Objects from the ancient site of Qalat Rabah (Calatrava la Vieja): a case study on the characterization and conservation of Islamic gilded bronzes from Spain

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Abstract

The recent archaeological excavations at Qalat Rabah (Calatrava la Vieja, Spain) brought to light a number of gilded pieces – harness and personal ornaments – of very high aesthetic and technological quality. These artefacts are being studied from different points of view, as they unquestionably represented the state of the art in the Mediterranean Europe of the Middle Ages. Selected pieces were investigated, mainly by scanning electron microscopy (SEM-EDXA), with regard to the corrosion structures and the gilding technique. The identification of the corrosion products and their distribution provided information for the conservation treatments, whereas the simultaneous presence of gold leaf and mercury lead to hypothesize either a gilding technique known as "cold mercury gilding" or a traditional leaf gilding in which mercury is already contained in the gold.

Resumen

Las últimas excavaciones en Qalat Rabah (Calatrava La Vieja, España) han sacado a la luz numerosas piezas sobredoradas (adornos personales, apliques para muebles e indumentaria, etc.) de gran calidad estética y tecnológica. Estos objetos ha sido estudiados desde distintos puntos de vista ya que constituyen una incuestionable representación del arte en el Mediterráneo europeo en la Edad Media. Se han seleccionado algunos de ellos para, mediante microscopio electrónico de barrido (SEM-EDXA), realizar un estudio de la estructura de la corrosión y la posible técnica utilizada en el dorado. La identificación de los productos de corrosión y su distribución aporta una valiosa información para la conservación y la restauración de piezas de estas características. Además, la presencia conjunta de una lámina de oro y de mercurio nos ha llevado a dos hipótesis distintas: una, que se trate de una técnica de dorado conocida como "cold mercury gilding"; y la otra, que sea una técnica de dorado con lámina de oro de tipo tradicional y que el mercurio ya estuviese presente en el oro desde el inicio.

Keywords: gilded bronzes, gilding techniques, conservation, Islamic artefacts, corrosion processes, SEM-EDXA

1. Introduction

Archaeological excavations started in 1984 in the Islamic city of Qalat Rabah (Calatrava la Vieja) in Upper Guadiana, Spain. The city played a starring role during the Middle Ages; being founded during the 8th century A.D. by the Omeyad Dynasty as a strategic point to protect Cordoba from the rebellious Toledo. It became the capital of the region during the three centuries of Omeyad domination of Al-Andalus. The city was annexed by the Christian kingdom of Castilla shortly before the battle of Las Navas de Tolosa, in 1212. Then Calatrava underwent an irreversible decay, ending with the final abandonment of the city at the beginning of the 15th

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century. The archaeological evidence points out the existence of a bronze workshop – which specialized in gilding techniques – placed in the Islamic part of the city.

So far a number of metallic objects has been recovered from the site, including a set of gilded bronze objects, outstanding for the high aesthetic and technological quality (Figure 1). They are small decorative elements, appliqués for clothes and furniture, buttons, etc.; with a few exceptions, they present poor conservation conditions and loss of the gilding.

Our research was designed with the aims of investigating the ancient gilding techniques, going deeper into the mechanisms of deterioration – including those of the gilding – and identifying optimum cleaning and conservation treatments. Following a previous study (Barrio et al., 2003) on a first group of objects, we continued and investigated a second group of recently excavated pieces.

Figure 1. Objects excavated at Qalat Rabah, significant for the high artistic and technological level.

2. Background on the gilding techniques

The high artistic and technical level achieved by the Islamic metal ateliers in the Mediterranean regions where this culture flourished in the Middle Ages (Allan, 1979, 1986), is clearly demonstrated by the wonderful gilded objects remaining from that period. The fact that even small ornamental objects were gilded, such as those from Calatrava la Vieja, points out the widespread use of this technique in Medieval Spain. Furthermore, the production of small gilded objects used as personal ornaments or harness appliqués became a specialization in the atelier of Qalat Rabat.

