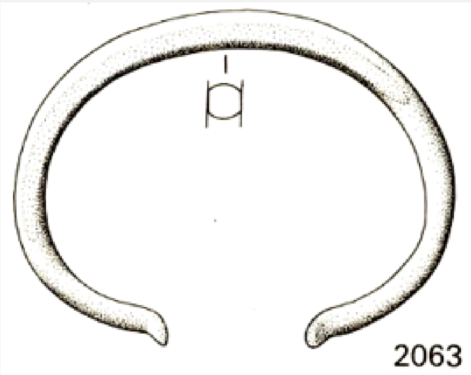
OVAL BRACELET WITH A ROUNDED DIAMETER B B3474 - LEADED BRONZE - LATE BRONZE AGE - SWITZERLAND

Artefact name Oval bracelet with a rounded diameter B B3474

Authors Marianne. Senn (EMPA, Dübendorf, Zurich, Switzerland) & Christian. Degrigny (HE-Arc CR, Neuchâtel, Neuchâtel, Switzerland)

Url /artefacts/344/

The object



Credit HE-Arc CR.

Fig. 1: Leaded bronze bracelet (after Paszthory 1985, Tafel 171),

Description and visual observation

Description of the artefact	Bracelet with round diameter after Paszthory (1985, 243). Ends shaped to form little paws, with a casting seam on the inside (Fig. 1). Dimensions: Øobject = around 6.2cm.
Type of artefact	Jewellery
Origin	Les Eaux-Vives, Genève, Geneva, Switzerland
Recovering date	None
Chronology category	Late Bronze Age
chronology tpq	1000 B.C.
chronology taq	----
Chronology comment	Hallstatt B2/3 (1000BC _ not defined)
Burial conditions / environment	Lake
Artefact location	Musées d'art et d'histoire, Genève, Geneva
Owner	Musées d'art et d'histoire, Genève, Geneva

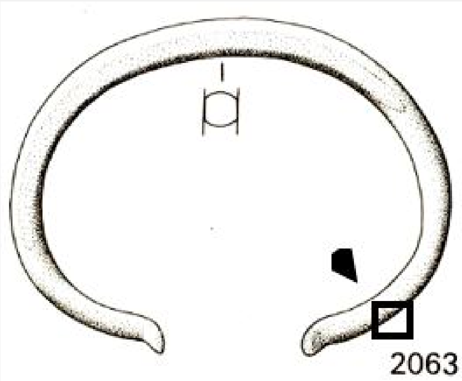
Inv. number B B3474

Recorded conservation data Not conserved

Complementary information

Nothing to report.

Study area(s)



Credit HE-Arc CR.

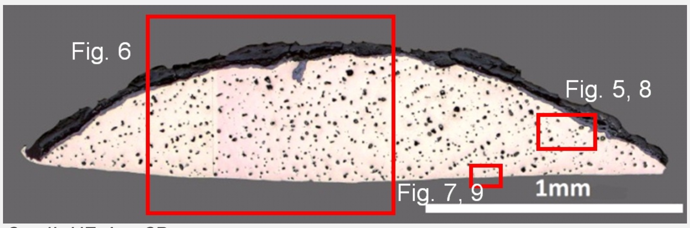
Fig. 2: Location of sampling area,

Binocular observation and representation of the corrosion structure

Stratigraphic representation: none.

MiCorr stratigraphy(ies) – Bi

Sample(s)



Credit HE-Arc CR.

Fig. 3: Micrograph of the cross-section showing the location of Figs. 5 to 9,

Description of sample The sample is a section from one end of the bracelet (Fig. 2). Its dimensions are: L = 2.3mm and W = 0.55mm. The corrosion layer is relatively thin (Fig. 3).

Alloy Leaded Bronze

Technology As-cast

Lab number of sample MAH 77-110-2

Sample location Musées d'art et d'histoire, Genève, Geneva

Responsible institution Musées d'art et d'histoire, Genève, Geneva

Date and aim of sampling 1977 and 1991, study of the corrosion layer, metal composition

Complementary information

Nothing to report.

Analyses and results

Analyses performed:
Metallography (etched with ferric chloride reagent), Vickers hardness testing, ICP-OES, SEM/EDS.

