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ARCHAEOMETALLURGICAL STUDIES OF BRONZE AGE OBJECTS FROM THE ROMANIAN CULTURAL HERITAGE

R. BUGOI[1], B. CONSTANTINESCU[1], A. D. POPESCU[2], F. MUNNIK[3]

[1] "Horia Hulubei" National Institute for Nuclear Physics and Engineering, PO BOX MG-6, Bucharest 077125, Romania, E-mail: bugoi@nipne.ro, bconst@nipne.ro
[2] "Vasile Pârvan" Institute of Archaeology of the Romanian Academy, PO BOX 22, Bucharest 010667, Romania, E-mail: ancadiana_popescu@yahoo.com
[3] Helmholtz-Zentrum Dresden-Rossendorf, PO BOX 510119, Dresden D-01314, Germany
E-mail: f.munnik@hzdr.de

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Abstract. This paper reports the chemical composition of some ancient metallic objects dated to the Bronze Age period and found on Romanian territory. Preliminary ED-XRF measurements were performed on cleaned areas of artefacts, while the nuclear microprobe experiments were conducted on tiny fragments detached from the same zones. The identified trace-elements led to some speculations about the employed metallurgical procedures and raw materials. Thus, the chemical composition of the Early Bronze Age dagger found at Ocnița suggests its manufacturing by smelting a mixture of copper and arsenic ores, while the Late Bronze Age artefacts have compositional patterns supporting the idea of connections and exchanges between the ancient populations living along the Danube river.

Key words: PIXE, archaeometallurgy, chemical composition, bronze, arsenical copper, Bronze Age.

1. INTRODUCTION

Metals played a significant role in society throughout the ages, their use strongly influencing the course of civilization and human history.

The ancient people observed that the properties of metals could be seriously improved by alloying or mixing them with other elements. Through metallurgical procedures, melting points can be lowered, leading to final products of enhanced hardness; other characteristics, such as strength, workability and resistance to corrosion, can be similarly improved [1].

The scientific study of ancient metallic objects – coins, weapons, tools or adornments – is of a special significance from archaeological and historical standpoint. Compositional analyses can identify the alloys made by the ancient people, help in the authentication of items with uncertain origin (i. e. not excavated from well-controlled archaeological environments), bring information on the employed metallurgical procedures, and, in the case of very ancient artefacts, provide hints about the raw materials provenance [1].

Native metals and those refined from ores are known as primary or virgin metals. Secondary metals are the ones derived from scrap re-melting, which, in turn, might have come from a variety of primary metal sources. The distinction between the primary and secondary metals is important if the chemical composition data are to be used for answering provenance questions. Thus, while analytical results on artefacts made of primary metals can be relied as yielding meaningful information on the origin of raw materials and the existence of ancient trade routes, considerations on provenance issues based on compositional data only become more speculative in the case of the secondary metals, because of the likely heterogeneous origin of the scrap [1].

During the last years, within the framework of ARCHAEOMET [2] and ROMARCHAEOMET [3] interdisciplinary research projects, a large number of ancient metallic objects from several Romanian museums were investigated with respect to their chemical composition [4–10]. In most of the cases, non-destructive Energy-Dispersive X-Ray Fluorescence (ED-XRF) measurements were performed using a portable spectrometer from Oxford Instruments [11].

The ED-XRF measurements provided accurate quantitative results for the major and minor elements only; these data were mainly used for the identification of the alloy from which the investigated artefacts were made – *e.g.* gold (refined or not), silver, electrum, arsenical copper, tin bronze, leaded bronze, brass, etc. and for establishing the fineness of gold and silver objects.

Since ED-XRF spectrometry with portable instruments inherently suffers from limited sensitivity, it was needed to resort to another analytical technique to accurately determine the trace-elements content. Thus, PIXE (Particle Induced X-ray Emission) measurements on some minute fragments (~ 100 μm^2) taken from a selection of Bronze Age objects were made to refine the previously obtained ED-XRF chemical composition data. Those tiny metallic chips were taken from Bronze Age objects – weapons and tools – from the small areas purposely cleaned to remove the superficial corrosion layers, a preparatory treatment making the artefacts suitable for ED-XRF analyses.

Taking into account the smallness of these samples, PIXE measurements were done at the microprobe facility of the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) – Tandetron accelerator [12]. The sought trace-elements were: nickel, cobalt, arsenic, lead, gold, silver, antimony, elements traditionally considered as indicative for the raw materials and ancient metallurgical procedures in the case of copper-based alloys [1].

