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Microanalyse
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STUDY OF A GOLD AND SILVER MASK WITH BLUE STONES
Assumed provenance and period: Peru, Sicán culture, 750 – 1375 CE.

Detail view of the object.

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NOTICE

The purpose of this study, performed following established norms of scientific integrity, is to carry out scientific investigations to provide analytical data concerning the manufacturing mode of the studied cultural property, the possible weathering of its constitutive material, either natural or artificial and to characterize the deposits or surface treatments on the object.

The investigations based on optical examination and physicochemical analyses of samplings of the object; follow the methods briefly described in the report, which are long-standing standards and protocols employed by the scientific community.

Comparison of the results obtained with the data actually available in the scientific community allows concluding if the physical evidences of the object are consistent or not with its supposed origin and period of time.

These scientific investigations are carried out not taking into consideration historical research, iconography and stylistics statements about the object. Information about provenance, period or attribution of the cultural property are under the responsibility of the owner or its authorized agent and written in the report only as indication. However, this given information is used in the discussion for final statement.

OBJECTIVES

Study of a gold and silver mask with blue stones
Assumed provenance and period: Peru, Sicán culture, 750 – 1375 CE.

Analysis of the metal to determine its composition. Analysis of the corrosion products, of the surface deposits and toolmarks to determine the preservation environment and detect whether artificial, modern altering processes have been used.

SYSTEMS USED

Inverted optical microscope; Stereomicroscope; Scanning electron microscope (SEM) with back-scattered electron (BSE, composition contrast) and secondary electron (SE, topographical contrast) imaging coupled with energy-dispersive X-ray element analysis (EDX); Semi-quantitative analysis (EDX).

SAMPLES

The following were analysed:

P1: metal sample taken at the top of the front, right side;
P2: metal sample taken at the top of the right ear;
P3: red deposit taken from the right cheek;
P4: green products taken from the back of the right ear;

Blue stone taken from the right ear;
Golden pendant taken from the left ear.

Sample P1 and P2 have been in first directly analyzed by SEM-EDX, then embedded in an epoxy resin to realize a microsection perpendicular to their surface.

The microsections and samples P3 and P4 were made conductive using carbon, for SEM examination.This is partly the cause of the carbon peak (C) observed in the elementary X-ray spectra.

The blue stone and the gold pendant have been analyzed directly, without any preparation.

ANALYSIS RESULTS

This study examined the composition of the metals, the condition of the surface, any surface deposits and toolmarks. The observations and analyses are illustrated on the following pages revealed that:

- The golden metal used to produce the object is a ternary gold based alloy. It has an average composition by weight of **61.4% gold, 34.9% silver and 3.3% copper with 0.4% nickel traces**. The same results are obtained for the golden pendant on the ears, indicating a probable contemporaneity of all the gold elements constituting the mask.

  The silver metal used to produce the ears of the mask is a binary alloy of **65.8% silver and 33.7% copper with 0.5% lead traces**.

  Both compositions are in accordance with alloys used in Sicán gold and silver objects.

- Numerous non-metallic inclusions have been observed on the silver alloy and result from a low refining of the metals used. This is compatible with ancient metallurgical techniques.

- The manufacturing of the mask is technologically in accordance with Sicán goldsmith techniques. Multidirectional and non-calibrated tool marks indicate a manual work with "traditional" uncalibrated tools.

- The blue stones decorating the mask correspond to "quartz chrysocolla". This type of stone exists in Peru and was used by pre-Columbians as "cultural turquoise".

- The surface of the mask revealed numerous corrosion products, principally silver chlorides, but also copper chlorides and copper carbonates.

Silver “whiskers” have also been observed on the gold surface and result from a corrosion in a very special environment with high sulfur and humidity.

- The depletion at grain boundaries, cracks and the blunt aspect of the tool marks on the surface of the gold sheets are signs of a probable antiquity of the object.

- Red deposits observed principally on the surface of the gold part of the mask are constituted of an ochre with iron oxides and reveal the high presence of sodium chloride salts that can originate from the environment or possibly from cultural preparation for burial.

- The presence of mineral phases in the corrosion product indicates that corrosion took place in a sandy burial conservation environment.

All these characteristics are consistent with the object's assumed age and origin.

Some restoration processes have been performed on the mask: a regluing of the blue stones and a probable deposition of a beige coarse grained material.

1. PRELIMINARY EXAMINATION

The mask is made out of a golden metal sheet (face, Fig. 2a) and dark grey metal sheets (ears, Fig. 2b).

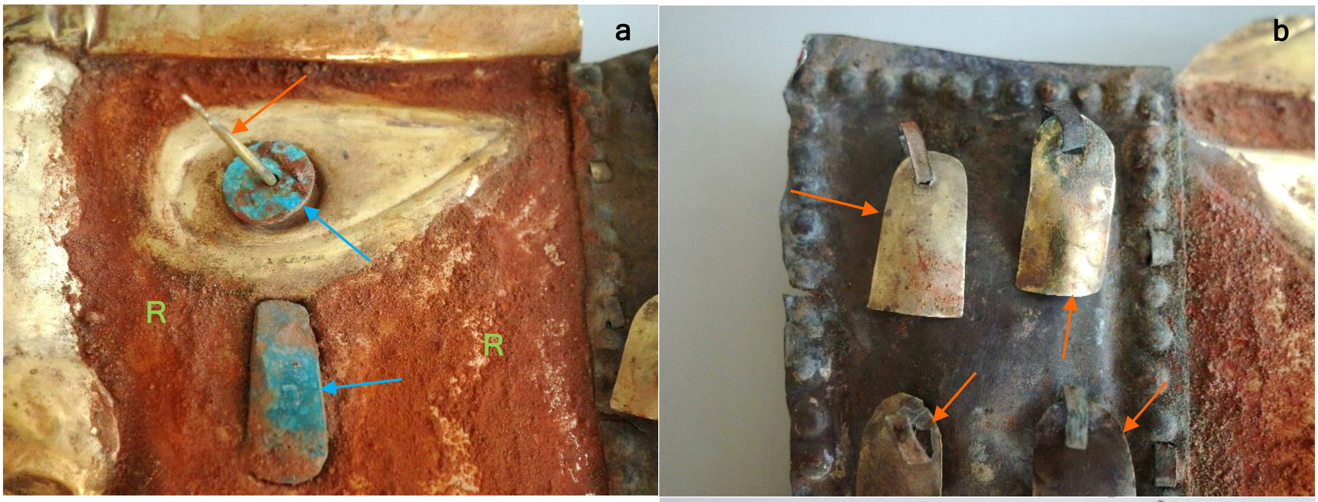


Figure 2. Detail views (photographs) of the surface of the mask.

Blue stones are fixed on the surface of the mask as decorative elements (Fig. 2a, blue arrows), as well as mobile elements, cut out of golden metal (Fig. 2a and b, orange arrows).

The golden face is partly covered with red product (Fig. 2a, **R**), also visible on ears surface (Fig. 2c, red arrows).

The ears are partially covered with green products (Fig. 2c, green arrows).

A beige deposit is also observed on every parts of the object (Fig. 2c, **D**)

Some cracks are visible on the edges of the gold part (Fig. 3a, arrows) and some desquamations of the black product (corrosion product) covering the ears reveal a shiny silver colored metal (Fig. 3b, arrows).

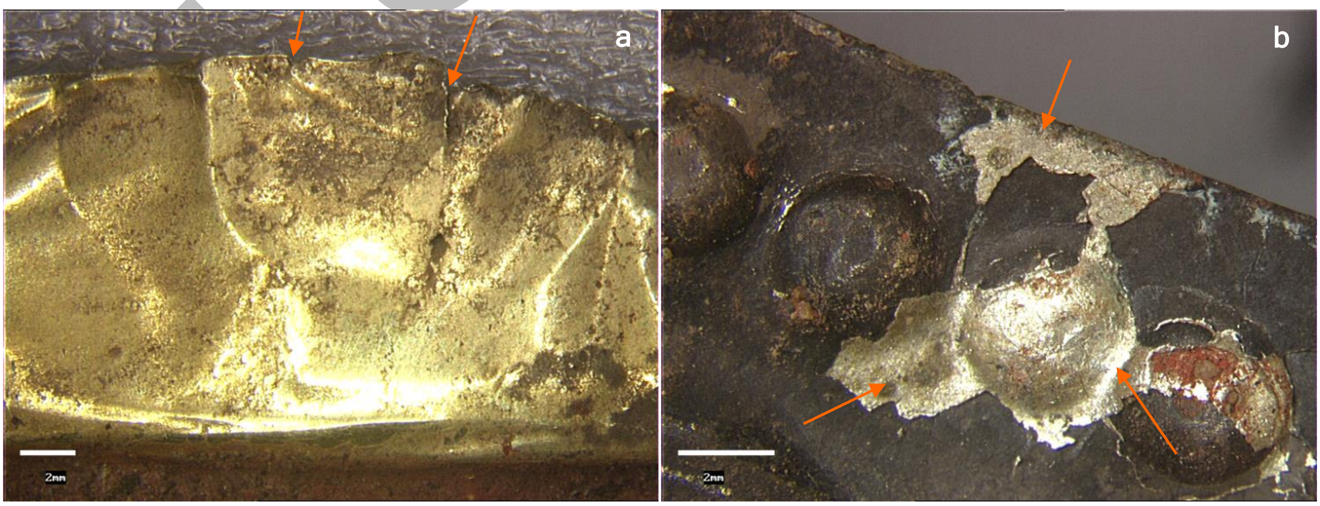


Figure 3. Detail views (stereoscopic microscope, **a-**, x5 and **b-**, x8) of the mask surface.