Non invasive analysis

Metal

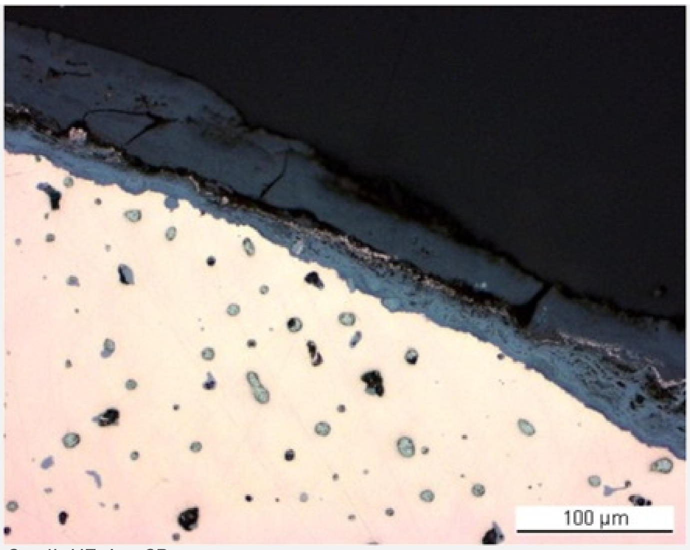
The remaining metal is a porous leaded bronze (Table 1). Under bright field light Pb and dark-grey copper sulphide inclusions can be seen (Fig. 5, Table 2). The copper sulphide inclusions are rather small with various forms, while the Pb inclusions are generally larger and round. The etched leaded bronze has the dendritic structure of an as-cast metal (Fig. 6) with an average hardness of HV1 80. After etching the Pb-inclusions turned dark grey and the copper sulphide light grey (Fig. 6).

Elements	Cu	Sn	Pb	Sb	As	Ni	Ag	Co	Zn	Fe	Bi
mass%	89.67	6.40	2.62	0.52	0.27	0.22	0.13	0.07	0.03	0.04	0.03

Table 1: Chemical composition of the metal. Method of analysis: ICP-OES, Laboratory of Analytical Chemistry, Empa.

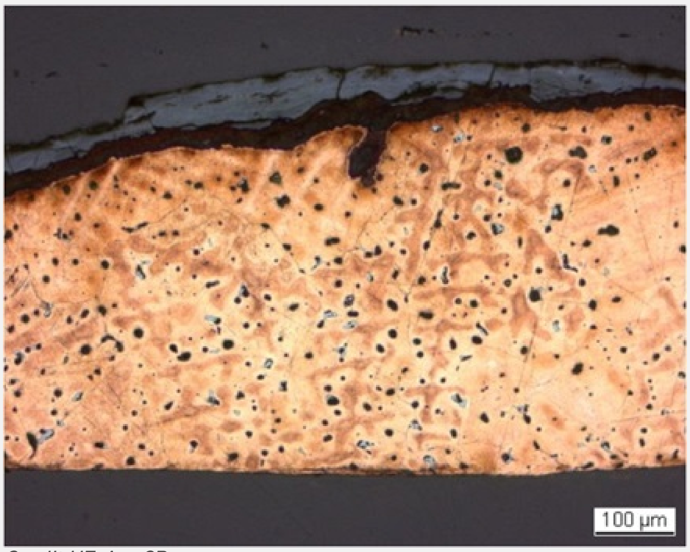
Elements	S	Cu	Total
Dark-grey inclusion	21	76	97

Table 2: Chemical composition (mass %) of dark-grey inclusions on Fig. 5. Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.



Credit HE-Arc CR.

Fig. 5: Micrograph of the metal sample from Fig. 3 (detail), unetched, bright field. In pink the metal with porosity (black), light-grey lead inclusions and dark-grey copper sulphide inclusions,



Credit HE-Arc CR.

Fig. 6: Micrograph of the metal sample from Fig. 3 (detail), etched, bright field. The dendritic structure is revealed with dark-grey lead inclusions and porosities (in black),

Microstructure	Dentritic structure with pores and inclusions
First metal element	Cu
Other metal elements	Sn, Pb

Complementary information

Nothing to report.