2. EXPERIMENTAL

The ED-XRF measurements were conducted with a portable spectrometer – model X-MET 3000 TXR+ from Oxford Instruments. This device contains an X-ray tube with a Rh anode (40 kV maximum voltage and 6 μA maximum current intensity) and a Peltier cooled Si PIN diode (FWHM ~ 275 eV at 5.9 keV) working as a detector.

For the in-vacuum micro-PIXE HZDR experiment, a 3 MeV proton beam provided by the 3 MV Tandetron accelerator has been used. The beam was focused to 10 μm diameter and 60×58 μm^2 areas on the metallic bits were scanned. These experimental parameters were chosen taking into account the smallness of the investigated samples, trying to get some "average" quantitative results and avoiding to measure the eventual inclusions that might exist in such inhomogeneous ancient alloys. A Si(Li) detector (FWHM ~180 eV at 5.9 keV), filtered with a 165 μm thick aluminum foil was used to detect the characteristic X-rays. The aluminum filter was chosen to reduce the pile-up peaks appearing in the PIXE spectra from the matrix elements (mainly Cu) and to optimize the Limits of Detection (LoD) for the trace-elements. The total accumulated electric charge on each sample was on the order of several μC, to obtain spectra of satisfactory statistics. In all cases, the analyzed areas were chosen as flat as possible. The elemental concentrations were obtained by processing the PIXE spectra with GUPIXWIN code [13, 14]. The micro-PIXE quantitative results are given in table 1, together with the ED-XRF data previously obtained by measuring the small cleaned zones on artefacts surfaces.

3. RESULTS AND DISCUSSIONS

Table 1 indicates an acceptable degree of agreement between the concentrations of major elements determined by PIXE and the ones obtained by ED-XRF. This cross-check was absolutely necessary, mostly to be sure of the representativeness of the small samples analyzed by PIXE, and considering the segregation phenomena that might appear in ancient copper alloys [15 and references therein].

3.1. ARSENICAL COPPER

3.1.1. Arsenical copper – general archaeometallurgical considerations

Copper alloyed with small quantities of arsenic, lead, antimony and tin appeared during the Eneolithic, indicating the first attempts of prehistoric metallurgists to improve the technical characteristics of native copper [1].

For many ancient cultures, the use of arsenical copper represented a transitional stage of development. Chronologically speaking, arsenical copper appeared after the initial employment of native copper only, while bronze (i.e. copper-tin alloy) started to be extensively used at the beginning of the Middle Bronze Age (MBA).

Arsenical copper alloy appeared at a certain moment during the 4th millennium B.C., nearly simultaneously in the Near East and in several regions of Central Europe. Arsenical copper can be considered the characteristic alloy of the Early Bronze Age (EBA) [16].

The presence of arsenic in copper alloys – usually in percentages up to 8 wt% is beneficial in maintaining the workability of the resulting metal. The intentional addition of arsenic improves the casting and working properties of copper. The presence of arsenic in copper increases the hardness of the metal, and also acts as an antioxidant which reduces the gas porosity formed during casting [1, 16–20].

The presence of arsenic might also change the color of the resulting alloy – for example, arsenical copper alloys with 4–12 wt% As are known to have a nice golden appearance [17].

There are large variations in the arsenic content of EBA artefacts, which sometimes can amount to more than 15 wt%. More commonly, arsenic was encountered in such objects in concentrations well under 5 wt% [16–20].

There were two ways of obtaining relatively high arsenic concentrations in copper-based alloys: either by purposely selecting copper minerals particularly rich in arsenic, such as the sulfoarsenate ores enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$), or by adding arsenic minerals – *e.g.* orpiment (As_2S_3) or realgar (AsS) to the smelting mix [1]. However, copper objects with high arsenic content could not have originated from the utilization of arsenic – containing copper ores only, because arsenic in small quantities would have oxidized during the smelting process into the easily volatile compound As_2O_3 and therefore evaporate [16].

It is very likely that EBA metallurgists recognized that the use of arsenic-rich copper ores or the incorporation of arsenic-rich ores into the copper-smelting mixture would result in a metal of particular properties, and consequently they would purposely select such ores with the intention of producing a superior class of material [1].

For EBA artefacts, one of the main questions of research is whether the arsenical copper alloy was intentionally made or whether it was the mere result of using arsenic-containing copper ores [1, 16].

The limit between the naturally obtained *i.e.* by the use of copper-arsenic ores only and purposefully produced arsenical copper was set by the previous archaeometallurgical studies to be roughly 2 wt% As [16 and references therein].

Arsenic, antimony, and silver are associated with copper only in the sulfoarsenate ores and not in other copper ores, where usually arsenic is absent.

