Query Details

Back to Main Page

1. Please check and confirm that the authors and their respective affiliations have been correctly identified and amend if necessary.

Everything was checked and modified accordingly.

2. Please confirm if the author names are presented accurately and in the correct sequence (given name, middle name/initial, family name) [Mariana Calderon Mejia, Dolores Gonzalez Pondal]. Also, kindly confirm the details in the metadata are correct.

Corrected, thanks. Now all the names are presented accurately.

3. References Amigo (2011), Annino (2003), Langdon (2011), Malosetti Costa (2011), Spear (2004), Vazquez (2003) was provided in the reference list; however, this was not mentioned or cited in the manuscript. As a rule, if a citation is present in the text, then it should be present in the list. Please provide the location of where to insert the reference citation in the main body text.

Thanks for pooionting this out,

- Amigo 2011, Malosetti Costa 2011, Annino 2003 and vazquez 2003 were deleted from the references.

- Langond 2011 and Spear 2004 were added in the introduction section.

4. Kindly provide the complete details for reference Langdon (2011) if possible.

Yes, please replace by:

Langdon H (2011) The representation of philosophers in the Art of Salvator Rosa. kunsttexte.de, 1, 12

Non-Destructive Techniques for Cultural Heritage

The role of restoration and scientific examination for the accurate attribution of a European painting in South America

Mariana Calderón Mejía, [1]

Marcos Tascon, [1,2]

Damasia Gallegos, [1]

Dolores Gónzalez Pondal, [1]

Mariana Bini, [1]

Lucia Liccioli, [3]

Serena Barone, [3,4]

Lorenzo Giuntini, [3,5]

Marielena Fedi, [3]

Francesco Taccetti, [3]

Fernando Marte, [1]✉

Email fmarte.iipc@gmail.com

[1] Instituto de Investigaciones Sobre El Patrimonio Cultural (IIPC-Tarea), Universidad Nacional de San Martín, B, Quinquela Martín, 1784, San Martín, Buenos Aires, Argentina

[2] Instituto de Investigación e Ingeniería Ambiental (IIIA-CONICET), Universidad Nacional de San Martín, Buenos Aires, Argentina

[3] Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Firenze, Florence, Italy

[4] Dipartimento di Chimica "Ugo Shiff", Università degli Studi di Firenze, Florence, Italy

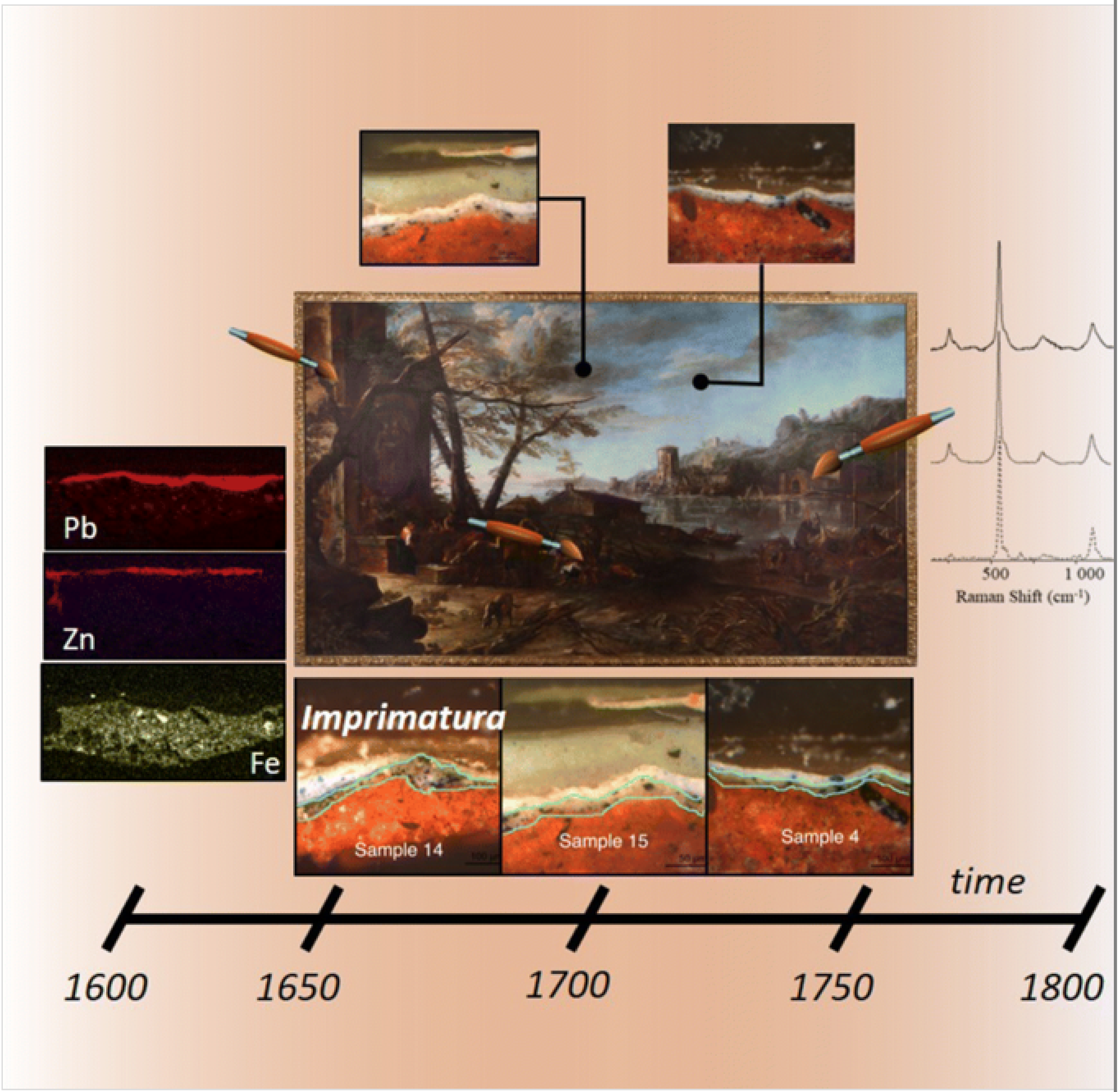
[5] Dipartimento di Fisica e Astronomia, Università degli Studi di Firenze, Florence, Italy

Received: 23 August 2019 / Accepted: 17 April 2020

Abstract

This work presents the interdisciplinary research and intervention of a big format painting attributed to Salvator Rosa. In addition to the challenging nature of the restoration, due to its format and state of conservation, the painting is a good example of the proliferation of art commerce in Argentina by the end of nineteenth and early twentieth centuries. Art collection and art dealing in this particular period has been studied from the historical point of view; however, extensive material investigation on the paintings that arrived in Argentina in this period of time has not been performed yet. When these pieces go from the private sphere to the collections of public institutions, it is important to conduct an in-depth investigation about them, to offer accurate information and to insert cultural heritage pieces into historical and national context. Restoration led to a deeper comprehension of the painting's historical and technical features; the pigment samples analyzed by Raman spectroscopy and polarized light microscopy, together with the contributions of the restoration field, cast a doubt over the Salvator Rosa attribution. However, considering technical aspects like the artisanal grinding of pigments, how the color was applied and the absence of synthetic pigments in the original layers, as well as the relationship between iconography and format, the piece can be identified as a no later than eighteenth century European painting. It is doubtful that the piece was made with intentions of forgery; however, it is more likely that the attribution comes from fraudulent documents and registration when the painting was sold.

Graphical Abstract



Keywords

14C Dating
Conservation
Raman spectroscopy
Restoration
Salvator Rosa
Technical art history

This contribution is a peer-reviewed version of a paper presented at the international meeting of the Non Destructive Techniques on Cultural Heritage (NDT-CH 2018) held October 12, 2018 in Buenos Aires (Argentina).

1. Introduction

In 2017, the Institute of Research in Cultural Heritage (IIPC-Tarea, by its Spanish abbreviation), part of the University of San Martin (UNSAM), was commissioned to restore a large format painting attributed to the Italian baroque painter Salvator Rosa (Fig. 1); the painting was donated by a private owner to the permanent collection of the Museo Castagnino in Rosario, Santa Fe province, Argentina.

