

FUNERAL MASK IVC 11595 – CU/AG, WITH SURFACE ENRICHMENT (AG)

Artefact name Funeral mask Ivc 11595

Authors

Url /artefacts/400/

∨ The object



Fig. 1: Funeral mask, front and back face to the left and right respectively,

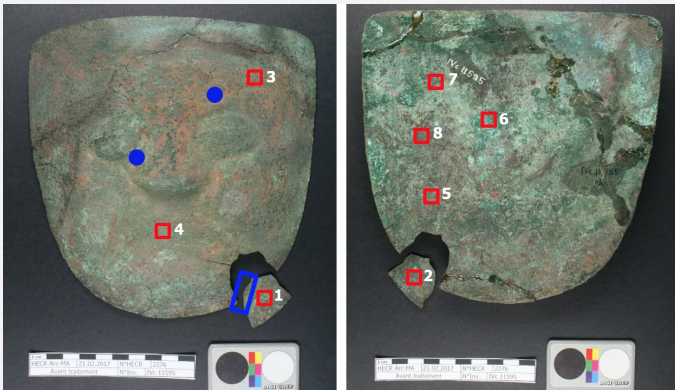
Credit HE-Arc CR, N. Gutknecht.

∨ Description and visual observation

Description of the artefact	The object is a funeral mask made from a copper alloy (Fig. 1). There are remains of red pigment and of a mineralised textile on the both sides of the object. It is heavily corroded in green and red corrosion layers. It is deformed and broken. Dimensions: Length = 180mm; Width = 170mm; Height = 20 mm; WT = 158,6g.
Type of artefact	Funeral mask
Origin	Peru, north coast
Recovering date	Date of excavation unknown, acquisition in 1967
Chronology category	None
chronology tpq	<input type="text" value=""/> ---- ▾
chronology taq	<input type="text" value="1500"/> A.D. ▾
Chronology comment	Tpq (earliest): unknown, Taq (latest): 1500

Burial conditions / environment	Unknown
Artefact location	Museum der Kulturen, Basel
Owner	Museum der Kulturen, Basel
Inv. number	IVc 11595
Recorded conservation data	No recorded conservation data.

Study area(s)

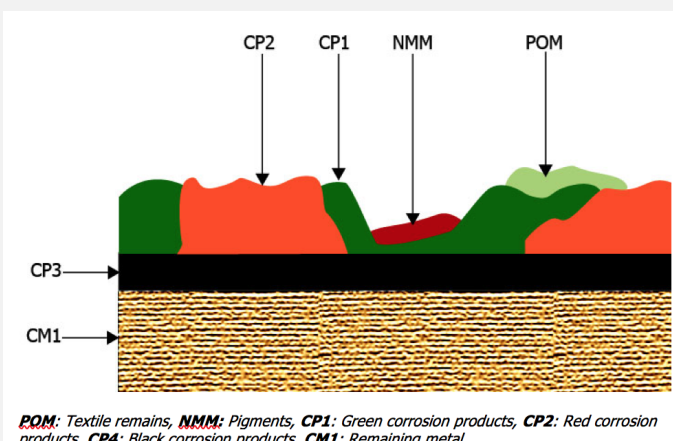


Credit HE-Arc CR, N. Gutknecht.

Fig. 2: Location of XRF analyses (red squares), cross-section area (blue square) and sampling areas for SEM-EDS (blue points),

Binocular observation and representation of the corrosion structure

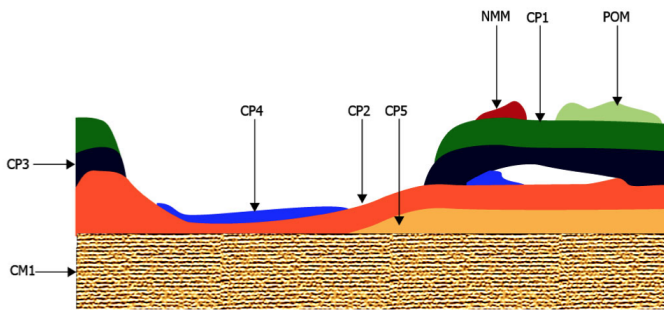
The schematic representation below gives an overview of the corrosion layers encountered on the object from visual macroscopic observation. The first stratigraphy (Fig. 3a) is for the front, while the second (Fig. 3b) represents the back.



Credit HE-Arc CR, N. Gutknecht.

