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"Hearts of gold" (Cuori d'oro): The case study of the leather *corami* of Palazzo Chigi in Ariccia ☆

Monia Vadrucci[a], Massimo Chiari[b], Anna Mazzinghi[b,*], Alessandro Rufoloni[c], Cristina Cicero[d]

[a] *Particle Accelerator for Medical Application Laboratory, ENEA Frascati R.C., Frascati (RM), Italy Italian Space Agency (ASI), Science and Research Directorate, Rome, RM, Italy*
[b] *University of Florence, Dept. Physics and Astronomy, Via G. Sansone 1, 50019 Sesto Fiorentino (FI) and National Institute of Nuclear Physics, Florence Division Via G. Sansone 1, 50019 Sesto Fiorentino, FI, Italy*
[c] *Superconductivity Laboratory, ENEA Frascati R.C., Frascati, RM, Italy*
[d] *Department of Literary, Philosophical and Art History Studies, University of Rome "Tor Vergata", Rome, RM, Italy*

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ABSTRACT

In this work we present the results obtained by different technical analysis in order to perform the characterization of the chromatic richness, the employed materials and the iconographic elements of different fragments of decorated and gilded leather *corami* coming from the archive of *Palazzo Chigi* of Ariccia (Rome) and employed, during the 17th century, as wallcoverings. Different microscopic and spectroscopic analyses have been performed by means of Ion Beam Analysis (IBA) and Macro Area X-Ray Fluorescence (MA-XRF) techniques available at the INFN LABEC ion beam laboratory in Florence and the Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDX) of the Superconductivity Laboratory of the ENEA Frascati Research Center. The results aim to provide the scholar information about the manufacturing process and the materials employed for the production of these peculiar artefacts, also in order to plan the best and most appropriate conservation protocol. In particular, thanks to the SEM-EDX analysis it has been possible to characterize the layered structure of the samples and, specifically, the interface between the leather of the substrate, the metal foil of the so called *meccatura* and between these and the overlying pictorial layer. The IBA and MA-XRF techniques has helped in characterizing the painting palette employed while IBA has allowed to determine the conservation condition of the silver layer with the hypothesis of the incorporation of the silver leaf into the organic compound of the *mecca* as its main deterioration phenomena. These complementary techniques provide, therefore, a comprehensive understanding of the materials and iconographic elements of these leather-based artefacts, which is essential for their preservation and restoration as well as they contribute to a better understanding of the deterioration processes they incur.

1. Introduction

The use of leather artefacts has been extremely diffuse since the start of the history of the mankind. The capability to convert a raw material into a non-rotting and resistant one by means of tanning process led to a frequent employ of leather for different furniture and artwork such as clothes, books and others [1]. After being mechanically flayed from the animal, the skin is dried by means of sodium chloride (NaCl) in order to preserve the skin by dehydration until the next step of manufacture (the curing). To proceed in the manufacturing process, the raw skin needs to be rehydrated by repeated washing with cold water. The subsequent step, called the soaking, consists in a bath in a caustic solution of calcium hydroxide $Ca(OH)_2$ (slaked lime) during which the chemical reaction of saponification takes place. During this step, of about two weeks in duration, all the non collagenous materials such as hair and the lipids are removed making easier the next step, the scraping, during which epidermal and hypodermal structures are mechanically removed by a crescent-shaped blade [2]. After being

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* Corresponding author.
E-mail address: anna.mazzinghi@unifi.it (A. Mazzinghi).

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immersed for some days in a bath of clean water to adjust the pH of the skin, the product is ready for tanning. Until the 19th century, when chrome tanned leather started to be produced, the tanning process was carried out through the use of vegetable tannins extracted from different plants, like mimosa, oak, or chestnut tree, able to react, through the phenolic molecules in these, with the collagen within the skin. The skin was immersed for a month in different baths with increasing concentrations of tannins and then washed and dried [3].

A very particular use of this material regards the art of the gilded leather intended for the creation of wall coverings and other furniture starting in Spain after the Arab conquest of the 8th century and the construction of the Caliphate of Cordoba (929–1031), from which the name of *cordovani* originated [4]. The first attempts seem to start in the city of Ghadames, a Libyan oasis, known for the production of a valuable kind of alum-tawed skin, from which can be traced back the traditional name of this kind of artefacts, *guadamacies*. Other sources traced this term to the fusion of the words *gueld* (leather) and *masir* (to decorate). Both hypotheses lead back to the post-conquest Spanish-Arab world, where this art had its origins or, in any case, spread to Europe [5]. Since the 14th century, the leather of *guadamacies* was replaced by a vegetable tanned one for its capability to be better punched and its lower cost. It was probably during the 16th century that the use of metallic leaf started to be employed in the decoration of these artefacts when the art of leather gildings was yet extremely diffuse in the Netherlands. Here starts to be employed, from the 17th century, the use of wood matrix to impress the leather decoration for the production of the so-called *embossed leather* [4]. In the same years the production is diffused in all Europe such as, for example, in Venice where these artefacts are known as *cuoridoro* (from "cuoi" and "oro", gilded leather) [6]. From the 18th century, this kind of decorated objects starts to be abandoned to be replaced by fabric and then paper [7]. For the production of this particular type of artefact was frequently used the *morocco* leather or the *cordovan* one: the moroccan leather was usually produced with goatskins tanned with sumac, while Cordovan was tanned with oak bark rather than gall. The latter was particularly suitable for receiving gilding and was more convenient than the former [6]. At this point, the leather was prepared to receive the metal leaf. It was generally employed a silver leaf (cheaper than the golden one), glued to the leather with starch [6] or parchment glue [7], burnished and then covered with egg white to be protected against oxidation. By woodcut printing or printing with a matrix under the press, the design of the decoration, typically floral and arabesque motifs, was being transferred onto the silver leaf and then a golden paint was applied to make the silver leaf look like gold. This method is called "*meccatura*" from the application of "*mecca*", an oil-resinous mixture with natural pigments (like saffron) in imitation of gold. Leaving the silver leaf free from the *mecca* paint, it was possible to have at the same time some silvered and some gilded areas [6,7]. The impressed and silvered leather was then painted, mainly with lacquers with oil binder and then impressed with decorative punches [7]. Once prepared, the leather was squared and sewn together, or glued during the second half of the 15th century [4], to form the wall covering.

In the present research, the *corami* of *Palazzo Chigi* in Ariccia (Rome, Italy) have been investigated. In this palace, delivered by Agostino Chigi to the municipality of Ariccia in 1988, it is still possible to appreciate a unique use of the gilded leather wall covering in many rooms of the palace, expression of the opulence and artistic taste of the family itself. *Palazzo Chigi* preserves also an exceptional archive of fragments from which the samples analysed for this work come, and some of the wooden and metal matrix employed for the impression of the decorative motifs. The building, bought by the Chigi Family from Giulio Savelli in 1661, was completely renewed in the subsequent years on the basis of a project attributable to Giovan Lorenzo Bernini. Some of the rooms were still covered by gilded leather, while, with the purchase by the Chigi and the expansion of the palace, the use of leather coverings was implemented also with the employ of panels from buildings in Rome belonging to the family [4,5]. In these rooms, it is possible to identify different styles of decorations from renaissance tradition, Venetian style or Dutch embossed ones, traceable to Roman baroque style and manufacture [4,8].