As regards the gilding techniques concerned with the objects discussed here, those involving cold hammering of gold sheets – documented in very few Islamic coins – can be excluded, as mercury was detected. Rather we had to focus on those artefacts involving this element that is, cold mercury gilding and fire gilding. The techniques can be shortly described as follows (Oddy, 1993):

- cold mercury gilding: the mercury is spread over the object's surface, then gold leaf is applied so that the amalgam is formed *in situ* at the interface between the leaf and the object; mercury is allowed to evaporate at room temperature;
- fire gilding: the gold-mercury amalgam is prepared separately and applied to the object's surface; subsequently the object is heated to allow for mercury evaporation.

Though the former technique has been mentioned since Pliny the Elder (Natural history, XXIII, 64-65, 100), replication experiments carried out by Anheuser (Anheuser, 1996) show that Oddy's description of the process may be oversimplified; in particular the word "cold" is questioned, as Anheuser could not avoid the complete amalgamation of the gold leaf. Consequently heating followed by burnishing was necessary to remove excess mercury and obtain a good quality golden aspect. As regards the latter technique, we have references in ancient sources from the 4th century A.D. Fire gilding seems to be the most frequently used method during the Middle Ages (Oddy, 1993). It was early in history mastered by the Islamic metal workers – it is mentioned in the texts of Al-Hamdani (A.D. 942) – although gilding methods were probably known in Al-Andalus even earlier. This is demonstrated by a fake dinar coin from the conquest period (A.D. 711-755) that shows a gilded layer of about 5 microns (Paredes, 1998), which is not too far from the 2-4 microns measured on the first group of Calatrava objects (Barrio et al., 2003). A later text, *Al-Muqaddimah* by the Sevillan historian Ibn Khaldoum (1332-1402) (Ibn Jaldún, 1977), sheds light on the methods that contemporary alchemists used to produce fake coins: among them it includes amalgam silver plating, which is identical to the technique used for gilding; numerous material evidences are available concerning the use of this method.

Analytical methods simply based on the detection of mercury do not help much to distinguish the two techniques, as mercury is present in both cases (Oddy, 1993, 2000). To obtain significant information one has to go further and consider the microstructure of the gilded layers and their immediate environments.

3. Description and preservation state of the objects

As gilding is usually hidden by the corrosion products of copper, we carried out a preliminary selection of those objects or fragments that, for their morphology, could be supposed to have gilding. Finally the following five objects were chosen by also taking into account the conservation conditions, in order to provide different corrosion situations.

Object A (Figure 2): fretted ornament, gilded on the obverse, measuring 70mm (length), 24mm (width), 1mm (thickness). The decoration repeats a geometrical pattern based on the square as a main figure. The reverse, which is not shown, is not gilded. A punched decoration goes across the whole decorative scheme. The samples were taken after restoration, to be more significant to the gilding technique. The preservation state is excellent with a sound metallic core and an almost complete gold layer.

Figure 2. Object A: fretted ornament.

Object B (Figure 3): Similar to object A, with a geometrical pattern, measuring about 46mm (length), 24mm (width), 3mm (thickness). It differs greatly from object A as regards the preservation state: it is completely mineralized – and therefore extremely fragile – and no remains of gilding were visible in the preliminary optical examination. Samples were taken from loose fragments prior to treatment. Analytical investigations proved that it was gilded.

Figure 3. Object B: fretted ornament.

The different preservation states of the two objects allowed us to comparatively evaluate the corrosion processes and the fabrication technology. No remains of gilding were observed on the other three (C,D and E) objects prior to restoration. Only Object E, further investigated by optical microscopy after restoration, showed the presence of gold.

Object C (Figure 4 left): buckle in very poor preservation state, fragmented and incomplete, measuring about 41mm (length), 28mm (width), 2mm (thickness).

Object D (Figure 4 centre): disc-shaped button or appliqué with a central rounded protuberance, fragmented and incomplete, measuring about 45mm (diameter), 1mm (thickness).

Object E (Figure 4 right): unidentified object with a flattened conic shape, measuring 60mm (length), 29mm (maximum width), 15mm (minimum width) and 9mm (thickness).

Figure 4. Objects C, D and E: buckle (left), button or applique (centre), unidentified object (right).

The initial preservation state of these objects is generally poor and the surface is severely deteriorated. Preliminary optical examination showed, above the gilding, a layer of corrosion products hiding completely the original surface. As the cleaning progressed, we could characterize the corrosion products and go deeper into the deterioration processes.