The simultaneous presence of these elements in the final product might be indicative for a deliberate use of sulfoarsenate ores for the manufacturing arsenical copper objects [1, 17].

3.1.2. Arsenical copper – analytical results and interpretation

One of the artefacts investigated in this study is a dagger with three rivet-holes, found in a settlement at Ocnița, Vâlcea county, together with Coțofeni and Glina pottery, and dated to the Early Bronze Age (EBA) [21]. The artefact was made from arsenical copper, featuring a relatively high content of arsenic (6.7 wt%) – see the results from Table 1 and the PIXE spectrum shown in Fig. 1.

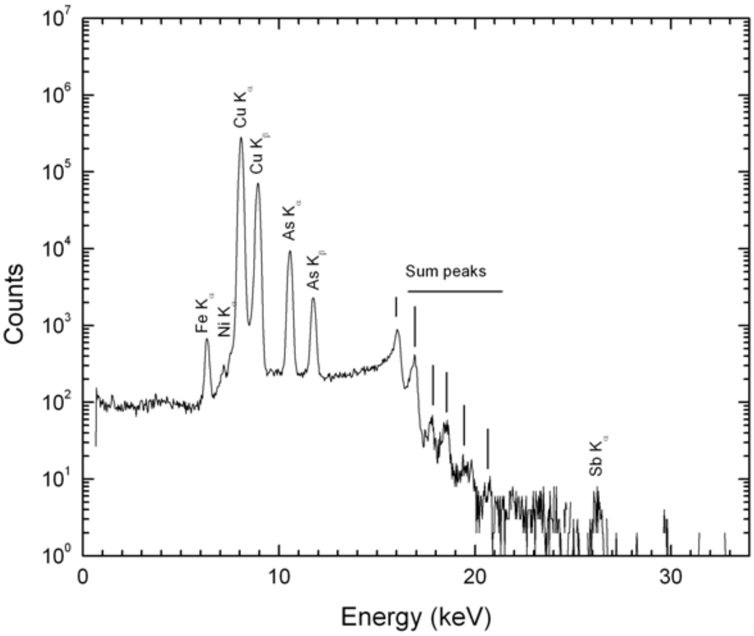

Fig. 1 – PIXE spectrum of a fragment from the arsenical copper dagger from Ocnița.

The overall appearance of the Ocnița dagger indicates a rather careful manufacturing of this object. The dagger has a nice golden color – in agreement with its relatively high arsenic content. Though made from a hard metallic alloy, this dagger does not seem to have been actually used as a weapon. Arguments pleading for this idea are its reduced dimensions (the overall length of the blade is 11.2 cm, from which at least 2 cm had been covered by hilt), but mostly its rounded point. The particular shape of this object suggests that it might have been used as a cutting tool in the domestic space [22–23]. It is also worth mentioning here that most of the EBA daggers discovered in the Lower Danube region came from settlements and just few of them were found in graves.

Table 1

Chemical composition of the analyzed objects
The relative statistical uncertainty of the reported concentrations is less than 5% for major elements and around 30% for trace-elements

Object	Fe(µg/g)	Co(µg/g)	Ni(µg/g)	Cu(wt%)	Zn(µg/g)	As (wt% or µg/g)	Ag(µg/g)	Sn(wt%)	Sb(µg/g)	Pb(µg/g)
Ocnița Early Bronze Age dagger (PIXE)	855	N.D.*	618	92.9	1822	6.7 wt%	N.D.	N.D.	429	N.D.
Ocnița Early Bronze Age dagger (ED-XRF)	700	N.D.	500	88.9	N.D.	10.8 wt%	100	N.D.	300	N.D.
Oinacu Late Bronze Age socketed axe with vertical ribs (PIXE)	5481	611	3956	94.0	N.D.	1884 µg/g	692	4.2	1142	4377
Oinacu Late Bronze Age socketed axe with vertical ribs (ED-XRF)	9000	N.D.	N.D.	93.6	N.D.	N.D.	N.D.	5.1	N.D.	3000
Oinacu Late Bronze Age socketed axe with vertical ribs inv. no. I 6007 (PIXE)	2493	292	5439	90.2	1425	3996 µg/g	1301	7.0	3918	8454
Oinacu Late Bronze Age socketed axe with vertical ribs inv. no. I 6007 (ED-XRF)	5000	N.D.	6000	86.30	9000	1500 µg/g	1000	10.8	N.D.	4000
Oinacu Late Bronze Age sickle fragment (PIXE)	552	345	4540	87.7	N.D.	7808 µg/g	700	9.8	4648	4712
Oinacu Late Bronze Age sickle fragment (ED-XRF)	4000	N.D.	N.D.	90.8	N.D.	N.D.	N.D.	8.7	N.D.	N.D.

