300), from left: black colour suggested by G. Salemi Pace (1872); Pompeian red (cinnabar) altered in black published by B. Pace (1934); yellow-orange background proposed after the conservation treatments by Camerata Scovazzo et al. (2005).

Fig. 4. Localization of the measurement areas analysed by XRF (white circles) and of the sampling point of the S1 sample (yellow rhombus) analysed by EMPA-EDS on three (from left) I.n. 2301, I.n. 2299, I.n. 2297 wall paintings panels. The diagnostic investigation was carried out after a preliminary cleaning of the pictorial surfaces.

Figure 5. Panel I.n. 2297; Infrared images (a, b) and comparison with a photographic detail of *tympanum* (c) to highlight the gain of readability in the infrared range (1000 nm) of the subject painted in the centre of the musical instrument as well as the volume and *chiaroscuro* effect of the entire representation.

Figure 6. Panel I.n. 2299; Infrared images (a, b) and comparison with photographic details (c, d) to highlight the gain of readability thank to IR imaging diagnostics for tracing particular of the mask, volume and *chiaroscuro* effect on the ribbons and decorations of the garland.

Figure 7. Panel I.n. 2301; Infrared images (a) and comparison with a photographic image of the musical instrument detail (b). The yellow dashed lines (b) indicates the area with two strings with which the *tibia* is attached to the garland.

Fig. 8. Typical XRF spectrum acquired on green pictorial layer (I.n. 2299) and digital optical microscope images of the analysed surface; the grains of blue pigment are clearly visible (magnification 200×).

Fig. 9. Panel I.n. 2297: XRF spectra acquired respectively on from bottom: a) yellow background layer, b) red pictorial layer, and c) outermost yellow pictorial layer.

Fig. 10 The digital optical microscope images (magnification 50×) shown the presence of light red pictorial layer below different colour layer on all three analysed panels: from left, blackened red background of the panel I.n. 2301; decoration frame of the panel I.n. 2297; green frame of the panel I.n. 2299.

Fig. 11. Panel I.n. 2301, comparison between the XRF spectra (13 and 14 measurement area, see Fig, 4) acquired on not altered (dotted line) and blackened (line) cinnabar pictorial layers.

Fig. 12. EMPA-EDS acquired on not altered (1) and blackened (2) cinnabar pictorial layers of the S1 fragment sampled on the upper part of the pictorial background (panel I.n. 2301, see Fig. 4).