The corrosion layer was formed by a heterogeneous mixture of soil, calcium carbonate, chlorides, copper oxide and copper carbonate. This is quite a frequent combination in archaeological copper or copper based alloys. The original gilding appeared during the cleaning underneath these products. The gilding was in different preservation conditions depending on the progress of the core corrosion.

For gilded objects much of the corrosion is due to the galvanic cells that are produced in the presence of humidity, between metals with different electrochemical potentials - namely copper and gold. During this process gold is cathodically protected and causes the progressive corrosion of copper (Selwyn, 2000). The gilding deterioration is due to the volume increase of the corrosion products – mainly basic copper chlorides (atacamite) – at the interface with gold. This produces a progressive swelling that finally results in the gilding detachment. This is not the case for Object A: the minimum chloride attack has kept the metallic core almost uncorroded and the gilding continuous. However, Object B has suffered a complete mineralization, so that remains of the gilding can only be observed by scanning electron microscope and microanalysis.

4. Cleaning and conservation techniques

Our restoration criterion had two clear objectives:

1. recovering the intact gilded areas so as to read adequately the original surfaces; and
2. achieving a good metallic stability to provide for the future integrity of the pieces.

The initial decay state of each of the objects called for individualized interventions, although all of them were carried out along common lines. The working protocol has varied for each object depending on the mineralization conditions and the presence or absence of a sound metal core. A combination of mechanical cleaning and physical-chemical cleaning (organic solvents – Acetone 50%/Xylene 50% – plus ultrasonic bath), already used in the restoring of great golden bronzes such as the statue of Marcus Aurelius (Fiorentino, 1994), has also proved itself effective on these Islamic bronzes.

The use of optical instruments such as binocular microscopes is a must when working on these small objects, where intact gilding might appear underneath the visible surface any time during the cleaning process. Mechanical cleaning methods, complemented with the advance of optical instruments, are today considered a very suitable solution for the cleaning of copper-based objects (Scott, 2002). The aim of the cleaning methods is to detect and recover all the gilding remains which can not be seen due to the corrosion of surfaces, as was the case in the analysed and restored sample objects from Calatrava. They are highly safe methods as they allow effective and constant control of the process, a specially desirable characteristic when working with deeply mineralized pieces.

Prior to mechanical cleaning, an optical examination was made and some cleaning probes were done. After establishing a gilding zone mechanical cleaning was performed under the microscope lens. The mechanical cleaning was totally manual using surgical scalpel blades and an organic brush. After finishing mechanical cleaning the objects were prepared for analysis in order not to disturb the results with the chemical products used in stabilization. The process ended with a stabilization and inhibition treatment with BTA in a 3% ethanol solution. Afterwards the pieces were stove-dried at 105ºC and covered in a protective double coating of Paraloid B-72 in a 5% xylene solution and micro-crystalline wax in W.S. at 5%, 60°C. Both Paraloid and the wax were vacuum-applied to guarantee an adequate penetration. The use of a double protective layer of acrylic resins and micro-crystalline mineral waxes has proved itself effective to protect copper-based metals from different aggressive atmospheres (Mourey, 1997; Díaz, 1997).

4.1 Microstructural investigations

Samples from the objects were investigated at the scanning electron microscope (SEM) to study the gilding technique and collect more information on materials and corrosion products. In one case (Object E) it was also possible to identify the remains of textiles fibres.

Sample CV-01 26-64 (Object A): This is the most significant sample as regards the gilding technique; in a previous publication (Barrio et al., 2003) the investigation of other samples lead to the hypothesis of a technique similar to the so-called “cold mercury gilding” (Oddy, 1993); here we have the same experimental evidence, but the discussion tries to discern greater knowledge.

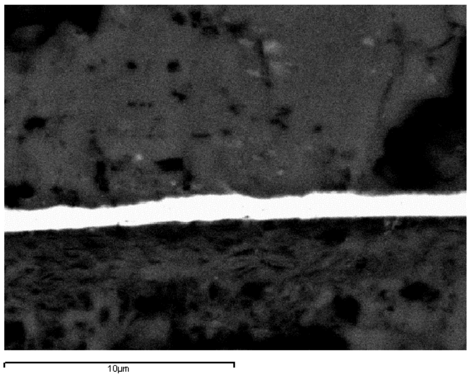

Figure 5. Sample CV-01 26-64 (object A), back-scattered electrons image of the gold layer.