Few years ago, in the frame of the ADAMO project financed by the *Regione Lazio* for the Technological District of Cultural Heritage (DTC Lazio), a series of investigations had been carried out on leather fragments coming from the archive of *Palazzo Chigi*. In particular, this research reported on the materials and methods employed in the production of the leather coverings of *Palazzo Chigi* [9] and the presence of eventual microorganism capable of causing biodeterioration and developing a method to perform disinfection treatment based on the use of X-ray irradiation [10].

In this work, we present some further technical investigations on different fragments of these decorated *corami* from the archive of *Palazzo Chigi* in order to analyse the materials of these artefacts as well as their peculiar manufacturing techniques. Different microscopic and spectroscopic analyses were performed by means of the Ion Beam Analysis (IBA) and Macro Area X-Ray Fluorescence (MA-XRF) techniques available at the INFN LABEC ion beam laboratory in Florence [11] and the Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDX) of the ENEA Frascati Research Centre (Superconductivity Laboratory).

More in general, as every collagen-based product like parchment or alum tawed skin, ancient and historical leather can incur in many deterioration phenomena of chemico-physical and biological nature [12-16], it is necessary to deeply understand the preservation state of the artefact itself in order to stop the progression of the deterioration with, for example, specific restoration treatments [17]. In the last few years, different methods and analytical techniques have been applied in order to describe and understand the mechanism of deterioration of leather [18-21], also in the case of decorated and gilded artefacts [9,22,23].

In this particular case, from the analysis of these fragments it was thus possible to characterise also the peculiar deterioration processes that incur in these artefacts due to their multi-layered nature and, in particular, in the interface between leather and metal foil and between these and the overlying pictorial layer.

2. Research aim

This study aims to add information for scholars on material and structural characteristics of the leather wallcovers (*corami*). More specifically in this study fragments from the archive of *Palazzo Chigi* in Ariccia (Rome) have been analysed following a multianalytical approach in order to extensively investigate the materials of these artefacts as well as their peculiar and poorly studied manufacturing techniques. The SEM-EDX analysis has helped in the surface characterization of the samples, in checking the presence of silver and its distribution and in evaluating the preservation condition of the decoration layer. MA-XRF analysis allowed the identification of the main elements of the samples, providing their distribution over the scanned area as elemental maps. Elemental distribution maps give information also on the production technique of the gilded leathers and insight on later interventions (i.e. pictorial retouchings). IBA was also employed for quantitative analysis of main and trace elements in the near-surface region of the samples exploiting the Particle Induced X-Ray Emission (PIXE) technique, while Elastic Backscattering Spectrometry (EBS) was used for the study of the stratigraphy of the decorative layers, especially where metal foils are present.

3. Materials and methods

3.1. Gilded and painted leather samples from Palazzo Chigi

The gilded and painted leather samples analysed in this work come from the archive of fragments available in *Palazzo Chigi*. The samples seem to differ for manufacturing process and technique employed, but they are all considered as subjected to "*meccatura*". As mentioned in the introduction section, the process of *meccatura* regards the application of a special varnish to convert the colour of a metal leaf, for example silver, in order to make it look like gold. This technique was employed since the Middle Ages not only to decorate gilded leather, but also for a variety of different artworks: fabrics, brocades, polychrome statues etc. [24,25]. It is clear that there are multiple recipes to produce the yellow varnish of the "*mecca*" and they depend on the historical period, the geographical location and the availability of the raw material. The *mecca* varnish was mainly composed of resins, dyes and, sometimes, a plasticizer. Until the 16th century sandarac was the resin employed and its use in Italy is documented until the 19th century when it was generally replaced by shellac. Among the dyes, turmeric, saffron, blood tarragon, gamboge, aloe etc. were generally used, while beeswax and more recently carnauba were used as a plasticizer [26].

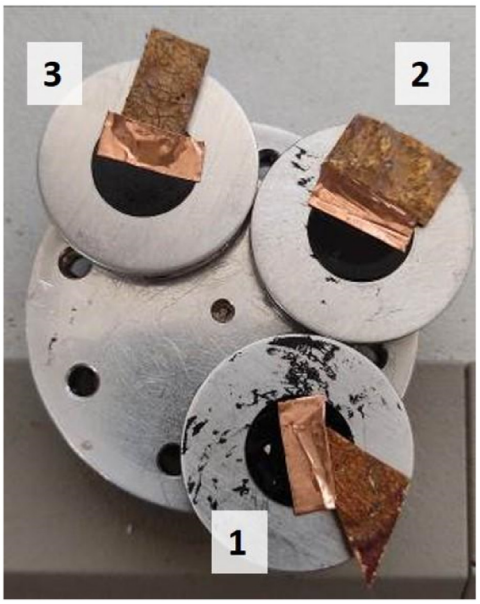

Fig. 1. The three samples investigated by SEM-EDX analysis.

3.2. Analytical methods

3.2.1. SEM-EDX analysis

In this work the microstructural analysis was carried out using a Leo 1525 field-emission SEM equipped with Oxford X-act 10 mm^2 Silicon Drift Detector (SDD) for energy dispersive spectroscopy. EDS signals were handled by AZtec ver. 3.2 HF1 software. To avoid distorted images or artefacts, a thin (of about 10 nanometers) conductive coating of carbon has been sputtered on the samples.

The analyses involved 3 different fragments from the gilded leather that has been investigated, probably coming from artworks with different techniques of manufacturing. All the samples present areas with gildings apparently produced by *meccatura* (Fig. 1).

3.2.2. IBA

IBA techniques, such as PIXE and EBS, can provide information on the elemental composition and distribution of materials in the artefact at a high spatial resolution, which can be used to identify the sources of the materials and their potential degradation. These techniques are particularly useful for identifying trace elements that may not be detectable with other techniques. IBA techniques are typically performed simultaneously, following the so-called "Total-IBA" [27] or "Global-IBA" [28] approach: when employed together, these analytical methods allow a comprehensive characterization of the elemental composition and depth distribution of the analysed material. The fact that IBA can be performed in external beam mode, with the ion beam extracted into ambient pressure from the in-vacuum beamline of the accelerator, makes them truly not invasive and not-deliberately destructive [29].

