AXE HEAD N11 – TIN BRONZE – MIDDLE BRONZE AGE

Artefact name	Axe head N11
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Url	/artefacts/387/

⌄ The object

Fig. 1: Bronze axe head n°11,

Credit HE-Arc CR_E.Forster.

⌄ Description and visual observation

Description of the artefact	Bronze axe head covered with a brown patina (Fig. 1). A uniform darker green corrosion product as well as a green powdery corrosion product appear locally in some areas. Dimensions: L = 90 mm; W max = 40 mm ; WT = 154.32 g.
Type of artefact	Tool
Origin	Unknown
Recovering date	Date unknown
Chronology category	Middle Bronze Age
chronology tpq	3300 B.C. ⌄
chronology taq	600 B.C. ⌄
Chronology comment	Bronze Age
Burial conditions / environment	Soil
Artefact location	Neues Museum, Biel/Bienne
Owner	Neues Museum, Biel/Bienne

Inv. number	N11
Recorded conservation data	No information, the object might have been treated in the past.

Complementary information

Nothing to report.

Credit HE-Arc CR, E.Forster.

Fig. 2: General view of the axe head showing the location of Fig. 4 (sample 1),

Credit HE-Arc CR, E.Forster.

Fig 3: Side view of the axe head showing the location of Fig. 5 (sample 2), Fig. 6 (sample 3) and Fig. 7 (sample 4),

Credit HE-Arc CR, E.Forster.

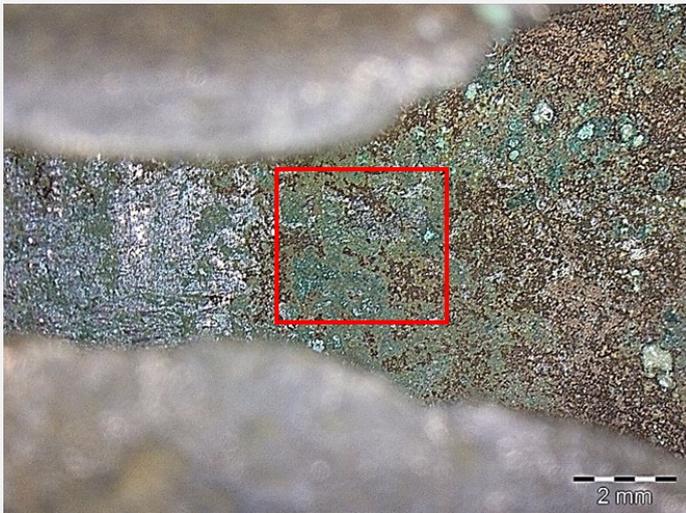Fig 4: Local corrosion (diameter: 2 mm) where sample 1 has been taken,

Credit HE-Arc CR, E.Forster.

Fig. 5: Local corrosion (length max: 30 mm) where sample 2 has been taken,

Credit HE-Arc CR, E.Forster.

Fig. 6: Local corrosion (length max: 10 mm) where sample 3 has been taken,

Credit HE-Arc CR, E.Forster.

Fig 7: Green dark corrosion layer where sample 4 has been taken,

⌄ Binocular observation and representation of the corrosion structure

The schematic representation below gives an overview of the corrosion layers encountered on the head axe from a first visual macroscopic observation.
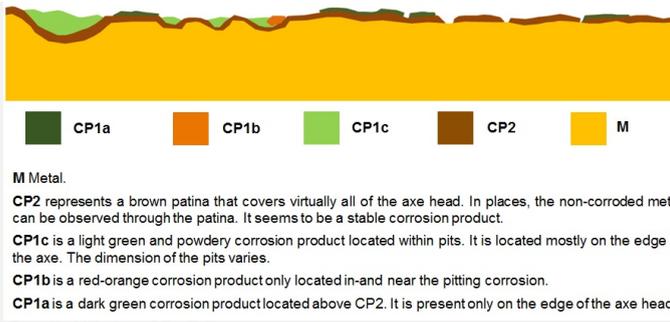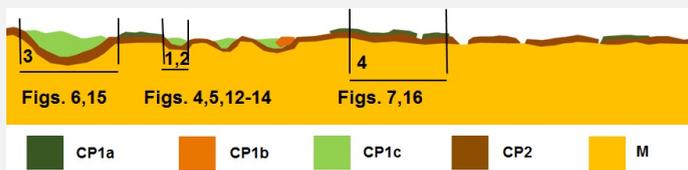
Fig. 8: Stratigraphic representation of corrosion products of the axe head (based on visual observations),

CP1a | **CP1b** | **CP1c** | **CP2** | **M**

M Metal.