Figure 5 shows a detail of the gold layer: it is approximately one micron thick and contains Hg. The thinness as well as the absence of any apparent granular structure seem to exclude proper fire gilding (Cowell et al., 1991; Jett, 1993). The use of gold leaf also seems to be confirmed by Figure 6 that shows the leaves overlapping in different parts of the sample. Hg is homogeneously distributed over the leaf thickness with a concentration ratio Au/Hg between 10 and 12. Given these facts one can propose different hypotheses, all in need of further investigation:

a) it is a leaf gilding in which the adhesion was obtained by mercury; the latter was applied to the surface in such small amounts to avoid the complete amalgamation of the leaf described by Anheuser. The homogeneous distribution of Hg over the leaf thickness may be due to the spontaneous diffusion of this element, possibly enhanced by a thermal treatment; or

b) it is a traditional leaf gilding; mercury took no part in the gilding process, as it was already present in the gold before the leaf application.

It has to be remarked that, given the sound aspect of the Au layer and the leaves overlapping, no complete amalgamation seems to have occurred here. The composition of the object's body metal is: Cu 92%, Pb 6%, Sb 2%; the latter seems related to Pb, as it has the same distribution. The presence of Pb is quite unusual and contradicts the practice, common to several cultures and periods, that avoids significant amounts of this element in alloys suitable for mercury gilding. This would confirm the latter hypothesis ie, that we are in the presence of a traditional leaf gilding, for which it is irrelevant whether the bronze is leaded or not.

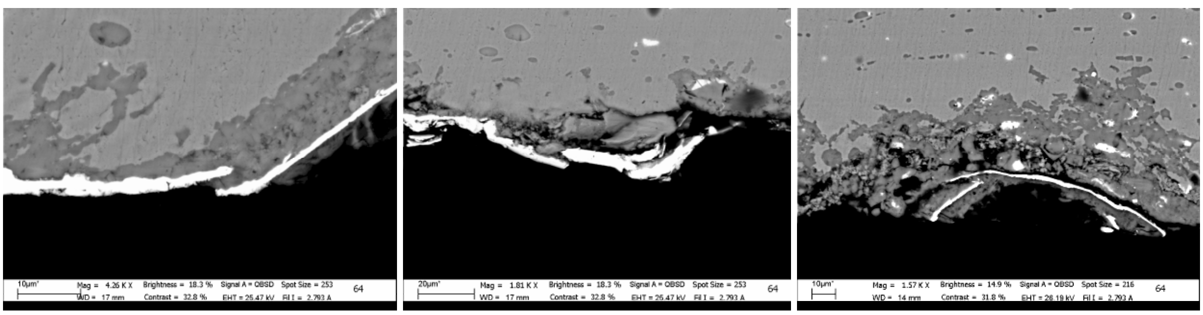

Figure 6. Sample CV-01 26-64 (object A), back-scattered electrons images showing partial overlapping of the gold leaves in different parts of the sample.

Sample CV-03 15-461 (Object B): the sample (Figure 7) shows a corrosion pattern typical of wires, actually two wires of 1.5-2 mm in diameter, possibly twisted and hammered. The gilding is visible in the lower part of the cross-section: it is 2-4 microns thick (see detail) and contains Hg in higher concentration with respect to the previous sample, the ratio Au/Hg being around six.

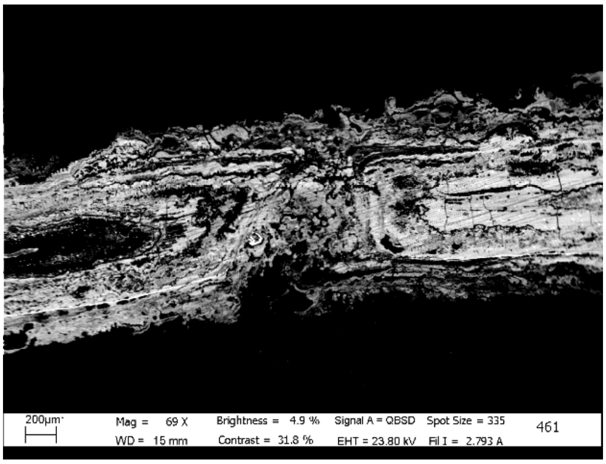

Figure 7. Sample CV-03 15-461 (object B), back-scattered electrons image showing two contiguous elements (possibly wires) with concentric corrosion structures

