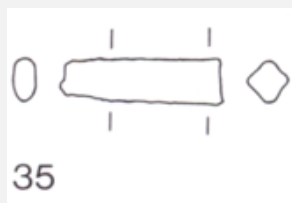


TANG FRAGMENT OF A KNIFE HR-6246 - TIN BRONZE - LATE BRONZE AGE - SWITZERLAND

| | |
|----------------------|---|
| Artefact name | Tang fragment of a knife HR-6246 |
| Authors | Marianne. Senn (EMPA, Dübendorf, Zurich, Switzerland) & Christian. Degriigny (HE-Arc CR, Neuchâtel, Neuchâtel, Switzerland) |
| Url | /artefacts/224/ |

∨ The object



Credit HE-Arc CR.

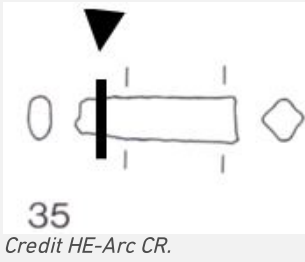
Fig. 1: Tin bronze tang fragment (after Rychner-Faraggi 1983, plate 35.35),

∨ Description and visual observation

| | |
|--|--|
| Description of the artefact | Tang fragment with lake (shiny brown) and terrestrial (granulated green-blue) crust. Dimensions: L = 2.7cm; Ø = around 5mm; WT = 5.8g. |
| Type of artefact | Knife |
| Origin | Hauterive - Champréveyres, Neuchâtel, Neuchâtel, Switzerland |
| Recovering date | Excavation 1983-1985, object from layer 1 (layer with material from Bronze Age till 20th cent.) |
| Chronology category | Late Bronze Age |
| chronology tpq | <input type="text" value="1050"/> B.C. ∨ |
| chronology taq | <input type="text" value="800"/> B.C. ∨ |
| Chronology comment | Hallstatt A/B (1050BC_ 800BC) |
| Burial conditions / environment | Lake |
| Artefact location | Laténium, Neuchâtel, Neuchâtel |
| Owner | Laténium, Neuchâtel, Neuchâtel |
| Inv. number | Hr 6246 |
| Recorded conservation data | Not conserved |

∨ Study area(s)

Fig. 2: Location of sampling area,



∨ Binocular observation and representation of the corrosion structure

Stratigraphic representation: none

∨ MiCorr stratigraphy(ies) – Bi

∨ Sample(s)

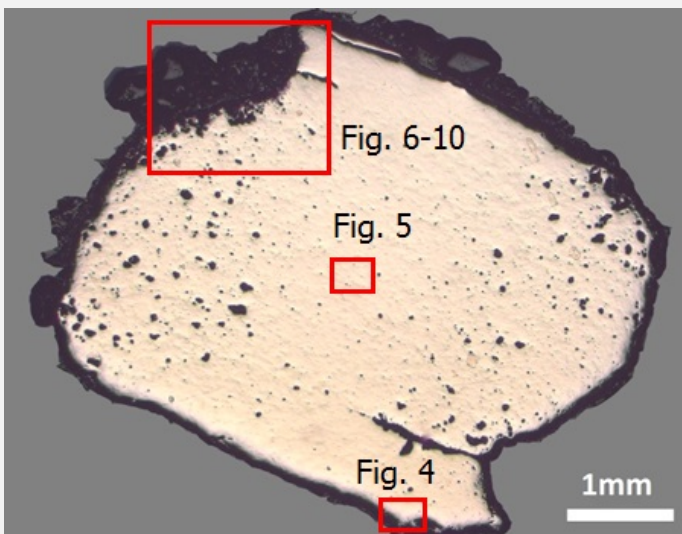


Fig. 3: Micrograph of the cross-section showing the locations of Figures 4 to 10,

| | |
|---------------------------------|--|
| Description of sample | The cross-section corresponds to a lateral cut. The surface is covered with a thick corrosion crust. |
| Alloy | Tin Bronze |
| Technology | Cold worked after annealing |
| Lab number of sample | MAH 87-197 |
| 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 | 1987, metallography and corrosion characterisation |

Analyses and results

Analyses performed:

Metallography (etched with ferric chloride reagent), Vickers hardness testing, ICP-OES, SEM/EDX, XRD.