IBA measurements were performed at the external beamline dedicated to cultural heritage applications of the 3 MV Tandetron accelerator of INFN LABEC laboratory in Florence [11]. The set-up at the end of the beamline includes, among the others, two X-ray detectors for PIXE technique: one is a 10 mm^2 Ketek SDD with He flow for light and major elements analysis, and the other is a 150 mm^2 Ketek SDD, with a 425 μm thick Mylar absorber for heavy and trace elements; and one particle detector for EBS technique, an Hamamatsu Si pin diode 10 × 10 mm^2 active area, placed at 135° scattering angle and mounted in an aluminium case, kept at 10^{-1}

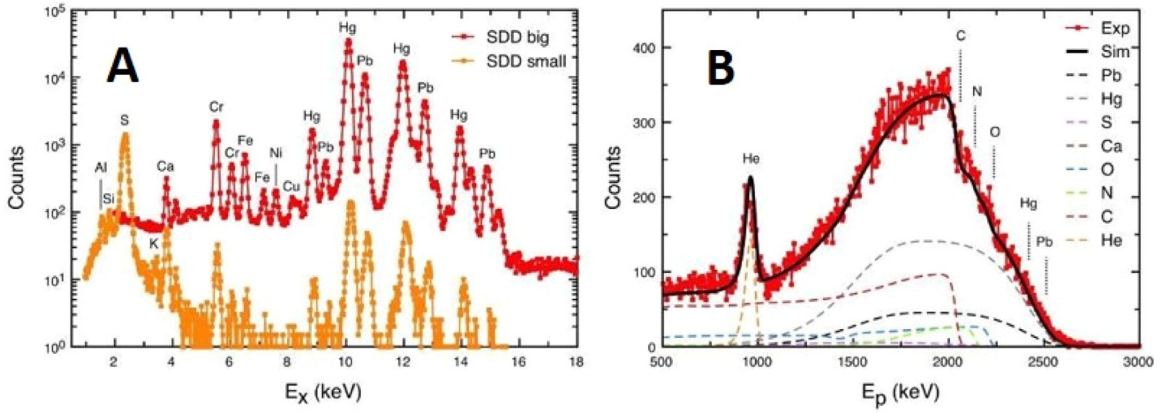

Fig. 2. (A) PIXE spectra collected with the two SDDs of a red pigment in the leather fragment 3, obtained with 3 MeV protons. (B) corresponding EBS spectrum together with the SIMNRA simulation. The contribution of the different elements to the simulation is also shown. He is not present in the sample itself, but it is a "parasitic" element, common to EBS spectra when measurements are performed in an external beam set-up under helium flowing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

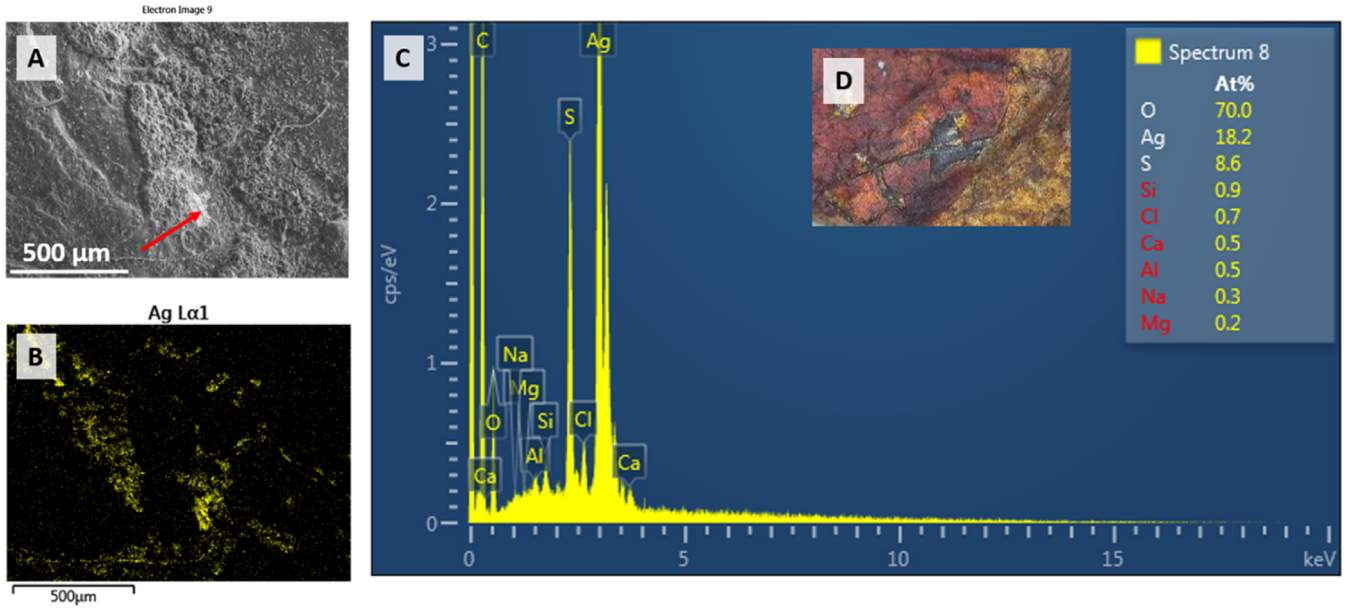

Fig. 3. Sample 1 micrograph (A) and map of the surface distribution of Ag (B) on the corresponding area, EDX spectrum of the exposed underlying silver leaf (C) indicated by the arrow in A where it is detectable the presence of sulphur (S) due to typical deterioration process of sulphuration of silver. Optical images of a different area of the same sample where it is possible to see the blackened exposed silver leaf (D).