Fig. 3a: Stratigraphic representation of the artefact in cross-section by macroscopic observation, face of the object,

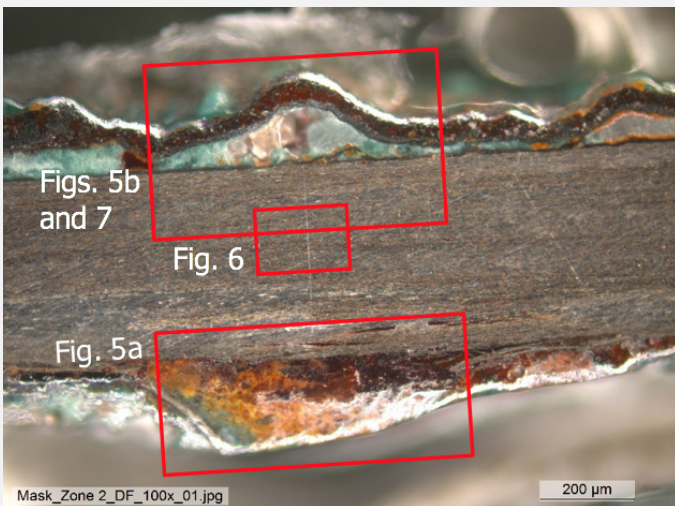
Fig. 3b: Stratigraphic representation of the artefact in cross-section by macroscopic observation, back of the object,



POM: Textile remains, **NMM:** Pigments, **CP1:** Green corrosion products, **CP2:** Red/orange corrosion products, **CP3:** Black corrosion product, **CP4:** blue corrosion product, **CP5:** Orange corrosion, **CM1:** Remaining metal
 Credit HE-Arc CR, N. Gutknecht

∨ MiCorr stratigraphy(ies) – Bi

∨ Sample(s)



Mask_Zone 2_DF_100x_01.jpg
 Credit HE-Arc CR, N. Gutknecht.

Fig. 4: Micrograph of the cross-section showing the locations of Figs. 5a (corresponding to the front of the object), Fig. 5b (back of the object), Figs. 6 and 7,

Description of sample

A polished section was made from an already detached fragment that was temporarily embedded in resin (Fig. 2). On Fig. 4 the upper part of the sample corresponds to the exterior (front) face of the object. Both sides have developed subsequent layers of corrosion. In areas, these have buckled and become detached.

Alloy

Cu/Ag, with surface enrichment (Ag)

Technology

Hammered and annealed, surface depletion

Lab number of sample

None

Responsible institution

Museum der Kulturen, Basel

Date and aim of sampling

2017, metallography and chemical analyses

∨ Analyses and results

XRF with portable X-ray fluorescence spectrometer (NITON XL3t 950 Air GOLDD+ analyser, Thermo Fischer®), SEM/EDS (with an acceleration voltage of 20 kV) and Raman spectroscopy.

∨ Non invasive analysis

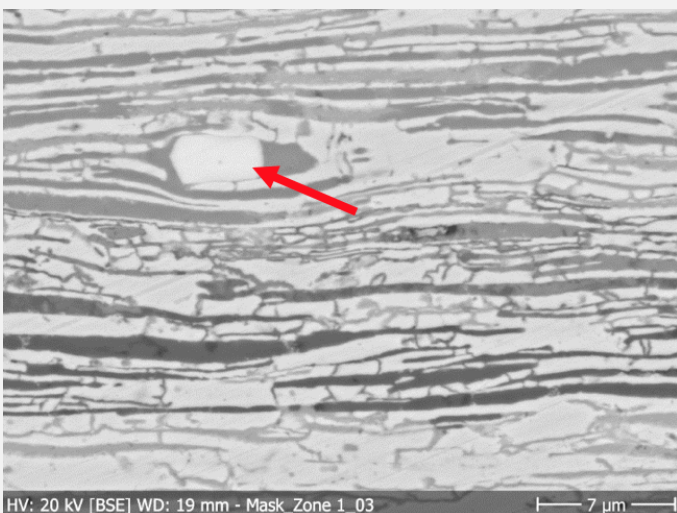
∨ Metal

The metal is a copper-silver alloy with traces of Pb and As. The surface has been decuprified according to the tumbaga making process (Scott, D. (2000) and McEwan, C (ed.) (2000)). This pre-Columbian surface enriching technique results in a silver looking object, even though the general silver content is low (about 30%). The metalsmith would repeatedly hammer and anneal the metal, which would create a copper oxide scale on the surface. The latter was then dissolved in acidic plant juices (Scott, D. (2000)). This process was repeated until the surface was enriched with silver, giving it the appearance of a silver artefact.