Non invasive analysis

Metal

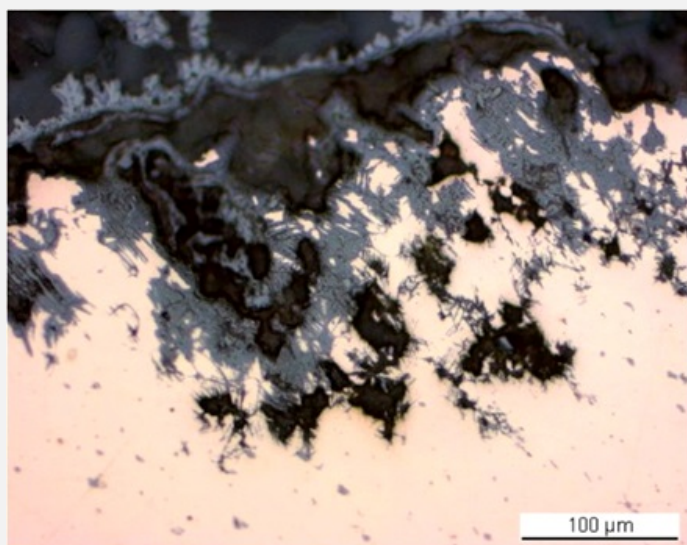
The remaining metal is a tin bronze (Table 1) with high porosity and large cracks both on the left and right edges of the sample (Fig. 3). The metal contains small, elongated copper sulphide (Table 2) and Pb inclusions that are oriented parallel to the cracks. Near the metal surface, slip lines are outlined by the development of intergranular corrosion (Fig. 4). The etched metal shows small, elongated grains with slip lines (Fig. 5). Annealing is visible in areas near the surface. The average hardness of the metal is HV1 145, but significant variations are observed, depending on where the measurements are taken.

| Elements | Cu | Sn | Sb | Ni | Pb | As | Ag | Co | Fe | Zn |
|----------|-------|------|------|------|------|------|------|------|------|------|
| mass% | 89.85 | 8.02 | 0.60 | 0.55 | 0.34 | 0.34 | 0.18 | 0.10 | 0.02 | 0.01 |

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

| Elements | O | S | Cu | Total |
|----------|-----|----|----|-------|
| mass% | 0.9 | 20 | 77 | 98 |

Table 2: Chemical composition of inclusions. Method of analysis: SEM/EDX, Laboratory of Analytical Chemistry, Empa.



Credit HE-Arc CR.

Fig. 4: Micrograph of the metal sample from Fig. 3 (inverted and reversed picture, detail), unetched, bright field. Corrosion products are in dark-grey whereas the metal is in pink. Slip lines are outlined by the development of intergranular corrosion,

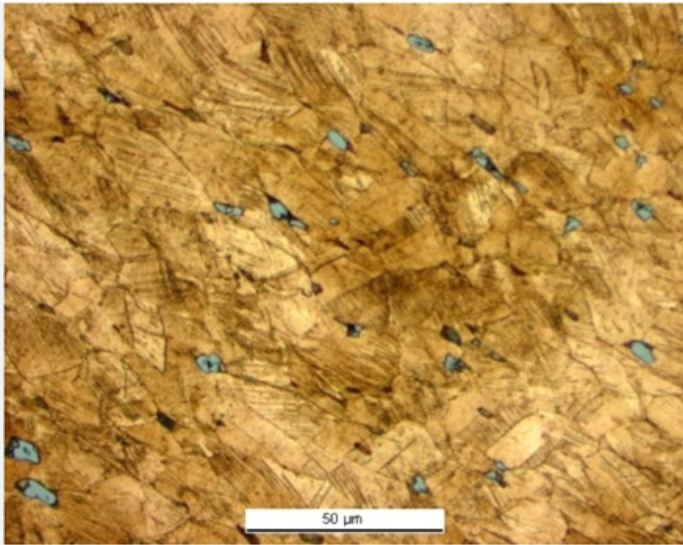


Fig. 5: Micrograph of the metal sample from Fig. 3 (detail), etched, bright field. We observe elongated grains with slip lines as well as grey copper sulphide inclusions,

Credit HE-Arc CR.

| | |
|-----------------------------|--|
| Microstructure | Elongated grains + strain lines with pores |
| First metal element | Cu |
| Other metal elements | Sn |

Corrosion layers

The corrosion crust has a thickness between 0.1mm and 0.7mm (Fig. 3). In bright field (Fig. 6), one can observe that the metal has been replaced by light-grey corrosion products. Adjacent to the metal is a thick, heterogeneous, dark-grey layer with a band of light-grey corrosion products. In polarised light (Fig. 7), all corrosion products which were previously light-grey appear brown-orange, the dark-grey layer turquoise. The elemental chemical distribution of the SEM image (Figs. 8 and 9) reveals that the inner corrosion products are Sn-rich whereas the adjacent band is Cu and S-rich (Fig. 10). The outer layer contains large inclusions (quartz and others, Si, Al and Na, see Figs. 9-10) and is most probably composed of malachite/ $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ (only Cu and O are detected – Fig. 10). S is distributed throughout this layer. XRD analyses indicated the presence of posnjakite/ $\text{Cu}_4\text{SO}_4(\text{OH})_6\text{H}_2\text{O}$, chalcocite/ Cu_2S and djurleite/ Cu_3S_2 (Schweizer 1994).

