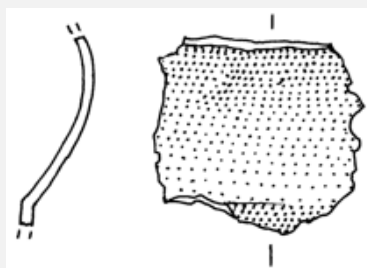


# DEFORMED FRAGMENT OF METAL SHEET WT10-M305 - TIN BRONZE - IRON AGE - SWITZERLAND

|               |   |
|---------------|---|
| Artefact name | Deformed fragment of metal sheet WT10-M305  |
| Authors       | Marianne. Senn (EMPA, Dübendorf, Zurich, Switzerland) & Christian. Degriigny (HE-Arc CR, Neuchâtel, Neuchâtel, Switzerland) |
| Url           | /artefacts/219/   |

## ≡ The object



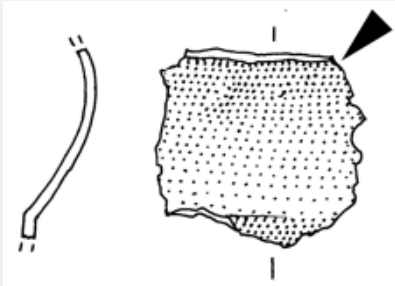
Credit HE-Arc CR.

Fig. 1: Tin bronze sheet fragment (section and front side) (after Department of Prehistory, University of Zurich),

## ≡ Description and visual observation

|                                 |   |
|---------------------------------|---|
| Description of the artefact     | Sheet fragment with a dark green and grey powdery surface (patina) that might have been caused by exposure to high temperatures. A green layer appears below the dark surface. Dimensions: L = 2.4cm; W = 2.3cm; WT = 4.8g. |
| Type of artefact                | Metal sheet   |
| Origin                          | Ritual place Wartau Ochsenberg, Sankt Gallen, Saint Gallen, Switzerland   |
| Recovering date                 | Excavation in 1991  |
| Chronology category             | Iron Age  |
| chronology tpq                  | 500 B.C. ▼  |
| chronology taq                  | 401 B.C. ▼  |
| Chronology comment              | 5th Century BC  |
| Burial conditions / environment | Soil  |
| Artefact location               | Kantonsarchäologie, Sankt Gallen, Saint Gallen  |
| Owner                           | Kantonsarchäologie, Sankt Gallen, Saint Gallen  |
| Inv. number                     | WT10-M305   |
| Recorded conservation data      | Not conserved   |

Study area(s)



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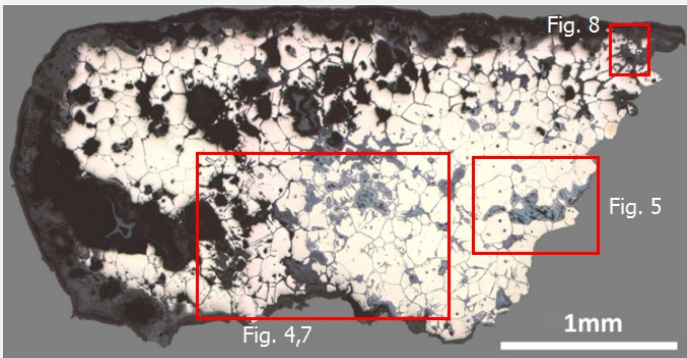
Fig. 2: Location of sampling area,

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 locations of the Figures 4, 5, 7 and 8,

Description of sample

The sample is a section from the top right corner of the sheet (Fig. 2). Its dimensions are: L = 2.5mm and W = 2.3mm. The metal is surrounded on three sides by corrosion products. Intergranular corrosion has developed throughout the metal section (Fig. 3).