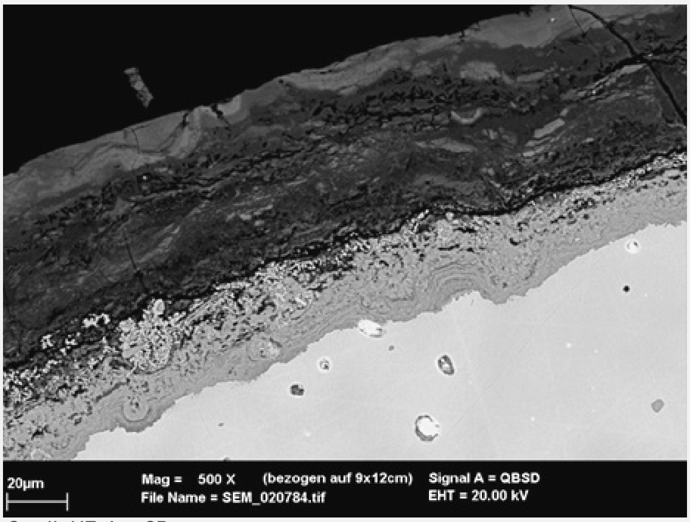
Corrosion layers

The corrosion crust has an average thickness of 60µm and is composed of two main layers (CP2 and CP3, Fig. 5). In bright field, the inner layer (CP3) has a slight blue hue (Fig. 5). The corrosion products are stratified and the outer part is porous (Fig. 7). In polarised light, the inner layer appears as a mixture of reddish and orange corrosion products (Fig. 8). This layer is Cu- and O-rich with some Sn, Fe and Si in the porous zone (Table 3, Fig. 9). In bright field, the outer cracked and stratified layer (CP2) is dark grey (Fig. 5). It is depleted of Cu and rich in Fe and Sn with significant amounts of O and Si (Fig. 9). In polarised light, large red angular crystals (possibly cuprite) appear clearly in this outer corrosion layer (Fig. 8). The surface of the outermost layer (CP1) is Sn and O and Fe enriched (CP1, Fig. 9).

Elements	O	Fe	Cu	Sn	Pb	Si	S	As	Total
CP2	40	30	<	25	3.1	5	<	0.6	104

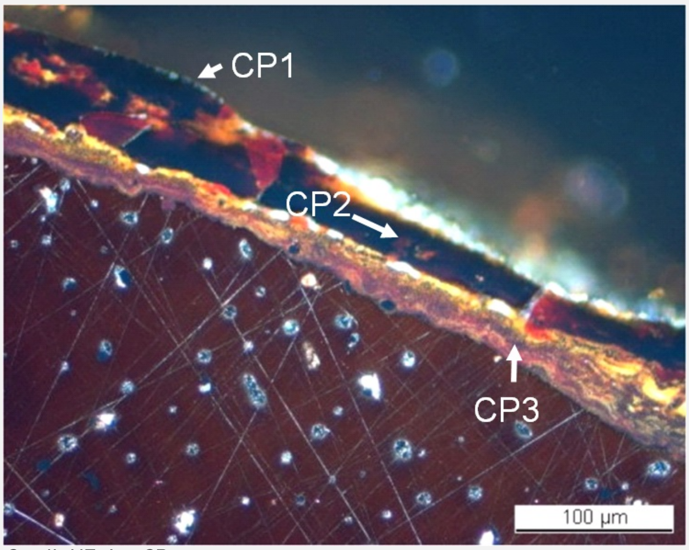
CP3	33	42	3.7	8.8	2.6	4.4	<	0.6	95
Red angular crystals in CP2	17	4.3	69	9.9	0.8	1.5	<	<	103

Table 3: Chemical composition (mass %) of the corrosion layers from Figs. 7 and 8. Method of analysis: SEM/EDS, Laboratory of Analytical Chemistry, Empa.



Credit HE-Arc CR.

Fig. 7: SEM picture (detail of Fig. 3), BSE-mode. From bottom right to top left: the metal, the inner light-grey layer, the outer dark-grey layer with a lighter top zone,



Credit HE-Arc CR.