Fig. 1

Painting before treatment

AQ1

The intervention faced a number of challenges: the physical dimensions of the painting, the aged and altered previous interventions and the lack of reliable documents about provenance. Aside from treating the painting in its material aspects, the restoration process aimed, along with the historical context of the acquisition, at providing tools to elucidate the painting authenticity.

AQ2

The painting is a 2.52 × 4.60 (meters) oil on canvas. It faced different conservation issues: loss of aesthetic harmony due to several layers of oxidized varnish, local structural deformation, general abrasion in the color layer and several overpaints that caused a chromatic and stylistic discordance in the overall composition.

The motive of the painting, a Marine with a pastoral scene, is not entirely unrelated with Rosa's early paintings (Conisbee 1973). However, the amount of overpainting and previous interventions demanded a cleaning treatment in order to allow for a more extensive visual analysis. In the same way, analytical studies of the materials, from the chemical point of view, were crucial to generate a broader vision and establish an objective start line of the possible origins of the painting.

The first visual analysis of the painting raised doubts over the attribution.

We must consider that large format paintings were costly and required a considerable amount of work. In addition, the intricate motives of Italian painting in the seventeenth century in its complex iconography from biblical, mythological and literary scenes, suggest that a painting of this size was an opportunity for an artist of this period to seek for an unusual motive to distinct his work from other painters (Pigler 1939). This makes it unlikely that a painting of this size, has gone unnoticed in catalogues raisonnés. The lack of documents related to the piece or mentions on reliable bibliography reinforced the doubts of the supposed attribution.

The figure of Salvator Rosa, a notable painter from the Italian *Seicento,* became especially relevant at the end of eighteenth century and the beginning of the nineteenth, when the Romantic movement flourished in all the different artistic forms (Ozzola 1909). Rosa was well appreciated for the intensity and expression of his landscapes, considered quintessentially Romantic by many writers and artists. The appreciation of Rosa's work translated in a high demand of his works during this period.

In his active time, Salvator Rosa (born in Naples in 1615) was known for his particular approach to patronage and for trying to maintain an almost absolute freedom over the subjects in his painting, a very particular attitude for his time (Wallace 1965). At the peak of his career, Salvator Rosa wanted to be remembered as an historical painter (Grigaut 1948), probably the subject with highest esteem among painters and patrons. It is also important to note that the technique in painters of the seventeenth century was governed by the workshop and master-apprentice practices (Spear 2004). Therefore, the technical context of seventeenth century paintings follows certain rules; preparations were usually made in the workshop of each artist (although there may be exceptions) and made of locally sourced raw materials (Martin 2008). The data provided by these sources is a useful precedent to compare with the technical information of the studied painting, to formulate a hypothesis on the period in which it was created (Langdon 2011).

Later, during the mid-nineteenth century, Argentina's economic model was largely based on cattle and meat exports; as a consequence, wealth was accumulated in the region of the Río de la Plata, where the capital Buenos Aires and main grasslands were located. Being an important South American port, Buenos Aires soon became a symbol of modernity and American progress (Sempat Assadourian 2011). In addition, the influx of European migration brought notable changes to the country, both for economic and cultural reasons.

The phenomenon of art consumption also involved art dealers and European producers that saw in Buenos Aires a perfect market to sell all those pieces that did not find great success in Europe; press articles aided to keep art in the public's interest and also motivated the desire for certain pieces as well as rejection for some others. But even when the first art exhibitions in Buenos Aires were unorthodox and far from the well-established galleries in Europe, they were enough to set the basis for a sustained art consumption in the city (Baldasarre 2006).

This way, exhibitions soon professionalized and certain European galleries established links with their counterparts in Buenos Aires. In addition, auctions, which were only made before for properties or cattle, started to gain popularity among the art market (Amigo 1998). The excitement for art consumption in Buenos Aires eventually generated concern regarding the authenticity of the pieces for sale, since many dishonest dealers took advantage of the popularity of art and of the great number of pieces in the market.

In this scenario, Rosa's attributed painting arrived in Argentina, targeting a market avid of European pieces and most probably with only a superficial knowledge of seventeenth century painting. Probably, the lack of knowledge, intimately tied to the market interests back then, may have contributed to reinforce its attribution.

In this context, the aim of this work is to study the painting technique as well as its constituent materials to collect information useful to corroborate—or reject—the possible attribution of this piece of art to Salvator Rosa. For such a purpose, the first instance consisted in the restoration of the piece in order to fully see the painting. Secondly, after the restoration process and having a clear view of the original painting as well as the proper identification of the overpainted area, cross section analyses of the paint along with Raman spectroscopy studies were performed. Then, 14C dating using accelerator mass spectrometry (AMS) was employed to date canvas samples from the painting. In this manner, a holistic interpretation on the attribution of the paint was designed including the results obtained from the restoration, historical and physicochemical fields.

2. Materials and methods

2.1. Sampling and sample preparation

Samples were collected from different areas of the painting. Visual observations led to sampling different areas of interest on the painting. Criteria for sampling focused on those materials whose chemical identity could lead to specific information about period the painting was made. Sampling sites were selected after a meticulous observation with a magnifier (Opti VISOR, Donegan Optical Company, USA) aimed at detecting the most appropriate areas of the paintings, considering minimum invasiveness and representativity. In total, 35 samples were taken with a scalpel blade and stored in individual polyethylene tubes. In Fig. 2 the sampled areas of the painting can be observed. Different color areas were sampled (Fig. 3):

A. Light blue from the sky, both in overpaints and apparent original layers.

B. Green samples from the tree leaves.

C. Earth and dark tones.

D. Deep blue from figures' clothing.

E. The purest yellows present in the composition.

Fig. 2

Detailed picture of a sampled area as a representative sampling condition

Fig. 3

Sampling map of the painting

Once the micro-samples were collected, they were included in an acrylic resin Subiton® (Buenos Aires, Argentina) and polished with a decreasing particle size (until 12,000 mesh) sandpaper for cross-section analysis (Tascon et al. 2016).

2.2. Polarized light microscopy

Optical microscopy observations were performed using a polarizing microscope Leica DM EP to 500 × magnification. The microscope is capable to work on both transmitted and incident light modes. The incident illumination was made with a visible 100 W Tungsten lamp also from Leica. Photographs were recorded using the inbuilt camera system Leica DFC280. Size measurements were carried out by LAS (Leica Application Suite) software, Version 3.8.0 (Build:878) from Leica Microsystems.

2.3. Raman spectroscopy

Raman spectra were recorded on a Lab RAM HR Raman system (Horiba Jobin Yvon), equipped with two monochromator gratings and a charge coupled device detector. The spectral resolution was 1.5 cm^{-1} as a result of a grating of 1800 g/mm and a hole of 100 mm. The spectrograph was coupled to an imaging microscope with a 10 ×, 50 ×, and 100 × magnifications. The He–Ne laser line at 632.82 nm was used as excitation source and was filtered to give a laser fluence or density power at the exit of the objective lens varying from 0.1 to 2 W/mm^2. Several measurements were performed at low powers to ensure that the heating produced by the laser was minimized to avoid the alteration of the sample. Typically, for a 50 × magnification, the spot size diameter was about 2–3 μm. Each spectrum was averaged over five scans with a collection time of 30 s.

2.4. 14C dating by accelerator mass spectrometry

The sample was collected from the back of the canvas using a standardized procedure in the lab for this kind of samples (Fedi et al. 2013; Petrucci et al. 2016). Then, the selected sample was prepared and measured by accelerator mass spectrometry (AMS) at the LABEC Laboratory of INFN-Istituto Nazionale di Fisica Nucleare-CHNet network, at Florence, Italy (Fedi et al. 2007). Before a radiocarbon measurement, linen samples from the canvas were prepared to remove all the possible contamination and isolate the carbon portion intended to be dated. To that purpose, an acid–base–acid (ABA) purification process was applied (Scirè Calabrisotto et al. 2017). Briefly, the process consists in a succession of baths in acidic (HCl 1 M) and basic (NaOH 0.1 M) solutions to eliminate possible contaminations due to carbonates and/or to organics. Then, the purified samples were dried on an oven at 100 °C. Carbon was recovered as gaseous CO_2 by using an elemental analyzer (CHN Thermo Flash 1112), and then converted to graphite, i.e. solid carbon, exploiting the reaction of carbon dioxide with hydrogen (with iron as catalyst). The sample was analyzed and prepared in two separated fractions. 14C concentration from the unknown sample was expressed as pMC (percent of modern carbon) and it was determined correcting the measured 14C/12C isotopic ratios for isotopic fractionation and background. Then, the corrected values were normalized against a set of NIST Oxalic Acid II standards. All the measurements were calibrated using the IntCal13 reference calibration curve and analyzed using OxCal v.4.2.4 (Reimer et al. 2004).

