Red color characterization in several Roman frescos and paintings by in situ and remote LIBS, LIF and Raman Spectroscopies

Roberta Fantoni, Violeta Lazic, Francesco Colao, Salvatore Almaviva, Adriana Puiu

Abstract: Nowadays, in situ pigments characterization on a cultural heritage relevant surface is possible by using combined laser spectroscopies which are suitable to detect at high resolution both molecular (Raman, LIF) and atomic sample composition (LIBS), the latter with stratigraphic capabilities and high sensitivity for trace detection. Their applications are here reported regarding the identification of historical pigments and dyes on different substrates, particularly in wall paintings, from pre-historic times up to the XIXth century when the use of synthetic substances became common. In this paper attention is focused on red colors, known since antiquity for the additional ritual and medical use. Their pictorial use along the centuries is shown and in selected cases provenances hypothesis, based on historical information, could be supported by results of composition analysis and elemental trace detection made possible by the application of laser technologies.

Keywords: laser spectroscopies, red pigments, trace detection, provenance studies, wall paints

Caracterización del color rojo en varios frescos y pinturas romanas *in situ* y remotas mediante espectroscopías LIBS, LIF y Raman

Resumen: Hoy en día, la caracterización de pigmentos *in situ* en una superficie relevante del patrimonio cultural es posible mediante el uso combinado de espectroscopias láser las cuales son adecuadas para detectar en alta resolución tanto la composición molecular (Raman, LIF) como la composición atómica (LIBS) de la muestra, esta última técnica con capacidades estratigráficas y una alta sensibilidad para la detección de trazas. En este artículo se exponen sus aplicaciones en la identificación de pigmentos y tintes históricos sobre diferentes sustratos, particularmente en pinturas murales, desde la prehistoria hasta el siglo XIX cuando se generalizó el uso de sustancias sintéticas. El artículo se centra en los colores rojos, conocidos desde la antigüedad por su uso ritual y médico. Su uso pictórico a lo largo de los siglos es demostrado y, en casos seleccionados, la hipótesis de procedencia, basada en información histórica, podría ser apoyada por resultados de los análisis de composición y detección de trazas elementales gracias a la aplicación de tecnologías láser.

Palabras clave: espectroscopía láser, pigmentos rojos, detección de trazas, estudios de procedencia, pinturas murales

Introduction

Along human history, early cultural heritage (CH) is frequently associated to painted surfaces with the use of mineral pigments and organic colors, their receipts assuming often the role of markers for social and technological development. Since pre-history, medicine and art were tightly bound for ritual use of paints and even for dual use of the material, either as medicine or sacred ornament in tombs and temples. To this respect red color carriers deserve special attention, for the ritual use of this color reminding the blood in sacrifices, and some magical power associated to their effective or supposed medical performance.

The development of mobile analytical tools for characterization of immovable CH surfaces corresponds to a remarkable innovation in the field (Miliani *et al*. 2010; Vandenabeele *et al*. 2016). Remote and in situ characterization of different types of painted CH surfaces relied on the use of laser-based prototypes developed for optical and spectroscopic investigation (Anglos *et al*. 1999), with possibility to release 3D models, 2D images, and point data information on composition and stratigraphy (Fantoni *et al*. 2017). In a significant example reported in Ceccarelli *et al*. (2021), laser scanner prototypes, developed at ENEA, were applied to investigate a well-known Etruscan tomb from the Vth century b.C. In situ measurements

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were addressed to characterize the surface morphology and composition. More specifically, surface composition was investigated by Raman Spectroscopy (RS) and Laser Induced Fluorescence (LIF) Spectroscopy, while atomic composition was investigated by X-Ray Fluorescence (XRF) spectroscopy. Complete information on the used pigments (iron-based earths, copper blue) was achieved, confirming the early use in Italy of the first synthetic pigment: cuprorivaite known as Egyptian blue.

Innovative analytical techniques for the preservation of CH were recently critically reviewed (Magdy 2021). Specifically, the application of laser spectroscopic techniques (Nevin *et al.* 2012), such as LIBS, to CH material characterization for archaeology (Botto *et al.* 2019) and archaeometry (Spizzichino *et al.* 2014) were discussed in detail. Significant examples of laboratory and in situ application of Laser Induced Breakdown Spectroscopy (LIBS) for compositional analysis and stratigraphy can be found for different historical findings such as ceramics (Lazic *et al.* 2018) and coins (Pardini 2012) from different ages. The complementarity of laser spectroscopies detecting atoms and molecular groups onto multilayered CH surfaces was previously stressed (Bruder *et al.* 2007), and recently confirmed in an in-situ campaign on a XIX century fresco (Romani *et al.* 2020).

Following, we introduce three widely used laser spectroscopies (RS, LIF and LIBS), suitable for in situ applications on CH surfaces. Innovative aspects of each commercial or prototype instrument are stressed in view of the considered application. As case study, we report information gained on red colors, utilized along the centuries from pre-history to modern times, with special attention to the red colors considered in the past for dual use, which was one of the subject of the recent Drugs and Colors conference*. The selected minimally invasive laser spectroscopic techniques were applied mostly in situ, in order to identify different historical red colors. The study is aimed to obtain information about the composition and realization technique of the painted surfaces and possibly to perform provenance studies, tracing commercial routes followed by the rough material.

Experimental

In this section the laser-based instrumentation utilized for laboratory and in situ spectroscopic analyses of CH painted surfaces is shortly presented, after recalling the respective expected analytical performance. Innovative aspects relevant to the considered CH surface to be characterized are stressed.

Laser Induced Breakdown Spectroscopy (LIBS) is a multi-elemental analysis technique, based on the detection of the plasma plume spectrum generated by laser evaporation and ionization of a small volume at the surface. Its only micro-destructive character coupled to

stratigraphy abilities, made it very suitable to the analysis of multi-layered painted surfaces. The need of calibration with reference samples for quantitative analysis, is not a major drawback for the application to this type of surfaces, since semi quantitative data and trace detection are often sufficient to infer the information relevant to the composition and the provenance of the material found in each layer (Lazic et al., 2020).

—*LIBS apparatus*. Nevertheless, prototypes of LIBS spectrometers for field use have been already developed (Gaona et al., 2013) and are available in our laboratory (Lazic et al., 2016), results here reported by LIBS have been obtained by a laboratory set up, since the technique was mostly applied to complete the investigation on fragments of Roman fresco's which could be safely transported to the laboratory where a microanalysis could be performed easily. The LIBS plasma was generated by an Nd:YAG laser (Quantel, CFR Ultra) emitting 6.5 ns long pulses at 1064 nm; the laser energy was fixed to 130 mJ. The beam was focused by a quartz lens $f = 100$ mm perpendicular to a horizontally placed target mounted on a micrometric X-Y table. The substrate height was slightly above the focal plane and the laser beam diameter was 0.30 mm, corresponding to a laser fluency of 42.5 J/cm^2 (6.5 GW/cm^2). The plasma emission was collected at 60° from the target plane by an optical system of 25.4 mm diameter and having two quartz lenses with focal lengths of 75 mm and 150 mm, respectively. The light was focused on a 1 m long fiber bundle containing four quartz fibers of 600 μm diameter each, that bring the signal to four compact spectrometers (Avantes AvaSpec-ULS2048L). The spectrometers cover the 200–796 nm range, with spectral resolution between 0.07 nm in UV and 0.16 nm in NIR. The sample support is mounted on a X-Y-Z micro-positioning system, and thanks to the on-line camera and the illumination system, it is possible to choose precisely spots on the targets to be analyzed. More details about the system are given elsewhere (Lazic *et al.* 2020). Micro-damages at the surfaces corresponded to holes with less than 1 diameter and analogous depth, as verified by the off-line optical microscope utilized for quantification of the ablation rate. On this type of samples, stratigraphy could be performed in the range 0 – 200 μm, with a resolution of about 1.2 μm. (Lazic *et al.* 2020).