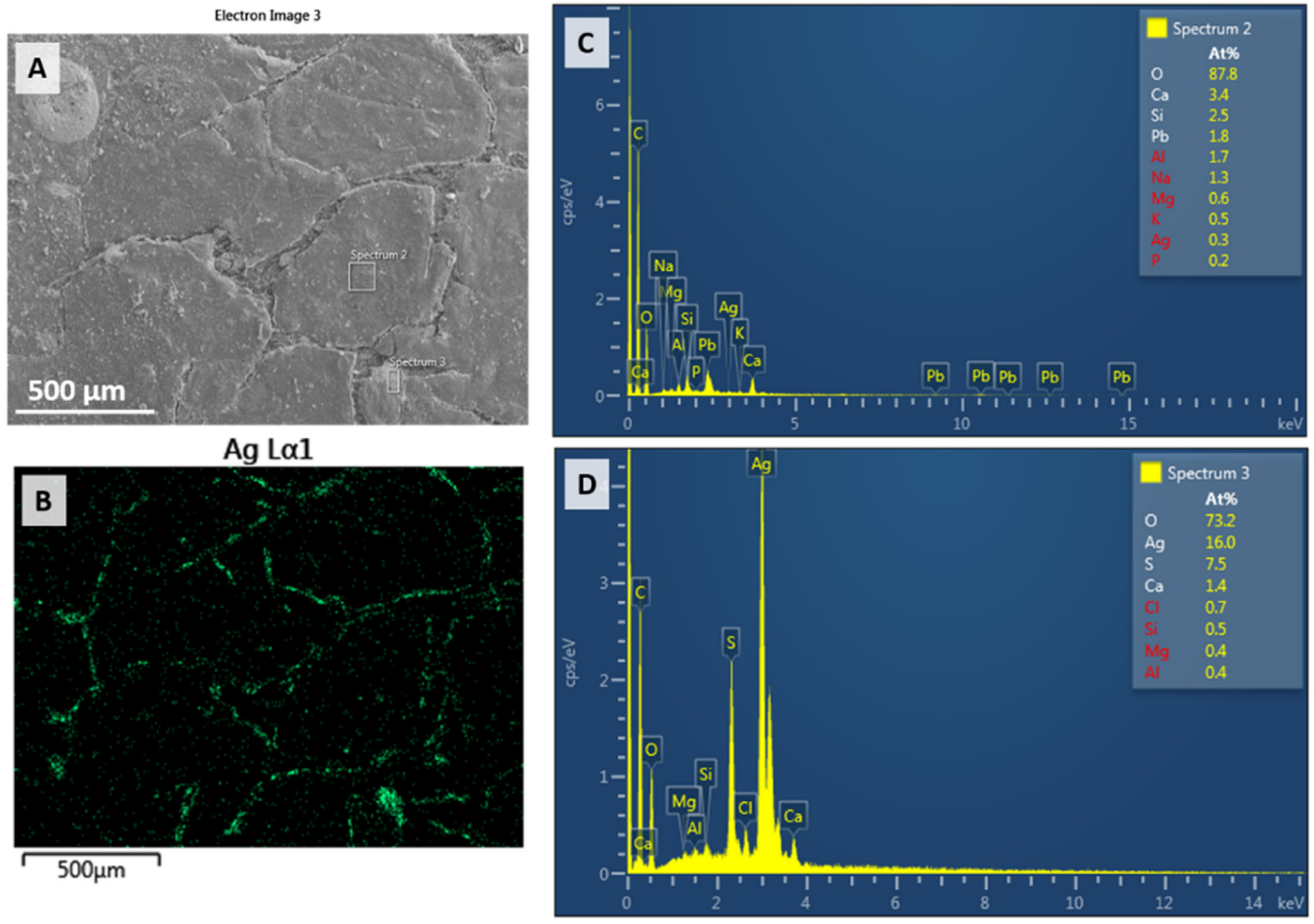

Fig. 4. Sample 2 micrograph (A) and map of the surface distribution of Ag (B) on the corresponding area. EDX spectrum of the area treated with *mecca* (C) and of the exposed underlying silver leaf (D) where it is detectable the presence of sulphur (S) due to typical deterioration process of sulphuration of silver.

mbar pressure. Measurements were carried out using a 3.0 MeV proton beam, 0.5 mm in diameter, extracted into ambient pressure through a 200 nm thick Si_3N_4 window, using a beam current ranging roughly from 100 to 500 pA (chosen to keep dead time and pile up corrections negligible), and lasted 150 or 300 s. Quantitative results were then obtained by accurate charge-equivalent normalisation measuring the weak extracted beam currents using a rotating chopper [30]. Quantitative IBA results based on the analysis of PIXE spectra were carried out using the GupixWin software [31], whereas the analysis of the EBS spectra was achieved using the SIMNRA simulation code [32], implementing evaluated cross sections for proton elastic scattering on He [33], C [34], N [35], O [36], S and Ca [37], whereas for the higher Z elements (Ag, Hg, Pb) a pure Rutherford cross section was considered. An example of PIXE and EBS spectra is shown Fig. 2.

3.2.3. MA-XRF

X-ray fluorescence (XRF) is a non-destructive and non-invasive analytical method that provides information on the elemental composition of an analysed material while MA-XRF, in particular, allows the analysis of a scanned area, providing distribution elemental maps. Though with the limit of being an elemental technique, in this study, MA-XRF has been useful for the characterisation of the pigments and metal foils employed in the decorations of the leather artefacts and also on their production techniques.

The INFN–CHNet instrument, thoroughly described in [38], is a light highly transportable device designed for in-situ heritage science applications. Briefly, the measuring head has a Moxtek X-Ray tube (40 kV maximum voltage, 0.1 mA maximum anode current) and an Amptek XR100 SDD (25 mm^2 effective active surface, 500 µm thickness). A telemeter (Keyence IA-100) is also installed for the continuous control and adjustment of the sample-instrument distance during measurements. The measuring head is installed on three linear motor stages by Physik Instrumente, 200 mm travel range in the x and y directions for this version, plus a 50 mm stage along the z perpendicular direction. The instrument has been successfully employed in several heritage science applications during the years [39-41]. The operating conditions of the X-ray tube for all measurements discussed here were: 38 kV anode voltage, 35 µA filament current, Mo anode with an 800 µm diameter collimator. Scanning velocity ranged from 2 to 5 mm/s and the equivalent-pixel size 1 mm. These X-ray tube settings correspond to the highest values compatible with a count rate which would not overload the electronics associated to the detector.

4. Results and discussion

4.1. SEM-EDX analysis of the sample surface

Three different samples coming from the archive of *Palazzo Chigi* have been investigated by SEM-EDX analysis in order to obtain information on the surface composition of the silver leaf treated by *mecca*. All the samples, in fact, present a gilded surface in poor conservation conditions. At the sample optical inspection, the gilded surface presents detachments and craquelure consisting of typical defects of these kinds of artefacts. The surface micrograph shows for all the samples the presence of Ag and, interesting enough, by mapping the presence of the element on the surface it is possible to notice the evidence of the silver coming from the cracks on the sample surface and not as a general distribution on the entire area. As it is possible to notice for instance in Fig. 3 for the sample 1 and Fig 4 for sample 2, the presence of

