An approach to the conservation of deeply corroded archaeological silver: the *polos* from Crucinia

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Abstract

This work presents a case study on the conservation of highly deteriorated archaeological silver objects; the subject is a *polos* that is, a rich and sophisticated headgear, made of silver laminae, embossed and gilded, belonging to a priestess' burial from Southern Italy, dated around the 6th century B.C. The conservation treatment was particularly complex due to a unique concomitance of different problems such as the extreme fragility and distortion of the pieces, the lack of comparisons, and the poor context information.
Scientific investigations concerned both the conservation-related aspects and the fabrication technique: radiographies allowed location of cracks and areas of deep corrosion, whereas scanning electron microscopy provided information on the corrosion patterns and the gilding technique.

Resumen

Este trabajo presenta el estudio de un caso de conservación de objetos de plata arqueológica fuertemente corroídos; se trata de un *polos*, esto es un rico y sofisticado casco hecho de láminas de plata, repujado y dorado, perteneciente al enterramiento de una princesa del sudeste de Italia, y datado en el siglo VI a.C. aproximadamente. El tratamiento de conservación fue particularmente complejo debido a la concomitancia única de distintos problemas como la extrema fragilidad y distorsión de las piezas, la falta de elementos de comparación y la poca información del contexto.
Las investigaciones científicas trataron tanto los aspectos relacionados con la conservación como las técnicas de fabricación: las radiografías permitieron localizar las fracturas y zonas de corrosión intensa antes de la limpieza, mientras que la microscopía electrónica proporcionó información acerca de las capas de corrosión y de la técnica de dorado.

Keywords: polos, archaeological silver, conservation, gilding, corrosion, Crucinia Metaponto

1. Introduction

In 1991 a rich burial site reputedly of a priestess (Guzzo, 1996, De Siena, 2000, Lippolis, 2002) dated around the 6th century BC, was excavated at Crucinia (Metaponto, Southern Italy). Among the objects, was one of outstanding archaeological and artistic importance: a headgear of the *polos* type, which is known to have a religious meaning. The shape of the *polos* was probably cylindrical (Figure 1, left); it was made of silver bands, some of which were gilded, decorated with appliques and a succession of *kouroi* (naked standing virile figures) and horses, embossed in silver lamina and gilded. The *kouroi* and horses are embossed in the form of closed shells, the two valves being obtained from a single folded lamina (Giumlia-Mair, 2001, Giumlia-Mair et al., 2001) Further *korai* (dressed standing feminine figures), constructively similar to the previous ones, are supposed to function as pendants at the head's sides. The metallic structure was fixed to a support made of organic material, possibly cloth or leather, which is now lost; the existence of this support proved by numerous silver staples inserted in the bands.

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A preliminary analysis of the object's conservation conditions found serious deterioration, due to the burial conditions (Figure 1, centre) but also caused by the urgency with which it was rescued (Figure 1, right) and to the incompleteness of previous cleaning treatments. The observed alterations include:

- the almost complete mineralization and the consequent fragility of the laminae;
- the presence of complex corrosion patterns involving thick layers of silver chloride hiding the gilding, sometimes alternated to calcium carbonate, also thick and adherent to the gilding;
- the distortion of some fragments and the incompleteness of the left-hand side, due to the pressure of the deceased preistess's head;
- the extreme and diffused fragmentation;
- the loss of the organic support material and of some joining elements.

Further problems related to the urgency of the rescue, to the consequent poor documentation of the excavation and to the loss of connections and pertinences experienced by the *polos* after the find.

These considerations provide a realistic idea of the complexity of the restoration – that the CO.RE.AR. group and A. Archi Olsoufieff were to carry out – not only as regards cleaning and consolidation of the laminae, but also – and mainly – as regards the assembly and recomposition of the artifact, given the exiguity of typological comparisons (CO.RE.AR. et al., 2002).

