Chemical composition of prehistoric copper artefacts from Transylvania, Romania

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Abstract

This work is part of a large archaeometallurgical project, which aims to study the beginnings of metalworking in Transylvania. Seventeen samples of Eneolithic and Bronze Age objects were analysed by Inductively Coupled Plasma - Atomic Emission Spectrometry and Inductively Coupled Plasma - Mass Spectrometry. The analyses disclosed high-purity copper for most of the heavy artefacts, a fact which has opened the discussion on distinguishing between native copper and smelted copper as raw material used for manufacturing Eneolithic artefacts.

Introduction

Transylvania is referred to in the literature as an important region for the prehistory of central and south-eastern Europe, being well known for its rich deposits of gold, copper and salt, which were exploited from early times. The beginnings of metal production in this area still raise a lot of questions as concerns the nature of raw materials, extractive activities, processing technologies, circulation of heavy artefacts, and intentional alloying of copper with arsenic and antimony. With regard to the development of independent metallurgical centres in the south-east of Europe, Chernykh (1978; 1992) defined a Balkano-Carpathian metallurgical province with several subprovinces and related them to the production centres of Ai Bunar, Rudna Glava and an unknown centre in the Carpathian Mountains. This concept is based on the optical emission spectroscopy analyses of typologically different heavy Eneolithic artefacts. According to Chernykh, differences in typology are accompanied by differences in the material composition, such as the concentrations of trace elements like arsenic, nickel, silver and gold. Todorova has completed the previous work with a detailed typological study and defined three metallurgical sub-provinces in south-eastern Europe, namely Transylvania, Serbia with Bosnia and parts of Dalmatia and Thrace (Todorova 1981; Pernicka et al. 1997).

While the Serbian and Bulgarian metallurgical centres have been described in monographic studies, in Transylvania such a systematic, multidisciplinary project for the identification of prehistoric mines and complex analytical studies of the Eneolithic and Early Bronze Age artefacts was never carried out. The prehistoric copper mines from Rudna Glava, Bor and Majdanpek in Serbia and Ai Bunar in Bulgaria and their relationships to the artefacts discovered in the nearby area have been investigated by interdisciplinary projects. There have been established comparisons between the chemical composition and/or isotopic composition of the sources of raw materials and archaeological finds (Pernicka et al. 1993; Begemann et al. 1995; Pernicka et al. 1997; Jovanovic 1976; Jovanovic 1978; Todorova 1999). This approach has in many cases rejected the simplistic standard geographical proximity of the raw sources considered in the existing archaeological models.

Transylvania has yielded an impressive amount of heavy copper objects (altogether 500 kg), objects belonging to Eneolithic cultures such as Petreşti, Tiszapolgár, Bodrogkeresztur, Herculane-Cheile and Turzii-Hunyadhalom. These artefacts have probably been produced by the exploitation of copper ore deposits from the Carpathians (Vulpe 1973: 220-234; Comşa 1987: 102-109). Evidence of local extraction and primary metallurgy of copper have motivated us to start an archaeometallurgical investigation within the Carpathian Arch. This project aims to establish the origin of raw materials used for the manufacture of Eneolithic and Early Bronze Age copper artefacts and to study the applied technologies within the Eneolithic and Early Bronze Age cultures of Transylvania, in comparison with technologies used in other

regions from south-eastern and central Europe. We have started in 1997 with the creation of a relational database system of copper ores from the Carpathians (Kadar 1999). The database has been continuously updated with Eneolithic and Early Bronze Age archaeological finds from Transylvania. Available analytical data has been entered into the database and further investigations have been carried out as concerns the chemical composition and metallographic structure of the objects in discussion (Kadar 2000).

This paper presents new data on the chemical composition of the heavy implements, mainly from south-western Transylvania. Analyses were carried out by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) at the European Large Scale Geochemical Facility, University of Bristol, Great Britain.

Catalogue of archaeological materials studied

The artefacts studied here belong to the south-west of Transylvania, a region very rich in Eneolithic metal finds (Figure 1).