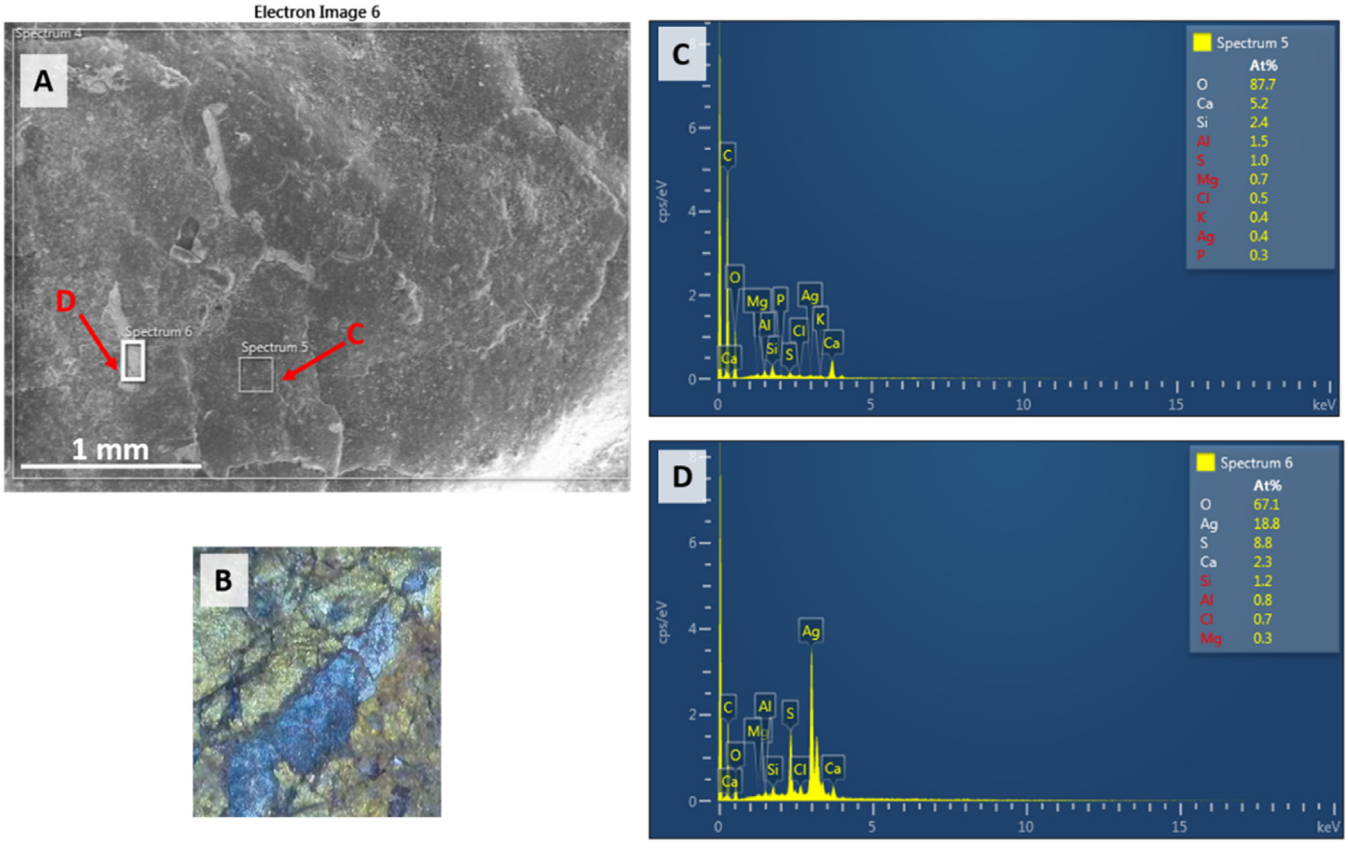

Fig. 5. Sample 3 micrograph (A) and optical images of a different area of the same sample where it is possible to see the blackened exposed silver leaf (B). EDX spectrum of the area treated with *mecca* (C) and of the exposed underlying silver leaf (D) where it is detectable the presence of sulphur (S) due to typical deterioration process of sulphuration of silver.

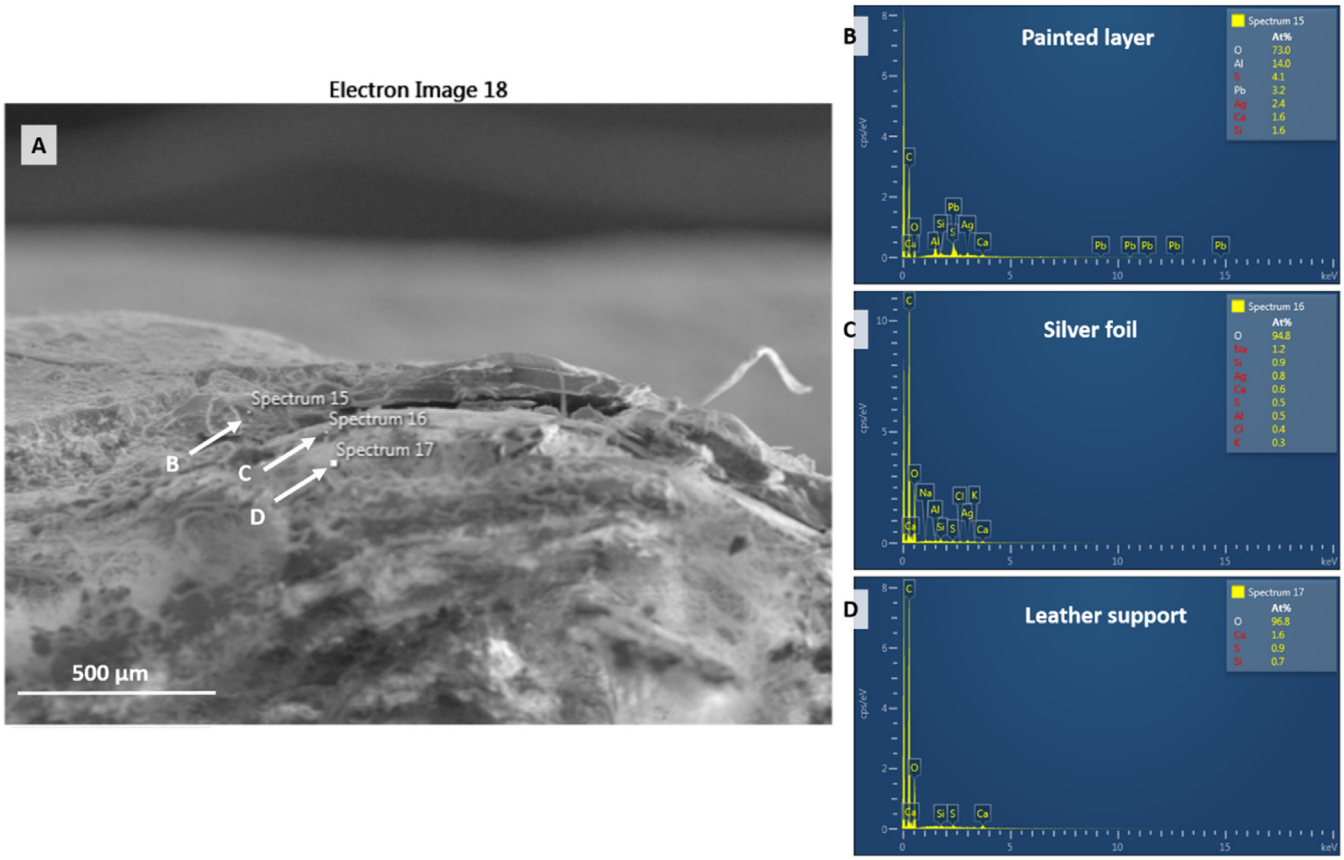

Fig. 6. Sample 1 micrograph of the sample cross section (A), EDX spectrum of the area pictorial layer (B), of the underlying silver leaf (C) and of the leather support (D).

silver becomes detectable only where the cracks expose the underlying layer of the foil. In all the analysed samples, the presence of silver is accompanied with the presence of sulphur (S) (Fig. 3C, 4D and 5D). As a matter of fact, the presence of this kind of element is strictly related to the preservation state of the exposed silver leaf. This is due to the typical process of sulfuration occurring when silver reacts with atmospheric hydrogen sulfide (H_2S), normally present as a pollutant in anthropic environments [42]. After the silver and hydrogen sulphide react, a black and dense layer of silver sulphide (Ag_2S) forms on the surface and the silver leaf begins to acquire a blackened colour [43]. As it is possible to see in the optical images obtained on different areas of the same samples (Fig. 3D and Fig. 5B), is not uncommon to find darker areas with exposed silver leaf in an advanced state of sulphuration.

The EDX analysis confirms the presence of organic compounds, as attested by the presence of C and O. Also, the other low-Z elements, such as Si, Cl, Al, Ma, Mg are common in the composition of such compounds (Fig. 4C and Fig. 5C).

With the help of the EDX spectra obtained analysing the cross section of the sample 1 reported in Fig. 6A it is possible, moreover, to explain the presence of the different elements resulting as a diffused pattern in the EDX maps and not directly attributable to a specific layer of these multilayered artefacts.

The presence of some elements such as Pb (Fig. 6B) can be, for example, ascribed to the presence of specific pigments (such as the red minium) or to the use of lead white as preparatory layer for the pictorial one. In both the cases, the diffused presence of these elements in the EDX maps can be easily explained. In some cases (as for sample 2 where no traces of pictorial layer can be found on the surface), it is also possible to hypothesize its employ as a preparatory layer for the silver foil [44,45].

Regarding the elements present in the EDX spectra of the silver foil layer (Fig. 6C), such as Si and Al, it is instead possible to hypothesize the use of a bole as a preparatory layer to apply the metallic foil. More specifically, for example, the use of the white bolus (*bolus alba*), an aluminum silicate frequently employed in gildings [46,47].