* N. D.= Not Detected

Until now, no dagger with exactly the same characteristics – namely the peculiar round hafting-plate and the general aspect of the midrib – was ever reported in the archaeological literature.

However, the chemical composition of this dagger resembles quite well the one of a dagger with triangular hafting-plate discovered at Băile Herculane, Caraş-Severin county, and attributed to the Coțofeni culture (~ 3 400–2 800 B.C.). This artefact was analyzed in 1968 at ICECHIM and the following chemical composition was reported: 6 wt% As, 0.1 wt% Fe, 0.01 wt% Ni, 2…6 μg/g Ag [24–25]. Unfortunately, reference [24] does not mention the analytical methodology followed to obtain these quantitative results.

Hafting-plate daggers with relatively high arsenic content (~5…10 wt%) were found in many settlements and graves from the Lower Danube region dated to the end of the Eneolithic period and beginning of the Bronze Age.

Thus, one can quote here a dagger found in Durankulak, Bulgaria, whose chemical composition was determined in Leningrad by Optical Emission Spectroscopy (OES) – a surface analysis technique – and also in Heidelberg, by Instrumental Neutron Activation Analysis (INAA) – a bulk analytical technique [26–28]. Unfortunately, the results of the analyses carried out on this object in the two laboratories led to very different arsenic percentages: 18 wt % and 8.4 wt%, respectively!

A possible explanation for these serious discrepancies might be found in the phenomena of arsenic superficial enrichment observed in ancient arsenical copper objects [17]. There are two possible reasons for the higher arsenic content of the surfaces of arsenical copper objects [29]:

- either the apparition of a so-called inverse segregation phenomenon of the copper-arsenic alloy, i.e. the arsenic-rich eutectic was forced to migrate to the surface as the casting solidified;
- or an arsenic-enriched layer was formed as the result of the corrosion processes that were either naturally-occurring or intentionally provoked by the ancient craftsmen in the final stage of artefact production.

Other daggers with relatively high arsenic content are the one found in the main grave from a barrow at Utkonosovka, Ukraine (~ 5.5 wt%) and the ones discovered in the burial mounds from Usatovo, Ukraine (As content ranging from 3 wt% up to 10 wt%) [26-27].

Copper objects with high arsenic content were also frequently encountered in the North-Pontic area and especially in the Caucasian region [30]. For example, tanged daggers excavated in some graves belonging to the Majkop culture from Northern Caucasus (dated to the second half of the 4th millennium B.C. – beginning of the 3rd millennium B.C.) contain arsenic from 4 wt% up to 8 wt% [29].

Starting with the second half of the 4th millennium B.C., objects made of arsenical copper have been found not only in Anatolia, in the Aegean Sea region, but also in Central Europe – *e.g.* Mondsee, Pfyn and Cortaillod cultures [28, 31].

A good example is the hafting-plate dagger found at Reute, South-Western Germany (middle of the 4th millennium B.C.), with an arsenic content ~5 wt% [32].

No traces of silver were found in this sample. The PIXE LoD for silver in this arsenical copper matrix were estimated using GUPIXWIN software to be around 140 μg/g. This apparent lack (or presence in very low amounts) of this element complicates taking a clear-cut decision about the types of the ores used to manufacture this artefact. Namely, on one hand, the relatively high amounts of antimony (429 μg/g) and nickel (618 μg/g) suggest the use of sulfoarsenate ores, but, on the other hand, it is hard to believe that such a high amount of arsenic (6.7 wt%) would have been obtained just by smelting sulfoarsenate arsenate ores without any intentional addition of arsenic minerals [1, 17].

To summarize, taking into account the typological and compositional similarities reviewed in the above paragraphs, one might speculate that the investigated Ocnița dagger was manufactured using the same raw materials and procedures as in the cases of other daggers and artefacts from the same period discovered in the North-Pontic area, in the Caucasian region or in some EBA sites from Central Europe. The composition of this arsenical copper dagger suggests the circulation of raw materials on large distances during the Early Bronze Age.

3.2. TIN BRONZE

As an alloying element for copper tin, has effects similar to the ones of arsenic, increasing the hardness of the resulting alloy and lowering the melting point. However the advantages of tin over arsenic are that this element is not volatile and that it can be smelted to a metal, thus increasing the control on the composition of the final alloy. Unlike arsenic, tin and its compounds are not toxic [1, 17-18].