Laser Induced Fluorescence (LIF) is used to remotely collect the emission induced by a monochromatic UV source onto a surface. Signals can be time (Nevin et al., 2014) or spectrally (Romani *et al.* 2010) resolved and LIF systems allow for collecting hyperspectral images. Due to the scarce penetration of the UV radiation inside solid samples, the signal is strictly coming from the outermost surface layers. Spectrally broad emission bands detected can be related to chromophore groups present in modern varnishes (Marinelli *et al.* 2017) and consolidant or colors (typically dyes), a few mineral or synthetic pigments present also peculiar fluorescence bands (Borgia *et al.* 1998).

— *Laser Induced Fluorescence scanner*. For remote time and spectrally resolved LIF imaging a compact and easily transportable prototype has been developed by ENEA (Fantoni *et al.* 2013) and used on fresco's also inside a Roman catacomb (Almaviva *et al.* 2018). This hyperspectral LIF-art prototype is equipped with a Nd:YAG laser operating at 266 nm as excitation source with an energy of 1.5 mJ, a pulse duration of 8 ns, and 20 Hz repetition rate. A spectrometer (Jobin-Yvon CP240) allows collecting the light in the range of 190–800 nm with a spectral resolution of about 2 nm. The laser spot is focused on the target by a quartz cylindrical lens, resulting in a linear blade of light, allowing scanning linear sections of the target instead of single points. With a FOV of 5.7°, an image of 1.5×5 m^2 can be scanned in less than 2 min at 25 m distance (spatial resolution 2 mm). This one dimension focusing has also the advantage to drastically reduce the energy at each target point, thus avoiding any damage at the examined surface. The ICCD detector is an ANDOR iStar DH734 with squared pixels (1024 x 1024 pixels. 13 x 13 μm^2 each), mounted behind a slit parallel to the laser line footprint during the scanning. Time resolved LIF measurements are implemented by modulating the trigger signal of the CCD intensifier. At each selected time gate, the entire spectrum is acquired in the considered monochromator range. Reflectance images can be collected by the same apparatus after switching off the laser source. The prototype is completed by a customized software (SAGACE) with algorithms for image processing and automatic extraction of features relevant to conservation problems (location of bio attacks, of former consolidants and retouches, of discoloration and detachments).

Raman Spectroscopy is a consolidated technique used to identify molecular groups onto a painted surface (Sodo et al., 2010). The low efficiency in generation of the Raman shifted emission bands restricts the application of the technique to point measurements use or micro-imaging. For CH applications portable devices have been commercially developed, which are equipped with a hand probe, alternatively the technique is used for high resolution laboratory measurements inside a microscope and referred as microRaman (Villar *et al.* 2005).

— *Laser Raman probe*. The Raman commercial spectrometer utilized is an *i*-Raman system (B&W TEK Inc., Newark, DE, United States) provided with a 785 nm GaAIAs solid state diode laser with power scalable in the range 3–300 mW (Almaviva *et al.* 2018). The detector is a 2048-pixel thermoelectrically cooled CCD (10 °C), equipped with a notch filter to cut the elastically-reflected Raleigh radiation. The spectrometer has a resolution of 3.5 cm−1 and covers the spectral range 175–3200 cm^{-1}. For in-situ measurements a Raman probe with 1 m long optical fiber is used, choosing the point of interest after visual inspection and focusing the laser beam in a 90 μm spot diameter, with a working distance of 5 mm. For all measurements here reported, the laser power was set to few mW, to prevent photodecomposition of pigments at the painted surface, with typical exposure times between 30 and 75 s for each spectrum and summation up to 3 spectra to increase S/N.

Results and discussion

In this section results obtained on different painted surface along the centuries are reviewed as significant case studies, since red colors utilized reflected material availability from natural resources and trades, and successive technological developments. The choice of the equipment was different in different campaigns, depending on the main objective in each case study pursued (which was not limited to the color palette identification), on the instrument's availability and on geometrical constraints of the examined site. Additional laboratory spectroscopic analyses were also performed upon availability of movable fragments.

Among the most common red mineral pigments and colors considered in the present work, dual use is well known for the widely used hematite and cinnabar (cosmetics, medicine), and for carmine (food and textile coloration, ritual use on bones in pre-Colombian burials). No reference to dual use for the other red colors was found.

— *Early Etruscan painted tombs.* The Tomb of Roaring Lions in Veio (nearby Rome) is the most ancient painted Etruscan tomb, dating back to the VIIIth century b.C. (between 700 and 690 b.C.- during the so called Villanovian period in Italy). Drawings, representing rows of animals (lions and ducks) with yellow, red and black colors, still appear on the walls. The roof of the tomb is red painted, as shown in the picture in Figure 1(top). Raman in situ analysis demonstrated the use of most ancient pigments: all earths based on different iron oxides, specifically hematite for the red and goethite for the yellow [Figure 1 bottom left and right]. No evidence of a calcite preparatory layer, typical for tombs painted later from the Vth century b.C. and on, was obtained. While black and yellow pigments were mostly used to paint the animals, a ritual use of hematite might be related to the red painted roof. A local origin of the iron-based pigments may be assumed, without any specific treatment for material purification.

— *Roman mural paintings and fresco's.* Later Raman in situ investigation on Etruscan tombs (Ceccarelli *et al.* 2021) and Roman paleo-Christian catacombs (Almaviva et al. 2018) revealed the use of calcite in the preparatory plaster and the addition of minium (red lead: Pb_3O_4) to the red palette. We may notice that with the progress of mining technology a new bright red color starts to appear on painted walls: the mineral cinnabar (HgS).

• Mitreum at Marino

In the second half of the last century, an underground temple dedicated to the cult of the God Mitra was discovered in Marino, a town on the Roman hills. The

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importance of the discovery is mostly related to the pictorial representation of the God in the end wall of the structure, dating back to the IInd-IIIrd century A.D.. An inscription reports that the temple was attended by slaves working in a nearby Peperino marble caves, that partially explain the simple realization of the wall painting without evidence of a proper plaster background. Nevertheless, in situ Raman investigation performed on the red colors demonstrate the use of the precious cinnabar together