B1. Small copper chisel belonging to the Tiszapolgár culture, discovered at Şeuşa-Gorgan near Alba Iulia, Alba County. Exhibition Room of the University of Alba Iulia (Ciută et al. 2001).

B2. Axe-adze, Jászladány type, Petreşti variety, History Museum of Sebeş; Inv. No. 247 (88). Vulpe 1975, 5, 41, no.150, pl. 20/150.

B3. Axe-adze, Jászladány type, Bradu variety, stray find, History Museum of Sebeş; Inv. No. 1491. Vulpe 1975, 5, 44, nr. 185, pl. 25/185.

B4. Shafthole axe, Şasa, Sălaj county, History Museum of Zalău, Inv. No. CC.18/1975.

B6. Hammer axe, Plocnik type, discovered at Turda, History Museum of Transylvania Cluj Napoca, Inv. No. P 848 (Junghans No. V 9567-8985, 1974) (Beşliu, Lazarovici, Olariu - L12, 1992).

B10. Fragment of axe discovered at Ghirbom, in a settlement belonging to the Petreşti culture, phase AB, History Museum of Alba Iulia, Inv. No. 5648. Vulpe 1975, 5, 53, no. 244A, pl. 31/244A, and Aldea and Ciugudean (1986).

B12. Wedge-axe, History Museum of Alba Iulia, Inv. No. 6945.

B13. Axe-adze, Jászladány type, Petreşti variety, discovered at Şpălnaca, Alba County, History Museum of Alba Iulia, Inv. No. 4235. Vulpe 1975, 5, 41, no.151, pl. 20/151.

B15. Copper knife blade from Sibişeni, Eneolithic layer, Alba County.

B16. Axe-adze, discovered at Cetatea de Baltă, stray find, History Museum of Aiud, Inv. No. 5117.

B17. Axe-adze, discovered at Ormeniş, stray find, History Museum of Aiud, Inventory No. 5043.

B20. Fragment of axe-adze, stray find, discovered at Cetea, Alba County, History Museum of Aiud, Inv. No. 2654.

B25. Chisel, Middle Bronze Age, History Museum of Aiud, Inv. No. 858.

B27. Copper ingot from a hoard discovered at Şpălnaca, Alba County, Hallstatt A, History Museum of Aiud, Inv. No. 1235.

B28. Fragment of axe discovered at Ungurei, Alba County, History Museum of Aiud, Inv. No. 58.

B32. Small copper ingot discovered in a settlement with several levels of occupation, at Pietri-Cetea, Alba County, History Museum of Aiud, Inv. No. 2502.

B34. Knife blade, stray find, Căpud, Alba County, Bronze Age, History Museum of Aiud, Inv. No. 979.

Methodology

Seventeen samples were analysed by both ICP-AES and ICP-MS. Bulk chemical analyses were carried out by ICP-AES and trace elements such as Ag, Co, Ni, Hg, Zn, Au, Pb were measured by ICP-MS. The advantages of both methods are an overall good precision, accuracy and rapidity when compared to other analytical techniques such as neutron activation or atomic absorption spectrometry.

Samples were removed from each artefact by drilling a one millimetre diameter hole and collecting the turnings. The first two or three millimetres of material were discarded to exclude metal corroded by inter-granular corrosion or chemically altered by corrosion processes. Only one hole