Fig. 8: Micrograph similar to Fig. 5 and corresponding to the stratigraphy of Fig. 4, polarised light. From bottom left to top right: the metal (in brown with white porosities and blue Pb inclusions), the inner layer (CP3) appearing as stratified red and orange layers followed by an outer layer (CP2, black with red angular crystals) and a superimposed light green layer (CP1),

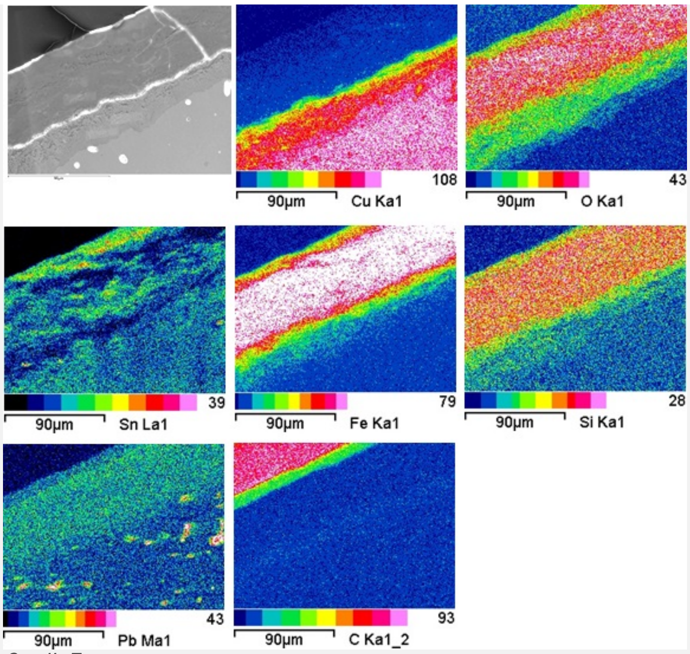


Fig. 9: SEM image, SE-mode, and elemental chemical distribution of a selected area of Fig. 7. The Pb mapping includes the Pb and copper sulphide inclusions, because of a peak interference. Method of examination: SEM/EDS, Laboratory of Analytical Chemistry, Empa, *Credit Empa.*

Corrosion form Uniform - pitting

Corrosion type Type I (Robbiola)

Complementary information

Nothing to report.

MiCorr stratigraphy(ies) – CS

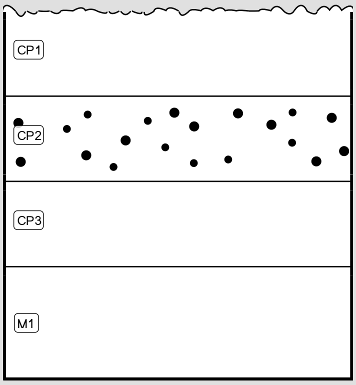


Fig. 4: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 8.

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

Corrected stratigraphic representation: none.

Conclusion

The leaded bronze artefact shows an as-cast structure. The outer layer is typical for a lake patina (though in this case formed under aerobic conditions), containing principally Fe as well as other contextual elements (such as Si). The absence of Cu in the corrosion layer could be due to its re-crystallisation in large cuprite crystals. Surprisingly the top of the outer layer is enriched in Sn, which was not the case in the study carried out by Schweizer (Schweizer 1994). The additional presence of C in this top layer could indicate a secondary, terrestrial patina formation phase. The corrosion is a type 1 according to Robbiola et al. 1998.

References

References on object and sample

Reference object

1. Paszthory, K. (1985) Der bronzezeitliche Arm- und Beinschmuck in der Schweiz. PrähistorischeBronzefunde X-Bd. 3, München, 243, Tafel 171.

Reference sample

2. Empa report 137'695/1991, P. Boll.
3. Rapport d'examen, Laboratoire Musées d'art et d'histoire, Genève (1977-110), 1977 and 1991.

References on analytic methods and interpretation

4. Robbiola, L., Blengino, J-M., Fiaud, C. (1998) Morphology and mechanisms of formation of natural patinas on archaeological Cu-Sn alloys, Corrosion Science, 40, 12, 2083-2111.
5. Schweizer, F. (1994) Objets en bronze provenant de sites lacustre: de leur patine à leur biographie. In: L'œuvre d'art sous le regard des sciences (éd. Rinuy, A. and Schweizer, F.), 143-157.