with much cheaper hematite in some of the red painted parts. As Figure 2 shows, for instance the hat of Cautes the "dadoforo" (torch bearing) keeping the torch high and representing the day (on the left of the picture) is painted with cinnabar (HgS), as detected in the Raman spectrum reported on the right of the same figure. It seems that at the time of the realization of the painting the availability of cinnabar in Rome was such that it could be used even to decorate a temple attended by slaves.
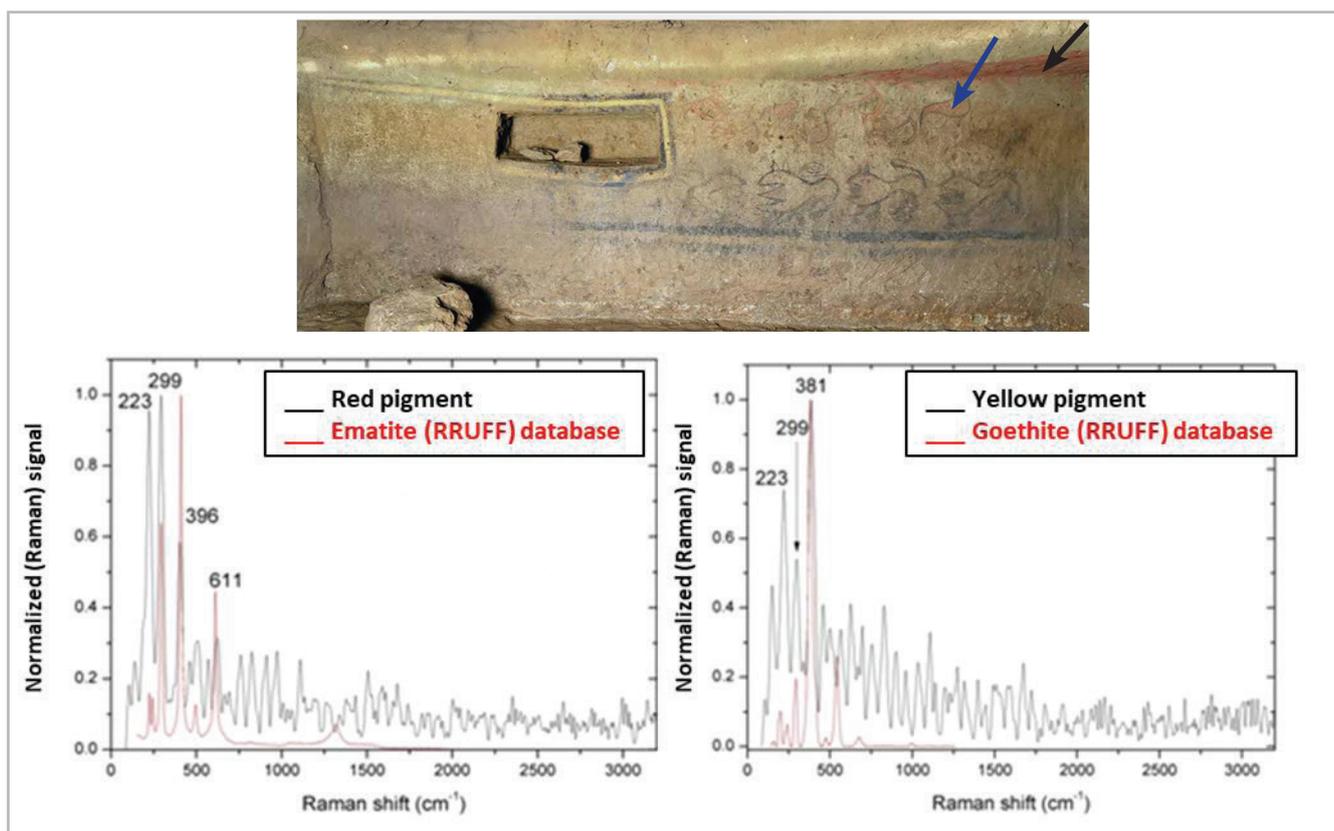

Figure 1.-The Roaring Lion Etruscan Tomb – Picture of the wall painted with lions and ducks rows, blue and black arrows indicate at the respective measurement points on the yellow and red decorations (top); Raman spectra after fluorescence background subtraction (bottom), the reference spectra (RRUFF database) used for the assignment are also shown: on the left from the red spot, on the right from the yellow spot.
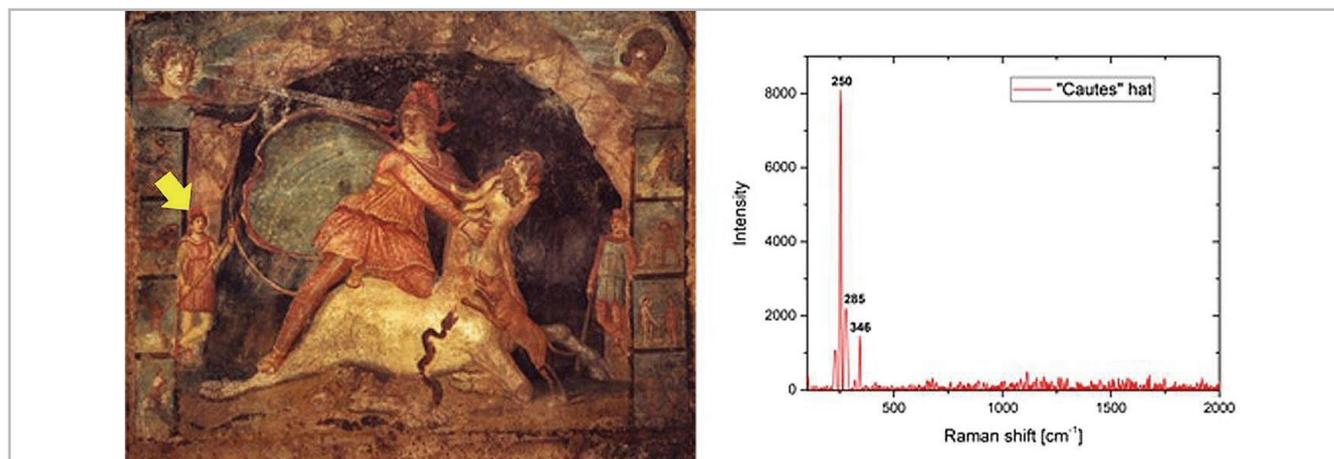

Figure 2.- Mitreum at Marino – Left picture of the wall painted with Mitra killing the bull, the yellow arrow marks Cautes's hat where the Raman spectrum was collected. - Right Raman spectrum, where all peaks are unambiguously assigned to HgS.

• Fresco's in the thermal area of Roman "Villa della Piscina"

Fragments of Roman fresco's from Villa Della Piscina (a suburban villa in Rome) coming from a thermal bath complex with rooms from the Ist and IIIrd century A.D. were available for study addressed to the possible reconstruction of decorative motifs on the walls. Hundreds of painted fragments were found in a former swimming pool basin from middle-age demolition. Attempts to reconstruct original painted rooms rely on both materials identification and stylistic considerations.

First spectroscopic investigations were carried out in the place where the fragments were stored, by using in situ different spectroscopic technique ranging from optical reflectance spectroscopy and XRF, to LIF, FT-IR and Raman spectroscopy. The main components of the color palette were assigned (Sbroscia *et al.* 2020): the use of natural (malachite) and synthetic copper based colors (Egyptian blue and green) was ascertained for blue and green colors. Concerning the red, the bright and dark colors were related respectively to the presence of cinnabar and red ochre (a mixture of hematite and magnetite). The contemporary presence of both type of red suggested deeper studies, which were conducted on selected fragments with more complex laboratory set-ups.

A green-white-red striped fragment from a room ceiling (n. 40) was examined at LABEC-INFN (in Florence) by PIXE (Proton Induced X-ray Emission). The obtained results (Vadrucci *et al.* 2020) showed that the red pigment could be associated to the presence of both cinnabar (HgS) and red ochre (F_2O_3, Fe_3O_4). However, using a single proton energy, it was not possible to establish if the red pigment was a mixture of large cinnabar grains with fine ochre powder or two separated layers have been painted on top of each other. Arsenic traces were detected in the red pigment, thus either of the two minerals might have origin from Monte Amiata in Tuscany. From the space distribution of lead traces, clearly detected in this case, no evidence of a specific lead based pigment was obtained, so these might come from the calcite substrate as impurity, and not be related to minium addition.