Figure 1. Graphical interpretation of the *polos* (left); detail of the conservation conditions of bands A and B after the rescue (centre); the *polos* during the urgent rescue (right); photographs: courtesy of the Soprintendenza Archeologica della Basilicata.

2. Conservation treatment

Before the conservation treatment, a number of preliminary activities took place; these included:

- photographic documentation of the material as received;
- sorting, visual identification and typological grouping of all the pieces, carried out with the aid of the poor pre-existing documentation. During these operations many connections among the fragments were found;
- establishment of an identification system related to the bands; these were identified with the letters A to G starting from the top (Figure 2).

Following these preliminary operations, the pieces were radiographed.

Figure 2. First recomposition of the polos resulting from the preliminary identification of the fragments (photograph by P. Rizzi).

2.1 General principles

Different cleaning strategies were considered, with special regard for mechanical and chemical methods; these had to be suitable to remove the thick layers of silver chloride that hid most of the gilded surfaces, thus preventing their readability (Figure 3). In this phase considerable support was provided by radiographies and scanning electron microscope investigations.

Figure 3. Details of the corrosion products and deposits covering the fragments (left and centre) and of the gilding conditions (right).

Mechanical cleaning was mostly used, due to the possibility of better controlling the cleaning level. Optical aids for the magnification of the concerned areas were extensively used. A mechanical and chemical combined cleaning was used for those areas with alternate stratification of silver chloride and calcium carbonate and on the appliques, that were particularly delicate due to the small dimensions and thin lamina (Plenderleith et al., 1971; Angelini et al., 1987; Marabelli, 1995).

Due to the almost complete mineralization and the consequent fragility of the pieces, it was decided to limit the cleaning treatment of the laminae to the front surface only. For the non-gilded bands and where the gilding was missing, the deep corrosion made the identification of the original surface particularly complex. It was therefore decided that the optimum cleaning level was the one that left a thin layer of chloride allowing a view of the underlying details of the original surface.

2.2 Operational aspects

The general sequence of the operations is as follows:

- removal of the materials resulting from the previous conservation treatments by means of suitable solvents and mechanical cleaning;
- mechanical removal of soil and incoherent corrosion products from the rear surface of the laminae;
- in case of chemical cleaning, the rear of the laminae was consolidated and protected from the chemicals by applying a layer of high concentration acrylic resin;
- before mechanical cleaning, the fragments were temporarily consolidated by back-veiling with cotton gauze stuck with acrylic resin (Figure 4, left); silicone rubber moulds were made to support the pieces and avoid concentrated stresses during mechanical cleaning (Figure 4, centre);
- removal of the thick layers of silver chloride and calcium carbonate by means of mechanical cleaning of the surfaces, carried out with surgical blades, abrasive micro-spheres mounted on a prosthetic drill, soft brushes (Figure 4, right). It was preferred to leave part of the silver chloride on the most fragile edges of the laminae;
- in the presence of extended alternate stratifications of silver chloride and calcium carbonate – particularly on the appliques – mechanical cleaning was alternated with immersions in 10% sodium thiosulphate and 10 to 20% trisodic EDTA solutions (Marabelli, 1995). Localized concretions of calcium carbonate on the gilded surfaces were treated with ion-exchange strong cationic resins;
- surface finish with damp pads and bicarbonate of soda and/or ethanol pads and silversmith pastes of different fineness;
- removal of the temporary veilings with acetone;
- removal of the products residues by rinsing in distilled water and/or ethanol;
- drying with infra-red lamps;
- consolidation of the fragments by means of low concentration (1.5%) acrylic resin;
- completion of the search of connections among the fragments;
- gluing of the fragments and integration of little lacunae with epoxy resin, suitably coloured by inorganic pigments;
- consolidation of the recomposed laminae by back-veiling with polyester fabric and 10% acrylic resin (Marabelli, 1995);
- final protection of non-gilded surfaces with acrylic resin;
- gluing of the detached decorations – rosettes, ram heads, doric *kimation* – to the bands A, C and D by nitrocellulosic resin; the latter was used because it is easily reversible and commercially available at the right concentration (Marabelli, 1995).