2.5. Scanning electron microscopy (SEM–EDS)

The samples were observed and analyzed using a scanning electron microscope Philips SEM 505 obtaining the photomicrographs, mappings, and corresponding elemental spectra. Samples were metalized with gold.

2.6. Treatment proposal and cleaning

With knowledge of Salvator Rosa's Italian seventeenth century technique and the analysis of other works of his authorship, the need to answer an initial question arose: how many layers of further interventions and overpaint does the painting have and what are their properties? A comprehensive visual analysis of the back and front took place, with different light incidences (natural light, shallow angle, UV-rays).

A solvent gel method of cleaning was chosen, based on the Cremonesi test (Cremonesi and Signorini 2012), due its advantages over other cleaning methods: better penetration control; the possibility of performing the cleaning in gradual stages; better effectivity of the solvent in its gel form, due to increased retention time over the surface; the possibility of being used in a vertical surface, due to the size of the painting and less exposure of restorers to solvent vapors (Dusan and Stulik 2004). For such purpose, different formulae with variations in polarity from 100% non-polar (ligroin) to 10% (acetone and ethyl alcohol) were tested. Table 1 shows the results of the most relevant preparations.

Table 1

List of preparations used in the cleaning tests and the results they provided

Formulae	Polarity[a]	Results
Ligroin 70 Ethyl alcohol 30 Carbopol 2 g Ethomeen 20 ml	78.7 FD	Effective solubilization of top layer varnish
Ligroín 60 Acetone 40	77 FD	Effective solubilization of top layer varnish/blanching of subsequent overpaint layer
Ethyl acetate 50 Methyl-ethyl ketone 50 Klucel (4 g each 100 ml)	52 FD	Effective solubilization of the contemporary overpaint and the subsequent varnish simultaneously
Benzyl alcohol Klucel (4 g each 100 ml)	48 FD	Effective solubilization of the contemporary overpaint and the top layer varnish simultaneously. Better response over oily overpaint

[a]Polarity values are based on Teas triangle of polarities. FD means dispersive strength and it is measured from 0 to 100

Formulae	Polarity[a]	Results
Dimethyl sulfoxide 60 Benzyl alcohol 40 Klucel (4 g each 100 ml)	43.8 FD	No positive outcome in removing oldest overpaint layer
Isooctane 50 Benzyl alcohol 24 Dimethyl sulfoxide 24 Carbopol 2 g Ethomeen 20 ml	68.36 FD	No positive outcome in removing oldest overpaint layer
Cyclohexane 50 Benzyl alcohol 24 Dimethyl sulfoxide 24 Carbopol 2 g Ethomeen 20 ml	68.36 FD	Unsatisfactory formulae for its use

[a]Polarity values are based on Teas triangle of polarities. FD means dispersive strength and it is measured from 0 to 100

Removal of the upper oxidized varnish layer had good results with a mixture of ligroin and ethyl alcohol in a 70/30 proportion. Overpaints were removed in different stages. The most contemporary was effectively solubilized altogether with the varnish of the top layer with a gel based on ethyl acetate and methyl ethyl ketone (MEK) in 50/50 proportion. The second area of overpaint, extended widely, especially over the bottom half of the landscape, was solubilized with benzyl alcohol in Klucel. This gel was also effective for the removal of a hard-oily plastering (Stavroudis and Blank 1989), which was intended to mend tears and gaps. When using benzyl alcohol, residue of the solvent gel was removed with ligroin and benzyl alcohol in a minor proportion (90/10, 92.1FD). In the case of the oldest overpaints, located in large patches over the sky which provoked notorious color mismatch (Fig. 2), the test with solvent gels was not successful. For its removal, a method based on abrasion by air and temperature was used in these particular areas, a technique recommended only in cases where more traditional methods have failed (Dusan and Stulik 2004). Table 2 shows the list of relevant materials used during the whole treatment.

Table 2

List of materials employed during the conservation process, recipes and manufacturers

Material	Activity	Recipe	Manufacturer
Saliva	Initial cleaning tests	–	–
Benzyl alcohol gel	Varnish and overpaint removal	Benzyl alcohol Ethomeen (4 g × 100 ml of water)	BA and ET: Sigma-Aldrich
Methyl-ethyl ketone gel	Varnish and overpaint removal	Ethyl acetate 50 Methyl-ethyl ketone 50 Klucel (4 g each 100 ml)	EA and MEK: Biopack K:
Ligroin/ethyl alcohol gel	Initial cleaning tests	Ligroin 70 Ethanol 30 Carbopol 2 g Ethomeen 20 ml	L, ET: Sigma Aldrich ETOH: Biopack CP:
Dammar varnish (different dilutions based on initial formula)	Final and intermediate coatings	Dammar resin 100 g Turpentine 300 g	DM and TRP:
Rabbit glue	Facing/stucco preparation	100 g of glue in 1 l of water/diluted in half for lining	–
Beva Film 370	As adhesive for strip lining	–	–
Plextol B500	For mending tears and losses	Plextol 50 ml Water 50 ml	
Gamblin colors	For the second phase of reintegration	–	Gamblin conservation Colors
Isopropanol	As solvent for second phase of reintegration	–	J. T. Baker
Pure linen fabric	For strip lining and loose lining	–	–
Watercolor	First face of reintegration	–	Winsor and Newton
Calcium carbonate	Inert filler for stucco	$CaCO_3$	Sigma-Aldrich
Linseed oil	Additive for stucco and plaster		–