These first observations indicate an alteration of the metal sheets that have induced some fragility.

Eyes spikes have been made by rolling gold sheets (Fig. 4a) and ears pendants have just been cut out and slightly curved.

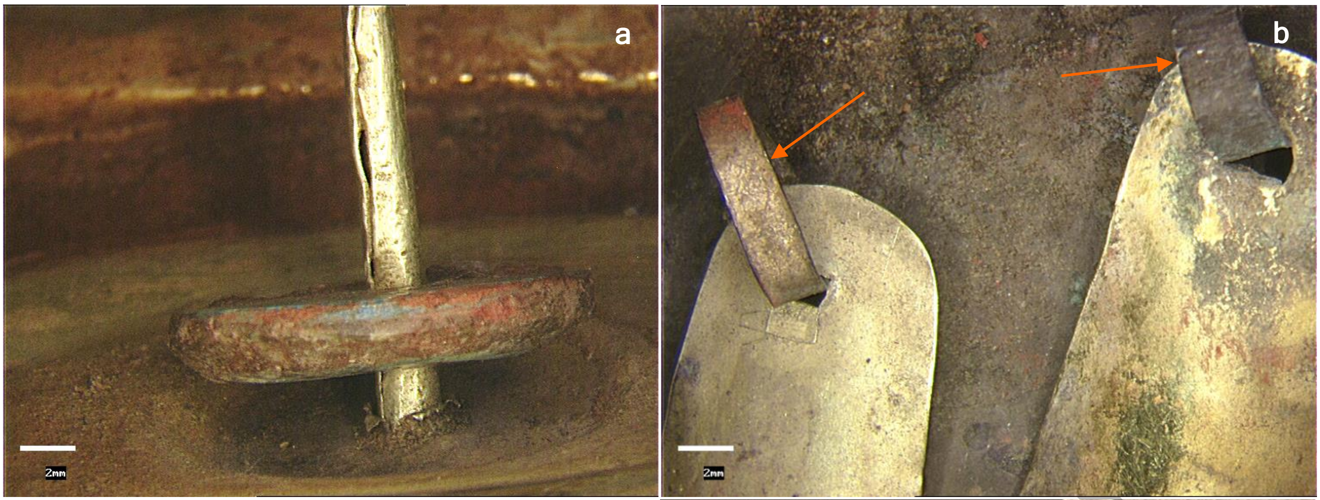
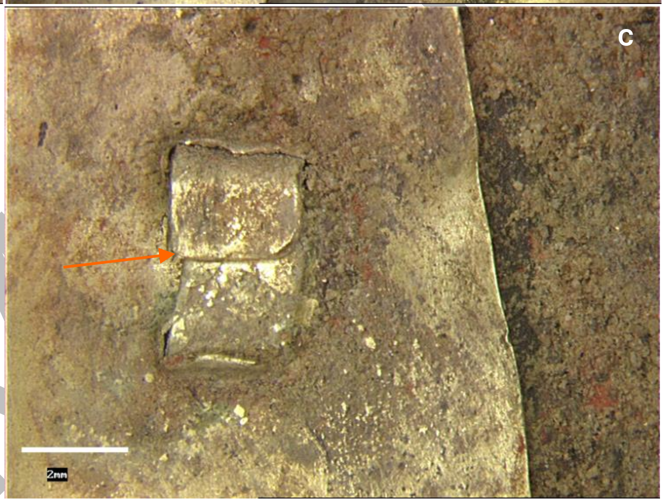


Figure 4. Detail views (stereoscopic microscope, **a-**, x5, **b-**, x5 and **c-**, x8) of the object surface.



The eyes spikes fixation consists to passing the spike through a hole cut in the gold sheet constituting the mask. The spikes are blocked in the back of the hole by flaring their base and in the front by placing a pierced blue stone.

Thin gold bands (tabs) are used to attach the pendants to the ears (Fig. 4b, arrows) and ears to the mask (Fig. 3c, arrow) through slots in the metal sheet.
The raised designs on the face and the ears were obtained by *repoussé* technique.

These elements are technologically in accordance with Sicán goldsmith techniques.

The close observation of the red products reveals that they overflow from the gold part to the silver ears (Fig. 5a, arrow).

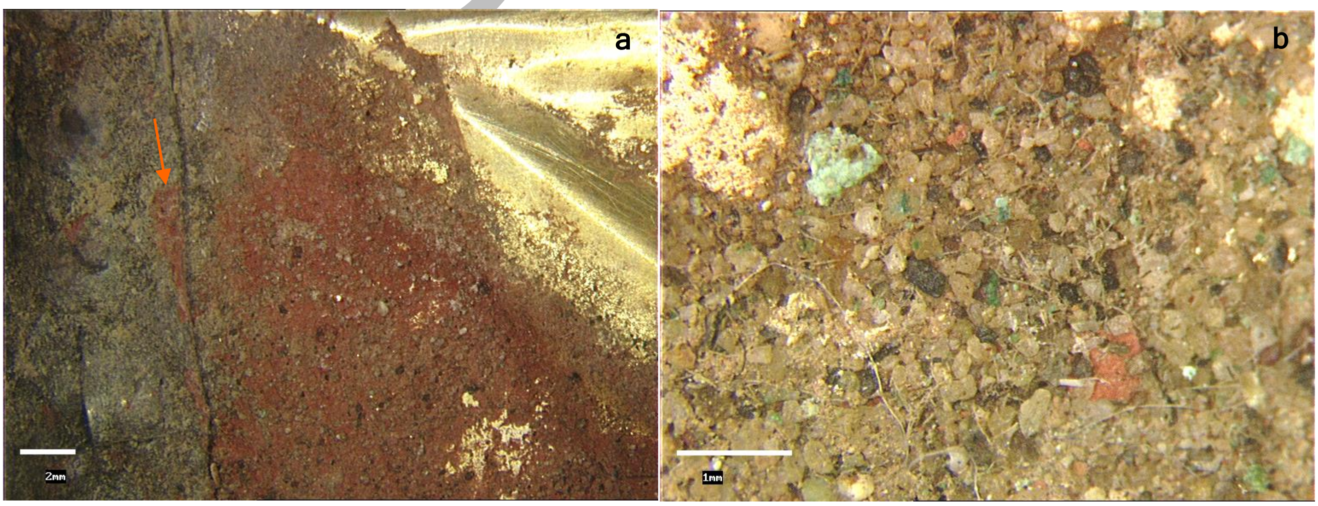


Figure 5. Detail views (stereoscopic microscope, **a-**, x12 and **b-**, x20) of deposits on the pendant surface.

The beige deposits, covering all the other products observed, has a coarse-grained aspect and seem to be an artificial mixing of beige, green, black and red particles with white fibers (Fig. 5b).

2. ANALYSIS OF THE METALS - CORROSION PROCESSES

Analysis of the metal and corrosion processes have been realized on a gold sample (Fig. 6a), a silver sample (Fig. 6b) and directly on a metal pendant (Fig. 6c).

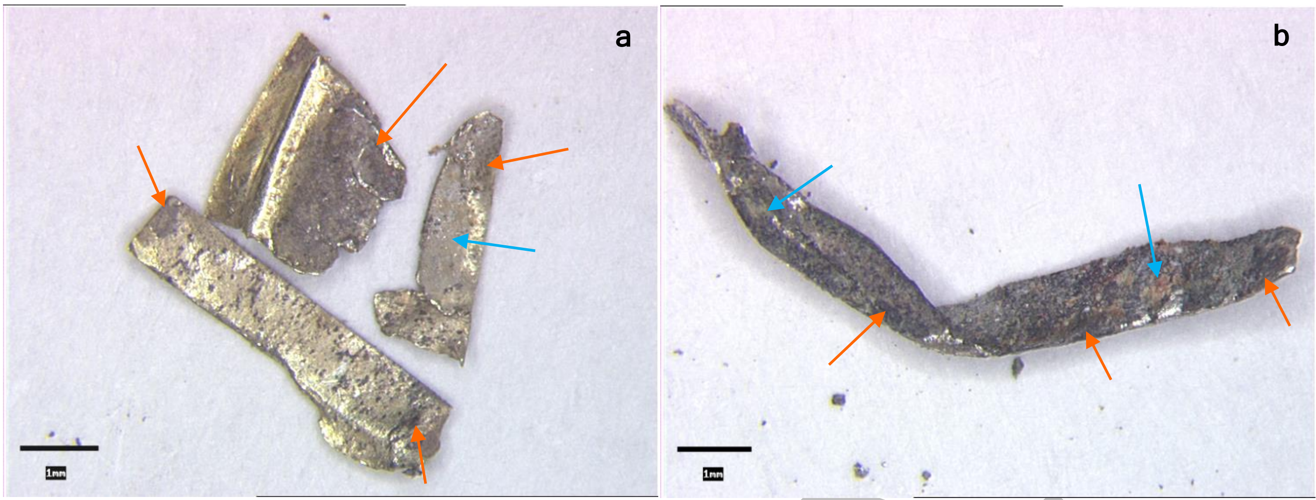


Figure 6. Overal views (stereoscopic microscope, x14) of sample P1 (**a-**), sample P2 (**b-**) and the golden pendant (**c-**).