Figure 4. Temporary back-veiling of the fragments (left); piece supported by a silicone rubber mould during mechanical cleaning (centre); result of the mechanical cleaning with respect to uncleaned areas (right).

Before the final back-veiling of the laminae, all the recomposed elements were graphically documented (by C. Damiani, Roma) as placed in their final position. Special consideration was made for the position of the staples and the holes used to connect the *kouroi* and the horses to the laminae and the laminae to the organic support.

3. Reconstruction hypotheses and final lay-out

The conservation treatment and recomposition of the fragments allowed a more accurate interpretation of the surfaces, as well as the collection of more information concerning the original positions of the *polos*' elements. The identification of the connections among the bands allowed to accurately estimate the headgear height to 25 cm. The circumference is more uncertain: given the deceased priestess' skull dimensions, it is probably about 54 cm.

Four hypotheses were proposed for the object reconstruction, differing from one another mainly as regards the positions of the *kouroi* and horses on band B. The uncertainties are related to problems of symmetry and to the fact that, among the 22 *kouroi* and horses, only 12 had an identified position.

The lay-out resulting from the final hypothesis is shown in Figure 5. Given the deformations in the central part of the *polos*, it was impossible to arrange the fragments on a support structure that would suggest a headgear. It was therefore decided to set the pieces on four separate plexiglass bands, provided with suitable templates to support the distorted parts; all the elements were attached to the plexiglass by nylon threads; an inclined plexiglass plane supported the whole.

Figure 5. Polos recomposed on the support system: full view (left) and detail (right); photographs by P. Rizzi.

4. Scientific investigations

The polos was investigated in two steps: the first one was commissioned from AB2 Art, the results will be referred to as "(AB2 Art 2001)"; the remaining investigations were directly carried out by the authors within collaborations acknowledged in the due section. Radiography and scanning electron microscopy were employed to study both conservation-related aspects and the fabrication technique. In particular, given the unreadability of the surfaces, X-rays showed – before cleaning – cracks and areas of deep corrosion. It was also possible to identify some of the systems used to mechanically join the appliques to the bands. Further information on the gilding technique, the corrosion patterns, alternation of different layers of silver chloride and calcium carbonate and mineralization of the laminae was provided by scanning electron microscopy.

4.1 Radiographies

X-rays were carried out on all the pieces immediately after their preliminary classification. The working conditions are: high voltage 80kV, current 4mA, exposure time 5-8min (AB2 Art, 2001). Figure 6, left. shows the radiographic detail of one of the horses and part of the adjacent lamina: cracks and areas of deep corrosion are clearly visible. The radiographs also show (right) the details of the shape of a *kore*. Figure 7 shows different fragments of band D: the top-most fragment is relatively uncorroded and shows numerous staples – used to join the lamina to the organic support – in their seats. A flower and some empty loops are also visible; the band at the bottom of the image is more corroded and cracked; it only has empty loops. Besides the usual cracks, areas of deep corrosion and staples, Figure 8 shows an interesting – digitally processed – detail of a loose decoration element hidden behind a flower on band C.