CP2 represents a brown patina that covers virtually all of the axe head. In places, the non-corroded metal can be observed through the patina. It seems to be a stable corrosion product.

CP1c is a light green and powdery corrosion product located within pits. It is located mostly on the edge of the axe. The dimension of the pits varies.

CP1b is a red-orange corrosion product only located in- and near the pitting corrosion.

CP1a is a dark green corrosion product located above CP2. It is present only on the edge of the axe head.

Credit HE-Arc CR, E.Foster.

MiCorr stratigraphy(ies) – Bi

Sample(s)

Figs. 6,15   Figs. 4,5,12-14   Figs. 7,16

CP1a | **CP1b** | **CP1c** | **CP2** | **M**

Fig. 9: Location of the samples on the stratigraphic representation of Fig. 8,

Credit HE-Arc CR, E.Foster.

Description of sample	Particles were sampled (Figs. 4-7 and Fig. 9) with a scalpel from the areas where local corrosion has developed.
Alloy	Tin Bronze
Technology	Unknown
Lab number of sample	-----
Sample location	HE-Arc CR, Neuchâtel, Neuchâtel
Responsible institution	HE-Arc CR, Neuchâtel, Neuchâtel
Date and aim of sampling	March 04, 2013, chemical and structural analysis

Complementary information

Nothing to report.

Analyses and results

Analyses performed:
SEM-EDS, FTIR.

The FTIR device used is a Biorad Excalibur FTS 3000 spectrometer coupled to an IR microscope UMA500. The measurements were performed between 4000 and 650 cm-1.

Non invasive analysis

SEM/EDS analysis of corroded particles indicates that the alloy is composed of copper (Cu) and tin (Sn) with some arsenic (As).
The core metal is most likely a tin bronze.

Microstructure	?
First metal element	Cu
Other metal elements	As, Sn

Complementary information

Nothing to report.

Analyses by SEM/EDS indicate that the light yellow particles of sample 1 are predominantly composed of Sn and O with minor presence of C, Cu, Fe, S, Cl and As (Fig. 12), while the green and red particles of sample 2 are respectively composed of O, Cu, Cl, and Sn, with a minor presence of Fe and S (Fig. 13) and Cu, O (Fig. 14, possibly cuprite). Sample 3 consists of green particles composed mostly of Sn, Cl, Cu and O with S, Al and Fe as minor elements (Fig. 15). Sample 4 is constituted of green and white particles. The former have the same composition as the particles of sample 3 while the white particles are significantly different in composition: containing a large amount of C with a small amount of O, Cl, S, K and Cu (Fig. 16). The FTIR spectrum of the white particles (Fig. 17) shows several characteristic peaks of an organic compound: 2919 cm-1 and 2850 cm-1 (C-H- bond), 3445 cm-1 and 3323 cm-1 (O-H- bond) or 1030cm-1, 1006cm-1 and 951cm-1 (C-O-C- bond).

Table 1: Identification of chemical elements in the corrosion products on the head axe. Method of analysis: SEM/EDS, HEI-Arc.

|	Sample / particles	Major elements	Minor elements
Green powdery corrosion product	Sample 1	Sn + O	C + Cu + Fe + S + Cl + As
	Sample 2 – CP1c (Fig. 10) - Green particles	O + Cu + Cl + Sn	Fe + S
	Sample 2 – CP2 (Fig.10) - Red-brown particles	Cu + O	
	Sample 3 - CP1c (Fig. 10)	Sn + Cl+ Cu + O	S + Al + Fe
Darker green corrosion product	Sample 4 – CP1a (Fig. 11) - Green particles	Cl + Sn + Cu + O	S + C
	Sample 4 – CP1a (Fig. 11) - White particles	C	O + Cl + S + K + Cu

Credit HEI Arc, S.Ramseyer.
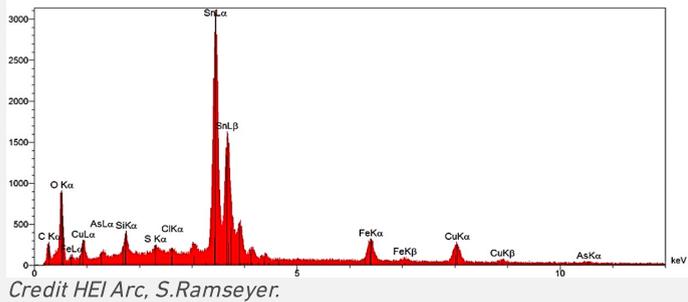
Fig, 12: EDS spectrum of sample 1 (yellow powder),