These samples principally reveals black products on their surface (Fig. 6, orange arrows).

The beige deposit is also observed (blue arrows).

2.1. Analysis of sample P1.

Microsection of sample P1 (Fig. 7) shows a very homogeneous monophasic metal but with visible surface layering (Fig. 7, arrows) with deposits on its surface (**D**)

EDX semi-quantitative analysis was performed on the sample and reveals that the metal used to produce the face is a ternary gold-based alloy. It has a composition by weight of 61.4% gold, 34.9% silver, 3.3% copper and 0.4% nickel traces (table 1).

This composition is in accordance with other sicán object analyzed (Cesareo and al, 2009).

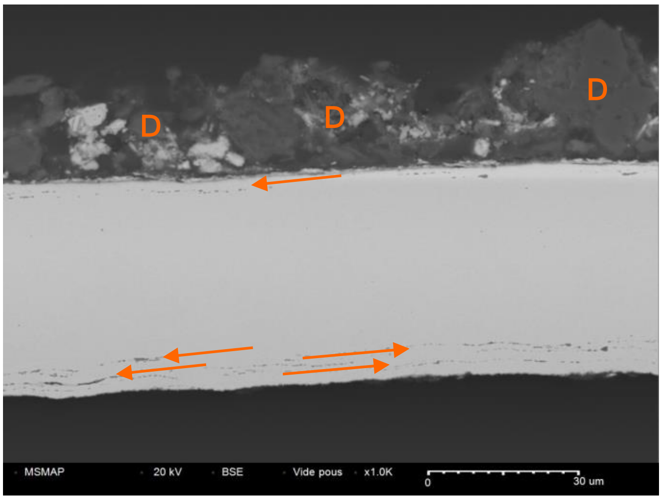


Figure 7. Vue de détail (MEB, ERD, x1000) de la microsection du prélèvement P1.

Elements	Au%	Ag%	Cu%	Ni%
P1	61.4	34.9	3.3	0.4

Table 1. Composition of the sample P1. Results are given in weight percent.

The surface layers correspond to copper oxide inclusions (Fig. 8a, arrows and Fig. 8b, **Cu**) of cuprite type.

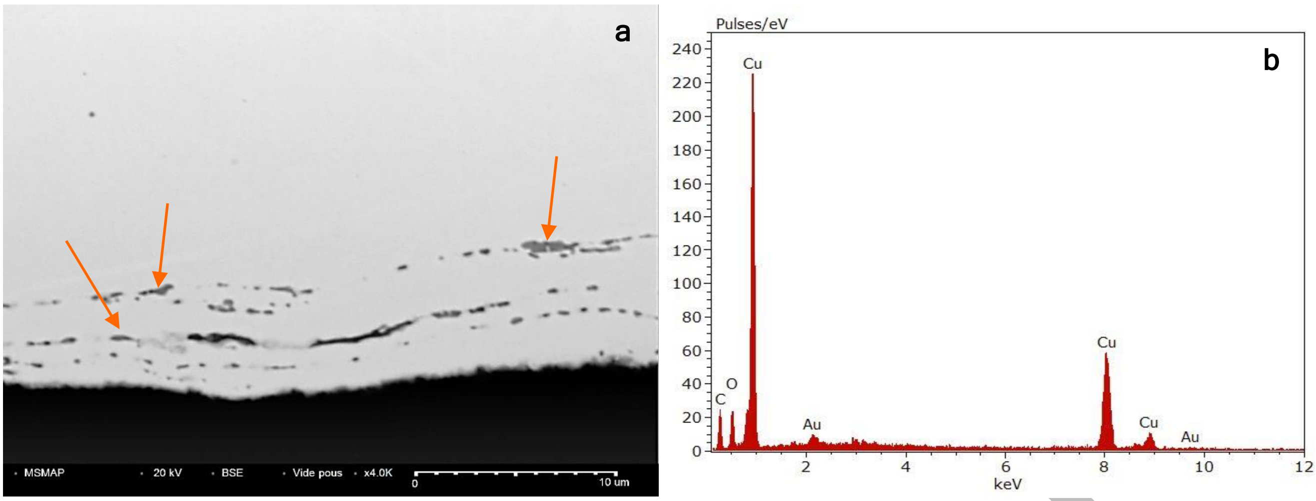


Figure 8. Detail view (**a-**, SEM, BSE, x4000) of the microsection P1 and EDX analysis spectrum (**b-**) of inclusions near the surface.

These inclusions are elongated and parallel to the surface and result from forging by successive hammering and annealing s to obtain the gold sheet out of an ingot.

The surface of the sample P1 (Fig. 9a) and corrosion products have been directly analyzed by SEM-EDX without any preparation of the sample.

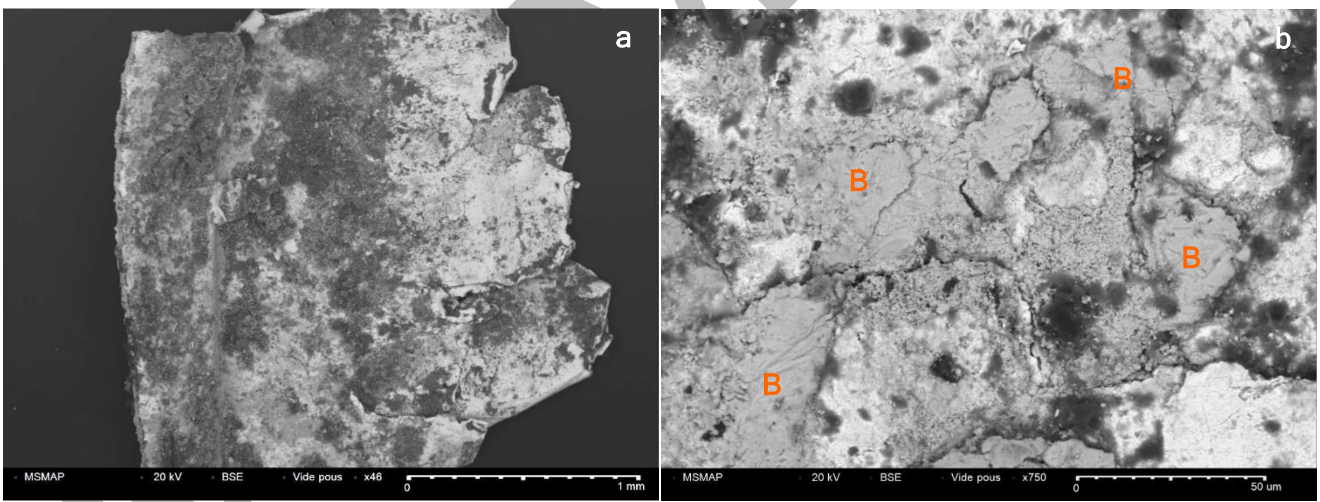
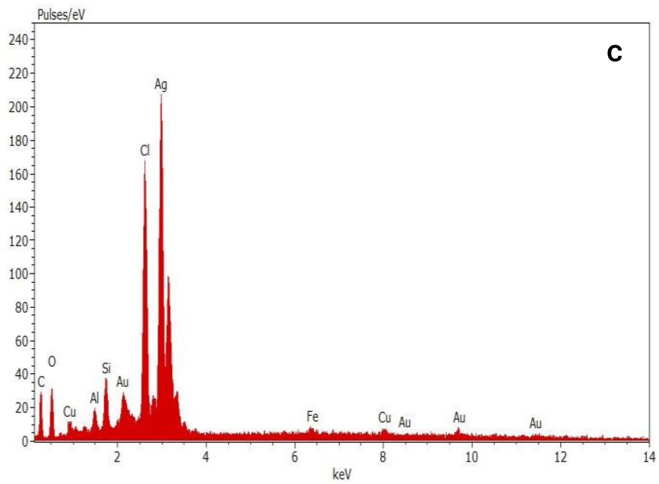


Figure 9. Detail view (SEM, BSE, **a-**, x46 and **b-**, x750) of the sample P1 and EDX analysis spectrum (**c-**) of the black deposits.



The black deposits (Fig. 9b, **B**) mostly observed on the surface of sample P1 are principally composed of silver chloride (Fig. 9c, **AgCl**), a natural corrosion product of the gold alloy, associated with aluminosilicate material (**Al**, **Si**, **Fe**) that may come from a burial conservation environment of the object.

Grey deposits are also visible on the surface of the gold sample and consist of filamentous structures (Fig. 10a) made of pure silver (Fig. 10b, **Ag**).