ED-XRF and PIXE were used to determine the composition of three Late Bronze Age (LBA) artefacts: a sickle fragment and two socketed axes with vertical ribs dated to the Late Bronze Age/beginning of the Early Iron Age (the second half of the 2nd millennium B.C.) – see Fig. 2. While the fragmentary socketed axe (inv. no. I 6007) certainly belongs to the Oinacu hoard[1], Giurgiu county, the socketed axe without inventory number and the sickle fragment were only probably found at Oinacu[2]. The socketed axe inv. no. I 6007 belongs to K-36 type, according to Chernykh's classification, while the second one shows the same features as the socketed axes grouped by Chernykh in K-38 type [33].

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[1] Though most of the objects from Oinacu hoard were published by S. Marinescu-Bîlcu in *Klad bronzovyh v Ojnake*, Dacia N.S. 7, 1963, 517-526, the socketed axe with inv. no. I 6007 remained unpublished.

[2] These two artefacts belong to the old collection (early 20th century) of "Vasile Pârvan" Institute of Archaeology of the Romanian Academy, Bucharest. Their actual finding place is not at all sure. The artefacts were recently rediscovered in a box on which the label *Oinacu* was attached.

Fig. 2 – 1) Socketed axe from the Oinacu hoard (inv. no. I 6007); 2) socketed axe; 3) sickle (fragmentary state). The socketed axe without inventory number and the sickle fragment were only probably found at Oinacu.

The chemical composition of the analyzed artefacts is reported in Table 1, while Fig. 3 presents the PIXE spectrum of a fragment from the bronze socketed axe with vertical ribs without inventory number.

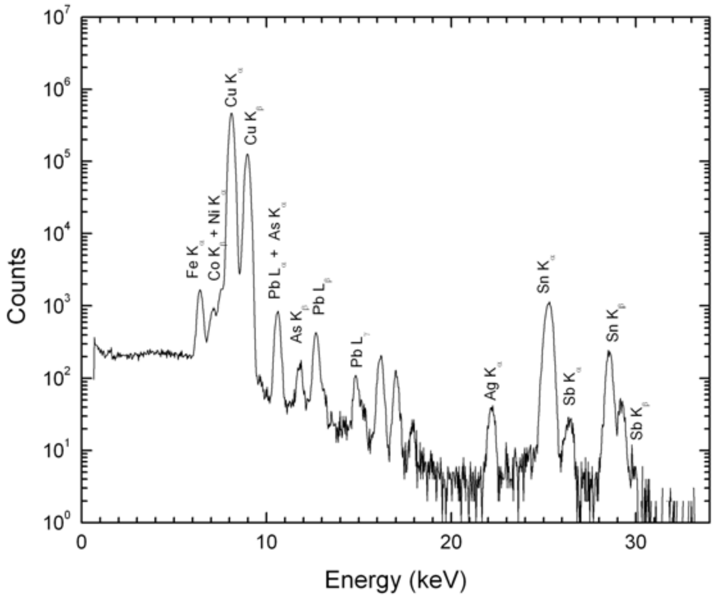

Fig. 3 – PIXE spectrum of a fragment from the Oinacu socketed axe with vertical ribs (without inventory number).

Arsenic and antimony, both volatile elements, are usually lost during the pyrometallurgical reprocessing of the copper ores. The presence at trace level (thousands of µg/g) of these two volatile elements in these Bronze Age artefacts indicates that these objects were not obtained through the re-melting of metallic scraps.

Socketed axes decorated with vertical ribs dated to this period were discovered in northern Bulgaria and in many sites from southern Romania located along the Danube.

The most likely sources for the copper ores used for manufacturing of these bronze artefacts should be sought among the ancient Serbian [34-35] and Bulgarian [28, 36] mines. However, to take a clear-cut decision regarding the provenance of copper used for making these Late Bronze Age objects, further determinations of the lead isotopes ratios should also be performed.

The chemical composition data reported in this paper, along with the occurrence of similar artefacts in other sites from the Lower Danube region can only support the hypothesis that vivid connections and exchanges existed between the populations living on both banks of this river during the Late Bronze Age.

4. CONCLUSIONS

PIXE measurements on tiny fragments from some Bronze Age metallic objects provided refined results on the chemical composition of these artefacts previously analyzed with a portable ED-XRF spectrometer. The additional chemical composition data were used to infer some conclusions regarding the way these ancient objects were produced raw materials, technology, possible ore sources, as well on the existence of exchange and trade links between the Bronze Age people.

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