Credit HEI Arc, S.Ramseyer.
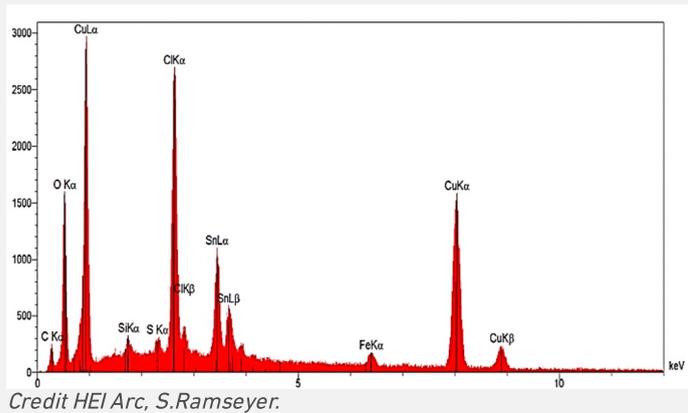
Fig. 13: EDS spectrum of sample 2 (green particle),

Credit HEI Arc, S.Ramseyer.
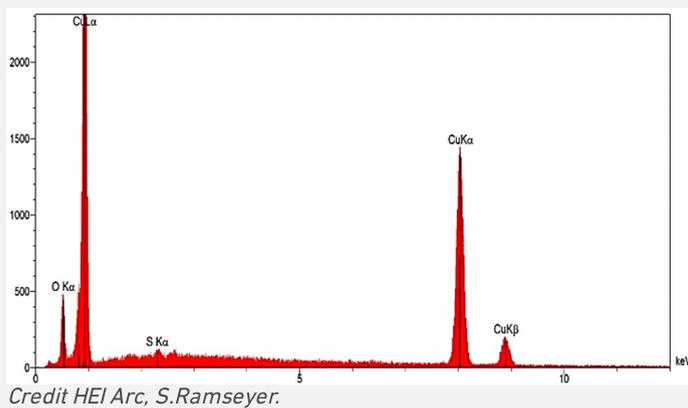
Fig. 14: EDS spectrum of sample 2 (red particle),

Credit HEI Arc, S.Ramseyer.
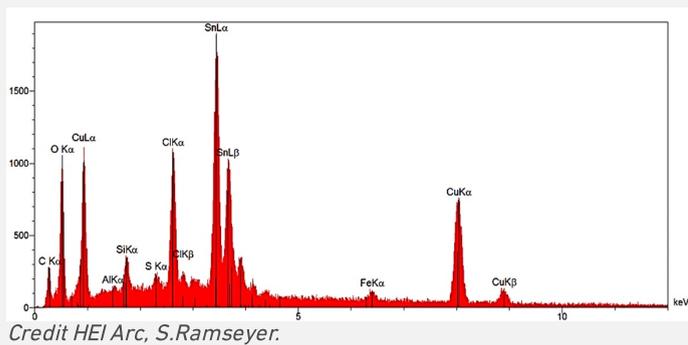
Fig. 15: EDS spectrum of sample 3 (green corrosion product),
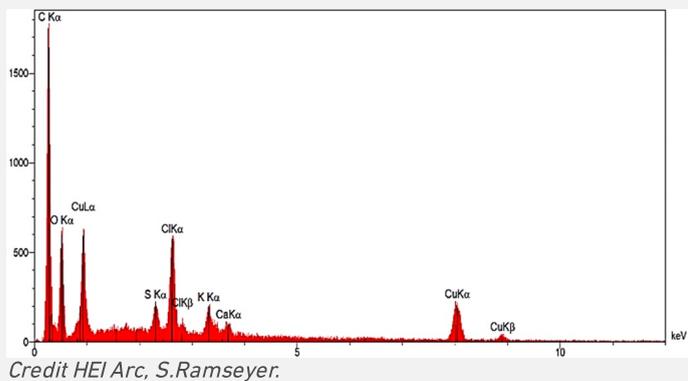

Credit HEI Arc, S.Ramseyer.

Fig. 16: EDS spectrum of sample 4 (white particle),
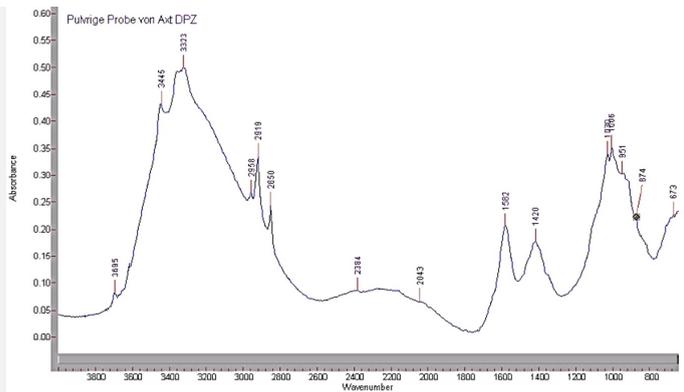
Fig. 17: FTIR spectrum of sample 4 (white particle),

Credit Lab of Swiss National Museum, Affoltern am Albis.