In order to disentangle the problem with the contemporary use of different red colors and possibly to obtain information about their provenance another sample (n. 35) [Figure 3 top] was examined by LIBS (Lazic *et al.* 2020). This sample was showing also the presence of more than one pigment in the green layer. Elemental semi-quantitative LIBS analysis confirmed the presence of both iron based green earth (Celadonite: K(Mg, Fe^{2+})(Fe^{3+},Al)(OH)$_2$) as main pigment and a copper and carbon based pigment, suggesting a mixture with Malachite (Cu$_2$(CO$_3$)OH$_2$). LIBS stratigraphy performed on a green spot confirmed the presence of both pigments in the same painted layer for the first 13 μm thickness.

On the red color composition, the present study required particular attention, since the detection of Hg (signature for cinnabar) in the presence of Fe (signature for red ochre) becomes tricky. In pigments containing Fe it is important to select analytical Hg I lines with minimum spectral interference. For instance, the most intense Hg I line at 253.65 nm fully overlaps with one intense Fe II line (not shown). There are other possible spectral features for detecting Hg I in common paintings, e.g. the Hg I lines at 312.57 nm and 313.18 nm have only a weak contribution of Fe I lines [Figure 3a]. In particular, the Hg I line at 313.18 nm is rather intense and without significant under laying peaks from other elements in the examined pigments, thus in the following we shall consider this Hg I for analysis. The Hg I line at 366.33 nm is too close to one also intense Fe I line [Figure 3b], and in this case the evaluation of Hg content in sample would require peak deconvolution. The analogue need for a peak deconvolution regards the Hg I line at 435.83 nm [Figure 3c]. On the other hand, the Hg I lines at 576.96 nm and 579.07 nm are free of interference [Figure 3d] but they are weak and their choice for tracking this element in samples would lead to high detection limits.

Once selected the proper Hg emission line, it was possible to solve the question of mixed or overlapping red layers containing different pigments. As shown in Figure 4 (left) on the examined sample, the final red color is obtained overlapping a back layer of cinnabar with an equally thin layer of red ochre. The detected alternation of Fe and Hg intensity in the stratigraphy at the first 9 μm, corresponds to red ochres in the outermost 5 μm on top of a 4 μm thick cinnabar layer.

In contrary, on the orange decoration added a secco with organic binders, an alternative use of cinnabar, within a thin 1.2 μm layer on top of goethite, was observed. In both cases the Ca I lines used for normalization were selected to have the closest excitation level with the analytical lines from the examined elements (Lazic *et al.* 2020).

Here the following question arises: why bright cinnabar was covered by darker hematite to obtain red colored areas when using the fresco technique? Since antiquity cinnabar was used in wall paintings, even if it was known to suffer from sunlight and humidity degradation leading to a blackening of fresco's (Plinio). Different mechanisms for the cinnabar blackening (Nõller 2014) were examined in a detailed study carried out by synchrotron radiation (Cotte *et al.* 2006), where the formation of chloride and sulfates was observed in fragments of fresco excavated from the Pompeian area. Specifically, the Cl addition might be related to the use of a protective wax on fresco, which was processed in salty water before use (Plinio), while sulfatation might come from gypsum added to the mortar. In our case no trace of gypsum was found in the mortar by X-Ray Diffraction (Sbroscia *et al.* 2020), so the observed unusual stratification might be attributed to the fear for blackening which might occur in the humid thermal environment where the fresco was located. Whatever reason may lead to the blackening of cinnabar, apparently the painter decided to cover cinnabar in the fresco with a layer of hematite for a protective purpose.
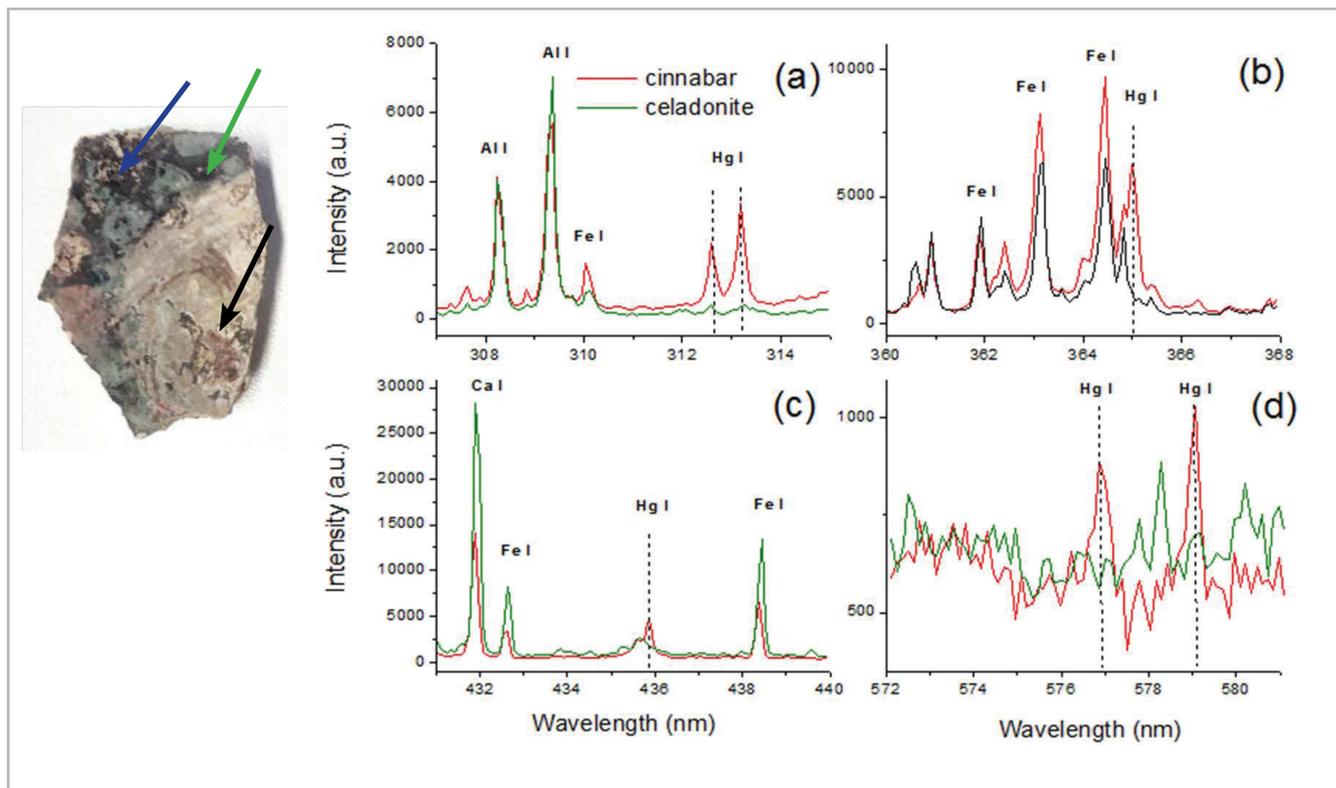
Figure 3.- Picture of the examined Roman fresco sample (top), blue and black arrows indicate respectively the dark red and light red investigated areas; Characteristic spectral intervals (a-d) for identification of Hg I in mixtures with iron based pigments: red line – spectrum on red area (blue arrow), green line – spectrum on green area (green arrow), both acquired by the 5th consecutive laser pulse on the same sample (bottom).
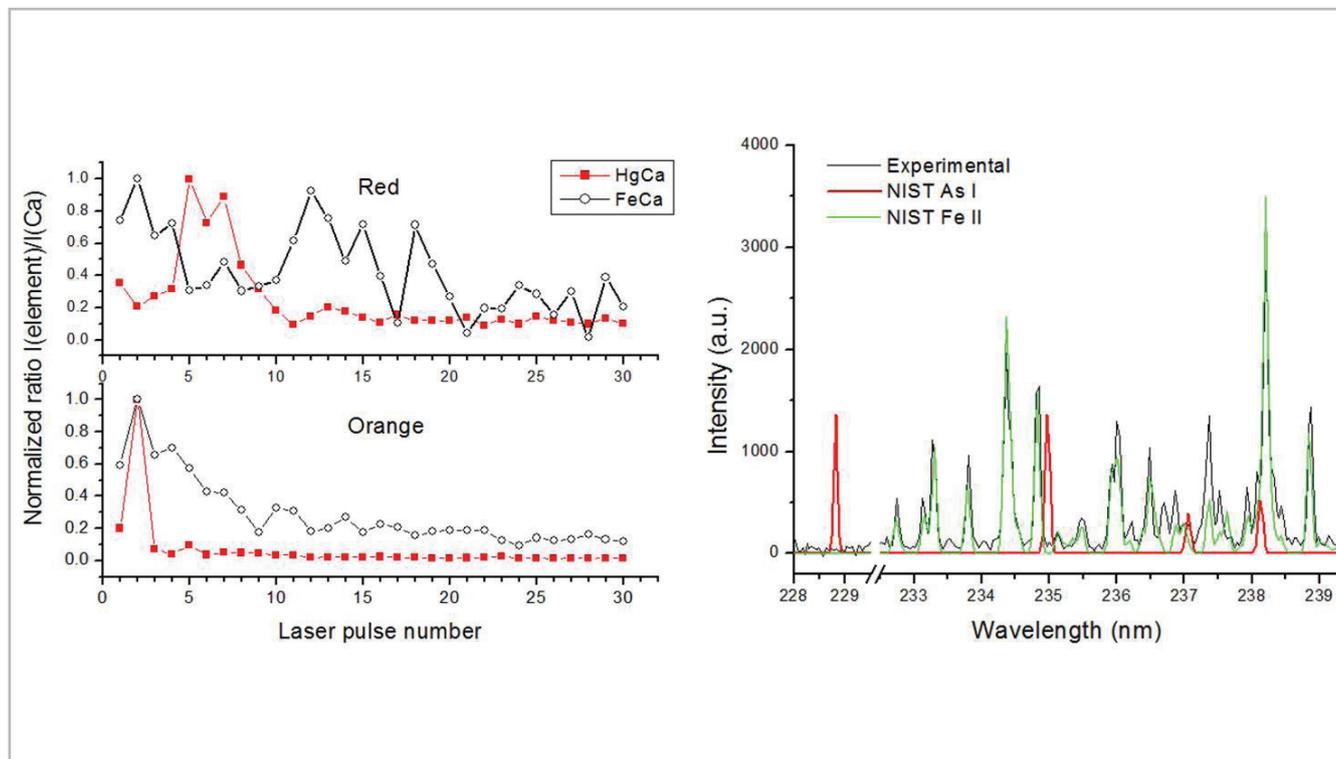