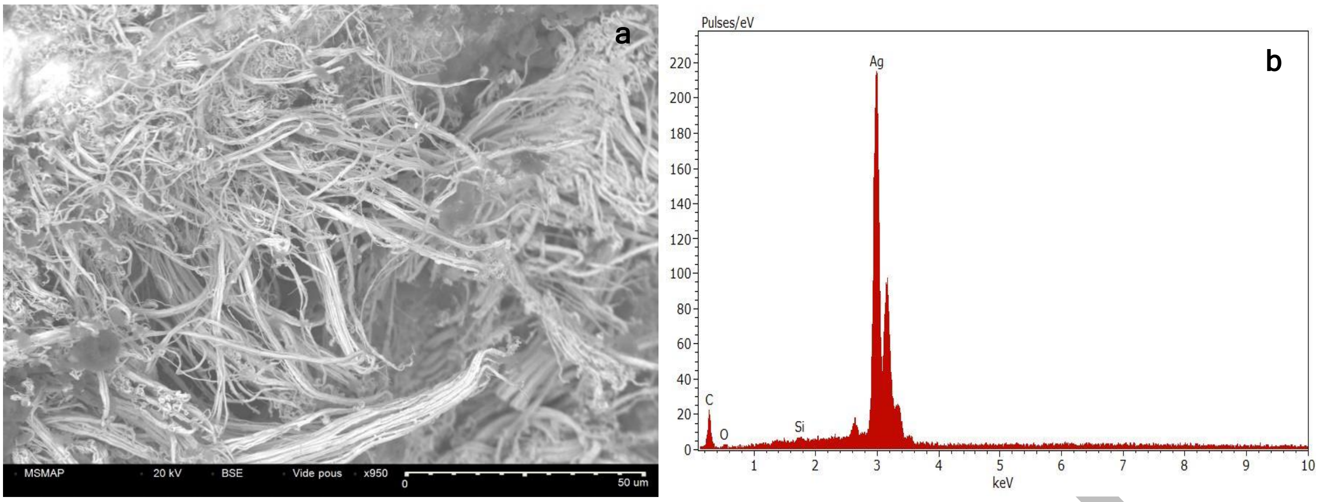
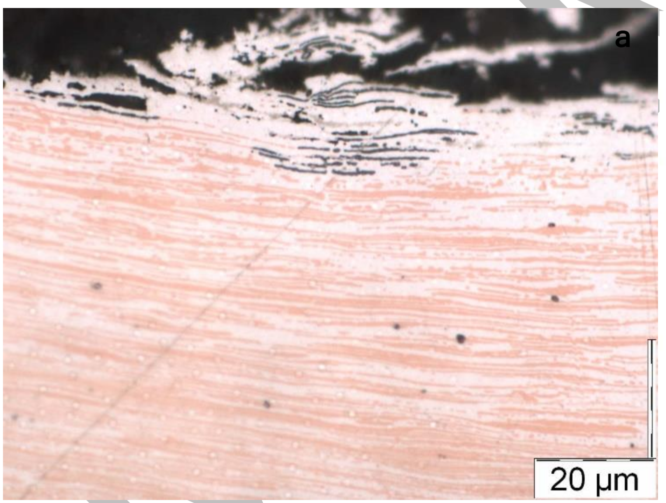


Figure 10. Detail view (**a-**, SEM, BSE, x950) and EDX analysis spectrum (**b-**) of filamentous structures growing up from the surface of the gold sheet. Sample P1.

These structures correspond to silver "whiskers" that can only appear on special conservation environment with high sulphur and high humidity content (Costa, 2001).

2.2. Analysis of sample P2.

Sample P2 revealed a biphasic structure (Fig. 11a) with a grey silver-rich phase (Fig. 11b, **Ag**) and a pink copper-rich phase (Fig. 11c, **Cu**).



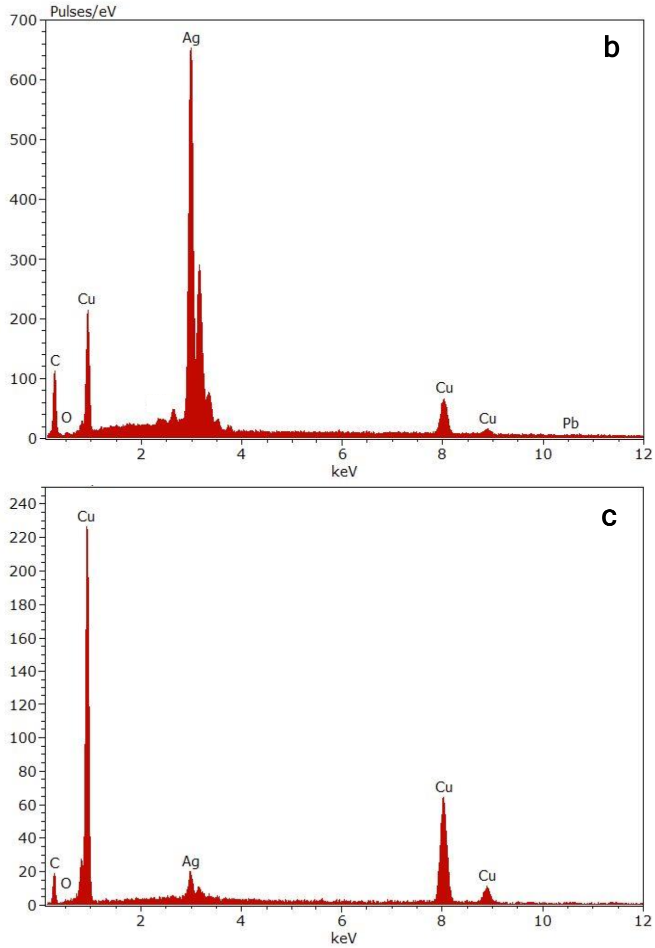


Figure 11. Detail view (**a-**, inverted optical microscope, reflected light, x1000) and EDX analysis spectra of the silver-rich phase (**b-**) and the copper-rich phase (**c-**). Sample P2.

The phases are elongated and parallel to the surface (Fig. 11a). This results from the extensive hammering and annealing to forge the silver sheet out of an ingot, as previously observed for the gold sheet.

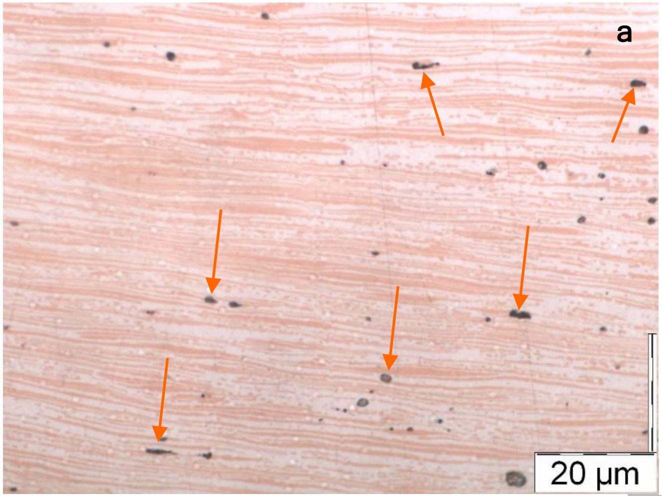
The surface of the sample reveals an important exfoliation (Fig. 11a, arrows) that results from the preferential depletion of the copper-rich phase.

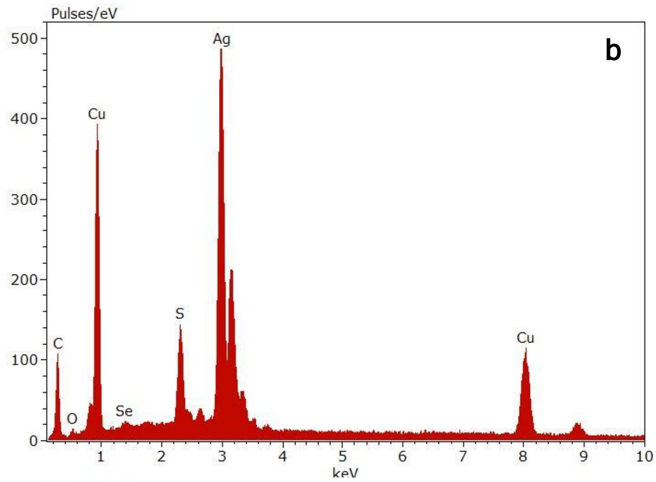
EDX semi-quantitative analysis was performed on the sample and reveals that the metal used to produce the ears is a binary silver-based alloy. It has a composition by weight of 65.8% silver, 33.7% copper and 0.5% lead traces (table 2).

Elements	Ag%	Cu%	Pb%
P2	65.8	33.7	0.5

Table 2. Composition of the sample P2. Results are given in weight percent.

The metal matrix reveals numerous non-metallic inclusions (Fig. 12a, arrows) that correspond to silver sulfo-selenide (Fig. 12b, **Ag**, **Se** and **S**) and arsenic copper associated with lead (Fig. 12c, **Cu**, **As** and **Pb**).