Material	Activity	Recipe	Manufacturer
Japanese paper	Facing tissue	–	–

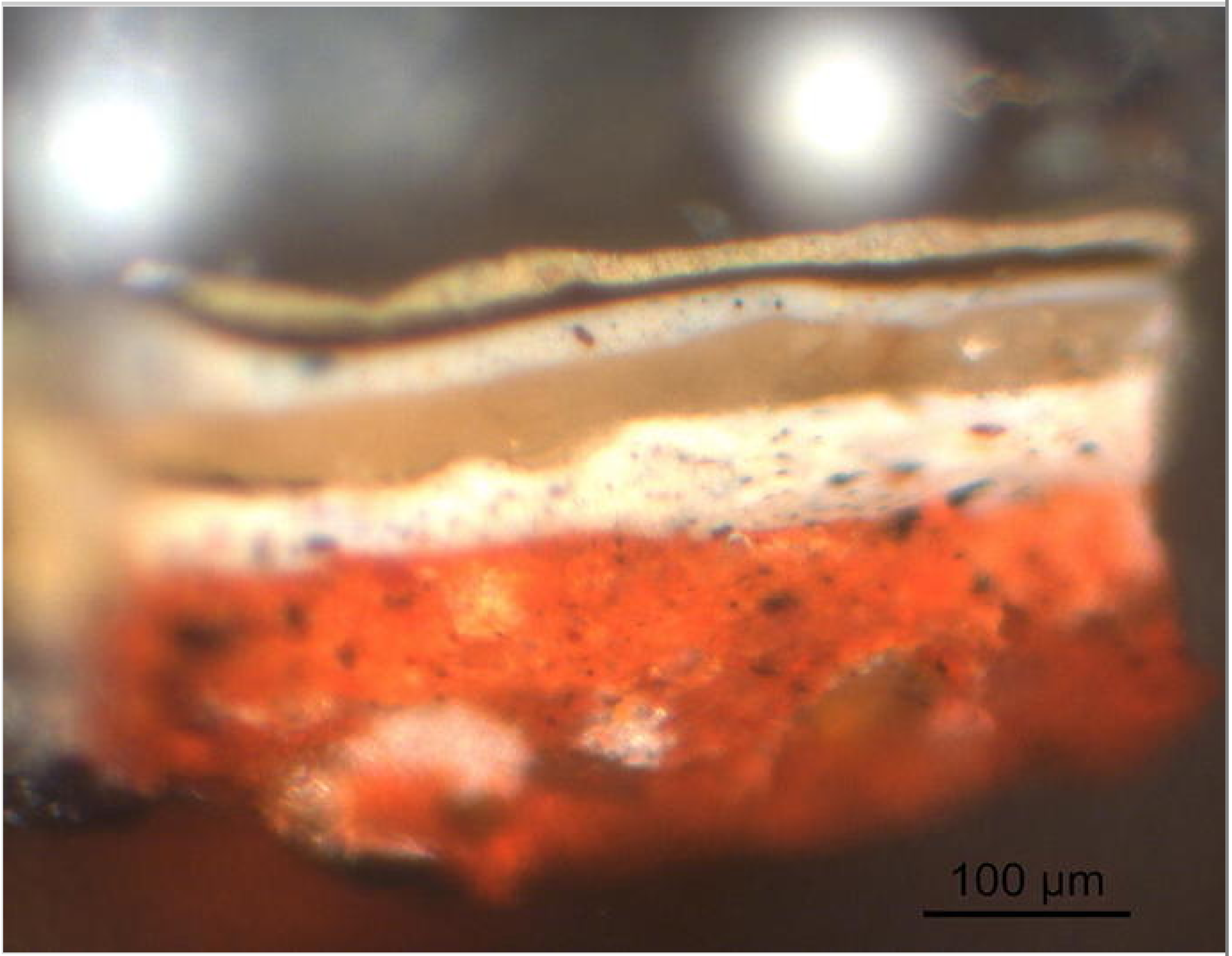
3. Results and discussions

3.1. Technical art history

Although many of the overpaint layers were visible to the trained eye, there were also further overpainted areas under the visible layers. The cross-section analysis accounted the quantity and depth of the layers; polarized and UV light analysis made possible an effective discrimination of every layer added to the original pictorial surface. Actually, it was found that some layers were made with the intention to amend abrasions or flaking, but many others were simply a free reinterpretation, which drastically modified the previous composition. Cross section analysis reinforced this interpretation; the amount of interventions can be seen in the sky-blue stratigraphy (Fig. 4).

Fig. 4

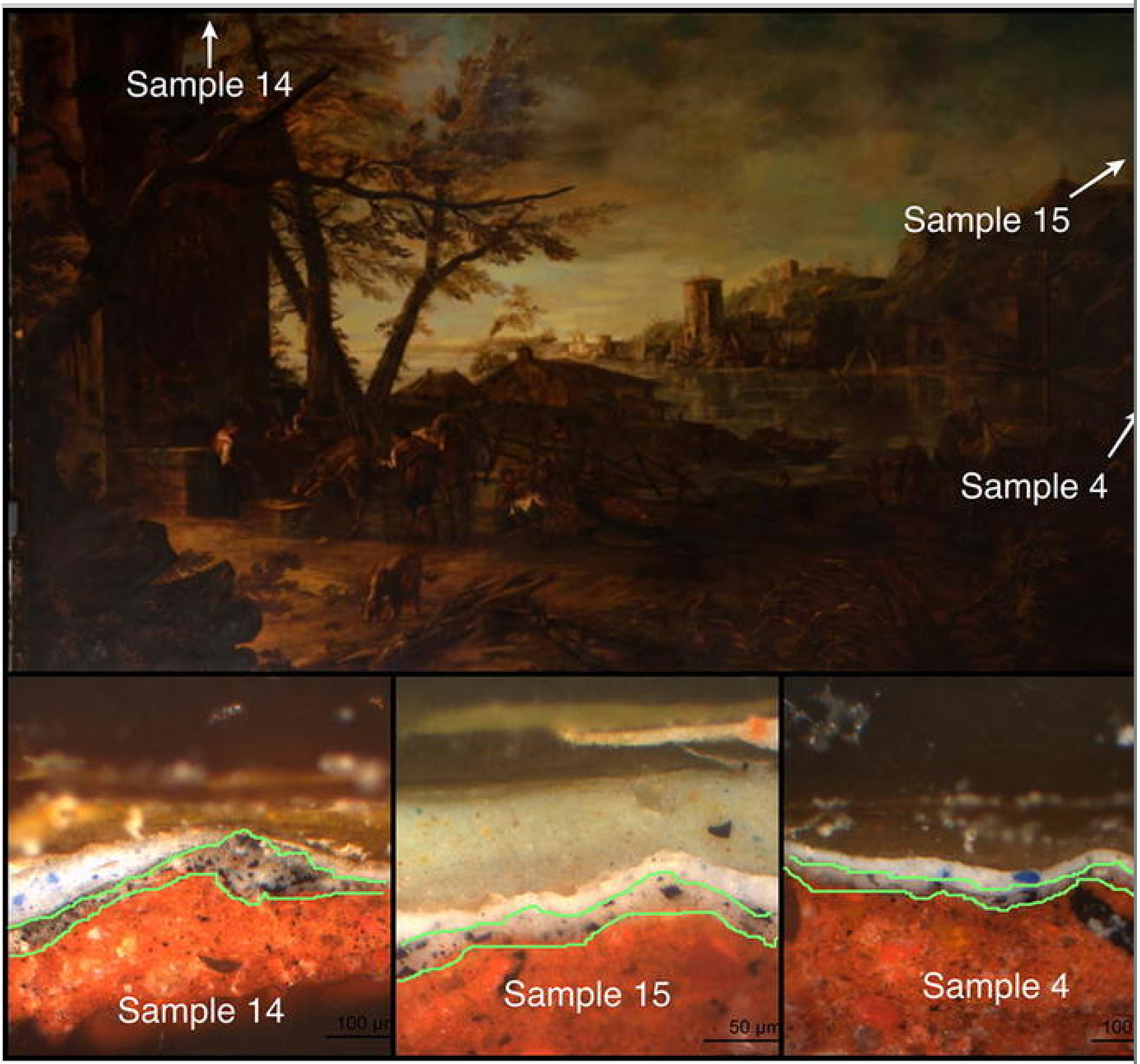
Stratigraphy of the blue sky showing the amount of interventions the painting has been through



Cross section analysis confirmed the presence of a dark earthy ground base. The ground, as well as the rest of the original layers, has large and uneven pigment particles, a common trademark of manual grinding. Reddish earth brown for the ground and the presence of localized light-colored *imprimatura* (Fig. 5) are in agreement with a technique common to different Italian painters from the seventeenth century like Caravaggio (Keith 1998), Correggio or Carracci (Keith 2008). However, this technique is not exclusive of the *Seicento;* it can be actually found also in the technique of Italian painters from the eighteenth century like Giovanni Battista Tiepolo or Bernardo Bellotto (Payne and Villis 2004).

Fig. 5

Stratigraphic localization of the grayish *imprimatura* in the brightest areas of the painting (indicated as dotted lines)



Having in mind the contrast of the pigment particles' size and shape between the overpaint and original layers, it was found that the size of particles in original layers corresponds to an artisanal manual grinding; the size of particles in overpainted areas corresponds to modern oil painting of industrial manufacture; in some areas of the painting there are at least two layers of varnish between overpaints. It was also found that the low mixture between color particles on the same layer corresponds to techniques from seventeenth and eighteenth century, where pigments were applied almost pure, with different levels of dispersion, depending on the chromatic intention of the painter (Joyce 1956). The discovery of artisan grinding posed a series of more specific questions about the pigments used in the painting, to get closer to the historic origin of the piece.