Fig. 1. Map of Eneolithic finds in south-western
Transylvania. Hammer axes (●) and axe-adzes (■).
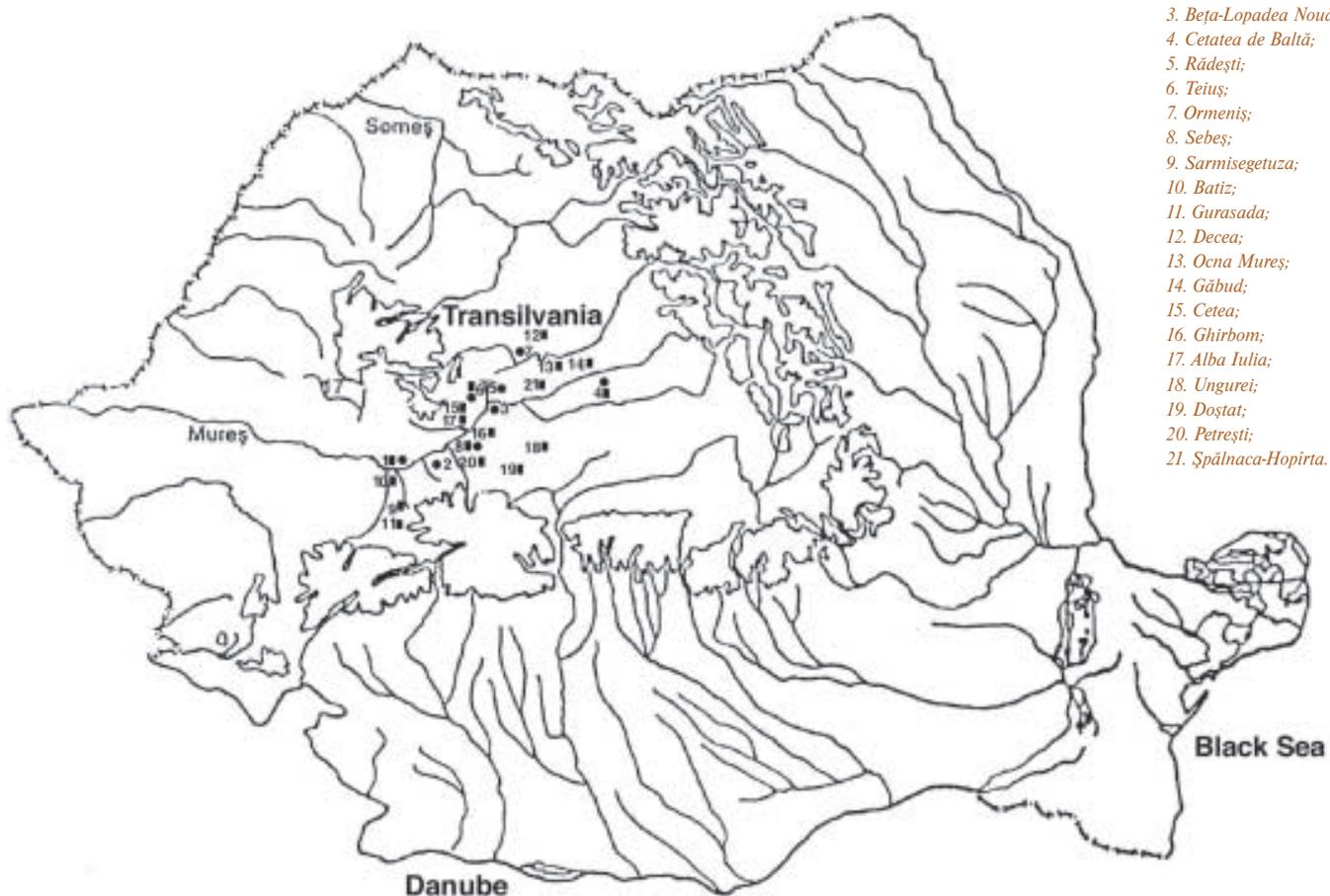
1. Turdaş;
2. Vinţu de Jos;
3. Beţa-Lopadea Nouă;
4. Cetatea de Baltă;
5. Rădeşti;
6. Teiuş;
7. Ormeniş;
8. Sebeş;
9. Sarmisegetuza;
10. Batiz;
11. Gurasada;
12. Decea;
13. Ocna Mureş;
14. Găbud;
15. Cetea;
16. Ghirbom;
17. Alba Iulia;
18. Ungurei;
19. Doştat;
20. Petreşti;
21. Şpălnaca-Hopirta.

was permitted in each artefact thus the place of sampling had to be carefully chosen in order to be representative for the object. Where the object to be sampled was too thin for drilling, a scalpel was used to scrape a sample from an edge, which had been previously cleaned mechanically.

