



AXE HEAD N11 - TIN BRONZE - BRONZE AGE

Artefact name Axe head N11

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Url /artefacts/536/

▼ The object



Credit HE-Arc CR_E.Forster.

Fig. 1: Axe head n°11,

▼ Description and visual observation

Description of the artefact 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 Bronze Age

chronology tpq

chronology taq

Chronology comment

Burial conditions / environment Soil

Artefact location Neues Museum, Biel/Bienne

Owner Neues Museum, Biel/Bienne

Inv. number N11





Complementary information

Nothing to report.



Credit HE-Arc CR, E.Forster.



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

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),

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

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.

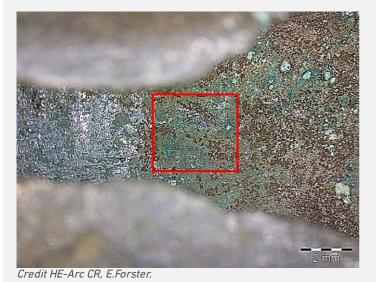


Fig 7: Green dark corrosion layer where sample 4 has been taken,

The schematic representation below gives an overview of the corrosion layers encountered on the head axe from a first visual macroscopic observation.

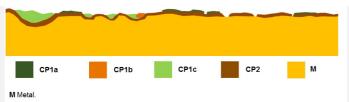


Fig. 8: Stratigraphic representation of corrosion products of the axe head (based on visual observations),

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



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

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 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.

P.4/8





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

Other metal elements As, Sn

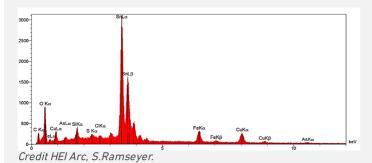
Complementary information

Nothing to report.

Analyses by SEM/EDS indicate that the light yellow particles of sample 1 are predominantly composed of Sn and 0 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).

	Sample / particles	Major elements	Minor elements
Green powdery corrosion product	Sample 1	Sn + 0	C + Cu + Fe + S + Cl + As
	Sample 2 – CP1c (Fig. 10) - Green particles	0 + Cu + Cl + Sn	Fe + S
	Sample 2 – CP2 (Fig.10) - Red-brown particles	Cu + 0	
	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 + 0	S + C
	Sample 4 – CP1a (Fig. 11) - White particles	С	0 + Cl + S + K + Cu

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

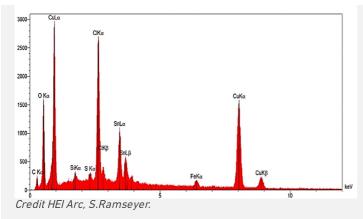


Fig, 12: EDS spectrum of sample 1 (yellow powder),

Fig. 13: EDS spectrum of sample 2 (green particle),







1500-Credit HEI Arc, S.Ramseyer.

Fig. 14: EDS spectrum of sample 2 (red particle),

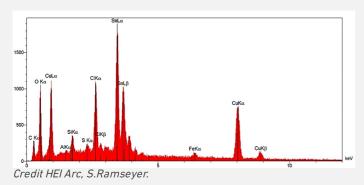


Fig. 15: EDS spectrum of sample 3 (green corrosion product),

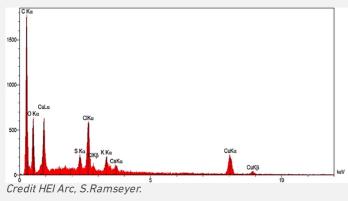


Fig. 16: EDS spectrum of sample 4 (white particle),

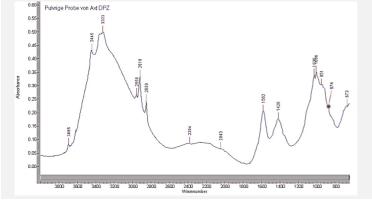


Fig. 17: FTIR spectrum of sample 4 (white particle),

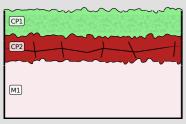
Credit Lab of Swiss National Museum, Affoltern am Albis.

Corrosion form Multiform - pitting

Corrosion type None

Complementary information

Nothing to report.



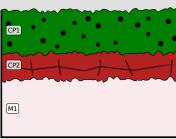
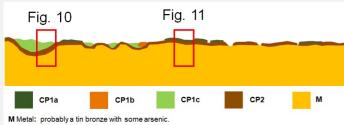


Fig. 10: Stratigraphic representation of the axe (sample 3) in crosssection using the MiCorr application. The characteristics of the strata are only accessible by clicking on the drawing that redirects you to the search tool by stratigraphy representation. This presentation can be compared to Fig. 18. CP1 corresponds to CP1c, Credit HE-Arc CR, C.Degrigny.

Fig. 11: Stratigraphic representation. of the axe (sample 4) in crosssection using the MiCorr application. The characteristics of the strata are only accessible by clicking on the drawing that redirects you to the search tool by stratigraphy representation. 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 of Fig. 8 integrating additional information based on the analyses carried out is given in Fig. 18.



CP2 Brown patina: could be cuprite.

 $\textbf{CP1c} \, \text{Local corrosion: powdery green corrosion products that could be related to active corrosion due to} \,$ 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

 $({\rm Cu_2O}).$ CP1a Green corrosion layer: the green particles are similar to CP1c. White particles might reflect the presence of an organic compound

Credit HE-Arc CR, E.Foster

Fig. 18: Improved stratigraphic representation of a virtual crosssection through the axe head based on visual observations and additional analyses and visualization of the two 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 metal and sample

References on analytic methods and interpretation

- 1. Bertholon, R. (2000) La limite de la surface d'origine des objets métalliques archéologiques. Caractérisation, localisation et approche des mécanismes de conservation. © Régis Bertholon, Paris.
- 2. Degrigny, C. and Senn, M. (2012) 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.
- 3. Selwyn, L. (2004) Métaux et corrosion Un manuel pour le professionnel de la conservation. Institut Canadien de Conservation, Ottawa.