It is impossible to know the original alloy composition, as the proportions have changed through corrosion and migration of elements. Nevertheless, the inner metal is reddish, which could indicate a 30% silver content for 70% copper. The silver-rich surface has been further enriched by the migration of copper ions that have formed the thick corrosion crust on top of the original surface.

The XRF analysis is a surface analysis that was done without any removal of the copper corrosion products. The proportions are given for the oxide on the surface. The SEM/EDS analysis shows that there are Cu-rich phases alternating with Ag-rich phases. There are inclusions of Pb and As (Fig. 6). Cl has been detected throughout the entire corroded metal, most likely in the form of Cu and Ag corrosion products.

A layer of mercury can be seen with EDS (Figs. 7 and 8). Mercury was not used by the pre-Columbians in metallic form (Scott, D. (2000) and McEwan, C (ed.) (2000)) but was common as a pigment in form of mercury sulfide (cinnabar).



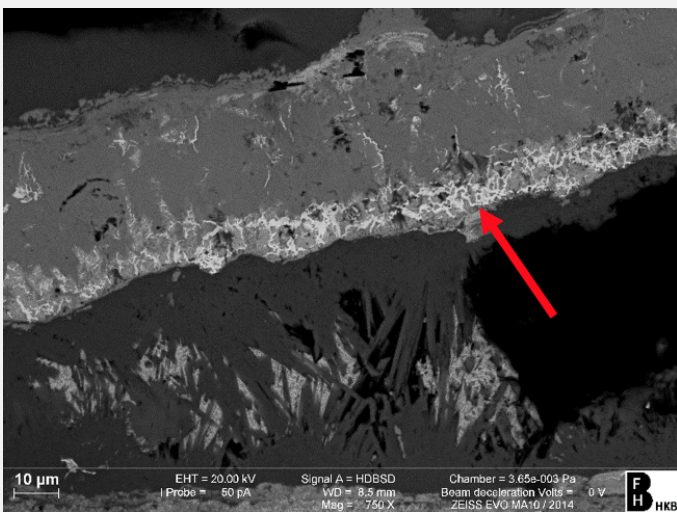
Credit HEI Arc, S. Ramseyer.

Fig. 6: SEM image (BSE-mode) of a selected area in the middle of the cross-section from Fig. 4 (detail), the elongated grains are the result of repeated hammering. Absence of strain lines indicates that the metal is annealed. The darker areas are Cu-rich phases and the lighter areas are Ag-rich phases. The arrow shows an As- and Pb inclusion,

Fig. 7: SEM image (BSE-mode) of the metal sample from Fig. 4 (detail), the mapped areas (Figs. 8, left and 9, right) are marked by red rectangles,



Fig. 8: SEM image of a partially refilled structural void with a silver-, copper- and mercury-rich layer (red arrow),



Microstructure	None
First metal element	Cu
Other metal elements	As, Ag, Pb

Corrosion layers

The remaining metal shows a preferential corrosion of copper and a presence of chlorides (Fig. 9, Table 1). There is a preferential corrosion of copper that has fragilized the structure of the sheet metal.

The silver enriched surface is entirely covered with copper corrosion products. The outer green layer (CP1) is a copper carbonate (Fig. 12, Table 1), while the red layers (CP2 in Fig. 5a ; CP4 and CP5 in Fig. 5b) are consisting of a copper oxide, most likely cuprite (Fig. 10). Below the cuprite and above the silver enriched surface on the front face a thin black layer is present (appears grey under polarized light). SEM-EDS analysis shows that in that stratum the mercury of the pigment (Fig. 14) has been transformed into a mercury-silver compound (Figs. 8 and 11a and b) which according to Raman spectrometry (Fig. 15) is not cinnabar anymore. In areas this silver- and mercury-rich surface has been pulled off by raising the corrosion layers, leaving structural voids that were subsequently filled by secondary corrosion products, most likely copper carbonates (Figs. 7 and 8)

The silver sulphide (HgS, cinnabar, Fig. 14), present as a red pigment on the silver surface, could have been reduced through an electrochemical process in the presence of chlorides (Keune, K. (2005)). The released sulfur recombined with the silver to form black silver sulphide. Above that layer a porous mercury- and silver rich stratum has formed (see Hg & Ag on cartography Fig. 9). It remains unclear if the limitos is located in the silver enriched surface or within this silver-mercury compound (Fig. 8).