3.2. Scientific analyses

Raman spectroscopy analysis of the ground layers evidences the presence of hematite as the main component, as shown in Fig. 6a), where the spectrum of the sample and of the standard of hematite (de Faria et al. 1997; Edwards et al. 2000) are shown. The use of this material is compatible with the expected seventeenth and eighteenth European century paintings (Hurlbut and Cornelis 1977). Moreover, in the ground layer, black charcoal particles were also found. Figure 6b shows the spectrum of the black particles where the characteristic broad bands of carbon at 1350 cm^{-1} and 1601 cm^{-1} (Lofrumento et al. 2011) can be easily observed. These bands are known as the graphitic band (1601 cm^{-1}) and the disorder band (1350 cm^{-1}), assigned to crystalline graphite and to structural disorder in the graphitic structure, respectively. One of the challenging aspects of this work is the characterization of blue paints, due to the large number of overpaints with different blue pigments. For such purpose, the first approach consisted in the overpaint identification by an exhaustive visual examination along with observation under UV light. The main sampling of blue color was made on the sky as well as on the deep blue in the character's clothing samples. The Raman analysis performed on the clothing's sample (Fig. 7) showed the characteristic bands of Prussian blue at 278, 533, 2094 and 2155 cm^{-1} (Chaplin et al. 2004). Noteworthy, this pigment was synthesized for the first time in 1704 and, its use in a work of art, was originally mentioned as Prussian blue in an anonymous paper in Latin in 1710 (Fitzhugh 2012). However, all the samples containing Prussian blue were characterized as overpaints, thus, the relevance of this pigment as a time marker for this specific work is not determinant. On the other side, there are two instances where lazurite appears in the sky-blue samples: a-in the original layers and b-in the sky overpaint. As can be seen in Fig. 8, the Raman spectra of both compounds are similar, showing bands at 258, 548, 580, 806 and 1094 cm^{-1} associated to lazurite. Also, from these spectra, it can be remarked that none of them seems to be natural lapis lazuli because, as previously reported by Osticioli et al. (2009), there is no evidence of calcite ($CaCO_3$) nor wollastonite ($CaSiO_3$) in the mineral pigments. These two markers, which are absent in purified lazurite, are commonly found in lapis lazuli minerals found in Chile and Afghanistan. However, it is possible to differentiate the nature of the original stratum from the overpaint by the size and shape of the particles. While the synthetic paint is characterized by very small, uniformly-sized pigment particles (Fig. 8a); original lazurite found in the original layers has relatively big particle size and heterogeneous shape, indicating a manual grinding (Fig. 8b) (Plesters 1966; Osticioli et al. 2009).

Fig. 6

Raman spectra of **a** sample containing hematite and standard of hematite and **b** Raman spectrum from a stratum containing carbon

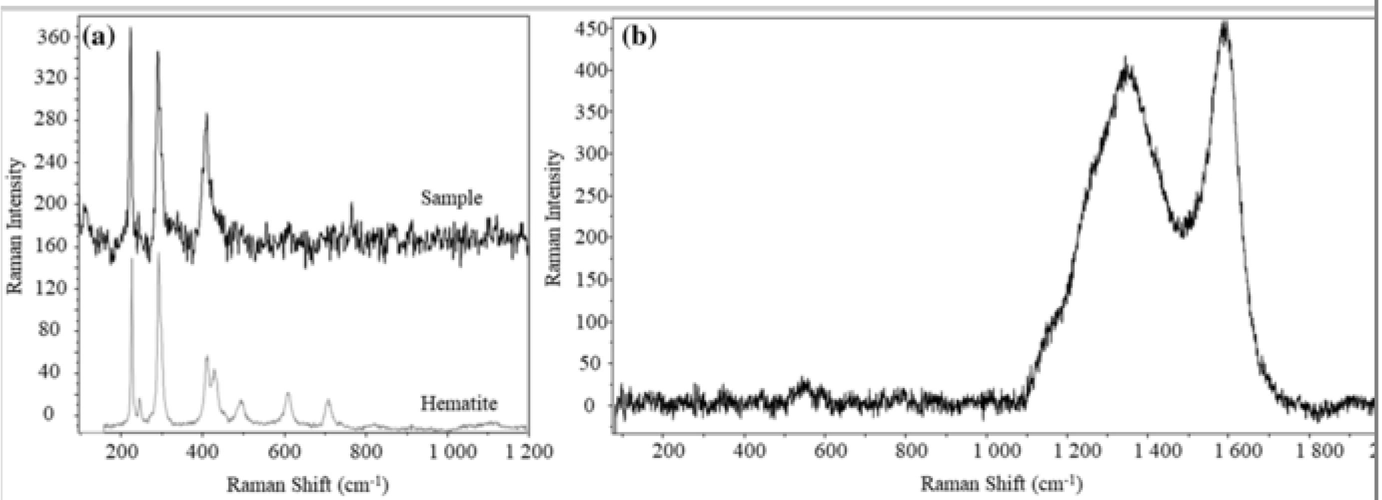


Fig. 7

Stratigraphy from a sample taken from the clothing. Raman spectrum of the blue layer as well as the spectrum of a Prussian blue standard

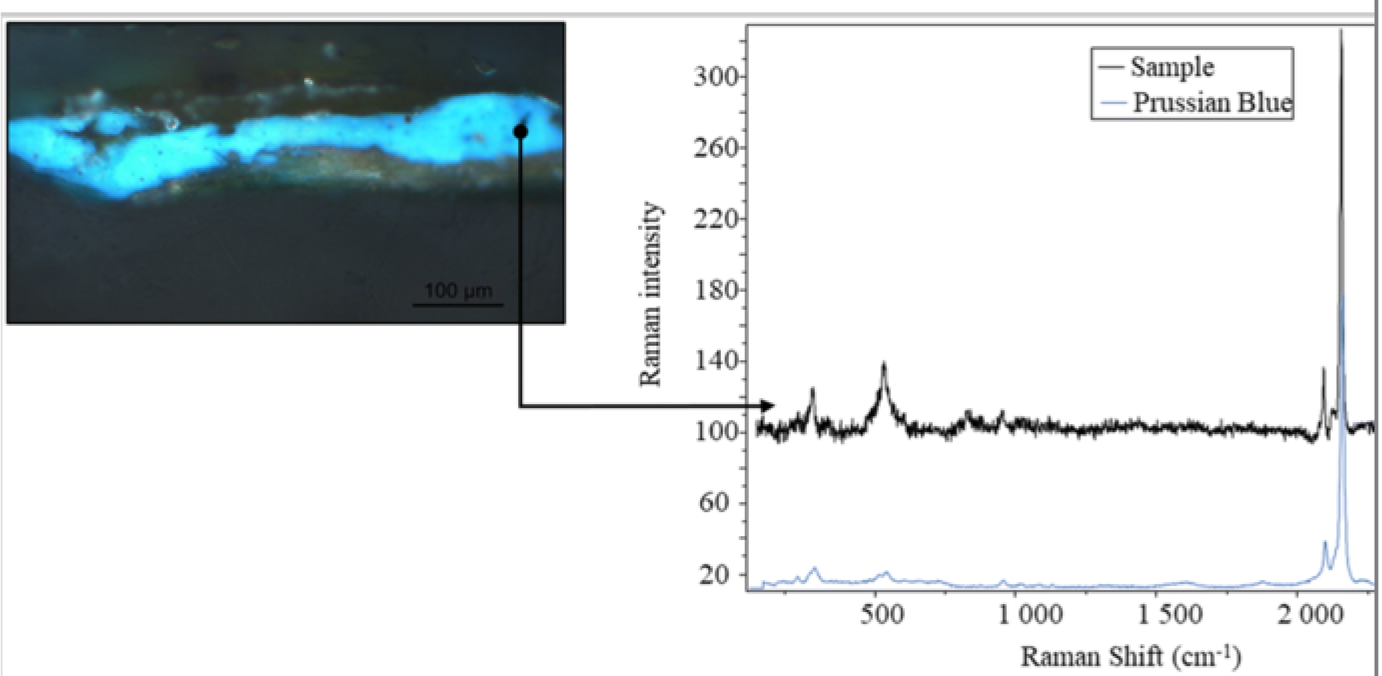
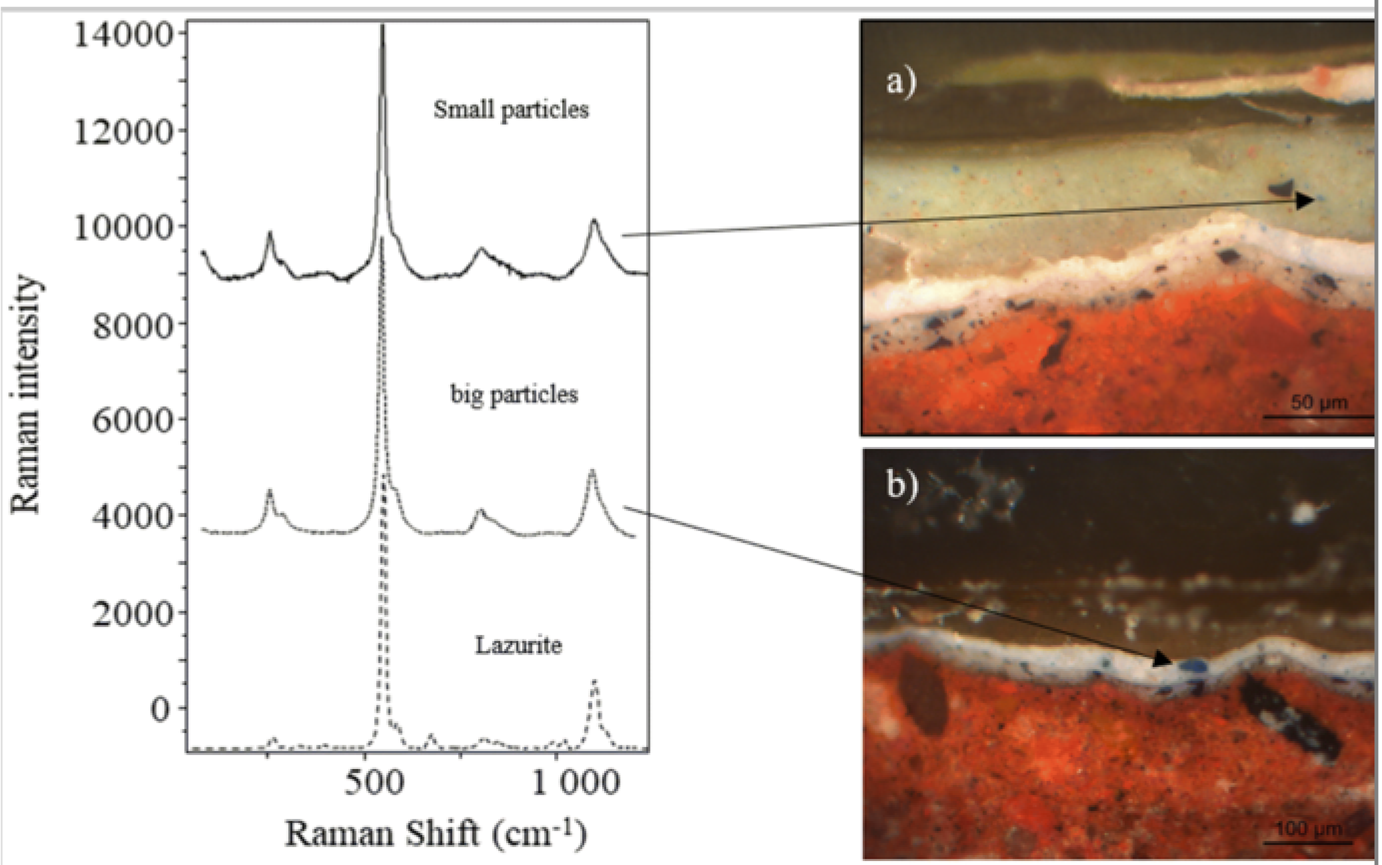