Sample preparation started with cleaning in excess of acetone, then 50 mg of each sample was weighed accurately into a PTEF beaker, 5 ml of aqua regia ($HCl + HNO_3$ mixture, 3:1) were added and then made up to 25 ml volume using deionised water. Some of the samples were microwave digested in order to keep possibly volatile trace elements in the solution.

Determinations were made using an Jobin Yvon JY 24 instrument for supposed major elements such as Cu, As, Fe, Sb and trace elements were determined by ICP-MS on a PlasmaQuad equipment. Synthetic multi-element standards were made up from commercial standard solutions. A series of five standards and a blank were made up to run first and to collect the count data for each concentration. Then the samples were run with standard reference materials at intervals. In order to monitor instrumental drift a "drift control" was also included every seven samples, which was a solution made up from synthetic standard solutions to a set series of concentrations for all elements analysed. Usually three standards were selected for the calibration. The instrumental drift was checked by plotting the individual measurements for the "drift control" and corrections have been applied where necessary. Standard reference materials were used to monitor the accuracy of the measurements and these were prepared in exactly the same way as the artefacts.

The precision of data (the relative standard deviation) is estimated at ± 1 % for major elements and for trace elements around ± 10 %. The wavelength used to analyse copper was 324.754 nm.

Results and discussions

One of the most debated problems is the nature of raw material used for the production of the Transylvanian Eneolithic and Early Bronze Age artefacts. To understand the early use of copper we have tried to identify objects as having been made from native copper and to distinguish them from objects made from smelted copper. Two techniques have been used in combination: trace element analyses and microstructure characterisation.

Here we will discuss only the chemical composition of the samples presented in Table 1. Some objects have been already analysed by emission spectroscopy at the Württembergisches Landesmuseum of Stuttgart (Junghans et al. 1974) and by neutron activation (Beşliu et al. 1992; Beşliu & Lazarovici 1995). As regards the Eneolithic artefacts, two of them, B1 and B12 present traces of mercury in the composition. The presence of mercury (0.62 ppm and 2.16 ppm), together with low concentrations of cobalt and nickel as impurities, would suggest that these objects have been made by cold hammering and possibly tempering of native copper. As stated recently by Pernicka et al. (1997: 118): "Smelting of copper removes mercury very effectively so this element might possibly serve as a useful indicator to distinguish between artefacts made of native copper and such made from smelted copper".

Other useful markers to distinguish between native and smelted copper are cobalt and nickel which are almost invariably higher in smelted copper, as indicated by analyses of copper prills found in Chalcolithic and Early Bronze Age slags from Feinan, Jordan (Hauptmann et al. 1992).

With regard to arsenic, one object (B4) presents higher concentration (7114 ppm), otherwise arsenic contents are much lower. We conclude that arsenic was not added deliberately but was a natural impurity in the ores used. The same is true

Table 1. Chemical composition of copper artefacts from Transylvania, Romania, obtained by ICP-AES and ICP-MS analyses.