More in general, some kind of elements are frequently found analysing skin-based products and can be easily ascribed to the manufacturing process of these substrates. As mentioned in the introduction section regarding the manufacturing process of leather, the diffuse distribution of some elements such as Na, Mg, or K, can be related for example to the preliminary step of conservation of the flayed skin with salt. Similarly, the presence of Ca is generally due to the treatment with slaked lime (calcium hydroxide) during the calcination step of the manufacturing, necessary to help in removing hairs before the tanning.

4.2. Analysis of silver leaf and meccatura (IBA and XRF)

The presence of characteristic X-rays of Ag detected with XRF confirms the use of silver foils in the decorative system of these leathers. Heterogeneities in the MA-XRF elemental maps are due to self-absorption effects in the pictorial layers (see Figs. 8 and 10). It is otherwise confirmed that no Au was detected in these samples, neither in golden coloured areas nor in others. Fe is detected in these same areas and is possibly related to the tanning process of the leather (see Figs. 8 and 10).

IBA measurements revealed Ag in most of the points analysed on the front of the leather fragments. Those points where Ag was not detected correspond to paint layers thicker than or close to the probed depth, so the 3 MeV proton beam did not reach the Ag containing layer at all or did it, but retaining minimal residual energy

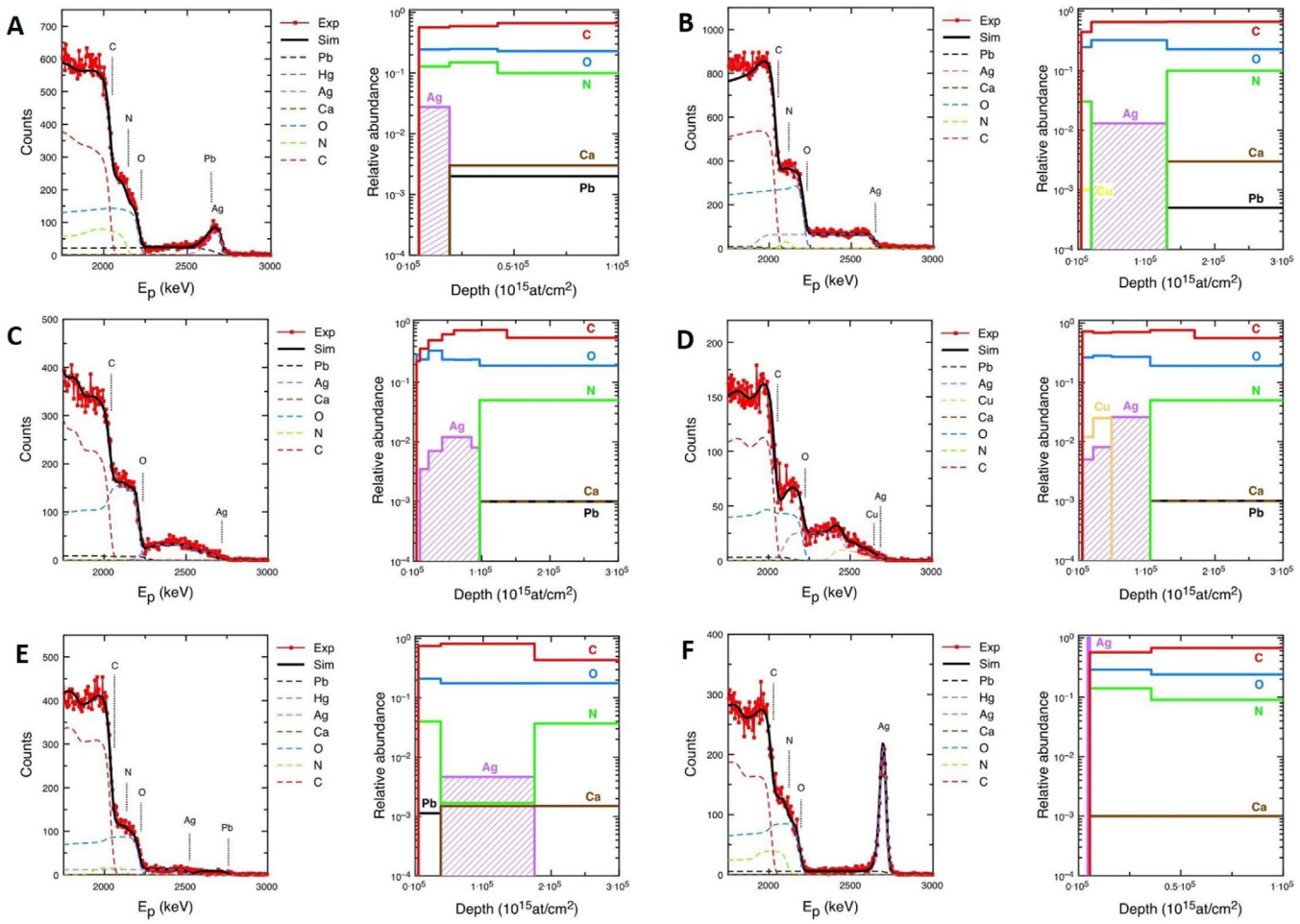

Fig. 7. Detail of EBS spectra together with SIMNRA simulations (the contribution of different elements to the simulation is also shown) and resulting elemental depth profile, with the Ag depth profile highlighted. The spectra were obtained with 3 MeV protons on different samples: (A) silver leaf, leather fragment 1; (B) golden point, leather fragment 1; (C) golden background, leather fragment 2; (D) dark green pigment, leather fragment 2; (E) golden point, leather fragment 3; (F) exposed silver vein, leather fragment 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