Fig. 8

Chemical composition of blue pigment from **a** layer containing small blue particles and **b** a layer containing big blue particles



It is well known that the scarcity and cost of natural lapis lazuli made it a material even more costly than gold (Barnett et al. 2006). The presence of natural ultramarine would point out that the piece was commissioned by someone with enough economical resources to use good quality materials. However, the depth of the color is faint, indicating the presence of a filler along with ultramarine particles or that the pigment has been mixed with something else. The cross section from Fig. 9 shows the typical stratum of lazurite dispersed in a white media. In fact, spectrum a shows the presence of lazurite while the SEM-EDAX mapping for lead demonstrates the presence of this element in the same stratum. Also, Raman analysis of lazurite original strata from different samples evidenced the presence of lead white as the main pigment giving the characteristic band at 1048 cm^{-1} (Burgio and Clark 2001). The preparation of this mixtures between lazurite and lead white was a common practice in seventeenth and eighteenth century techniques in order to produce different visual effects; the presence of lead white and more affordable kinds of blue, like azurite, are often common, even in those compositions where ultramarine blue is deeper (Plesters 1966). Due to its scarcity and cost, saturated ultramarine blue was always applied as a final glaze, to exploit its chromatic richness to the maximum. There are no areas in this painting where ultramarine blue is saturated. This reinforces the hypothesis that the piece might have been made in a time before both the nineteenth century and the creation and extensive use of synthetic ultramarine blue. In addition, in Fig. 9b a preparation layer of hematite is distinguished in the Raman spectrum as well as the identification of iron in the SEM-EDAX mapping. The use of a red preparation layer based on hematite was a common practice in this period. Noteworthy, in Fig. 9 spectrum c was identified as a modern overpaint, whose Raman spectrum gives the bands at 237, 257, 596, 680, 748, 951, 1145, 1341, 1451 and 1527 cm^{-1} attributed to blue phthalo PB15; a copper phthalocyanine blue synthetic pigment. This idea is reinforced by SEM-EDAX mappings where, as can be seen in Fig. 9, the overpaint exhibits high concentration of zinc, most likely as zinc white (ZnO). Finally, the presence of sodium in the SEM-EDAX mapping from Fig. 9 can be attributed to some additive of the painting. As Fig. 10 shows, analysis of yellow samples gave enough pieces of information to identify the pigment as an iron oxide yellow based on goethite, or ochre yellow, a color used since antiquity. The characteristic bands of goethite at 299, 388, 480, 550 and 695 cm^{-1} are in agreement with the standard database (Fig. 10) as well as with the reported literature (de Faria et al. 1997; Bikiaris et al. 1999; Edwards et al. 2000). The absence of synthetic yellow and the use of the color without any kind of mix with other colors, supports the hypothesis of a painting made when pigments were used almost pure, with the exception of lead white (Plesters 1956), and before the extended use of synthetic pigments, roughly before the nineteenth century. Finally, the dating of canvas gave a 14C concentration of 98.67 ± 0.48 pMC, corresponding to a conventional radiocarbon age of 110 ± 40 years Before Present. When we calibrate this measured radiocarbon age, we obtain a date which is compatible with a modern sample: the canvas is indeed dated to the period 1675–1940, at 95% level of confidence. Thus, considering that Salvator Rosa died in 1673, the present result suggests that it is not so likely that he used this canvas to paint. However, it is important to highlight that the results are not conclusive due to the radiocarbon calibration curve’s shape between the 1600s and the present.

Fig. 9

Sample representative of the original blue pictorial layer’s construction. Raman spectra of the pigment (**a**), preparation layer (**b**) and overpaint (**c**) and, SEM-EDAX micrograph (**d**) with elemental mappings of iron (Fe), lead (Pb), zinc (Zn) and sodium (Na)