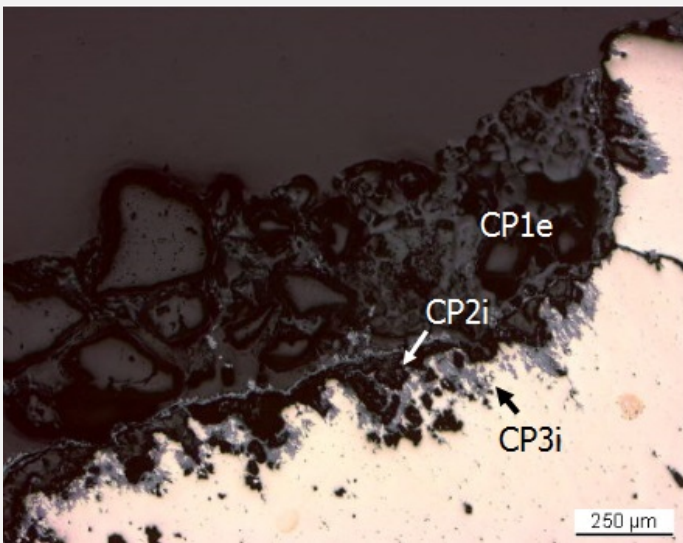
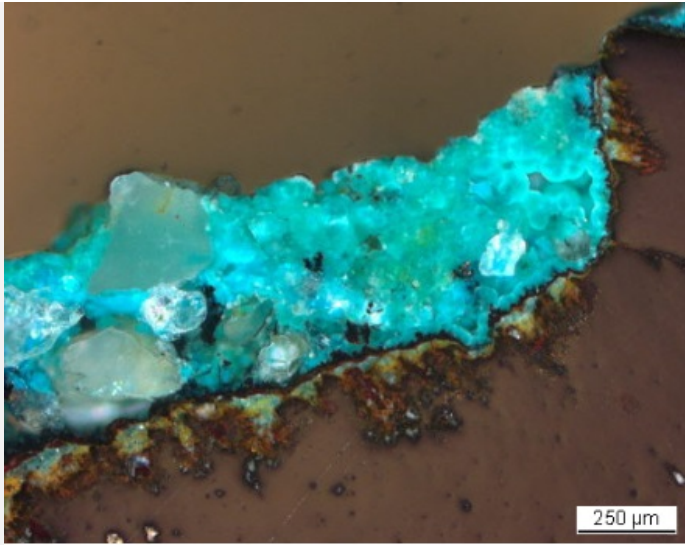


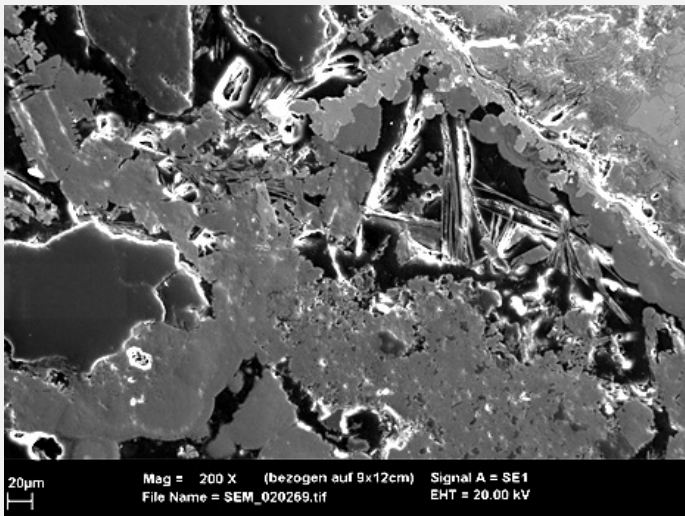
Fig. 6: Micrograph of the metal sample from Fig. 3 (detail), unetched, bright field. The inner light-grey corrosion products extend into the metal surface (in pink) and appear as a line within the dark-grey corrosion layer,

Credit HE-Arc CR.