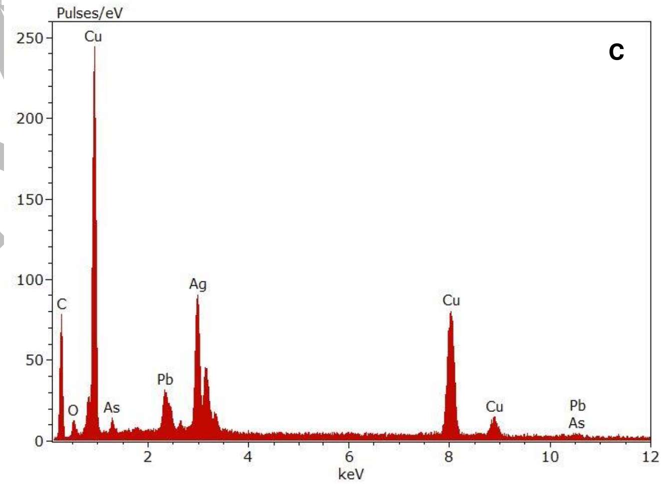


Figure 12. Detail view (**a-**, inverted optical microscope, reflected light, x1000) of the metal matrix and EDX analysis spectra (**b-** and **c-**) of non-metallic inclusions. Sample P2.

Sulfur (S), selenium (Se) and lead (Pb) also detected may originate from silver salts and lead copper ore (Palmer et al, 1998).

The presence of numerous inclusions can be indicative of a low refined alloy, in accordance with ancient metallurgical technique of refining.

A SEM-EDX analysis of the surface (Fig. 13) confirms that corrosion product of copper (**Cu**) principally, silver (**Ag**) and lead (**Pb**) have developed near the surface (Fig. 13a, **arrows**) and on the surface (**C**) of the metal.

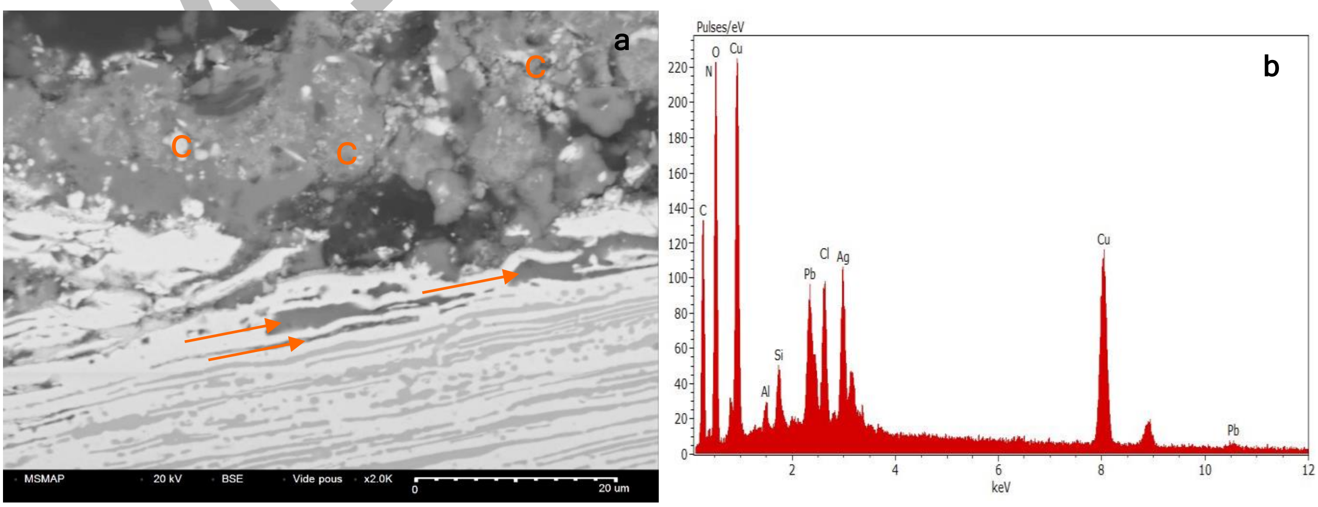


Figure 13. Detail view (**a-**, SEM, BSE, x2000) and EDX analysis spectrum of corrosion products near the surface of the metal. Sample P2.

The chlorine detected (Cl) is associated with silver chlorides. The presence of aluminum and silicon can be associated with an aluminosilicate material that may come from a burial conservation environment of the objects.

2.3. Analysis of the golden pendant.

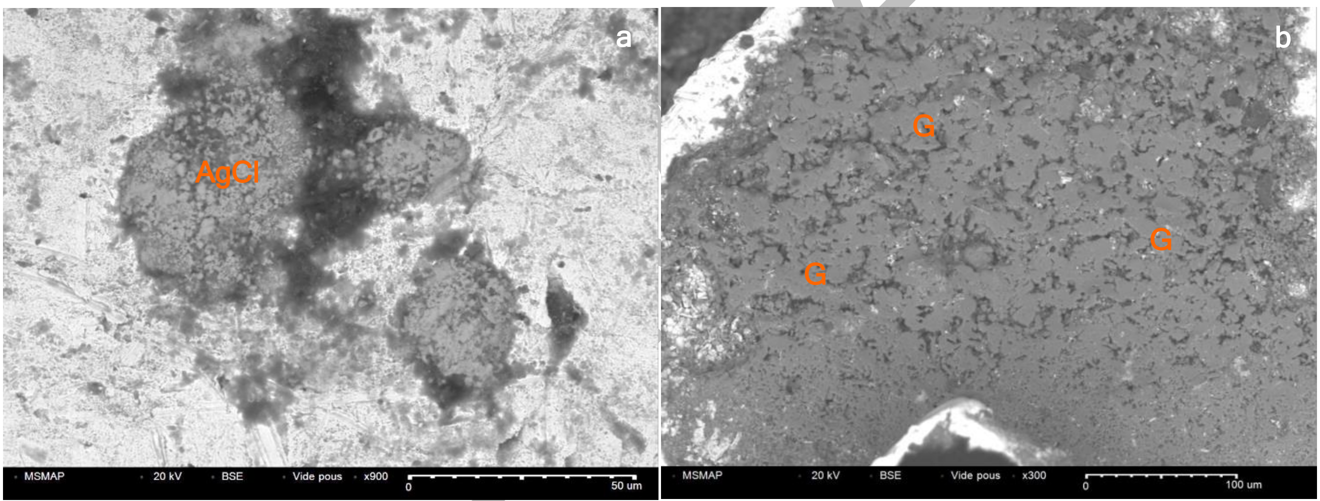
The golden pendant has been directly analyzed by SEM-EDX without any preparation. The EDX analysis of a clean area of metal reveals a composition (Table 3) similar to the alloy of the gold sheet used to make the face (cf. Table 1).

Elements	Au%	Ag%	Cu%
Pendant	61.0	34.9	4.1

Table 3. Composition of the pendant. Results are given in weight percent.

This indicates the use of the same alloy to create the golden part of the mask and the pendants. The very slight difference in composition and the absence of nickel detected may result from the direct analysis process, on the surface of the pendant instead of a microsection.

Black deposits are observed on the surface of the pendant and correspond to silver chlorides (Fig. 14a, **AgCl**).



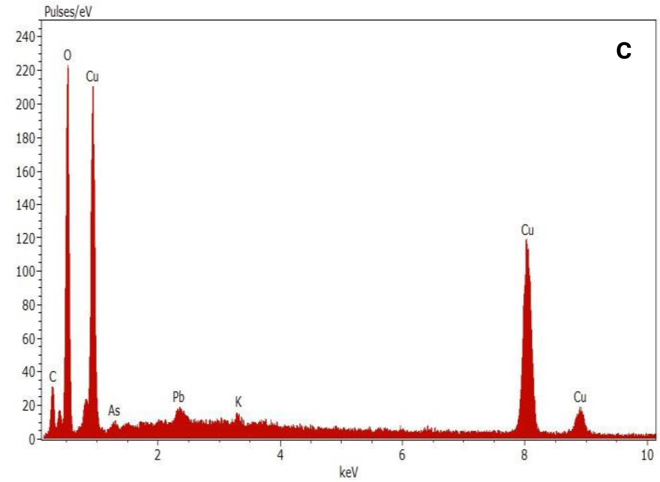


Figure 14. Detail view (SEM, BSE, **a-**, x900 and **b-**, x300) of the surface of the pendant and EDX analysis (**c-**) of the green corrosion products on it.

Green deposits also observed (Fig. 14b, **G**) correspond to copper carbonate recrystallizations (Fig. 14c, **Cu**).

*The flattened aspect of these copper carbonates seems to indicate that they have grown up between the pendant and another support. The presence of lead (**Pb**) and arsenic (**As**), only observed in the silver alloy, suggests these green products are in fact corrosion products from the silver sheet that have crystallized between the ear and the pendant.*

3. STUDY OF THE METALS SURFACE AND TOOL MARKS

Examination of **the surface of the gold sheets** (Fig. 15) reveals depletion at grain boundaries (Fig. 15a, orange arrows), micro-pitting (blue arrows) and cracks (Fig. 15b and c, arrows).