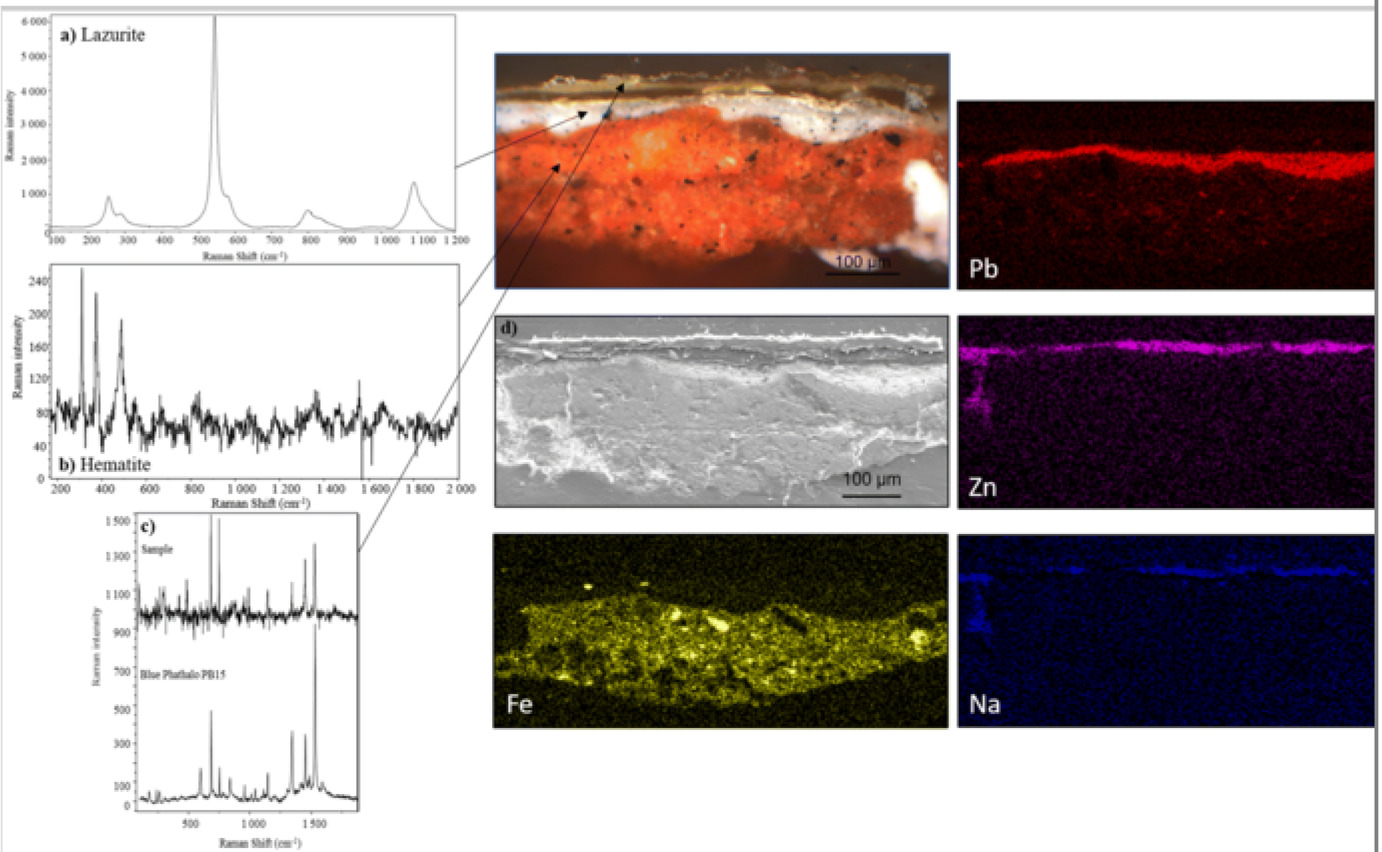
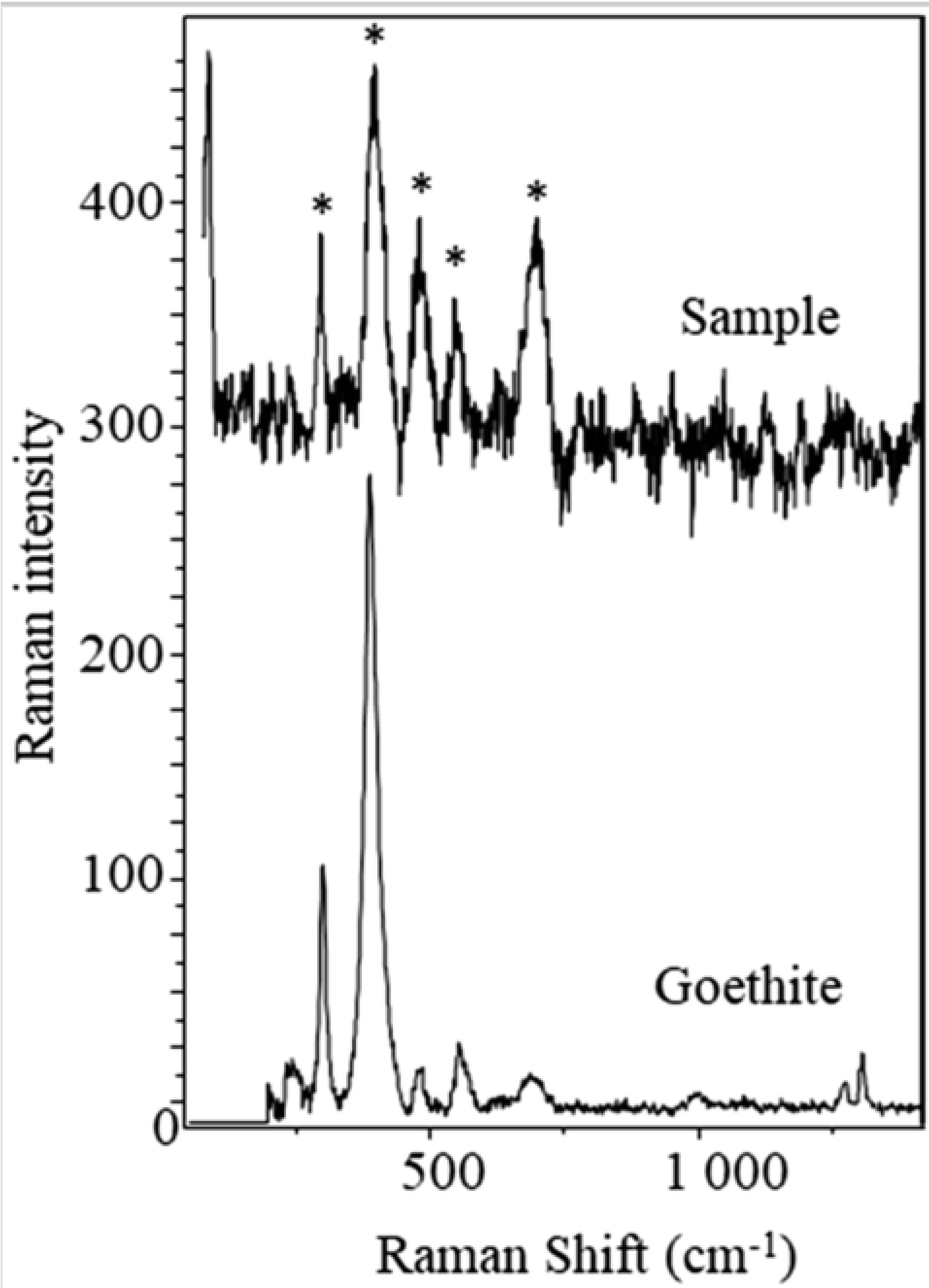


Fig. 10

Averaged Raman spectrum of different yellow pigment particles and a standard sample of goethite



3.3. Restoration results

The initial visual analysis pointed out that due to its format and the good condition of the fabric, it was more likely that the painting was made later than seventeenth century (a result confirmed by 14C AMS measurements). It is well known that large format old paintings usually have seams or joints to unite several pieces of fabric. In addition, the homogeneity of the fibers in the fabric also pointed out to a later piece, possibly from the eighteenth century. The palette and technique elucidation through stratigraphic samples did not contradict this hypothesis. The particle size of the original layers observed under microscope showed artisanal manual grinding. In fact, some pigments and the way they were applied, along with the subject and format, would also place the painting in a time after the Italian *Seicento*.

Once the oxidized varnish and overpaints were removed, the painting partly recovered its chromatic balance and the spatial representation. Nevertheless, the increase of the refractive index of oil painting over the years, made the color palette more translucent. This factor, combined with the dark red ground, contributed to a general dimness on the image, that made it loose its initial nuances. Both dark preparation layer and the increase in refractive index would be signs of a relatively ancient painting. Dark grounds were a common practice in the seventeenth century. However, calcium sulfate was not detected in the analyzed samples, an element with a rather extensive and well documented use in Italian grounds of the Seicento (Roy 1998). Figure 11 shows the painting after the treatment.