Figure 4.- Left: normalized in depth variation of LIBS line intensities from Hg I (313.8 nm) and Fe I (438.35 nm) measured on the dark red area marked by the blue arrow in fig. 3 (top) and orange area marked by the black arrow in fig. 3 (bottom) of the sample. Right: a portion of the LIBS spectrum collected at the 5th laser shot on red area, and the theoretical spectral lines (NIST database) from Fe II and As I.

The very low iron content in the mercury rich intermediate layer for the red painted areas of the fresco offered the possibility to further investigate cinnabar provenance. In the red area, the most intense Hg I lines occurs for the 5th laser pulse. Also here, we did not observe any presence of As, as shown in Figure 4-right where the experimental spectrum is compared with the theoretical most intense As I and nearby Fe II lines according the NIST database. Since no arsenic traces were detected together with Hg, the possible provenance of cinnabar from Monte Amiata could be ruled out and present data support the suggested cinnabar provenance from the Spanish Almadèn mine (Sbroscia et al. 2020).

— *The red color in paintings from XVIth-XVIIIth century.* In the middle age the color palette remained basically unchanged, with major or minor utilization of materials from Asia depending on the availability of commercial routes. The situation changed with America discovery and trades from the West India route towards Spain and Portugal. Specifically, a new red was introduced for different use, including paintings. The new color had an organic origin, carmine was indeed coming from the cochineal insect body and widely used as colorant in the Pre-Colombian American art (painting), ritual ceremonies (on bones in burials), and every-day life (dye for cloths). After diffusion in Europe it was used as well as food and beverage color up to modern times, as probably in Aquae Elixirs offered at Spezieria di Santa Maria della Scala in Rome since the XVIIth century, an ancient pharmacy run by the Spanish order of the Discalced Carmelite Friars.

• Spanish mural paintings

Remote LIF imaging campaigns were conducted on Spanish mural paintings in Andalusia, to ascertain their conservation status (Ortiz et al. 2015). Although most historical mineral pigments do not present detectable fluorescence emission in the plaster, one of the investigations was addressed to explore the chances of identifying the color palette by LIF

spectra collected (Gomez-Moron *et al.* 2020). To this aim, reference LIF spectra were first collected on pure color samples in powder and on models of their application in fresco made according the original receipt. For the red palette both carmine lake (from cochineal) and vermilion (being vermilion the modern name for synthetic cinnabar) were considered. In Figure 5, reference LIF spectra obtained from both type of samples are reported. The powder spectrum shows a characteristic red emission for carmine from cochineal, which persists in the fresco model and is well above the vermilion tail observed in the same spectral region; despite the substrates difference, significant variations in the intense fluorescence signature of carmine from cochineal were not detected. Note that in the fresco model, the blue-green band common to both the samples is useless to pigment identification because it is coming from the plaster (Gomez-Moron *et al.* 2020).