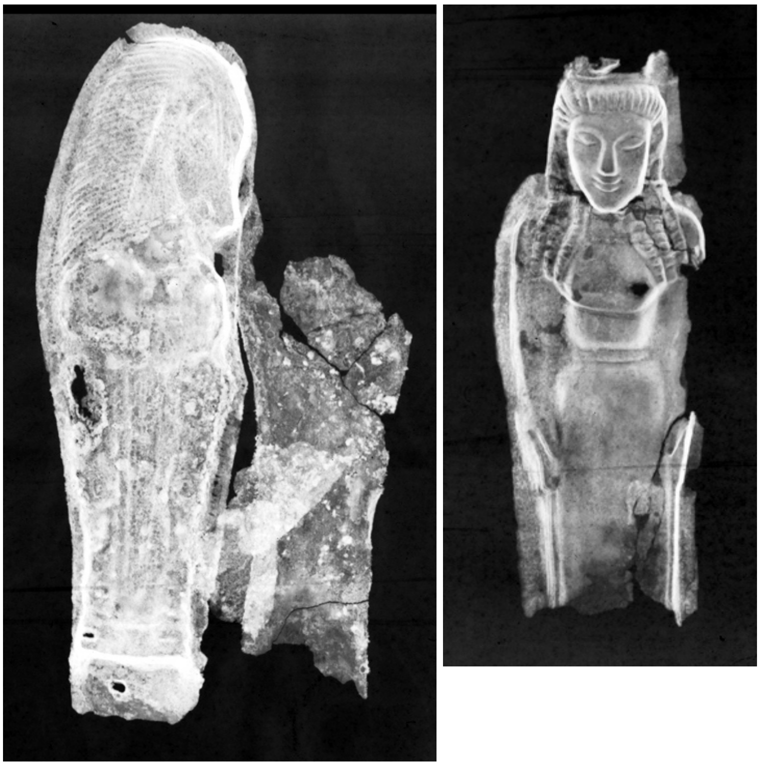


Figure 6. X-ray images of one of the horses with part of the adjacent lamina (left) and a *kore* (right).

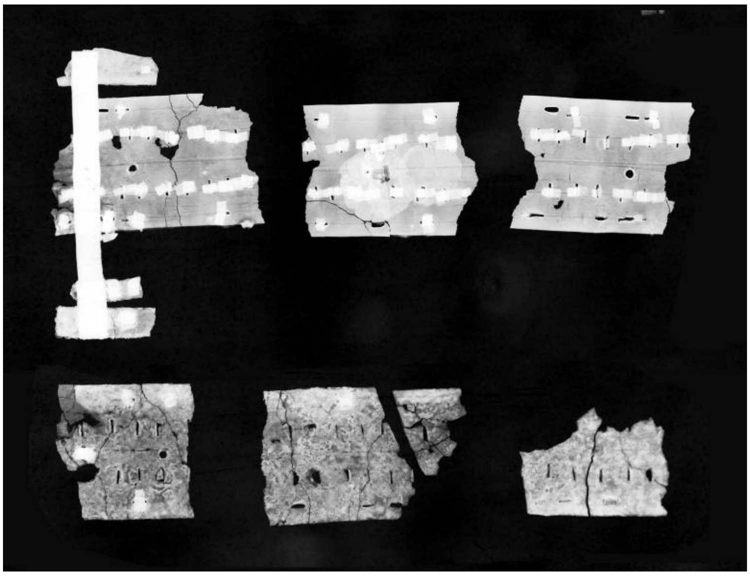


Figure 7. X-ray image of different fragments of band D.