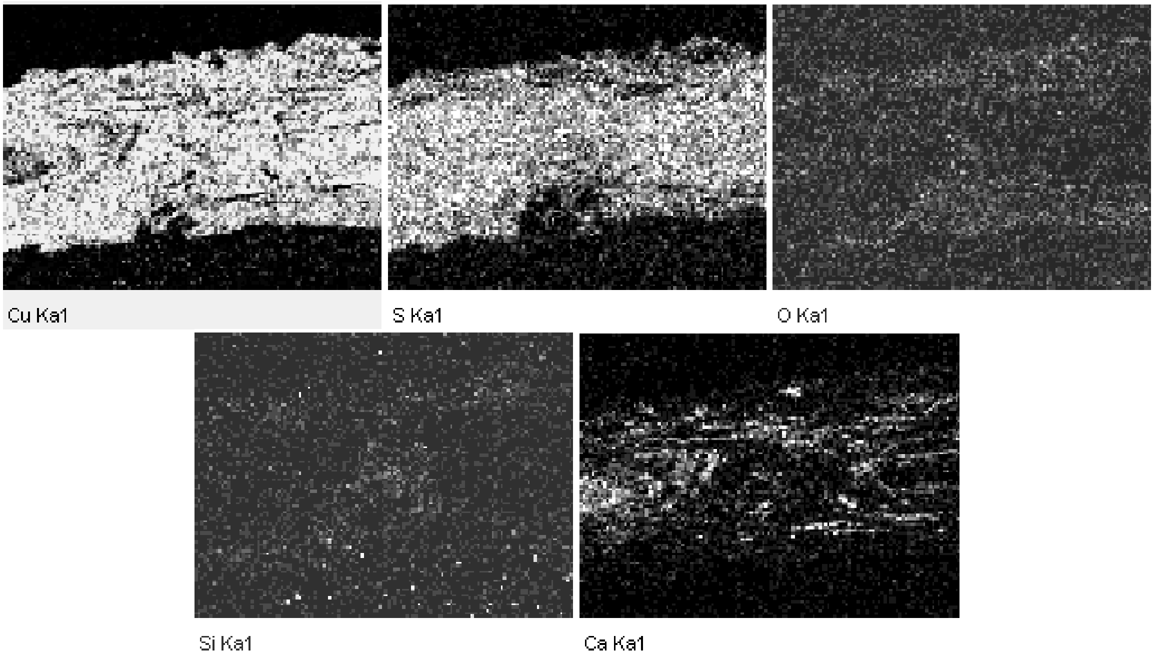

Figure 8. Sample CV-03 15-461 (object B), elemental maps concerning the area of Figure 7.

`The elemental maps (Figure 8) show that S and Cu are more or less homogeneously distributed all over the sample, whereas O is detected in the outer layers of the wires. Figure 9 shows the gold leaf and its surroundings; it is worth noting that among all the Calatrava samples, only this one has S above detection limits. The supposed copper sulphide appears both below and above the gilded surface, but it seems remarkably more solid in the interior parts (upper part of the image). Furthermore, the microanalysis shows 4-5% Au homogeneously distributed on the cross-section. No other elements, except those from soil contamination, are detected in significant amounts.

The interpretation of these data is not straightforward, as they are not completely consistent with the present knowledge of either niello or black-patinated bronze (Craddock et al., 1993), however the same reference, at p.120, reports a recipe, included in the Islamic texts of Zosimos, that involves the use of sulphur to produce a black-coloured copper. At present the experimental evidence only suggests the possible pertinence of the sample to a gilded decoration.