Alloy

Tin Bronze

Technology

Secondary recrystallization (produced by burning) after cold working

Lab number of sample

MAH 92-5-2-003

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

1992, examination of the corrosion layer

⌵ Analyses and results

**Analyses performed:**

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

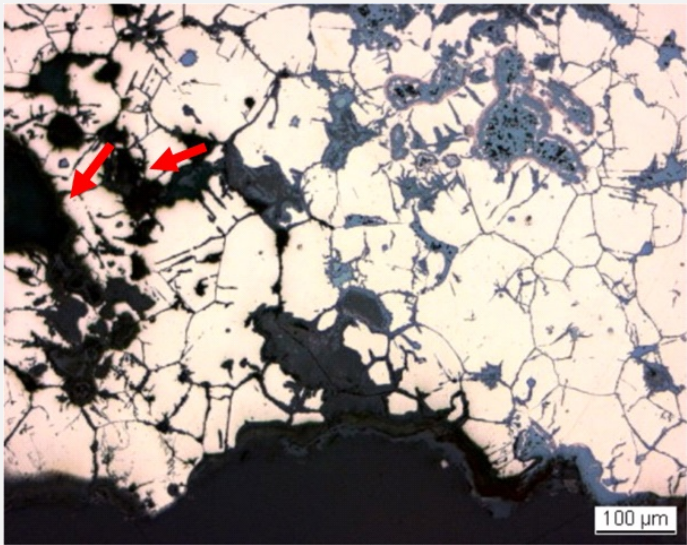
⌵ Non invasive analysis

⌵ Metal

The remaining metal is a porous (red arrows on Fig. 4) tin bronze (Table 1). Five analyses were made, including S in non-corroded metal (2 measurements), and P (3 measurements) in partially corroded metal. As no major difference in the composition was observed (comparison of RSD) all analyses were used to calculate the median value. Inter- and transgranular corrosion has developed so extensively that all grain boundaries and twin lines are outlined (Fig. 4). After etching, we observe annealed polygonal grains with a few twins and slip lines below the surface (Fig. 5). The slip lines are restricted to the right side of the sample where the metal is best preserved (Fig. 5). The grain size varies between 50 and 170µm, due to an excessively long or hot annealing procedure leading to a grain coarsening. Small copper sulphide inclusions appear in blue. The average hardness of the metal is HV1 90.

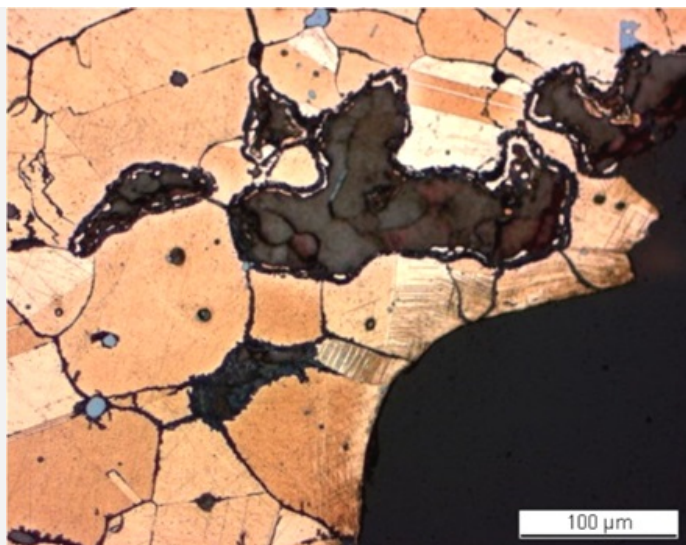
| Elements | Cu    | Sn | As   | S*  | P**  | Co    | Ni    | Pb   | Sb   | Ag    | Zn    | Fe | Bi    |
|----------|-------|----|------|-----|------|-------|-------|------|------|-------|-------|----|-------|
| mass%    | 83.13 | 16 | 0.26 | 0.1 | 0.07 | 0.032 | 0.025 | 0.02 | 0.02 | 0.009 | 0.002 | <  | 0.002 |
| RSD %    | 2     | 9  | 13   | 25  | 45   | 3     | 5     | 41   | 15   | 12    | 6     | <  | 43    |

Table 1: Chemical composition of the metal. Analytical method: LA-ICP-MS, Laboratory of Basic Aspects of Analytical Chemistry at the Faculty of Chemistry, University of Warsaw, PL. \*S is only present in the metal, whereas \*\*P indicates the presence of corrosion products in the analysed metal.



Credit HE-Arc CR

Fig. 4: Micrograph of the metal sample from Fig. 3 (detail), unetched, bright field. Extensive inter- and transgranular corrosion has developed within the metal. Large pores are visible (arrows) inside the remaining metal,



Credit HE-Arc CR.

Fig. 5: Micrograph of the metal sample from Fig. 3 (detail), etched, bright field. We observe pink-orange polygonal grains with twins and slip lines as well as copper sulphide inclusions (in blue),

|                      |  |
|----------------------|--|
| Microstructure       | Large polygonal grains with few twins + strain lines |
| First metal element  | Cu   |
| Other metal elements | Sn   |