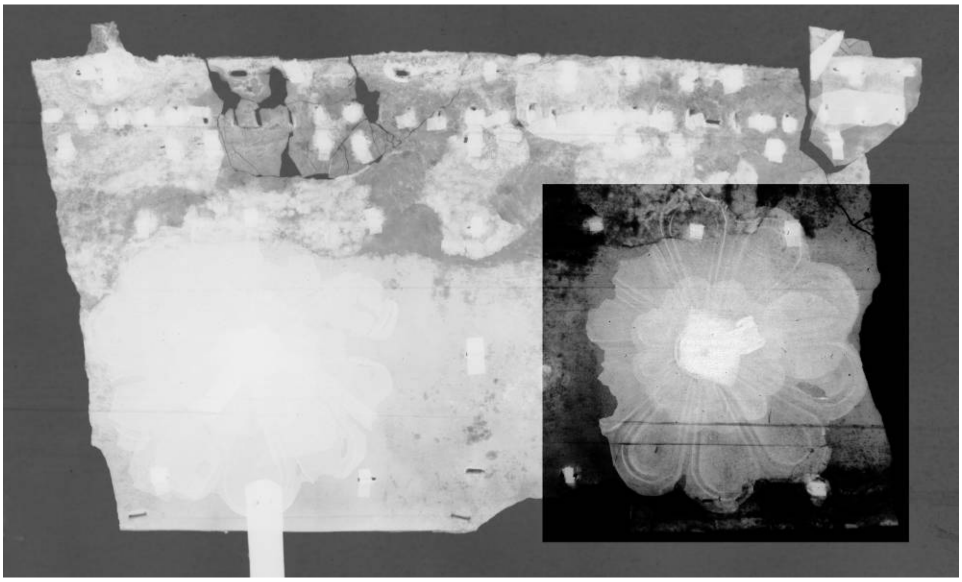


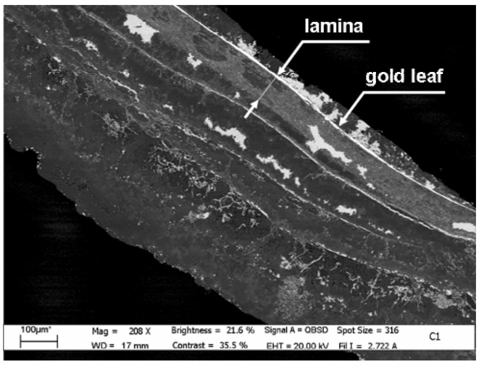
Figure 8. X-ray image of band C; digital processing of a detail showing a flower that hides a loose rosette behind the corolla.

4.2 Scanning electron microscopy

Band C, half-rosette, sample C1: Figure 9 left shows the corrosion pattern typical of this object: below the gilding, the lamina is entirely mineralized; further alternately stratified corrosion products (silver chloride) and deposits (calcium carbonate) grow on the non-gilded side of the lamina; the stratification is possibly related to the periodical floodings and droughts experienced in the tomb. A detail of the mineralized lamina is shown on the right: from the surface (right) inwards (leftwards), it is possible to observe:

- a deposit of calcium carbonate;
- a solid layer of silver chloride, just above the gold leaf;
- the gold leaf;
- just below the gold leaf, a spongy structure of silver chloride and calcium carbonate, corresponding to the original silver lamina; the calcium carbonate may precipitate due to the cathodic reduction of oxygen to hydroxyl in the presence of calcium ions and carbonic acid (Marabelli, 1995).Measured in different parts of the spongy structure, the relative concentration ratios of Ag, Cl and Ca appear reasonably constant;
- calcium carbonate alone and a solid layer of silver chloride.

The described corrosion structure and the concerned elemental maps are shown in Figure 10 at higher magnification: the leaf thickness is about 3 microns, no Hg is detected in any part of the cross-section.



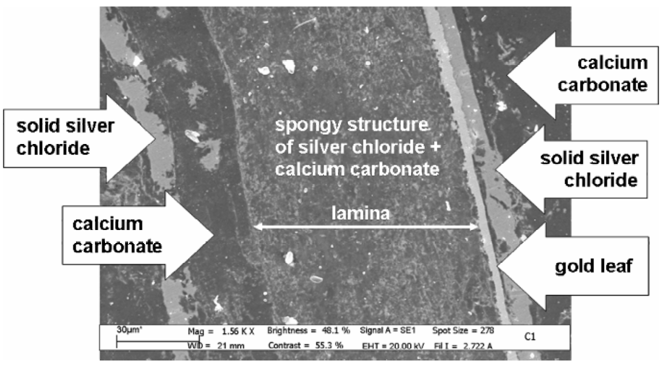


Figure 9. Band C, half-rosette, sample C1, cross-section: backscattered electron images of the corrosion pattern (left) and a detail of the lamina (right).