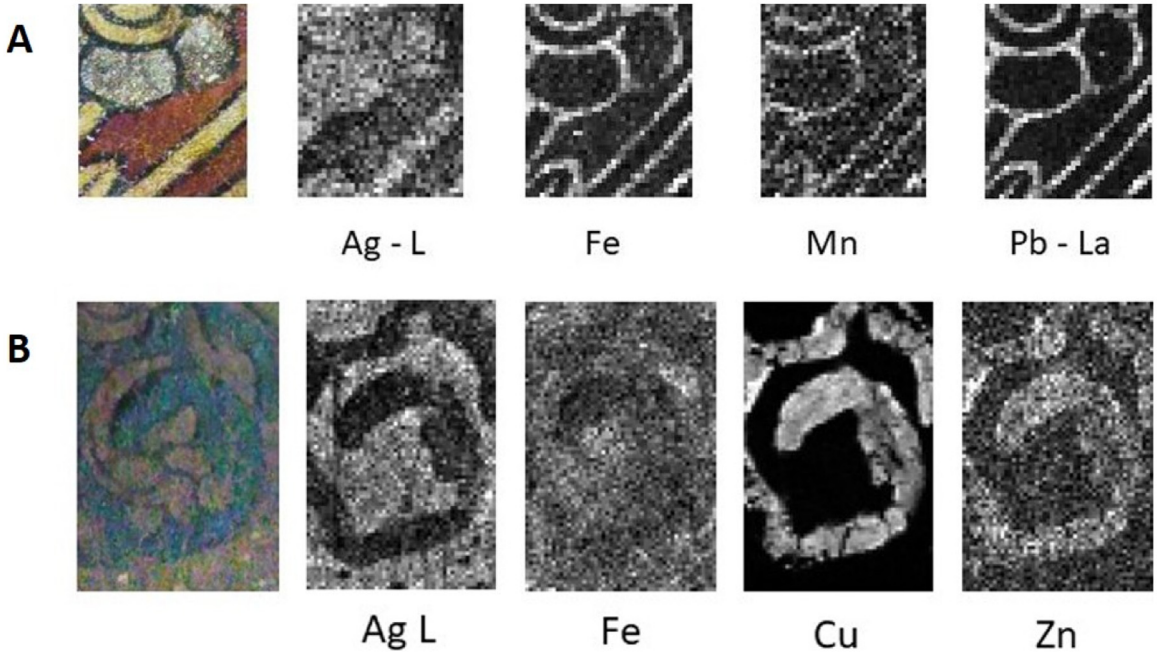

Fig. 8. (A) Leather fragment 1: elemental distributions obtained with MA-XRF. White is associated with maximum counts and black with minimum. (B) Leather fragment 2: elemental distributions obtained with MA-XRF. White is associated with maximum counts and black with minimum.

to induce, for instance, a detectable Ag X-ray yield. Ag concentrations in terms of areal density ranged from about 12.5 μm/cm^2 to 260 μm/cm^2, corresponding to 70·10^{15} up to 1450·10^{15} atoms/cm^2, in turn corresponding to an Ag foil of thickness in the interval from 120 nm to 2.5 μm. These values agree with those reported in [48] from the IBA analysis of silver leaves in gilt leather wall coverings.

However, from the analysis of the EBS spectra - some are shown for example in Fig. 7- it was possible to determine the depth profile of elements and of Ag in particular, in the surface layers of the samples. Only where the silver leaf is exposed, i.e. in correspondence to cracks of the *meccatura*, Ag is present as a thin metal foil (see for instance Fig. 7F), whereas in the other cases the silver atoms appear dispersed in a much thicker layer together with, for instance, C, N and O, as if the original silver leaf underwent a degradation process and mixed with the *mecca*.

4.3. Painted layers (XRF and IBA)

Outlines in leather fragment 1 are characterised (see Fig. 8A) by the presence of Fe and Mn, suggesting the use of iron oxides/hydroxides pigments (such as earth and ochres) – Mn being a typical trace of these compounds [49]. The presence of Pb in these outlines is less clear, it may be due to the use of lead white in mixture with dark pigments (earth/ochres and maybe also black C-based compounds), but also to the less usual grey galena [50] or other compounds such as massicot or minium, or degradation products of such materials as plattnerite [51].

Green areas in leather fragment 2 are characterised (see Fig. 8B) by the presence of Cu-based compounds showing Zn traces. This composition is consistent with the hypothesis of the use of verdigris/copper resinate rich in Zn traces, as typical of these compounds [48].

Painted leather fragments (samples 3 and 4) have a rich palette of pigments, most of which are consistent with the leather fragments production period.

Red areas, such as those of the red berries in sample 3 are painted with a Hg-rich compound indicating the likely use of vermilion.

The green garland (sample 3) and the green branch (sample 4) are characterised by the presence of Cu, consistent with the use of one of the numerous copper-based green pigments [52]. Fe is also detected in these areas, the presence of which may be related to the use of iron oxides/hydroxides pigments such as earth and ochres, possibly in mixture with the copper-based compound to give a different colour tone.

In addition, Ba, Cr and Pb are also detected in these green areas, elements that are not typical of pigments used in the 17th century. Pigments containing these elements are to list a few examples, barium yellow ($BaCrO_4$), chrome yellow ($PbCrO_4$ $PbSO_4$) and viridian (Cr_2O_3), in use since the 19th century [53]. A plausible hypothesis is that there is an original layer with a Cu-based compound which is over painted with a more recent pigment such as those listed above, as it can be hinted by the analysis of the EBS spectra shown in Fig. 9.

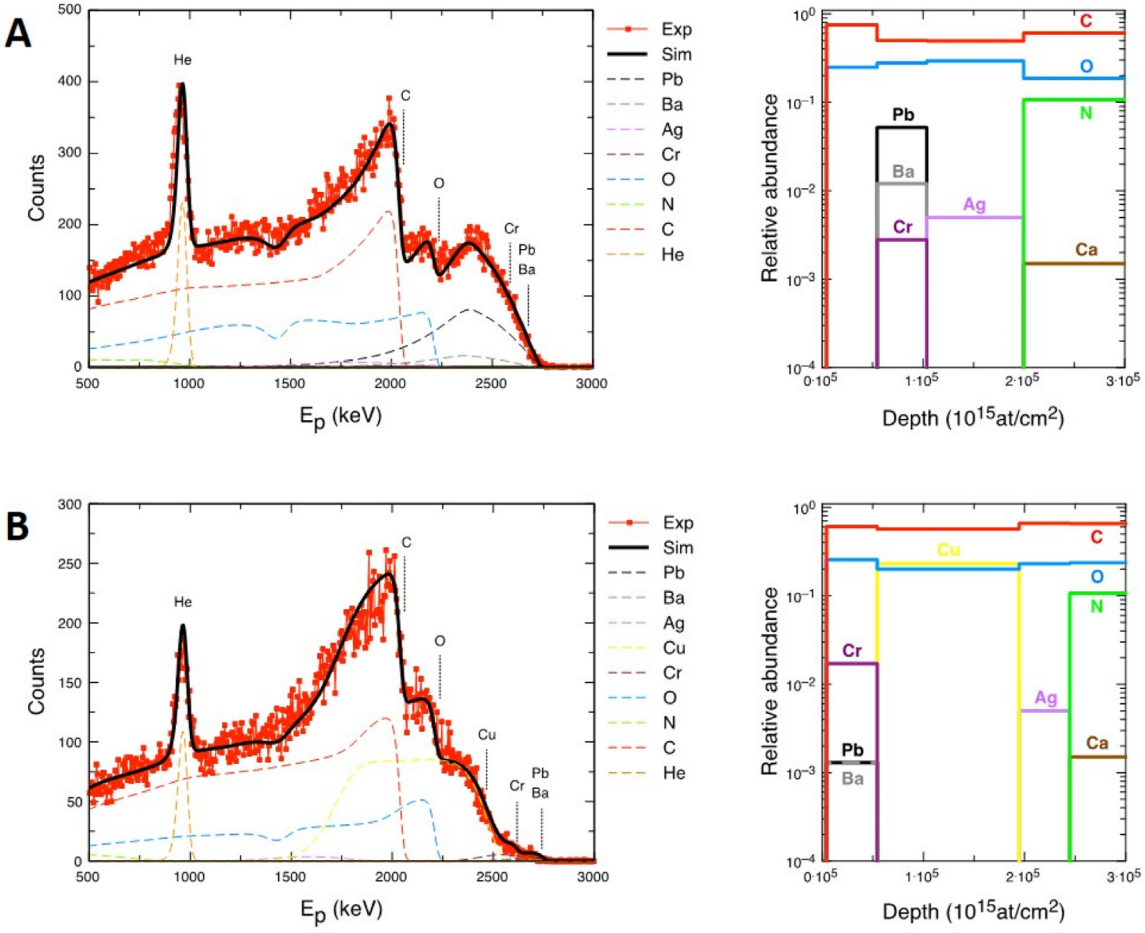

Fig. 9. EBS spectra together with SIMNRA simulations (the contribution of different elements to the simulation is also shown) and resulting elemental depth profiles, obtained with 3 MeV protons on samples: (A) green pigment, leather fragment 3; (B) light green pigment, leather fragment 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