Corrosion form   Multiform - pitting

Corrosion type   None

Complementary information

Nothing to report.

⌄ MiCorr stratigraphy(ies) – CS

Fig. 10: Stratigraphic representation of the object in cross-section using the MiCorr application. This presentation can be compared to Fig. 18. CP1 corresponds to CP1c, Credit HE-Arc CR, C.Degrigny.
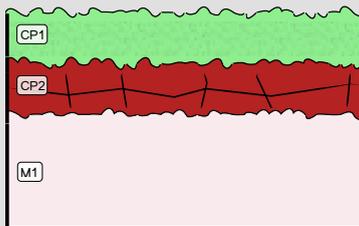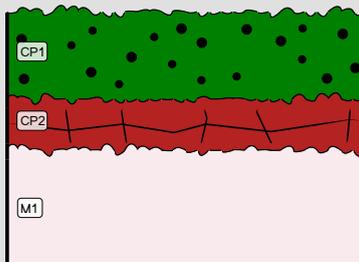

Fig. 11: Stratigraphic representation. of the object in cross-section using the MiCorr application. This presentation can be compared to Fig. 18. CP1 corresponds to CP1a, Credit HE-Arc CR, C.Degrigny.

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

The schematic representation of corrosion layers below integrates additional information based on the analyses carried out.

M Metal: probably a tin bronze with some arsenic.
CP2 Brown patina: could be cuprite.
CP1c Local corrosion: powdery green corrosion products that could be related to active corrosion due to the presence of large amount of chlorine (atacamite, paratacamite or clinoatacamite ($Cu_2Cl(OH)_3$)).
CP1b Red-orange corrosion: no analysis was performed, it could be a copper oxide, most likely cuprite (Cu_2O).
CP1a Green corrosion layer: the green particles are similar to CP1c. White particles might reflect the presence of an organic compound.
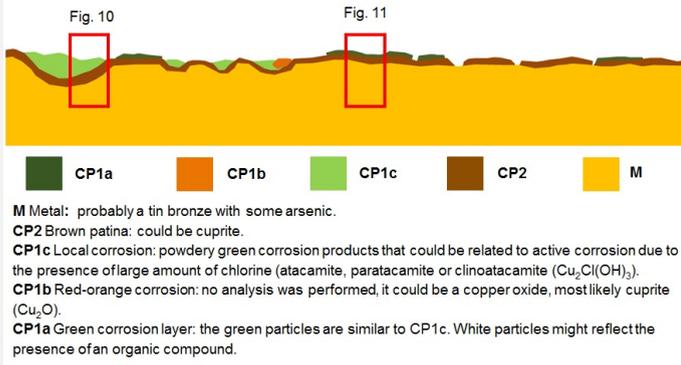
Credit

Fig. 18: Complementary stratigraphic representation of a virtual cross-section through the axe head based on visual observations and additional analyses with indication of stratigraphies of Figs. 10 and 11.

Conclusion

The axe head is probably a tin bronze containing a small amount of As. It is difficult to interpret the corrosion layer only by macroscopic observation. The analyses show that all green corrosion products contain chlorides that might originate from strip-cleaning by hydrochloric acid (although not documented). Active corrosion is not proved but we suspect the presence of atacamite, paratacamite or clinoatacamite (Cu2Cl(OH)3). FTIR revealed the presence of an organic compound on the metal surface (possibly a protective coating).

References

References on analytic methods and interpretation

1. Bertholon, Régis. La limite de la surface d'origine des objets métalliques archéologiques. Caractérisation, localisation et approche des mécanismes de conservation. ©Régis Bertholon, Paris, 2000.

2. Degrigny, Christian and Senn, Marianne. Methodology to study and analyse the microstructures and corrosion forms of ancient and historic metals: application to metallographic samples from Swiss collections MIFAC-Métal. Projet Sagex, Final Report, Haute école de conservation-restauration ARC, Neuchâtel, 2012.

3. Selwyn, Lyndsie. Métaux et corrosion Un manuel pour le professionnel de la conservation. Institut Canadien de Conservation, Ottawa, 2004.