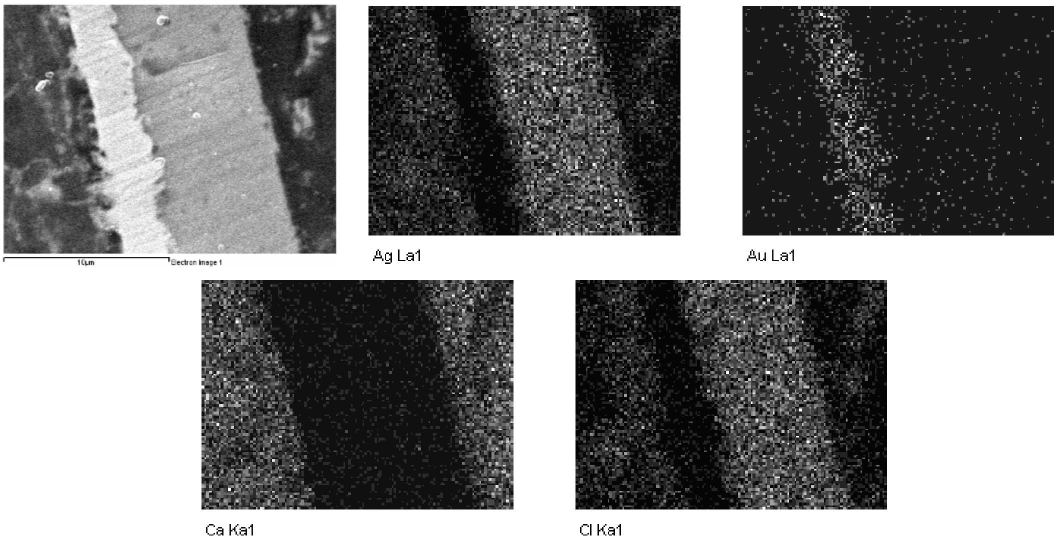


Figure 10. Band C, half-rosette, sample C1, cross-section: backscattered electron image and elemental maps of the leaf and its immediate surrounds

Further information about the gilding technique (provided by Figure 11) that shows the partial detachment between two gold leaves in an overlapping zone; this indicates the exclusion, with reasonable certainty, that the so-called diffusion bonding (Oddy, 1993) ever took place. It is likely that the gold leaf was applied after the embossing and no heating was carried out.

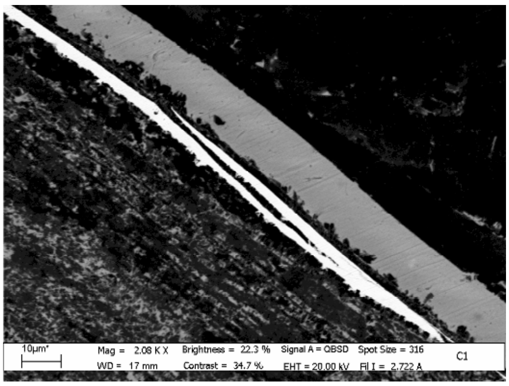


Figure 11. Band C, half-rosette, sample C1, cross-section: backscattered electron image showing the detachment between two gold leaves in an overlapping zone.

Band G, staple, sample C2: Figure12 shows the cross-section of a staple and the surrounding lamina, the concerned elemental maps are shown as well. Similarly to sample C1, it is possible to observe the complex corrosion pattern made of solid silver chloride and the spongy structure of silver chloride and calcium carbonate.