Sample ID	Description	Period	Location	Cu wt%	As ppm	Fe ppm	Pb ppm	Sb ppm	Sn ppm	Ag ppm	Co ppm	Ni ppm	Hg ppm
B1	Small Chisel	Eneolithic	Şeuşa-Gorgan Alba	96.2	79	284	11	11	90	41	4	75	0.62
B2	Axe-adze	Eneolithic	Sebeş-Alba	97.6	89	52	68	9	71	32	< 2	75	ND
B3	Axe-adze	Eneolithic	Petreşti-Alba	100.6	84	38	24	11	77	92	< 21	42	ND
B4	Shafthole axe	Bronze Age	Şasa-Sălaj	95.5	7114	62	247	863	123	720	2	186	ND
B6	Hammer axe	Eneolithic	Turda-Alba	93.6	41	51	4	25	75	4	8	27	ND
B10	Axe fragment	Eneolithic	Ghirbom-Alba	96.6	125	ND	22	26	69	136	ND	18	ND
B12	Wedge-axe	Eneolithic	Alba	98.4	25	6	9	3	76	50	49	79	2.16
B13	Axe-adze	Eneolithic	Spălnaca-Alba	97.7	22	16	9	8	70	59	< 1	61	ND
B15	Knife blade	Eneolithic	Sibişeni-Alba	97.1	35	27	39	16	165	49	798	56	-
B16	Axe-adze	Eneolithic	Cetatea de Baltă-Alba	97.9	17	16	454	449	< 3	11	79	35	-
B17	Axe-adze	Eneolithic	Ormeniş-Alba	97.3	6	14	449	421	< 3	5	87	30	-
B20	Axe fragment	Eneolithic	Cetea-Alba	98.4	15	548	437	453	< 3	34	77	157	-
B25	Chisel	Bronze Age	Râmeţi-Alba	93.0	257	2840	1646	1286	99300	24	295	1736	-
B27	Copper ingot	Hallstatt	Spălnaca-Alba	95.7	108	2010	585	568	< 2	17	146	33	-
B28	Axe fragment	Eneolithic	Ungurei-Alba	102.3	6	10	417	397	< 2	5	93	55	-
B32	Copper ingot	Late Bronze Age	Cetea-Alba	91.7	19420	45	3577	22417	22460	39	211	3691	-
B34	Knife blade	Bronze Age	Căpud-Alba	98.3	< 2	27	471	488	< 3	19	205	107	-

ND= not detected.

for antimony when talking about the Eneolithic objects.

Looking at iron, according to Junghans et al. (1974), an iron content below 1% seems to be typical of Eneolithic and Early Bronze Age artefacts. The low content of iron may have several reasons. It may be caused by smelting rich oxidic copper ores, i.e. relatively pure malachite with a low content of gangue from the matrix rock, or an originally high content of iron may have been reduced by a technological process. Another reason would be the remelting before casting, with the oxidation and slagging of iron as demonstrated experimentally by Tylecote and Boydell (1978) and by Merkel (1990).

The problem of distinguishing between native and smelted copper when dealing with high purity copper from south-eastern Europe has been raised in the last century, further studied by Otto and Witter (1952) by optical emission spectroscopy and presented by Junghans and co-workers in their study of prehistoric metal objects from all over Europe. These scholars are inclined to state that spectroscopically high purity copper in objects is indicative of native copper as source. Chernykh (1992) states that his chemical groups I and II derive from monometallic copper ores.

In Transylvania, evidence concerning the early smelting of copper ores starts with Eneolithic cultures and continues in the "transition period" and in the Early Bronze Age cultures.

For example, one of the finds, a piece of melted metal discovered at Livezile-Alba County, in the context of the chronological horizon of the Livezile group of the Early Bronze Age, has the chemical composition of an alloyed copper: 91.8 % Cu, 7.2 % Zn, 0.8 % Fe, 0.1 % Pb and 0.03 % As. Local communities have overcome the phase of processing native copper and have started to exploit local complex ores in which copper is associated with zinc, such as ores from Bucium and Săcărâmb (Ciugudean 1996: 119; Beşliu et al. 1992: 123, appendix 4).