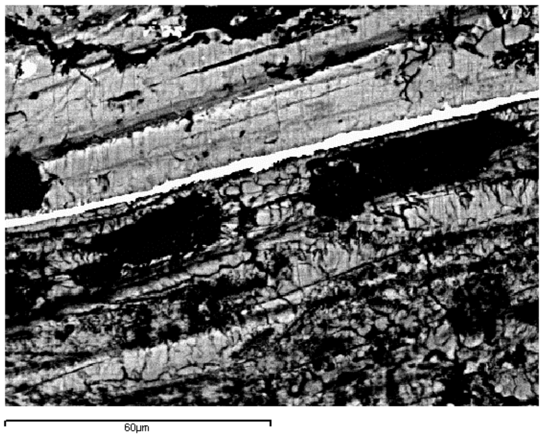

Figure 9. Sample CV-03 15-461 (object B), back-scattered electrons image of the gold leaf.

Sample CV-03 28-133 (Object C): the sample is deeply corroded (Figure 10); the alloy is a brass showing – in its uncorroded parts – the composition: Cu 87%, Zn 12%, Sn 1%. The most abundant corrosion products are copper chlorides, incorporating a few uncorroded grains; the maps in Figure 11 show a surface layer, probably made of redeposited metallic Cu and, above it an apparent Pb enrichment. The thinness of the latter layer suggests a deposition of Pb corrosion products (possibly carbonate) from the burial context, as the alloy does not contain significant amounts of Pb.

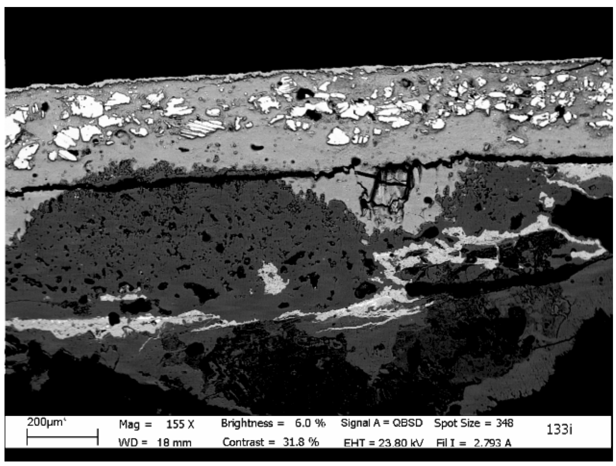

Figure 10. Sample CV-03 28-133 (object C), back-scattered electrons image of the sample's corrosion pattern.