Elements	Cu	Ag	O	Cl	Hg	S	As	Pb	Interpretation
Red layer (CP2, front & CP4-CP5, back)	+++		+						Copper oxide
Grey layer (CP3, front & CP2, back)		+++			+++	++			Pigment (HgS) and silver
Green layer (CP1)	+++		+	++					Copper carbonate
Black layer	+	++				++			Silver and copper sulfides
Nodules in the metal		+++		+++					Silver chlorides
Metal phases 1	+	+++							Silver-rich phases
Metal phases 2	+++	++	+	+					Copper-rich phase
Inclusion in metal			+				++	+++	AsPb impurities

Table 1: Chemical composition of the corrosion crust from Fig. 4. Method of analysis: SEM-EDS, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc (+++: high concentration, ++ medium concentration, + low concentration), credit MiCorr_HEI Arc, S. Ramseyer.

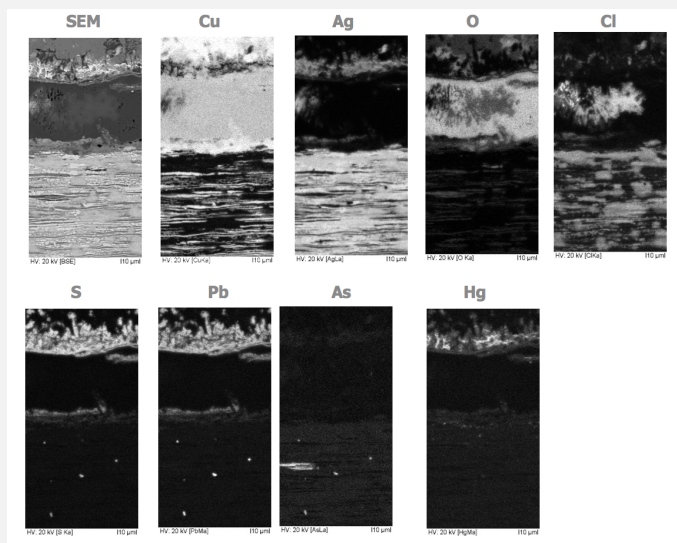


Fig. 9: SEM image (BSE-mode) and elemental chemical distribution of the selected area on Fig. 7. Method of examination: SEM/EDS,

Credit HEI Arc_S. Ramseyer

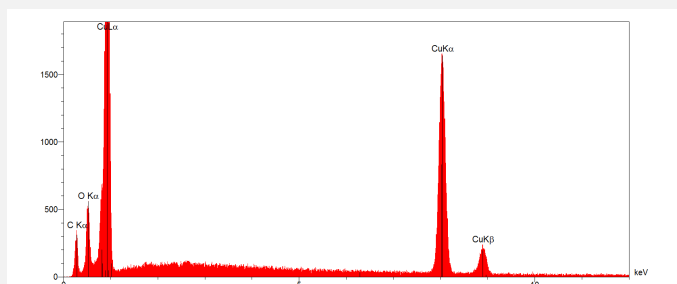
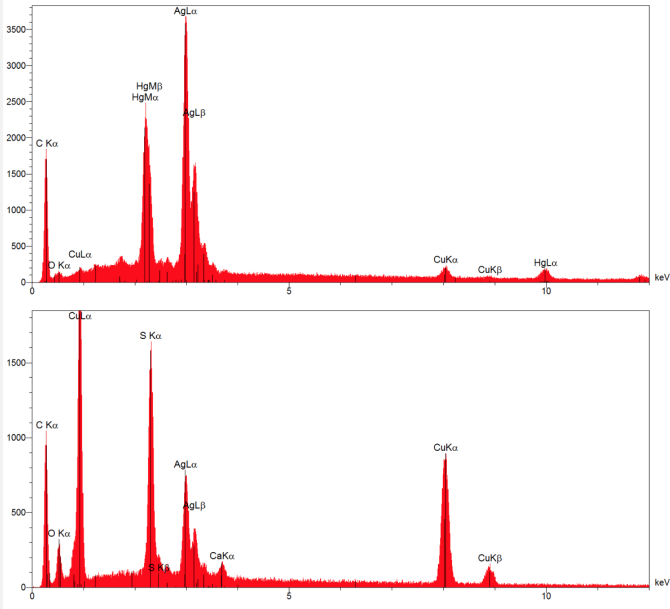