Considering the chemical composition of the investigated objects, the conclusion would be that most of the Eneolithic objects are made from pure copper, this result being in accordance with earlier studies. As regards the impurity levels in native copper compared to those in smelted copper, it has been demonstrated that concentrations of cobalt and nickel in native copper tend to be lower than in smelted copper (Pernicka et al. 1997: 124). Concentrations of cobalt in native copper have been shown as being below 10 ppm and for nickel below 100 ppm. Nickel especially is considered to be a useful marker in distinguishing between artefacts made from smelted copper and such made from native copper. In this respect, in addition to the two objects in which the presence of mercury has been found (samples B1 and B12), some other Eneolithic objects would qualify as native copper. The axe-adzes (samples B2 and B13), the hammer axe (sample B 6) and the axe fragment (sample B10) present concentrations of

B2 Axe-adze

B4 Shafthole axe

B1 Small Chisel

B10 Axe fragment
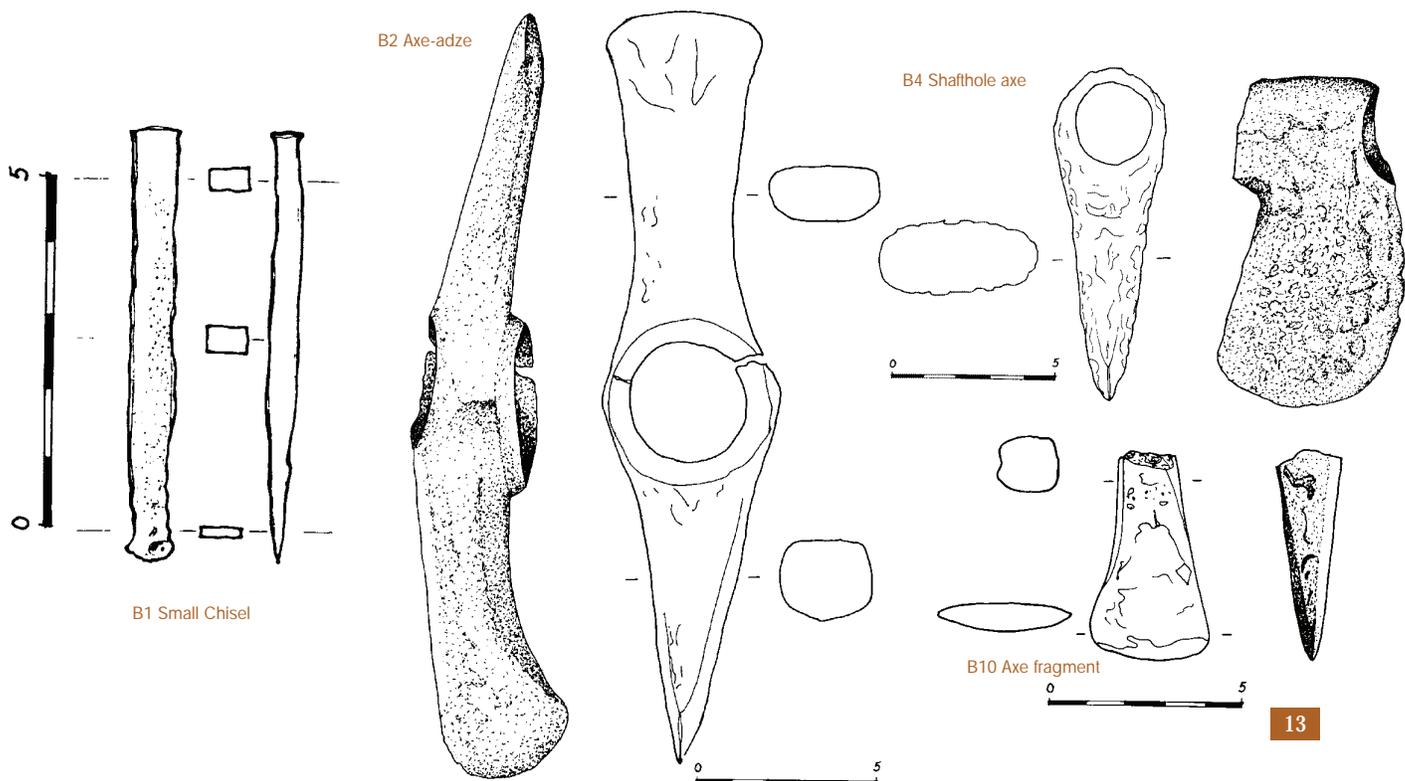
nickel between 18 and 75 ppm and concentrations of cobalt of less than 8 ppm, with one exception for cobalt (sample B12 in which the concentration is 49 ppm).