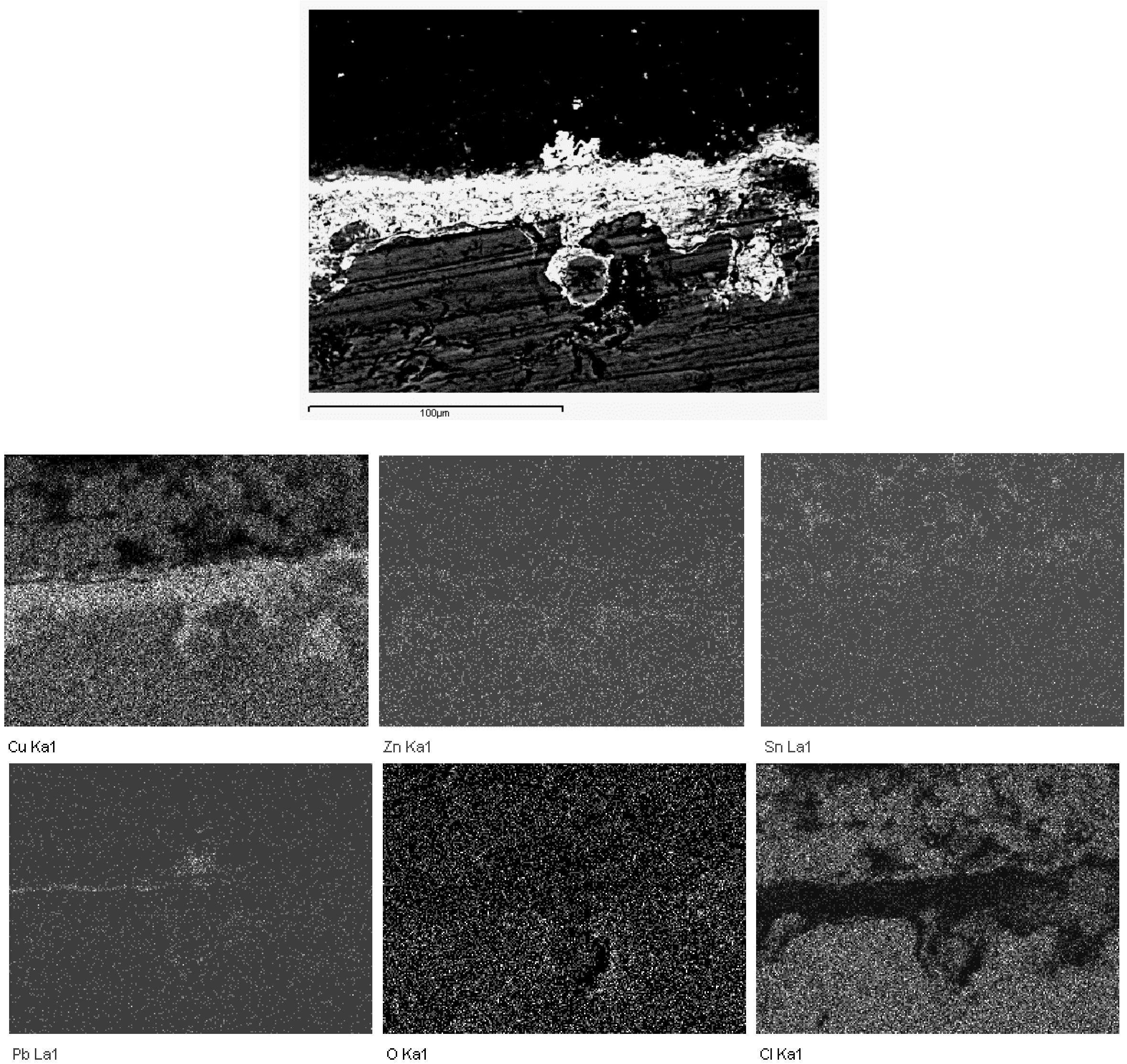

Figure 11. Sample CV-03 28-133 (object C), back-scattered electrons image and elemental maps showing form top to bottom: copper chlorides, a thin lead-enriched layer, a thicker layer of redeposited metallic copper, copper chlorides.

Sample CV-03 26-248 (Object D): this sample is deeply corroded (Figure 12); the alloy is a brass very similar to the previous one; its uncorroded parts show the composition: Cu: 86%, Zn 13%, Sn 1% with Pb just above the detection limits.

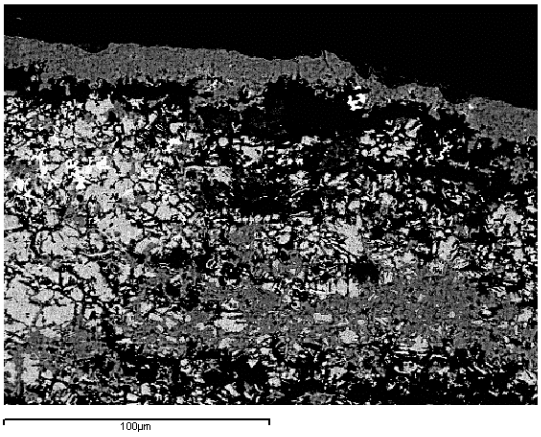

Figure 12. Sample CV-03 26-248 (object D), back-scattered electrons image showing the deep sample corrosion.

Sample CV-03 28-127 (Object E): the alloy (Figure 13) is a brass with composition: Cu 76%, Zn 18%, Sn 2%, Pb 4%. Before embedding the sample in the resin, it was also possible to observe the remains of fibres on the surface: these were identified as cotton (Figure 14).

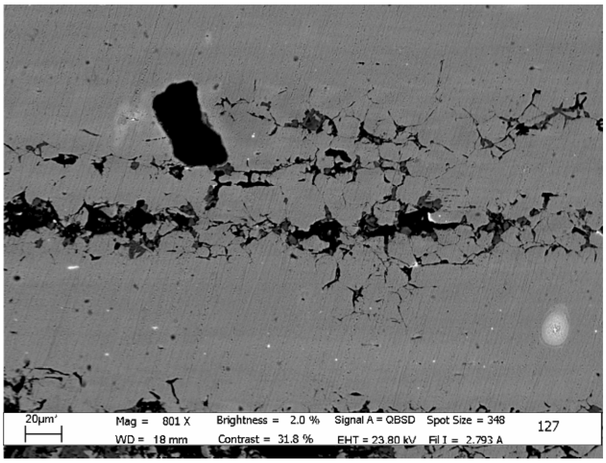

Figure 13. Sample CV-03 28-127 (object E), back-scattered electrons image of the cross-section.