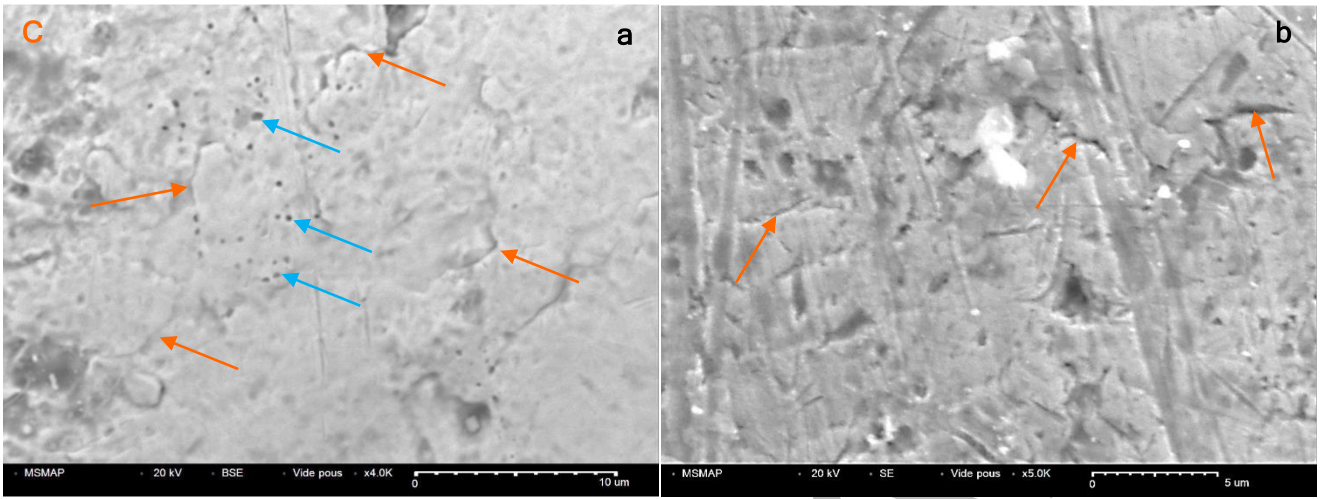


Figure 15. Detail views (SEM, **a-**, P1, ERD, x4000 and **b-** and **c-**, P2, SE, x500) of the surface of gold sheets.

These characteristics are significant of a long term weathering.

The tool marks observed on the surface of the gold are multidirectional and non-calibrated (Fig. 16a and b, orange arrows), they can correspond to a manual work with "traditional" uncalibrated tools.

The blunt aspect of the metal and of the tool marks is the indication of a certain antiquity of the metal.

Modern marks are visible (Fig. 16a and b, blue arrows) and come from the modern manipulation of the object.

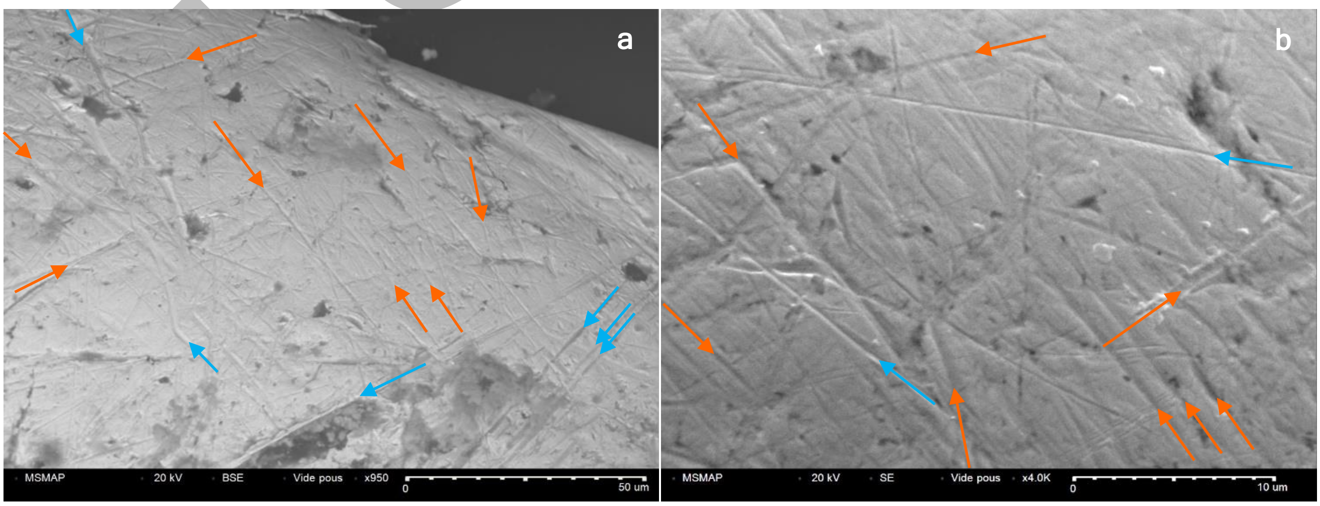


Figure 16. Detail views (SEM, **a-**, BSE, x950 and **b-**, SE, x4000) of the surface of the gold. Sample P1.

All these surface characteristics are in accordance with the antiquity of the object.

Examination of **the surface of the silver sheet** (Fig. 17) only reveals cracks (Fig. 17a, arrows) and exfoliations (Fig. 17b, arrows) resulting from the copper depletion previously observed on sample P2.

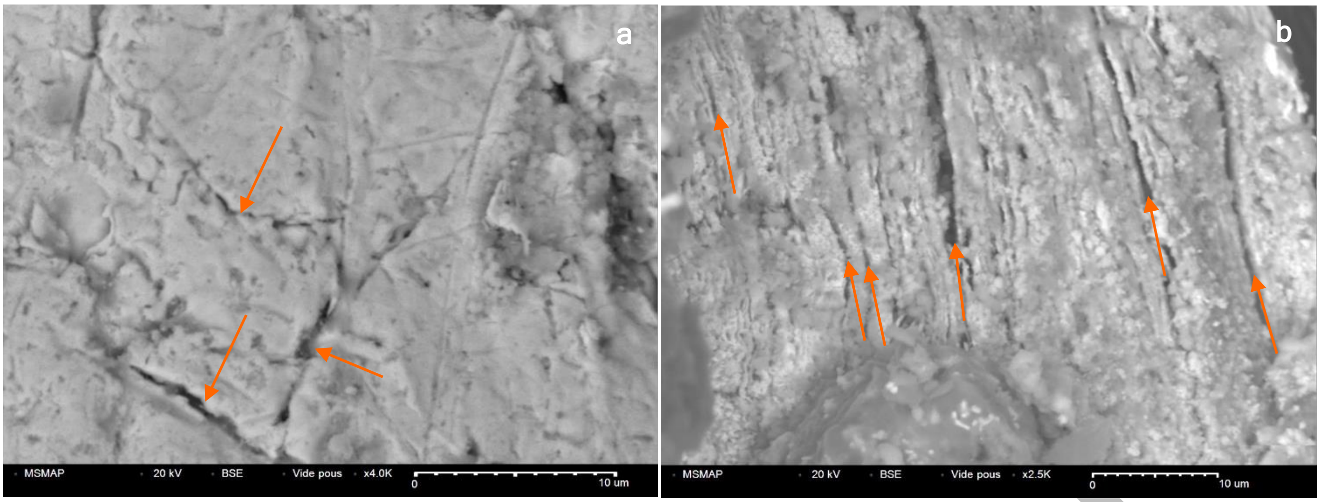
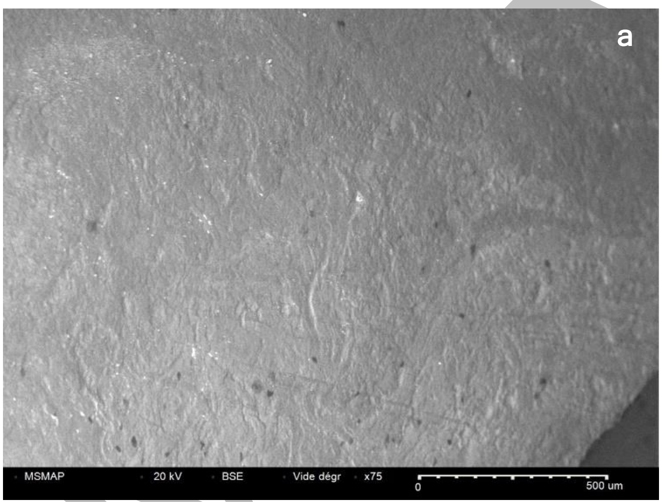


Figure 17. Detail views (SEM, BSE, a-, x4000 and b-, x2500) of the surface of the sample P2.

The conservation state of the silver sheet surface does not allow the observation a tool marks.

4 - STUDY OF THE BLUE STONES

The blue stones decorating the mask does not reveal crystalline structure (Fig. 18a) and has a high silicon content (Fig. 18b, **Si**) associated with copper (**Cu**) and aluminum (**Al**), and traces of magnesium (**Mg**), calcium (**Ca**) and iron (**Fe**). This cryptocrystalline mineral phase could correspond to **chrysocolla**.