Conclusions

Our research will be continued and extended to the eastern part of Transylvania in order to identify possible geological sources of raw materials in the Eneolithic and EBA and to reconstruct production and exchange systems at the level of Eneolithic and EBA communities. By updating our archaeometallurgical database with new analyses and finds we would like to fill, at least in part, a gap in the documentation of Romanian prehistoric metallurgy.

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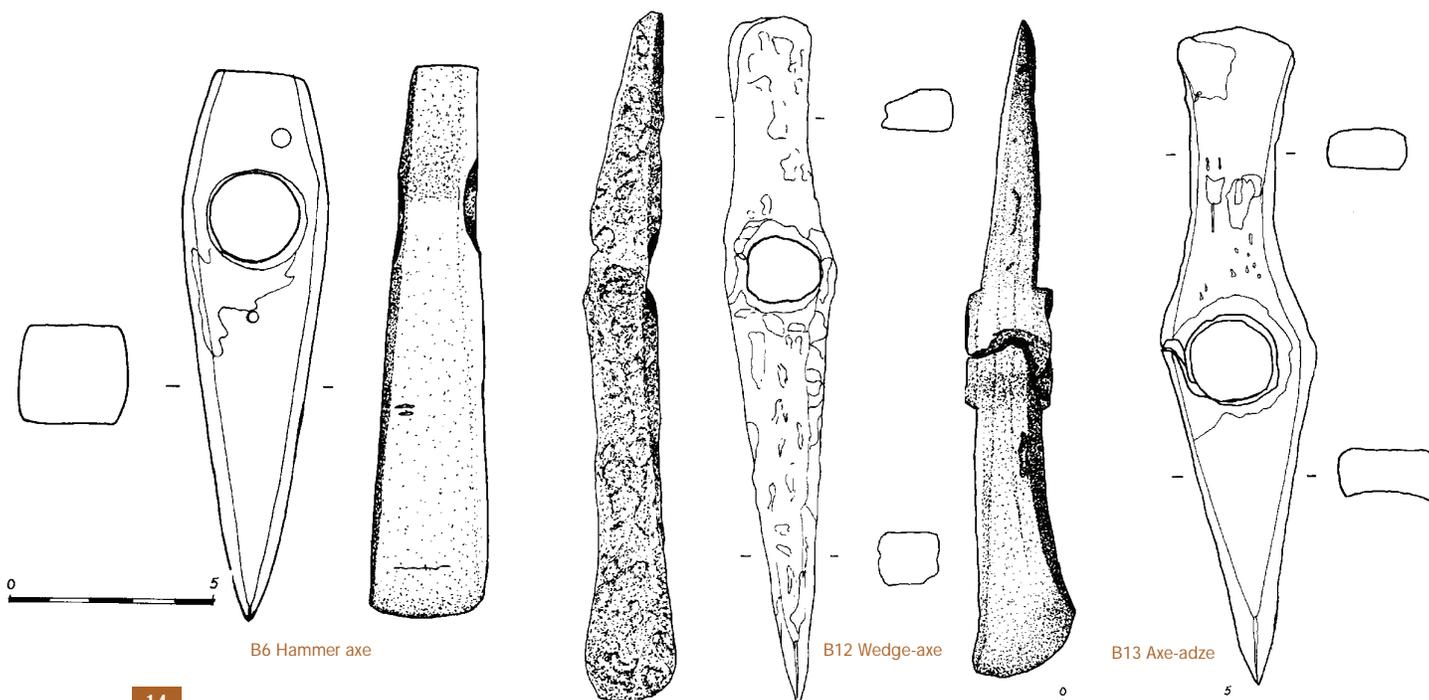
B6 Hammer axe

B12 Wedge-axe

B13 Axe-adze