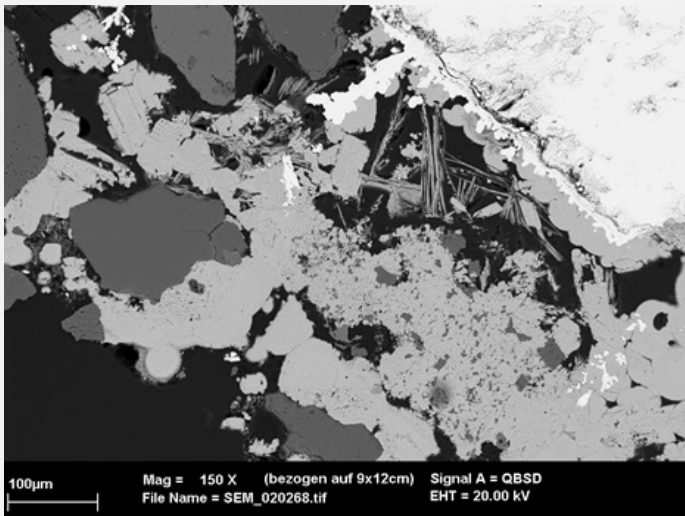
Credit HE-Arc CR.

Fig. 7: Micrograph similar to Fig. 6, polarized light. One can see that large mineral features are incorporated only in the corrosion layers above the brown-orange corrosion band,



Credit HE-Arc CR.

Fig. 8: SEM image (detail of Fig. 6), SE-mode. From bottom to top right: the thick, porous outer corrosion layer, the light-grey band and the remaining metal,



Credit

Fig. 9: SEM image, similar to Fig. 8, BSD-mode.

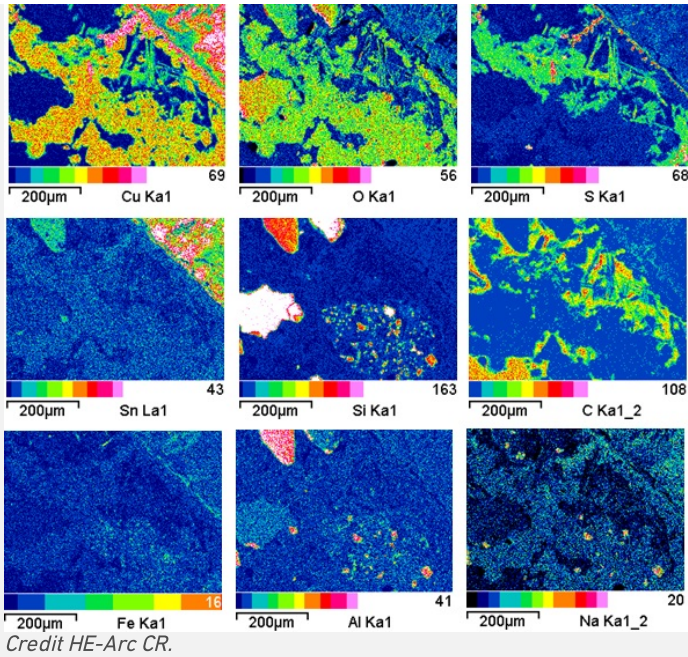


Fig. 10: EDX elemental chemical distribution of the SEM image of Fig. 8. Method of examination: SEM/EDX, Laboratory of Analytical Chemistry, Empa,

Corrosion form Uniform - transgranular
Corrosion type Type I (Robbiola)

✧ MiCorr stratigraphy(ies) – CS

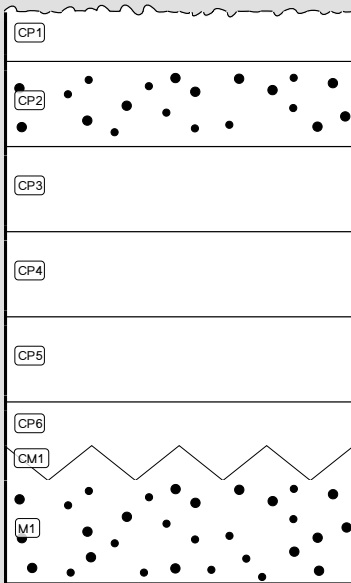


Fig. 4: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 8.

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

Corrected stratigraphic representation: none

✧ Conclusion

The tang fragment is made from a leaded bronze and has been cold worked on the top surface after annealing. The SEM/EDX examination and past XRD analyses indicate the presence of chalcopyrite in the corrosion crust, typical of lake context (Schweizer 1994), enriched with Sn close to the metal surface and depleted of Cu on the outer surface. This object was certainly abandoned rather quickly in an anaerobic, humid and S and Fe-rich environment, favouring then the formation of chalcopyrite. The limit of the original surface most probably lies between the Sn-rich inner layer and the Fe and S-rich outer layers. The presence of iron oxides on top of the copper corrosion crust has not yet been explained. The corrosion is a type 1 according Robbiola et al. 1998.

References

References on object and sample

References object

1. Rychner-Faraggi A-M. (1993) Hauterive – Champréveyres 9. Métal et parure au Bronze final. Archéologie neuchâteloise, 17 (Neuchâtel).

References sample

2. Rapport d'examen, Laboratoire Musées d'art et d'histoire, Geneva GE (1987), 87-194 à 197

3. 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.

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.