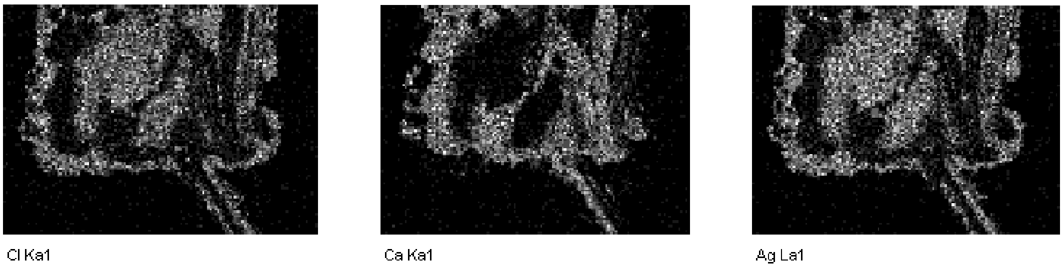


Figure 12. Band G, staple, sample C2, cross-section: backscattered electron image and elemental maps of a staple and the surrounding lamina.

Microanalysis shows the presence of Pb and Sn on the head of the staple (Figure 13, left). The method of joining some decorative components to the bands still remains unclear, as no joining elements were found; therefore it is possible that these are the remains of soft solder used for joining. Several areas of the sample (Figure 13, left and right) show a peculiar structure – whose nature is not understood at the moment – made by the alternate overlapping of numerous gold layers and silver chloride layers, the former being thinner than the gilding.

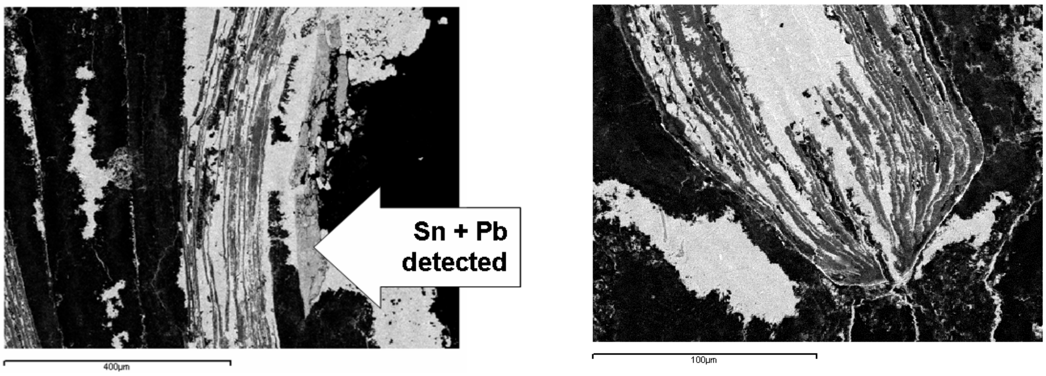


Figure 13. Band G, staple, sample C2, cross-section: backscattered electron image of the staple's head (left) and the tip of the wing (right).

Band D2, sample C3: the sample is almost uncorroded, the microanalysis shows almost pure silver, in particular there is no alloying copper. In the optical microscope view the etched cross-section shows the slipping planes due to cold-working (Figure 14, AB2 Art, 2001).

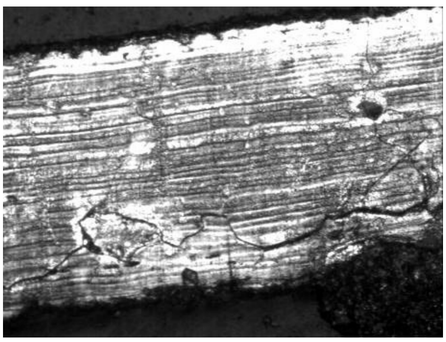


Figure 14. Band D2, sample C: optical microscope image of the etched cross-section showing the slipping planes due to cold-working.

Band C, fragment of flower: the images (Figure 15) are indications of the bad conservation conditions, frequently found on the gold leaf. They show the leaf edge detached and folded with the underlying silver chloride (left); and the working marks, left in the metal to assist the adhesion of the leaf to the substrate (right).