The case study reported in (Gomez-Moron *et al.* 2020) is relevant to the XVII century fresco on the vault of the Chapel of Our Lady of the Good Air in San Telmo Palace, Seville (Spain). Spectrally resolved fluorescence images were collected by using the hyperspectral ENEA LiF art prototype. Principal Component Analysis of the data collected from the entire image, revealed a significant red component peaked around 600 nm [Figure 6 top] in the PC4 and to a less extent also in PC5, supporting the use of carmine lake from cochineal in all red painted areas. The lack of a closer and more specific band overlap between the red component of the spectra of figure 5 and the corresponding one in the PC4 and PC5 in figure 6 is explained by considering that the PCA does not provide components with a physical sense like; indeed, it only shows trends occurring in form of bands which, in contrast with each other, originate from the underlying physical components. Projection by Spectral Angle Mapper (Dennison *et al.* 2004) of the fluorescence spectral signature obtained in red areas onto the entire images data set permitted to reveal the use of carmine not only on central character's red dress [Figure 6 bottom left] but also
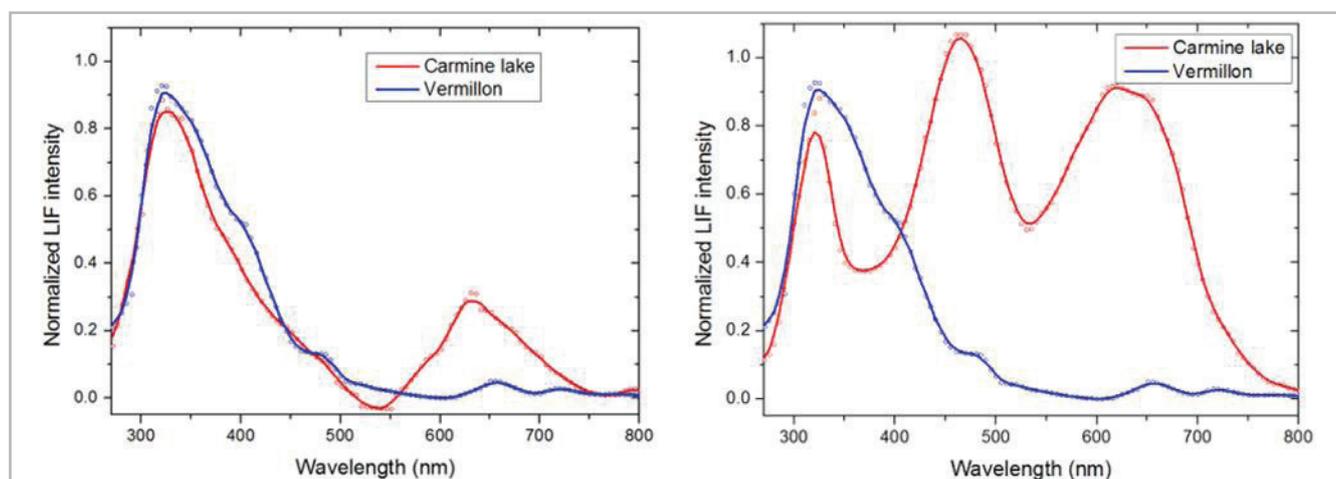

Figure 5.- LIF spectra of considered red colors in powder (left); the same spectra collected from model of red painted fresco samples (right). The used pigments are detailed in the legend.
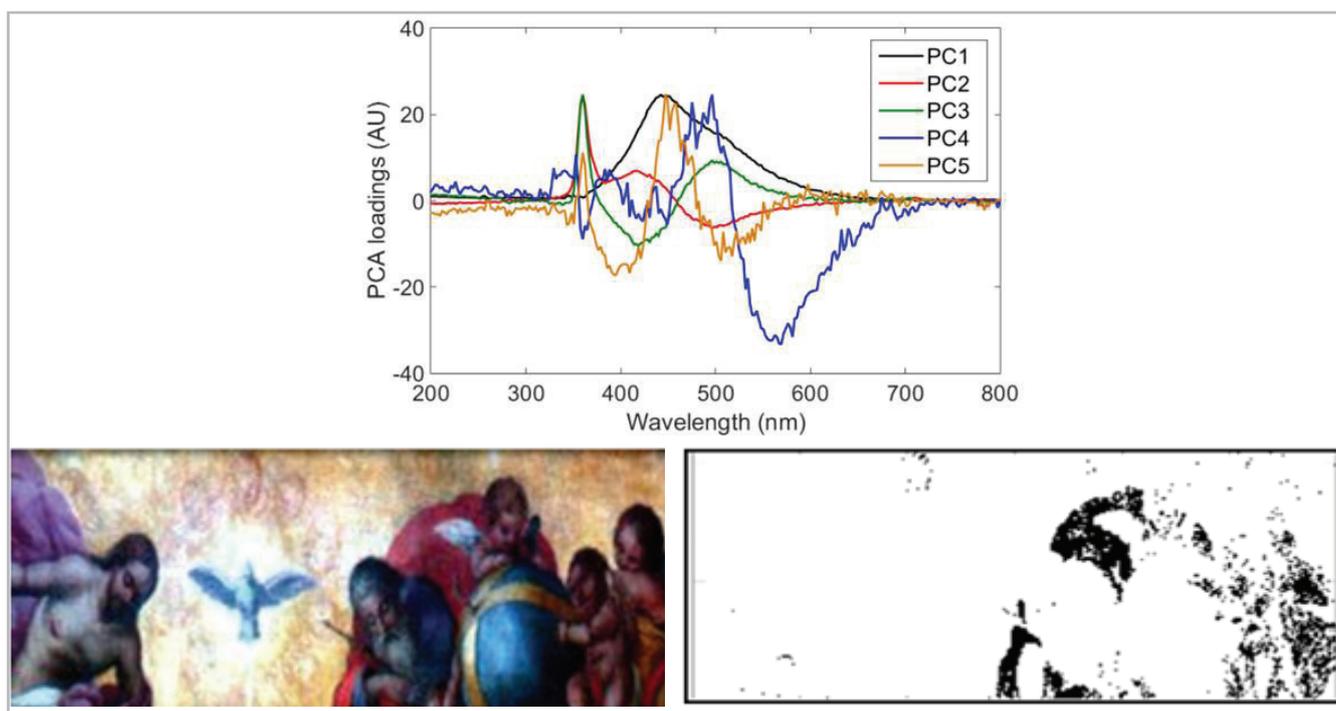
Figure 6.- Top PCA analysis of the spectra collected on the area shown in the reflectance image (bottom left); bottom right the carmine lake distribution in the same area as obtained by SAM projection of the reference LIF spectrum.

as spot in other areas [Figure 6 bottom right]. Analogous results were obtained on a different portion of the vault, considered in the analysis performed by (Gomez-Moron *et al.* 2020).

The use of carmine from cochineal witnesses the importance in Spain of trades from America in the XVIIth century.

• Italian oil paintings on canvas

Within a cooperation with the restorer EURESARTE s.l.r. two paintings (oil on canvas, realized between XVIIth and XVIIIth century in central Italy) were examined in situ at the restoration place in Macerata by the ENEA Laser Raman probe operating at 785 nm. The paintings were "Annunciation" by Giovanni Battista Brughi, "Emmaus Dinner" by Filippo Bellini, realized at the beginning of the XVII and of the XVIII century, respectively. Aim of the work was to identify the color palette and all materials used in the realization and in former restorations. Concerning red colors, main question was the use of cinnabar in red and pink painted area.

In situ spectra collected in red areas of Emmaus Dinner (XVIIth century) and Annunciation (XVIIIth century) revealed a diffuse use of cinnabar (named vermilion in modern times) for red and pink colors, from dark to light nuances, in combination with lead white or red ochre, respective Raman shifts are reported in Table 1. Examples, shown in Figure 7 and Figure 8, report results obtained on red cloths, skin and lips. Linseed oil was used as binder in these paintings on canvas, for which a strong fluorescence signal

was found in all the examined points and subtracted to the Raman features ascribed to the pigments. No utilization of carmine lake was detected either in the older nor in the more modern painting, since its characteristic Raman peak at 1318 cm^{-1} upon laser excitation at 785 nm (CHSOS database) was not present in any of the paintings.