Fig. 10: EDS analysis of the red corrosion layer (Fig. 4). Method of analysis: SEM-EDS, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc,

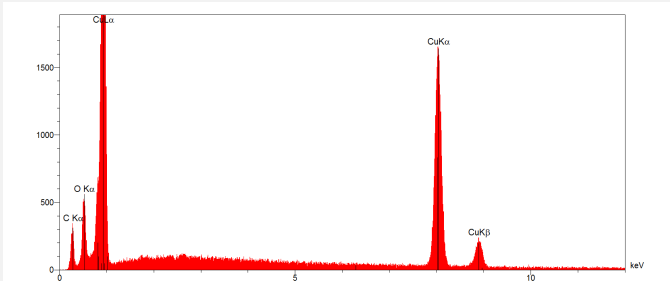
Credit HEI Arc, S. Ramseyer.

Figs. 11a and b: EDS analysis of the layer that appears light grey under polarized light, situated below the red layer (Fig.

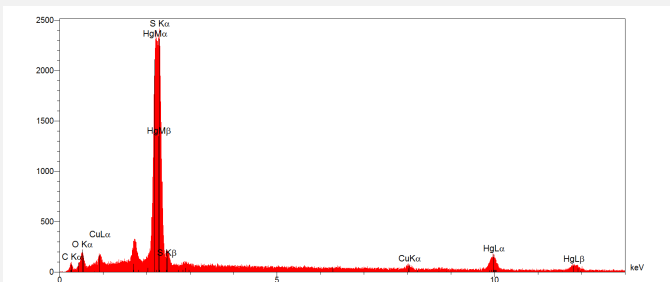
4). Method of analysis: SEM-EDS, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc,



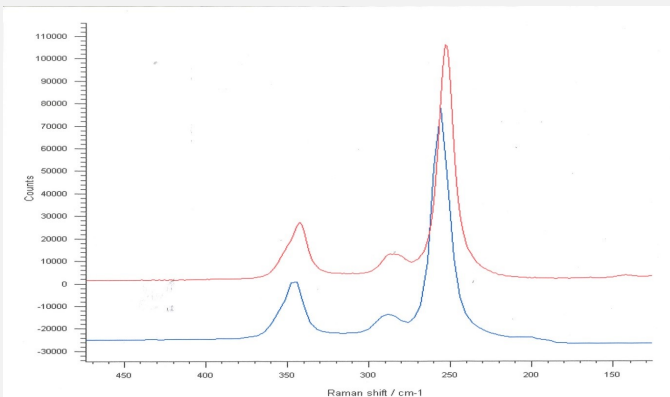
Credit HEI Arc, S. Ramseyer.



Credit HEI Arc, S. Ramseyer.



Credit HEI Arc, S. Ramseyer.



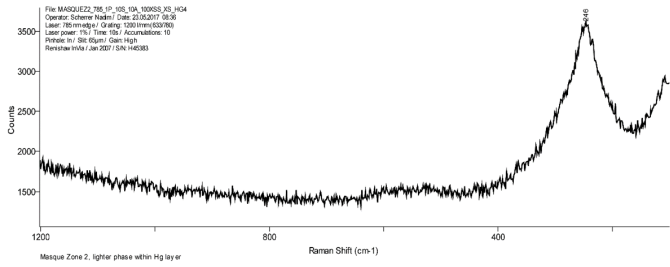
Credit HEI Arc, N. Scherrer.

Fig. 12: EDS analysis of the green corrosion layer that has filled the structural void (Fig. 4). Method of analysis: SEM-EDS, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc,

Fig. 13: EDS analysis of the red surface pigment from a surface sample. Method of analysis: SEM-EDS, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc,

Fig. 14: Raman analysis of the red pigment on the surface (red line) and the references for cinnabar (blue line). Method of analysis: Raman spectroscopy, HKB,

Fig. 15: Raman analysis of the mercury compounds from the cross section. Method of analysis: Raman spectroscopy, HKB,



Credit HEI Arc, N. Scherrer.