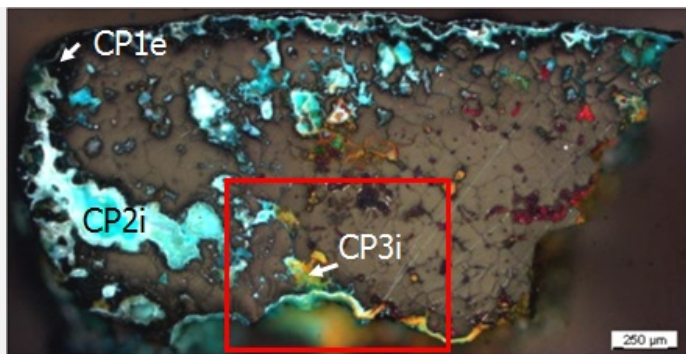
#### Corrosion layers

The corrosion crust varies in thickness between 60 and 150μm (Fig. 3). In bright field, it appears dark-grey (Fig. 4) and consists of two layers. The inner layer is dark-grey and dense while the thin outer layer is slightly lighter coloured. Within the metal, the corrosion products are light-grey (Fig. 4). Under polarized light, the corrosion layer turns blue-green with dark-blue areas (Figs. 6 and 7) whereas corrosion products inside the metal are either light-blue (Figs. 6 and 7) or red-orange (Figs. 6 and 7). The red corrosion products have the composition of cuprite/Cu<sub>2</sub>O while the orange compounds are enriched in Sn (Table 2). The blue-green corrosion products both within the remaining metal and on the surface are even richer in Sn and O, and contain some P (Table 2 and Fig. 8). The thin, irregular dark-grey surface layer is enriched in P, Fe, Si and Al (Table 2 and Fig. 8). XRD analyses of powdery particles sampled from the thin, dark surface corrosion layer indicate the presence of tenorite/CuO and cassiterite/SnO<sub>2</sub> (Museum report 1992). The Raman spectra of this layer (Fig. 9) confirmed the presence of tenorite.

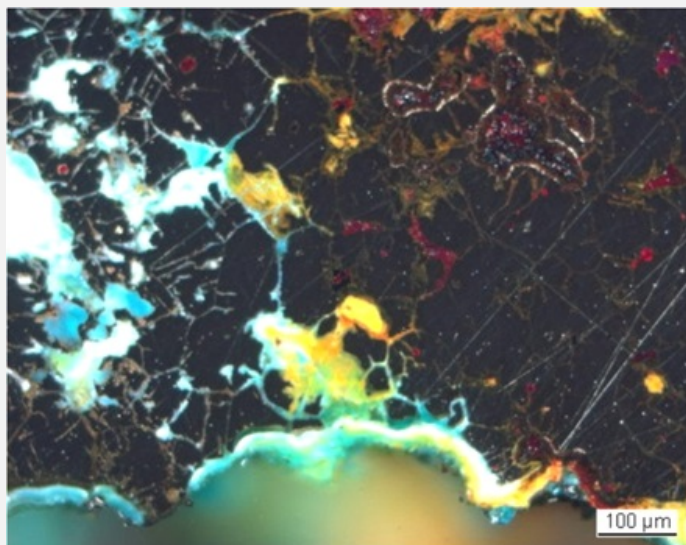
| Elements   | O  | Cu | Sn | Si  | Fe  | P   | As   | Total |
|--|----|----|----|-----|-----|-----|------|-------|
| CP1e, outer dark-grey corrosion layer. Fig 6                           | 34 | 16 | 49 | <   | 3.4 | 3.0 | 0.86 | 108   |
| CP2i, blue-green middle corrosion layer. Fig. 6                        | 40 | 21 | 41 | 1.4 | <   | 1.7 | 0.58 | 106   |
| CP3i, Red corrosion product (average of 2 similar analyses). Fig. 6    | 11 | 95 | <  | <   | <   | <   | <    | 106   |
| CP3i, Orange corrosion product (average of 2 similar analyses). Fig. 6 | 24 | 54 | 30 | 0.6 | <   | <   | 0.59 | 109   |
| Blue-green corrosion product. Fig. 7                                   | 32 | 21 | 51 | 1.1 | <   | <   | 1.0  | 106   |
| Blue-green inner corrosion layer. Fig. 7                               | 34 | 22 | 39 | 0.8 | <   | 1.4 | <    | 98    |

Table 2: Chemical composition (mass %) of the different corrosion products and layers from Figs. 6 and 7. Method of analysis: SEM/EDX, Laboratory of Analytical Chemistry, Empa.

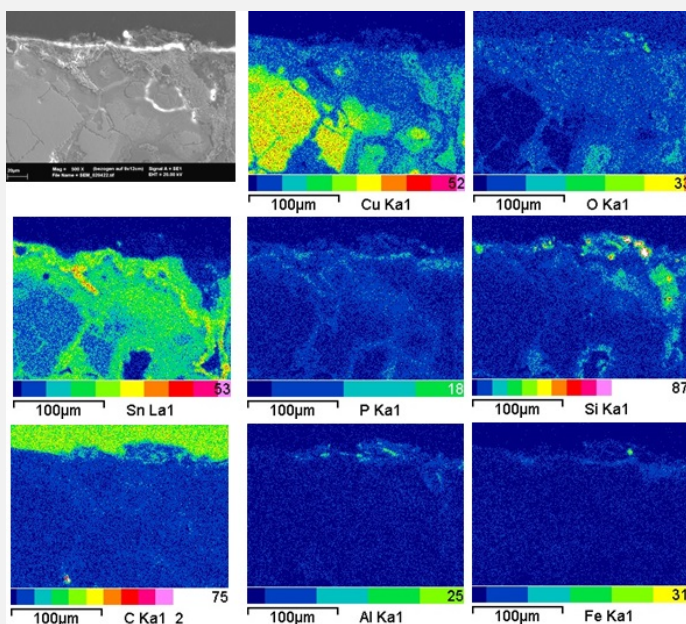




Credit HE-Arc CR.