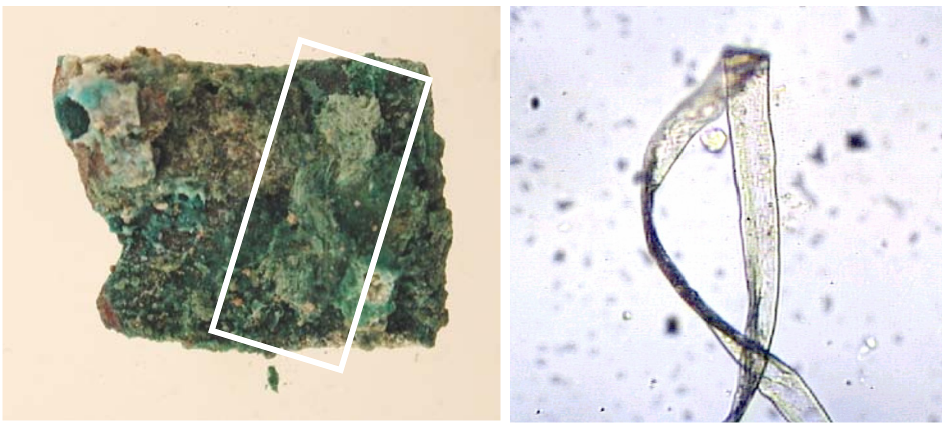

Figure 14. Sample CV-03 28-127 (object E), remains of textile fibres and (right) image of a single fibre (optical microscope, courtesy of A. Lentini, CNR-ITABC), identified as cotton.

5. Conclusions

The restoration of a second group of objects from the ancient city of Qalat Rabah (Calatrava la Vieja, Spain) was undertaken with the objectives of: first, recovering the intact gilded areas so as to read adequately the original surfaces; second, achieving a good metallic stability to provide for the future integrity of the pieces. The working protocol involved a combination of mechanical cleaning and physical-chemical cleaning and a final stabilization and inhibition treatment.

A further goal was to investigate the gilding technique, the alloys composition and the corrosion products. The presence of mercury and the partial overlapping of gold layers were observed; furthermore the gildings appeared solid, with no granular structure, and thinner than proper fire gildings. Such an experimental evidence is similar to that described in a previous work (Barrio *et al.*, 2003), however its interpretation needs to be someway revised. In the light of Anheuser's replication experiments, Oddy's theory of "cold mercury gilding" can be retained only if one assumes that mercury was spread in much lower amounts than Anheuser could achieve, which obviously opens the problem of how this was done. A second and opposing hypothesis is that of a traditional leaf gilding: where mercury has nothing to do with the gilding technique, it is already in the gold leaf and is possibly related to the techniques used to refine the gold or recover it from scrap materials. This hypothesis is also consistent with the fact that one of the gilded objects is made of leaded bronze (6% Pb), that in principle would be unsuitable for mercury gilding.

The sample (CV-03 15-461) from one of the two gilded objects is suspected to be a fragment of decoration: it seems to consist of two wires, twisted and hammered, with local gildings; the presence of gold and sulphur – this is the only sample from Calatrava in which sulphur was found. It evokes the Islamic texts of Zosimos and his recipe for the production of a black-coloured copper. As regards the composition of non-gilded objects, they are all made of brass; two (C and D) are compositionally similar; Object E provided the remains of textile fibres that were identified as cotton.

If one excludes the sample with sulphur, whose nature is not completely understood at the moment, quite common corrosion patterns were found; a peculiar structure was observed in one of the samples, consisting – from the surface inwards – in: a thin layer of lead corrosion products from the burial context, a thicker layer of redeposited metallic copper and, finally, copper chlorides resulting from the almost complete corrosion of the metal.

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