Raman shift (cm-1)	Assignment
106, 1050	Lead White 2PbCO$_3$·Pb(OH)$_2$
250, 285, 346	Vermilion (Cinnabar HgS)
398	Red ochre (hematite F2O3)

Table 1.- Assignment of red and pink color on the examined oil paintings on canvas. Measurements points are marked in figure 7 and 8.
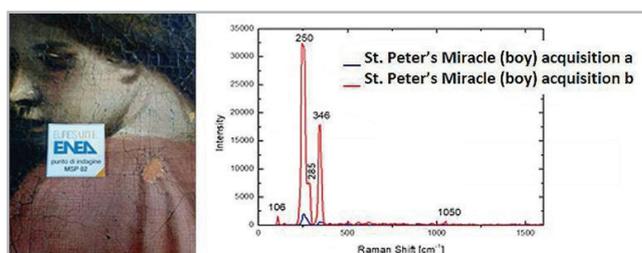

Figure 7.- On the left a detail of the "Emmaus Dinner" painting with label on the spot examined: orange arrow on the boy's dress (b), yellow arrow on the boy's face (a); on the right the respective Raman spectra collected after background subtraction, assigned as in Table 1.
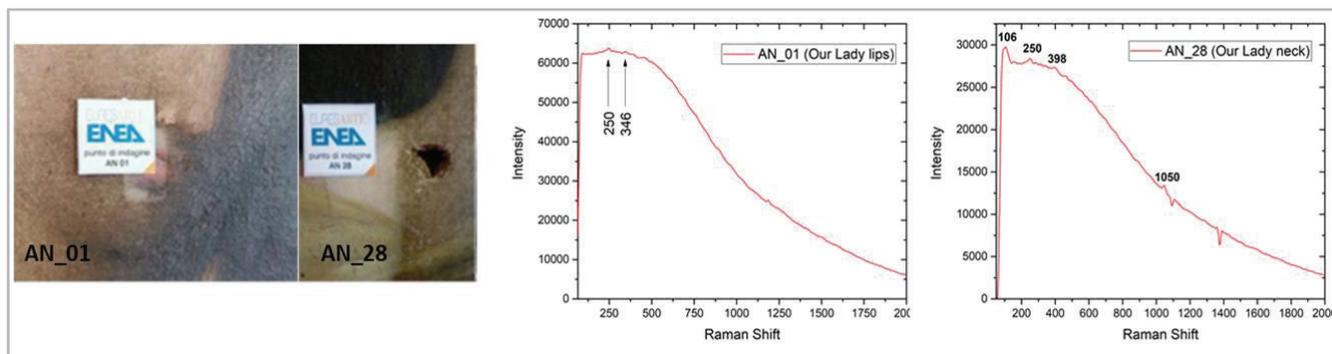
Figure 8.- Details of the "Annunciation" painting with labels on the red and pink spot examined in Our Lady image (lips and neck respectively); on the right the respective Raman spectra, assigned as in table 1, red ochre was found on the neck of Our Lady.

— Italian modern fresco from the XIXth century

Within an in situ diagnostic demonstrative campaign, carried out on Vincenzo Pasqualoni modern (middle XIXth century) fresco in San Nicola in Carcere (Rome), interest arose on the use of pigment and colors, due to the contemporary diffusion of chromium based synthetic materials in correspondence with the development of chemical industry. However, additional interest was remarked for provenance of peculiar pigments identified to obtain red, pink and orange colors (Romani *et al.* 2020). Raman spectroscopy could be used with the probe described in the experimental section since the fresco was under restoration and scaffolding were already installed, which could be climbed by the operator in order to place the probe in contact with the surface to be investigated.

Quite surprisingly we found a new red pigment of natural origin from South America in this spectra: phoeni-cochroite ($PbCrO_4 \cdot PbO$), used also in combination with ochres and calcite. The Raman spectra collected at different sample points are shown in Figure 9; the assignment of major structures detected is reported in Table 2. It is indeed historically known about a working visit of the painter in Chile, where a phenicochroite mine is located (Tocopilla Province).

Also other red based colors were obtained starting from phenicochroite (e.g. orange and violet) in combination with other ingredients. For instance, the addition of yellow ochre (goethite) to phenicochroite was used to obtain orange color [Figure 10], while the golden yellow contained goethite with traces of orpiment (As_2S_3). Once again the used pigment could have an American origin, since important orpiment mines are located in Peru.

Conversely, spectrally resolved LIF imaging, remotely performed on the same area after the scaffolding removal, did not show any presence of carmine in the red painted area, ruling out the use of this historical "American" color from cochineal in the fresco (Romani *et al.* 2020). Apparently the use this color in painters' palette did not spread from Spain to central Italy until the XIXth century, neither for oil painting nor for fresco, nevertheless the cochineal was already present at the Spezieria of Santa Maria della Scala in Rome for other uses.

Point	Raman Shift (cm-1)	Assignment
A	224, 290, 411 106, 144, 340, 380, 826	Fe2O3 (hematite) PbCrO4·PbO (phoenicochroite)
B	153, 280, 711, 1084 144, 342, 382, 828 225, 290, 407	CaCO3 (calcite) PbCrO4·PbO (phoenicochroite) Fe2O3 (hematite) - traces
C	153, 280, 711, 1085 225, 290, 407, 612 144, 342, 381, 828	CaCO3 (calcite) Fe2O3 (hematite) PbCrO4·PbO (phoenicochroite) - traces
D	106, 145, 342, 382, 825, 837 846, 1007	PbCrO4·PbO (phoenicochroite) CaSO4 (gypsum)
E	156, 280, 1084 233, 415, 497, 622, 1007, 1142 200, 350 300, 401	CaCO3 (calcite) CaSO4 (gypsum) As2S3 (orpiment) FeO·OH (goethite, yellow ochre)

Table 2.- Pigment identification in the red – yellow areas.