Fig. 11

The painting after restoration treatments

4. Conclusion

The multidisciplinary study of the large format painting attributed to Salvator Rosa made restorers and scientists of the IIPC-TAREA reach the conclusion that the piece is, in relation to its size and palette, coherent with the features of an eighteenth century European painting, with no clear signs of the piece being a forgery. This makes it possible that the documents in the acquisition transactions were manipulated to favor a more lucrative sale. This practice could be considered common in the middle of the effervescence of art collection in the early twentieth century region of the Río de la Plata, Argentina. It should also be emphasized that Rosa was a painter with great influence and was very much appreciated years after his death. Therefore, it cannot be ruled out that the painting could have been made by a school or authors close in time and in geography to its initial attribution.

Aging, conservation conditions and repeated treatments that the painting endured over time, could have also contributed to the loss of subtle glazes and brushstrokes that can dramatically influence the stylistic analysis of the piece, something which could easily lead to a wrong judgment of authorship.

Nevertheless, although the attribution to Salvator Rosa and its seventeenth century dating was questioned, the material analyses of the oldest pictorial layer placed the painting in a period before the nineteenth century. 14C dating studies pointed to a modern origin of the canvas. However, chemical and historical analysis does not endeavor to simply discredit an attribution. It is important to foment deeper reflection on the degrees of authenticity of cultural heritage pieces, without disengaging their historical and physical context. All the same time, we conclude that the uncertainties surrounding the piece could only be answered through the extensive interdisciplinary work that involves both restoration practice and analytical studies, which, together with historical accounts, have allowed a correct attribution of this work of art.

AQ3

Publisher's Note

Acknowledgements

We would like to thank the valuable collaboration of Néstor Barrio, Laura Malosetti, Mariana Bini and Noemí Mastrangelo with this project. Also, the group of authors is grateful to all the students and interns of UNSAM that worked in the restoration of this piece.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Amigo R (1998) El resplandor de la cultura del bazar. Razón Revol 1(3):57–64

~~Amigo R (2011) Imágenes sitiadas. Tradiciones visuales y política en el Río de la Plata. ERA 1:1830–1870~~

~~Annino A (2003) Pueblos, liberalismo y nación en México. Inven. la Nación Iberoamérica Siglo 21:399–430~~

Baldasarre MI (2006) Los dueños del arte: coleccionismo y consumo cultural en Buenos Aires. Edhasa, Buenos Aires

Barnett JR, Miller S, Pearce E (2006) Colour and art: a brief history of pigments. Opt Laser Technol 38:445–453. https://doi.org/10.1016/j.optlastec.2005.06.005

Bikiaris D, Daniilia S, Sotiropoulou S et al (1999) Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies : application on wall paintings at Meteora and Mount Athos, Greece. Spectrochim Acta Part A 56:3–18

Burgio L, Clark RJH (2001) Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. Spectrochim Acta Part A Mol Biomol Spectrosc 57:1491–1521. https://doi.org/10.1016/S1386-1425(00)00495-9

Chaplin TD, Jurado-Opez A, Clark RJH, Beech DR (2004) Identification by Raman microscopy of pigments on early postage stamps: distinction between original 1847 and 1858–1862, forged and reproduction postage stamps of Mauritius. J Raman Spectrosc 35:600–604. https://doi.org/10.1002/jrs.1208

Conisbee P (1973) Salvator Rosa and Claude-Joseph Vernet. Burlingt Mag 115(849):789–794

Cremonesi P, Signorini E (2012) Un approccio alla pulitura dei dipinti mobili. In: Rimozione parziale o totale di materiali filmogeni, Il pratto. Padua, pp 169–212

de Faria DLA, Silva Venancio S, de Oliveira MT (1997) Raman microspectroscopy of some iron oxides and oxyhydroxides. J Raman Spectrosc 28:873–878

Dusan V, Stulik D (2004) Solvent gels for the cleaning of works of art. The Getty, Los Angeles

Edwards HGM, Newton EM, Russ J (2000) Raman spectroscopic analysis of pigments and substrata in prehistoric rock art. J Mol Struct 550:245–256

Fedi ME, Cartocci M, Taccetti F, Mando PA (2007) The 14C AMS facility at LABEC, Florence. Nucl Instrum Methods Phys B 259:18–22

Fedi ME, Caforio L, Mandò PA et al (2013) May 14C be used to date contemporary art? Nucl Instrum Methods Phys Res Sect B Beam Interact Mater Atoms 294:662–665. https://doi.org/10.1016/j.nimb.2012.08.053

Fitzhugh EW (2012) Artists' pigments, vol 3. National G, Washington, DC

Grigaut P (1948) The Finding of Moses by Salvator Rosa. Bull Detroit Inst Arts City Detroit 27:63–67

Hurlbut CS, Cornelis K (1977) Manual of mineralogy. Wiley, New York

Joyce P (1956) Cross-sections and chemical analysis of paint samples. Stud Conserv 2:110–157. https://doi.org/10.2307/1505000

Keith L (1998) Three paintings by Caravaggio. Natl Gallery Tech Bull 19:12

Keith L (2008) Annibale Carracci's Montalto Madonna. Lond Natl Gallery Tech Bull 29:46–59

Langdon H (2011) The representation of philosophers in the Art of Salvator Rosa. kunsttexte.de, 1, 12

AQ4

Lofrumento C, Ricci M, Bachechi L et al (2011) The first spectroscopic analysis of Ethiopian prehistoric rock painting. J Raman Spectrosc. https://doi.org/10.1002/jrs.3096

~~Malosetti Costa L (2011) Los primeros modernos: arte y sociedad en Buenos Aires a fines del siglo XIX. Fondo de C, Buenos Aires~~

Martin E (2008) Grounds on canvas 1600–1640 in various European artistic centres. Preparation for painting: the artist's choice and its consequences. Archetype, London

Osticioli I, Mendes NFC, Nevin A et al (2009) Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. Spectrochim Acta Part A Mol Biomol Spectrosc 73:525–531. https://doi.org/10.1016/j.saa.2008.11.028

Ozzola L (1909) Works of Salvator Rosa in England. Burlingt Mag 81:146–150

Payne J, Villis C (2004) Finding light in the shadows, the cleaning and restoration of Tiepolo's The Banquet of Cleopatra'. Art Bull Vic 43:21–31

Petrucci F, Caforio L, Fedi M et al (2016) Radiocarbon dating of twentieth century works of art. Appl Phys A Mater Sci Process 122:3–6. https://doi.org/10.1007/s00339-016-0501-1

Pigler A (1939) The importance of iconographical exactitude. Art Bull 21(3):228–237

Plesters J (1956) Cross-sections and chemical analysis of paint samples. Stud Conserv 2(3):110–157

Plesters J (1966) Ultramarine blue, natural and artificial. Stud Conserv 2:62–75. https://doi.org/10.2307/1505446

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JWBC, Blackwell PG, Buck CE, Burr GS, Cutler KB, Damon PEER, Fairbanks RG, Friedrich M, Guilderson TP, Hogg AGHK et al (2004) Intcal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal Bp. Radiocarbon 46:1111–1150. https://doi.org/10.2458/azu_js_rc.46.4183

Roy A (1998) Painting techniques, history, materials, and studio practice. In: IIC Dublin congress

Scirè Calabrisotto C, Amadio M, Fedi ME et al (2017) Strategies for sampling difficult archaeological contexts and improving the quality of radiocarbon data: the case of Erimi Laonin Tou Porakou, Cyprus. Radiocarbon 59:1919–1930. https://doi.org/10.1017/RDC.2017.92

Sempat Assadourian C (2011) La economía del Río de la Plata durante el siglo XIX. Anuario de, Buenos Aires

Spear R (2004) Claude and the economics of landscape painting in Seicento Rome. Konsthistorisk Tidskr 73:147–157

Stavroudis C, Blank S (1989) Solvents and sensibility. WAAC Newsl 11(2):2–10

Tascon M, Mastrangelo N, Gheco L et al (2016) Micro-spectroscopic analysis of pigments and carbonization layers on prehispanic rock art at the Oyola’s caves, Argentina, using a stratigraphic approach. Microchem J 129:297–304. https://doi.org/10.1016/j.microc.2016.07.003

~~Vázquez JZ (2003) Una difícil inserción en el concierto de las naciones. Iberoamérica siglo XIX, Buenos Aires~~

Wallace RW (1965) The genius of Salvator Rosa. Art Bull 47:471–480. https://doi.org/10.1080/00043079.1965.10790783