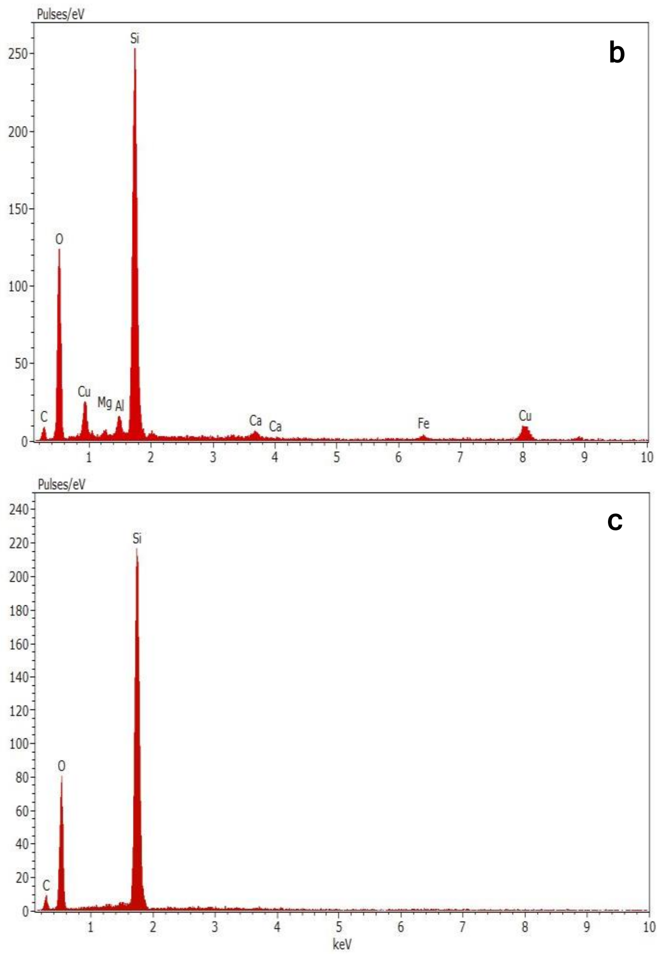


Figure 18. Detail view (**a-**, SEM, BSE, x75) of the surface of the blue stone and EDX analysis spectra (**a-** and **b-**) of the mineral phases analyzed.

Analysis of a white area of the stone also reveal presence of **quartz/chalcedony phases** (Fig. 18c, **Si**).

This stone must correspond to a “quartz chrysocolla”.

Chrysocolla exists in Peru and was used by Pre-Columbians as “cultural turquoise”.

No “modern” tool marks have been observed on the surface of the stones (Fig. 18b) which were thoroughly polished.

The stone was glued to the silver sheet with a thick brown material (Fig. 19a and b).

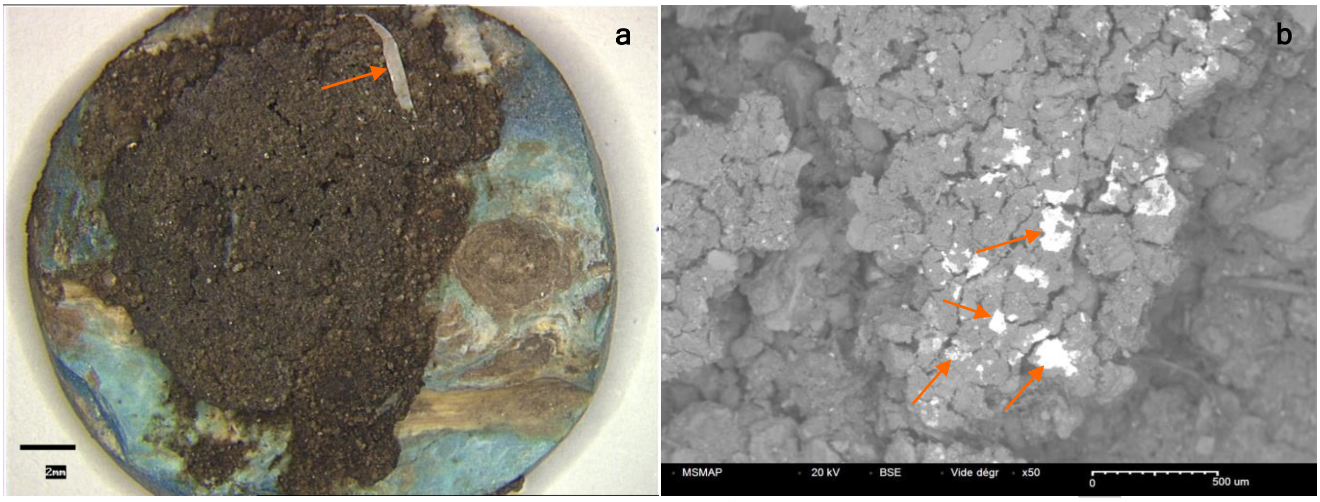
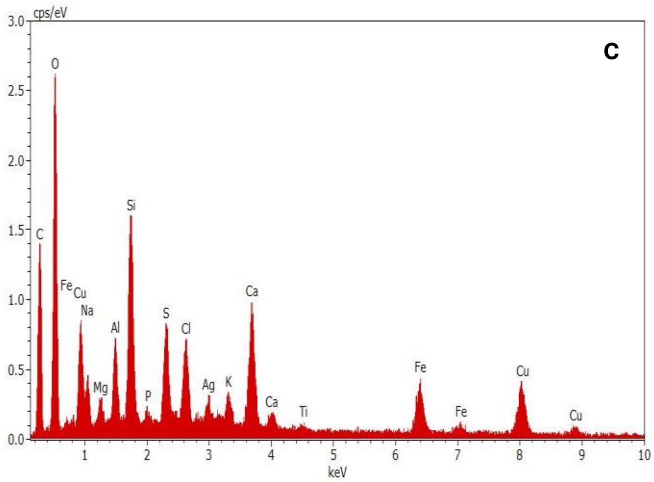


Figure 19. Detail views (**a-**, stereomicroscope, x5 and **b-**, SEM, BSE, x50) and EDX analysis spectrum of the brown material under the blue stone.



This material shows a complex composition (Fig. 19c) that reveals the presence of organic matter (**C**) probably a glue, aluminosilicate products (**Na**, **Mg**, **Al**, **Si**, **K**, **Ti**), probable calcium carbonates (**Ca**), important chlorine (**Cl**) and sulfur (**S**) probably associated with corrosion product of copper (**Cu**) and silver (**Si**).

The iron (**Fe**) is associated with chlorine (**Cl**) as "ferric chloride" (Fig. 19b, arrows). This product is generally used as an etchant product on the surface of metal.

Here, it is difficult to say if the origin of this product is artificial or natural because of the apparently natural high salinity of the conservation environment (see Fig. 21).

The white fiber (Fig. 19a, arrow) is modern (synthetic) and is completely enclosed in the brown material. This is evidence that there is a probable regluing of the stone.

The blues stones ("quartz chrysocolla") can result from an ancient manual work, compatible with pre-Columbian lapidary techniques. There is evidence of a modern restoration regluing.

5. STUDY OF THE DEPOSITS

Red, green and beige deposits have also been observed on the surface of the mask.

The red deposits (Fig. 20a) covering the face are constituted with aluminosilicate material (Fig. 20b, **Al**, **Si**, **K**) associated with iron oxides (**Fe**).

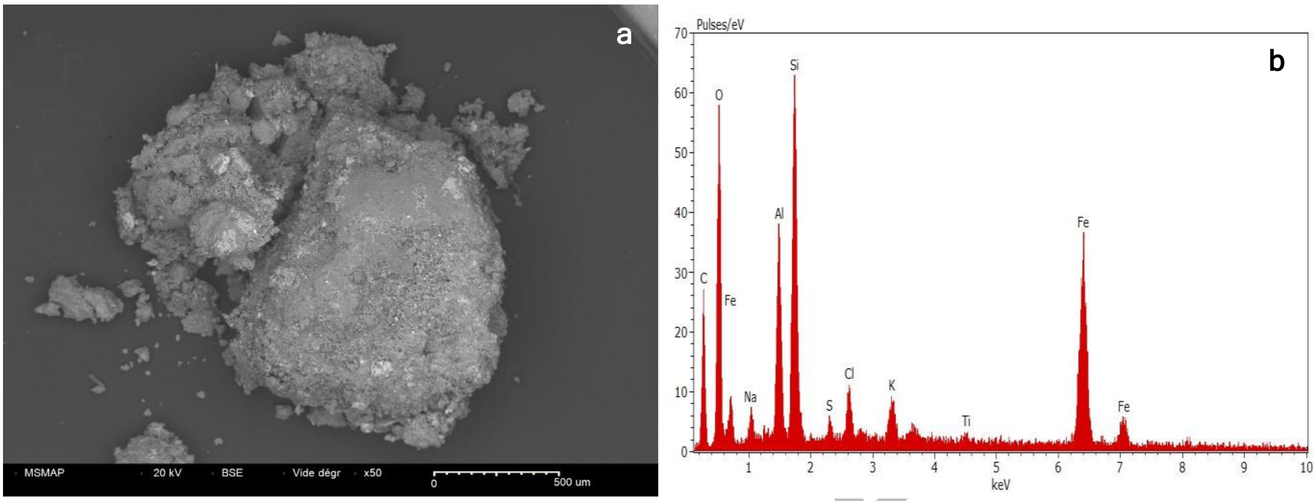


Figure 20. Detail view (**a-**, SEM, BSE, x50) and EDX analysis spectrum (**b-**) of the red deposit. Sample P3.