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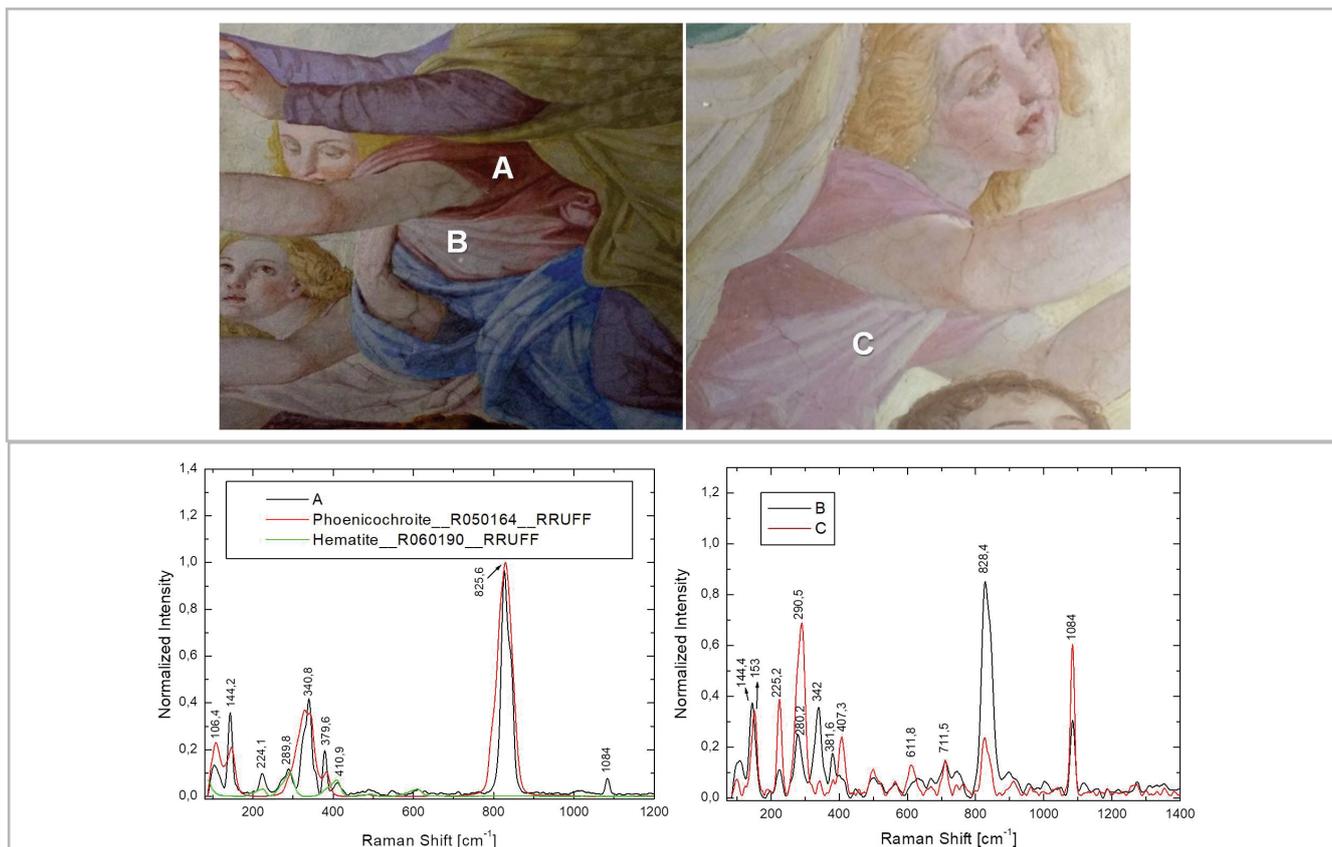
Figure 9.- Raman spectra of red (A) and pink (B and C) points sampled at respective letters. For the spectrum of the red pigment (A), reference spectra of two mineral pigments from the RRUFF database are also reported for comparison. Complete spectral assignment is reported in Table 2
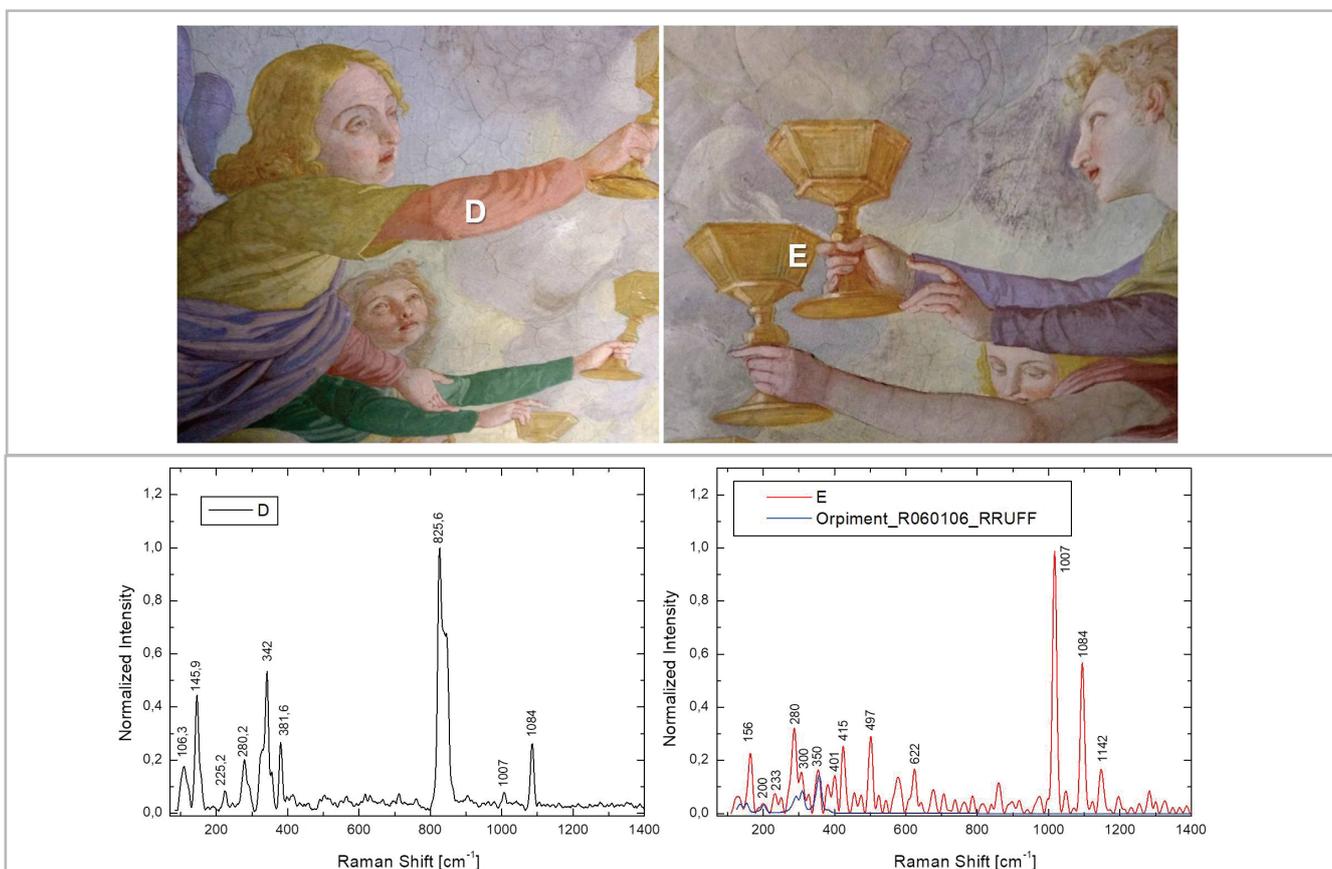

Figure 10.- Raman spectra of orange (point D) and golden yellow (point E). For the golden yellow pigment (E), reference spectra of one mineral pigment from the RRUFF database is also reported for comparison. Complete spectral assignment is reported in Table 2.

However, the beginning of a significant globalization in the XIXth century can be remarked from the use of peculiar South American pigments by the painter.

No dual use of phenicochroite has been reported, on the other hand the chromium presence makes it surely poisoning, as well as the arsenic presence in orpiment.

Conclusions

Innovative laser spectroscopic techniques have been used mostly in situ to characterizes painted CH surfaces. Information on red colors (red ochre, cinnabar, carmine and phoenicochroite) used from the antiquity to the XIXth century was gathered in different case studies, relevant to paintings realized on various substrates with different problems of accessibility. The techniques were applied in a fully non-destructive way, except LIBS which however resulted only micro destructive in the stratigraphy experiments.

By the adopted laser spectroscopies, it was possible to scientifically supported the utilization of the selected red substances with historical dual use in different types of painting. Information on their combination with other chemicals, either in mixtures of in overlapping layers (the latter revealed by LIBS stratigraphy) was achieved.

Provenance studies, based on trace elemental analysis coupled to historical documentation, improved our knowledge of ancient and modern travel routes, as well as the technology progress in painting on different substrates.

Acknowledgements

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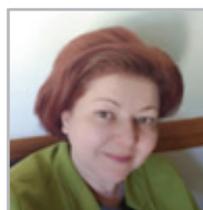Development (ENEA), Frascati, Italy

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