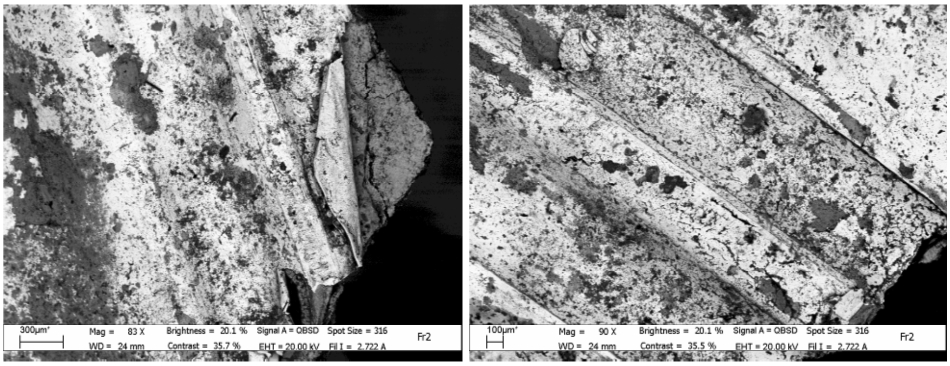


Figure 15. Band C, fragment of flower: backscattered electron images of the gold leaf showing a detachment (left) and the working marks (right).

Band C, petal of flower, sample C5: Figure 16 shows an example of lamina gilded on both sides (AB2 Art, 2001).

For the samples investigated, the thickness of the laminae ranges between 200 microns for band D – which has a structural function – and 50-80 microns for the decorations. Other parts such as band C and the vertical supporting sticks (E) were not investigated, but visually appear even thicker.

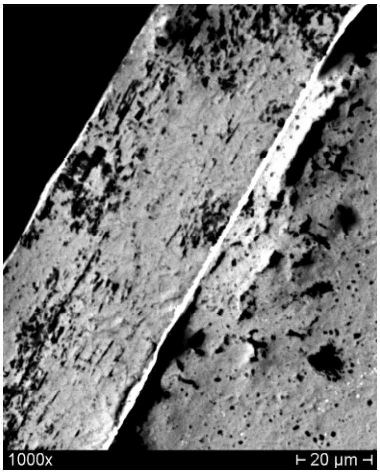


Figure 16. Band C, petal of flower, sample C5: backscattered electrons image of a lamina gilded on both sides.

5. Conclusions

The paper has discussed the case of the *polos* from Crucinia as a significant example of the problems concerned with the conservation of archaeological silver objects. The conservation treatment, the reconstruction and the study of the *polos* were particularly complex and delicate: the very bad conservation conditions and the fragmentation of the pieces were only two of the reasons. Further problems came from the poor documentation concerning both the excavation – carried out in conditions of extreme urgency – and the previous cleaning. The conservation treatment recovered the interpretation of the morphology by removing the thick layers of deposits and corrosion products and by consolidating the constituent materials. It also recovered the readability of the artefact as a whole by recomposing the pieces on a support system. The system – actually the availability of a plausible reconstruction hypothesis – was possible thanks to the extensive knowledge of the construction technique acquired during the restoration of the object.

An important contribution was provided by scientific investigations, mainly radiography and scanning electron microscopy; as the surfaces were almost completely visually unreadable. X-rays focused on the location of cracks and areas of deep corrosion; in a few lucky cases they also located loose fragments hidden below other pieces and allowed the identification of some of the systems used to mechanically join the appliques to the bands. Besides the assessment of the mineralization of the laminae, replaced by a spongy structure of silver chloride and calcium carbonate, scanning electron microscopy provided information on the corrosion patterns, mainly consisting in alternated layers of silver chloride and calcium carbonate. With regard to the gilding technique it was also possible to assess that the artefact was leaf-gilded after embossing: the detachment of two overlapped gold leaves shows that the so-called diffusion bonding was not used on this artifact.

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