The sodium (**Na**) and the chlorine (**Cl**) detected are associated to numerous sodium chloride phases (Fig. 21a and b, **NaCl**) present in the deposits.

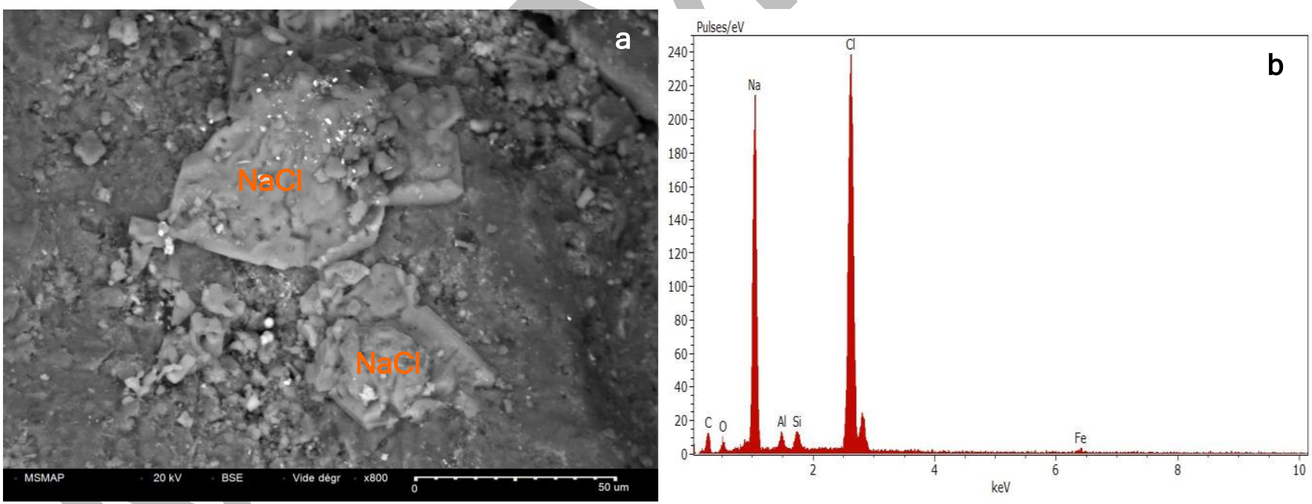
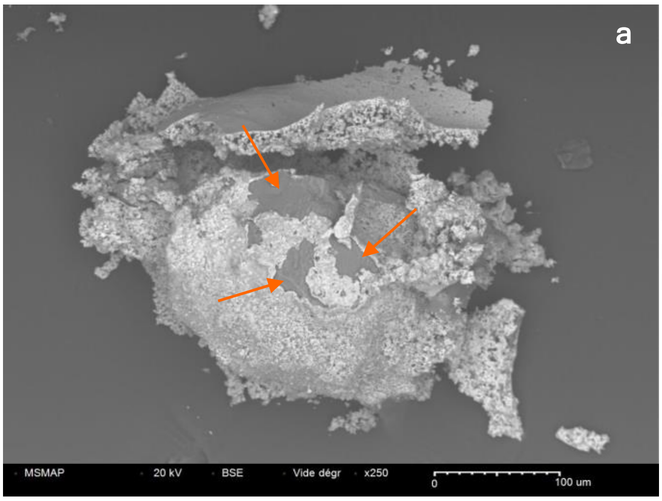


Figure 21. Detail view (**a-**, SEM, BSE, 800) of the sample P3 and EDX analysis spectrum of sodium chloride phase **(b-**).

The sodium chloride salts and the sulfur detected can originate from the burial environment or possibly from a cultural preparation for burial, as observed in Moche and Lambayeque coastal desert burial sites (Kempson, 2003).

The green deposits (Fig. 22a) coming from the surface of the silver ears are composed by copper chlorides (Fig. 22b, **CuCl**), a natural corrosion product of the copper constituting the alloy, in a chlorine-rich environment.



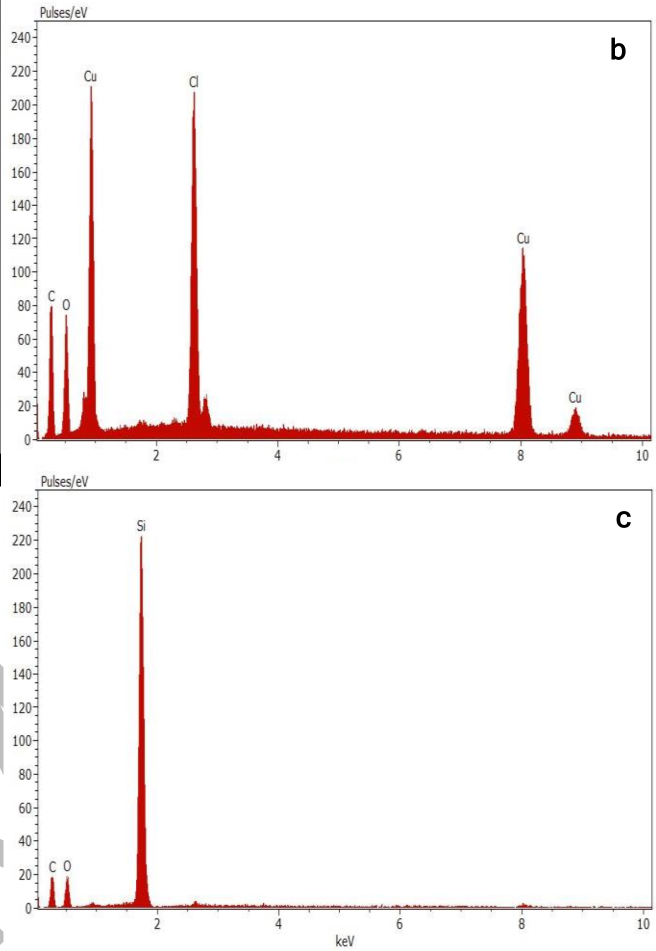


Figure 22. Detail view (**a-**, SEM, BSE, 250) and EDX analysis spectrum (**b-**) of the green corrosion products. EDX analysis spectrum (**c-**) of quartz taken by the corrosion products. Sample P4.

Mineral phases (Fig. 22a, arrows) are enclosed in the green corrosion products. There are mainly rounded quartz phases (Fig. 22c, **Si**).

This confirms that corrosion occurs in a burial environment, probably of sandy type.

The beige deposit, visible all over the surface of the mask contains particles of lead carbonates (Fig. 23a, arrows and Fig. 23b, **Pb**) corresponding to the use of white lead pigment.

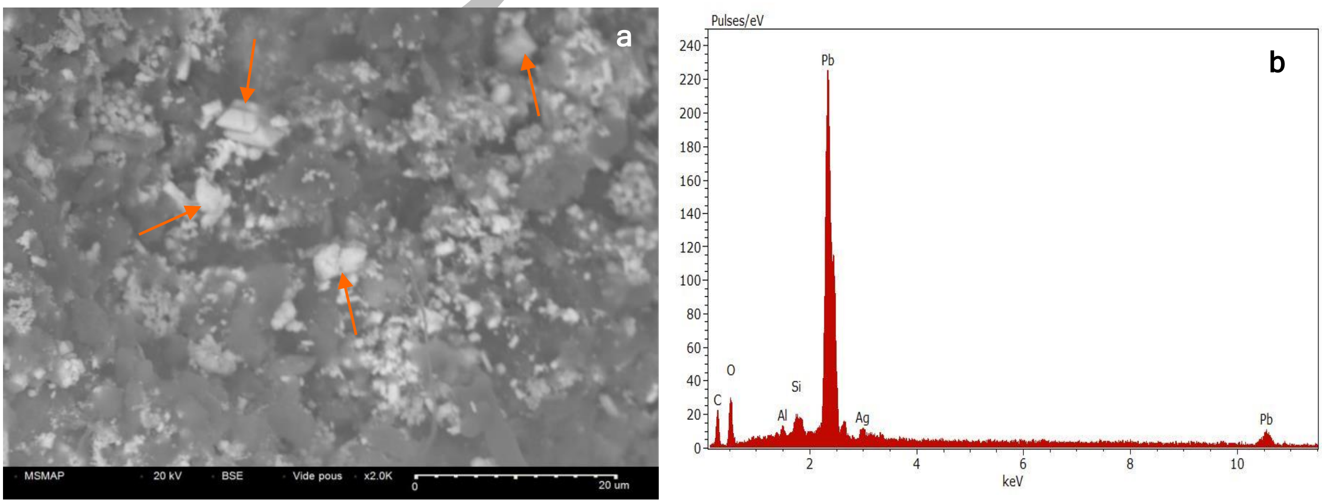


Figure 23. Detail view (**a-**, SEM, BSE, x2000) of the beige deposit and EDX analysis spectrum of white lead particles. Sample P1.

The white lead pigment was not knew and used by pre-Columbian civilization. *It is evidence that the beige deposit is artificial, probably related to a restoration phase of the object.*

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