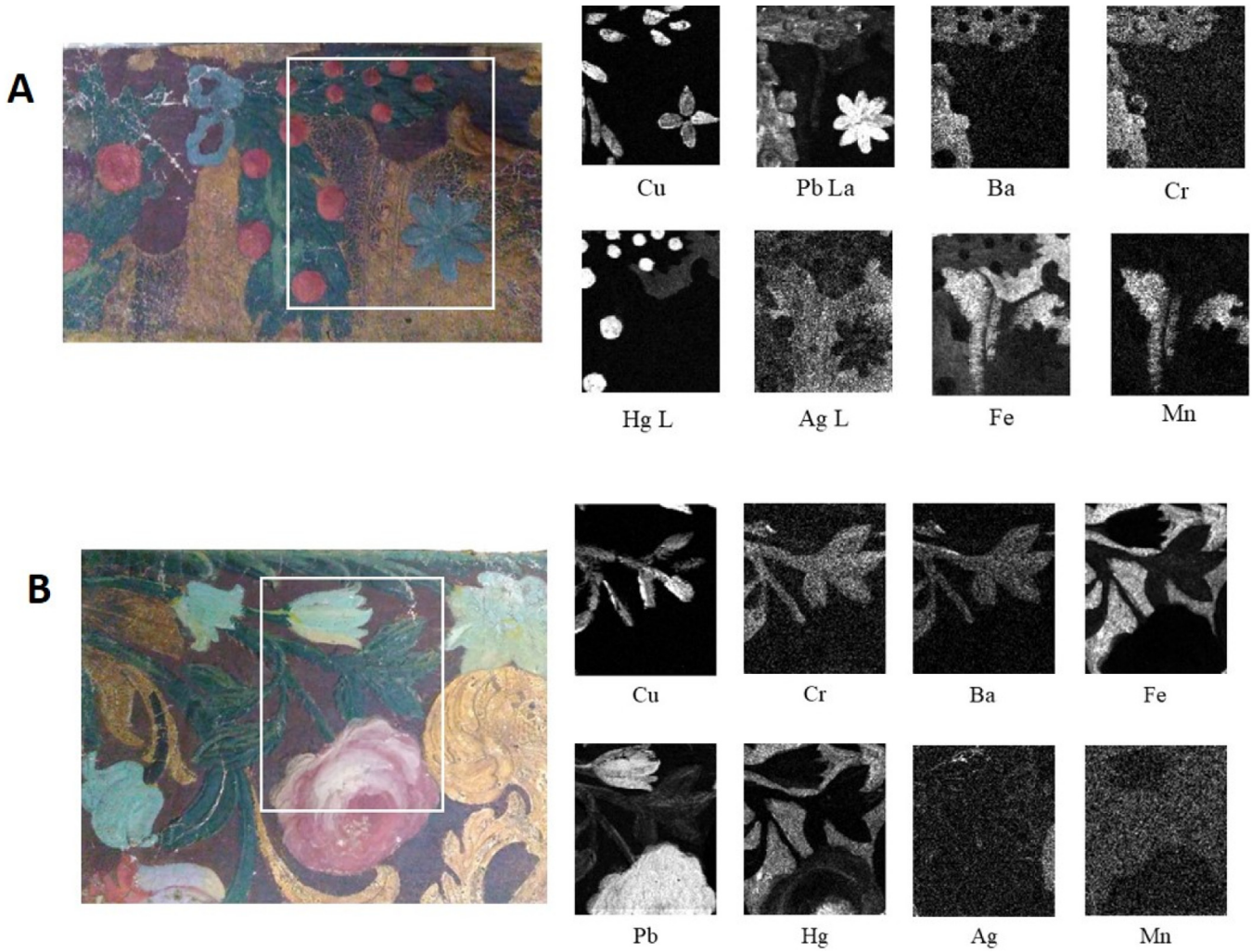

Fig. 10. (A) Leather fragment 3 and (B) Leather fragment 4: elemental distributions obtained with MA-XRF. White is associated with maximum counts and black with minimum.

This hypothesis can be addressed also in the case of the blue-greyish flower of sample 3, the petals of which are all characterised by the presence of Pb, but only four of them contain also Cu (Fig. 10A and B).

The brown backgrounds in sample 3 and 4 are characterised by the presence of Fe with Hg traces and may be related to the naked leather itself, maybe with little pigmentation of vermilion. The golden background in sample 3 has a brownish area which matches the distribution of Mn map. It is possible that compounds such as Burnt Sienna or van Dick brown have been employed.

5. Conclusions

In this work, we have reported on different analyses performed on different fragments of decorated *corami* from the archive of *Palazzo Chigi* in order to analyse the materials of these artefacts as well as their peculiar manufacturing techniques. The analyses also allowed the characterisation of eventual deterioration processes occurring in these artefacts and in their peculiar multi-layered structure. In particular, in the interface between leather and metal foil and between these and the overlying pictorial layer, thanks to the SEM-EDX it has been possible to obtain preliminary information on the structure and composition of the layers of some leather fragments worked by *mecca* and to evaluate the preservation condition of the surface layers characterised by cracks and detachments. It is precisely in the fractures of this layer that it has been possible to identify the presence of the silver leaf behind the gold painting appearance. In these areas, the presence of sulphur detected by EDX analysis reveals how the silver leaf undergoes deterioration when in contact with environmental hydrogen sulphide leading to the consequent formation of the silver sulphide patina that makes it darker.

IBA also gave important information on the conservation state of the silver layer. Indeed it is hypothesised that the silver leaf underneath the *meccatura* layer is degraded, possibly getting “incorporated” into the organic compound of the *mecca* itself.

Moreover, by means of IBA and MA-XRF, though being elemental techniques, it has been possible to evaluate also the composition of the pictorial/decorative layers. The painting palette hypothesised in these layers widely matches with that expected in the time of the production of the leathers, with the exception of few later retouchings. The original painting palette likely employs: iron oxides/hydroxides pigments (such as earth and ochres), lead white (or other Pb-based compounds), Cu-based compounds containing Zn traces (such as copper resinate) and vermilion. The layers with golden appearance confirm the presence of Ag and the absence of Au, as consistent with the *meccatura* technique.

Author contributions

M. Vadrucci designed and conceived the study and the experimental campaigns to which C. Cicero contributed and together they wrote the first draft of the manuscript.

M. Chiari and A. Mazzinghi performed the IBA and XRF analyzes and wrote the dedicated paragraphs.

A. Rufoloni, C. Cicero and M. Vadrucci performed the SEM-EDX analysis.

C. Cicero wrote the introduction on the history and processing of golden leather and, with M. Vadrucci, the discussion on the SEM-EDX analysis.

M. Vadrucci and A. Mazzinghi worked to the final version of the manuscript. All authors contributed to the revision of the manuscript, read, and approved the submitted version.

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Availability of data and material (data transparency)

Data will be made available on reasonable request.

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