Corrosion form Uniform - selective

Corrosion type None

✧ MiCorr stratigraphy(ies) – CS

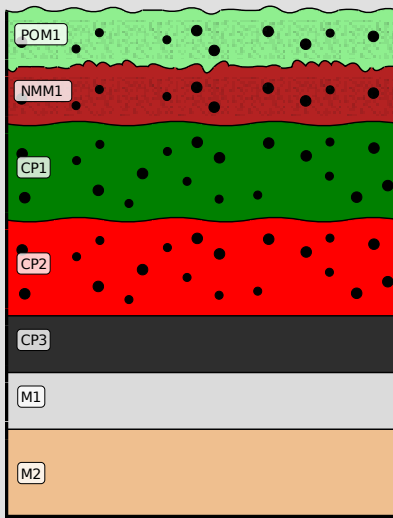


Fig. 5a: Schematic interpretation of the cross-section from 3a (front of the object), Credit HE-Arc CR, N. Gutknecht.

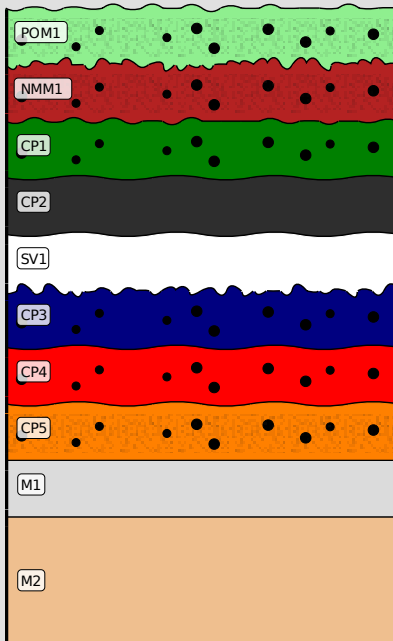


Fig. 5b: Schematic interpretation of the cross-section from 3b (back of the object), Credit HE-Arc CR, N. Gutknecht.

✧ Synthesis of the binocular / cross-section examination of the corrosion structure

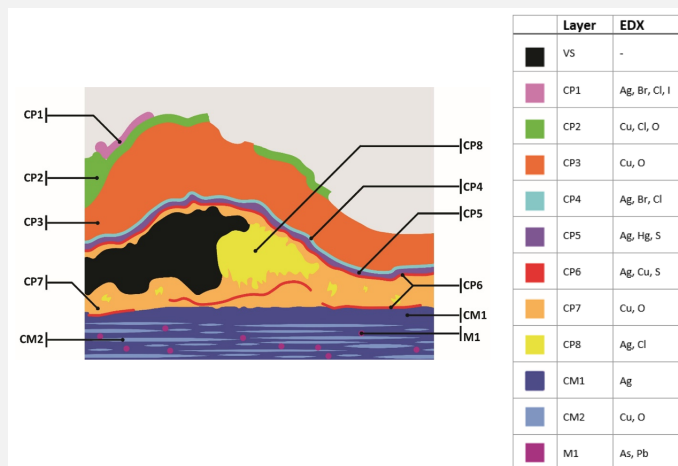


Fig. 16: Stratigraphic representation of Fig. 7 based on the results from the SEM-EDS analysis,

Credit HE-Arc CR, N. Gutknecht

Conclusion

The artefact is a repeatedly hammered, annealed and pickled Cu-Ag tumbaga. The cuprite and hydroxycarbonate layers and the presence of chlorides are typical for the corrosion of tumbaga alloys in an archaeological context. Cinnabar has been identified as pigment applied to the surface before burial. Over the centuries, it was partially incorporated into the growing copper corrosion layers.

Close to the enriched silver surface and below the cuprite layer a silver- and mercury-rich stratum has formed. Only one publication mentions the reaction of cinnabar with a gold-enriched tumbaga surface but does not go into details about the possible mechanism involved (Masuda, S. (ed.) (1997)).

The presence of a silver-sulphur compound below this silver-mercury stratum could indicate that the cinnabar was reduced by electrochemical processes to mercury, releasing sulphur that reacted with the silver enriched surface. The mercury itself formed a silver-mercury layer above the latter. More research is needed to fully comprehend this phenomenon.

References

- Keune, K. (2005) «Analytical Imaging Studies Clarifying the Process of the Darkening of Vermilion in Paintings». *Analytical Chemistry*, n° 77, 2005. p. 4742-4750.
- Scott, D. (2000). A review of gilding techniques in ancient South America. In: T. Drayman-Weisser (ed.) *Gilded Metals: History, Technology and Conservation*. London, Archetype Publications, p. 203-222.
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- Masuda, S. (ed.) (1997). *Sicàn - ein Fürstengrab in Alt-Peru: Eine Ausstellung in Zusammenarbeit mit dem peruanischen Kulturministerium*. Museum Rietberg, Zurich.