Credit HE-Arc CR.

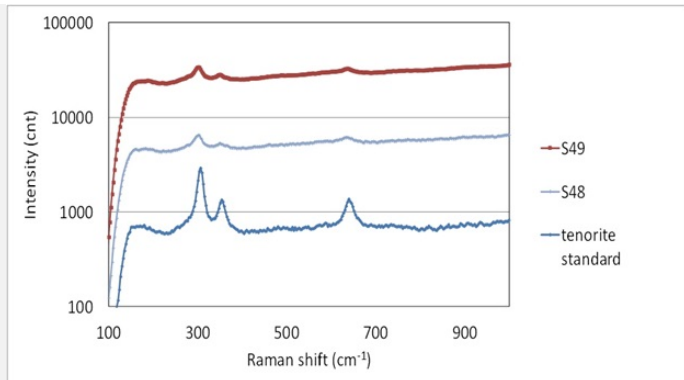


Credit HE-Arc CR.

Fig. 6: Micrograph of the cross-section (same as Fig. 3), polarised light, showing the location of Fig. 7,

Fig. 7: Micrograph (same as Fig. 4), polarised light. In black the metal. Blue-green, orange and red corrosion products are found in the porous metal and along the grain boundaries,

Fig. 8: SEM image, SE-mode, and elemental chemical distribution of the selected area from Fig. 3. Method of examination: SEM/EDX, Laboratory of Analytical Chemistry, Empa,



Credit HE-Arc CR.

Fig. 9: Raman spectra of the outer dark corrosion layer (S48 and S49) compared to a tenorite standard spectrum. Settings: laser wavelength 532nm, acquisition time 20s for S48 and 100s for S49, one accumulation, filter D1 (7.5-8mW), hole 500, slit 80, grating 600. Method of analysis: Raman spectroscopy, Lab of Swiss National Museum, Affoltern a. Albis ZH,

|                |   |
|----------------|---|
| Corrosion form | Uniform - intergranular                       |
| Corrosion type | Mostly type II with locally type I (Robbiola) |

#### ✧ MiCorr stratigraphy(ies) – CS

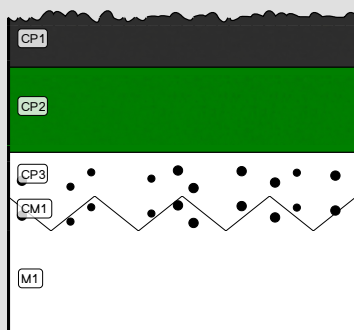


Fig. 4: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 7.

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

Corrected stratigraphic representation: none

#### ✧ Conclusion

The tin bronze sheet shows traces of cold working but has been exposed to an extended or excessively hot annealing process. According to Northover (Northover in preparation), the relative lack of twins and their large size confirm a prolonged annealing process. Furthermore large grains, large twins and extensive intergranular corrosion are characteristic of objects that have been exposed to a hot reducing flame either in a house fire or on a funeral pyre. All corrosion products except the cuprite are Sn enriched. The enrichment in P of the surface layer might be due to an environment rich in organic material (for example bones). Tenorite analysed by XRD and Raman spectroscopy is very rare in ancient Cu corrosion and must be interpreted as a further tracer for Cu corrosion in burning context. The original surface of the metal has been destroyed resulting in a type 2 corrosion layer after Robbiola et al. 1998. Only locally in the areas where tenorite is preserved does type 1 patina occur.

#### ✧ References

##### References on object and sample

##### Reference object

1. Publication in preparation (Biljana Schmid-Sikimic).

#### Reference sample

2. Degli Agosti, M., Santoro, I., Senn, M., Untersuchungen zur Brandpatina an Kupferlegierungen. In: Schmid-Sikimic, B. in preparation.

3. Northover, P., Untersuchungen an Fragmenten einiger Negauer-Helme. In Schmid-Sikimic, B. in preparation.

4. Rapport d'examen, Laboratoire Musées d'art et d'histoire, Genève 92-5-2 (1992).

#### *References on analytic methods and interpretation*

5. 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.