Studies on Bronze Pre-Monetary Signs using Micro-PIXE

A. Vasilescu\textsuperscript{1}, B. Constantinescu\textsuperscript{1}, D. Ceccato\textsuperscript{2}

\textsuperscript{1} Horia Hulubei National Institute for Nuclear Physics and Engineering, Bucharest (Magurele), Romania.
\textsuperscript{2} Dipartimento di Fisica dell’Università di Padova, Padova and\textsuperscript{3} INFN, Laboratori Nazionali di Legnaro, Legnaro (Padova), Italy.

INTRODUCTION

This paper refers to the micro-PIXE study of various bronze pre-monetary items: warfare arrowheads (fig 1a) and arrowhead-shaped signs (fig. 1b), found in Dobrudja, in the framework of the MicroArchaeoStudy project at the AN2000 accelerator of INFN-LNL.

The local trade between the Greek colonies (Histria/Dobrudja, Olbia/Southern Ukraine, etc.) and the “barbarian” Scythians, Getae, Thracians got more intense during the 7th – 6th centuries BC in Dobrudja and was characterized by the use of pre-monetary signs: arrowhead-shaped items were typical [1].

EXPERIMENTAL

The micro-PIXE study was performed in June and December 2015 using 2 MeV proton beam at the LNL-AN2000 accelerator. The typical beam-spot was about (3-4) x (3-4) \( \mu \text{m}^2 \).

The acquired point and map spectra (typically 2.5 mm x 2.5 mm) were analyzed using GUPIWIN.

RESULTS AND DISCUSSION

Besides the typical copper-tin-(lead) bronze, containing variable amounts of Sn (to increase hardness) and Pb (to facilitate casting), two unusual types like Cu-Sn-Mn-Pb and Cu-Sn-Sb-Pb were identified. These alloys were identified for both types of items and were found together in the same deposit!

Fig. 1. Pre-monetary items: (a) Scythian-type warfare arrowheads; (b) arrowhead (Histria) and dolphin (Olbia) - shaped signs.

The purpose of this work was to determine the alloy compositions and study the correlation between the various elemental components, in order to draw some conclusions on the origin of the metal and on the metallurgical skills mastered by the issuers of the items.

Warfare arrowheads and pre-monetary signs found jointly in various locations in Dobrudja: the Histria-area (Histria, Tariverde, Sinoe-Zmeica, Golovita, Cogealac) and Floriile (possibly Getic fortified settlement) on the Danube were investigated.

Figures 2 and 3 represent the result of mapping the sample Floriile 11. It is a Cu-Sn-Pb bronze, which contains also Mn. The Sn content in the sample is lower then the usual 10-12% for bronze. see fig 5.

One aspect of interest is related to the main metallurgical problem of those times: to obtain a homogeneous
microstructure, at least in the range of a few microns, i.e. to avoid elemental segregation.

Manganese is present mixed with Cu, but we also see in Fig. 3 a clear segregation/replacement in some parts of the matrix (missing Mn where Cu is signal is more intense).

Figure 4. Cu-Fe-Sn-Sb-Ni-Pb maps (2.5 mm x 2.5 mm by size), sample Sinoe-Zmeica 15

The second type of alloy is illustrated in Figs. 4-5. The composition of sample 15 Sinoe-Zmeica is more complex. Sn-Sb-Pb seem to be well-mixed, Ni is correlated with Cu, but anti-correlated with Fe.

A second aspect to investigate is connected to the origin of the metal, and this can be discussed trying to answer the question about how Sb and Mn can be present in the alloy. Sb is a component of polymetallic ores; its presence in the alloy indicates the use of secondary sulfide (Fahlerz) ore, which contains Cu, As, Sb, and in small quantities also Ag, Ni and Bi. Chernykh [2] connects arsenical and antimonial bronze in Southern Russia with sources in the Southern Caucasian Pyritic copper mines.

As such, a plausible hypothesis is to consider that these items are related to the Scythian presence in the Northern Black Sea area, who possibly obtained antimonial bronze by co-smelting Cu minerals with stibnite.

Figure 5. PIXE spectrum for sample Sinoe-Zmeica 15

The problem of manganese is even more mysterious and awaits an explanation. Could it be related to some other unknown sources of metal rich in Mn, or some specific technological recipe?

The copper minerals from Northern Bulgaria and Serbia (closer to Romania) do not contain Mn or Sb, thus these sources are excluded in our case.

In the case of Hystrian pre-monetary signs, the following time scenario based on the compositional analysis results is proposed:

- warfare Scythian arrowheads were used for trade between Greeks and the neighbouring populations;
- mechanically modified arrowheads were used safely in trade as pre-coins;
- dedicated cast pre-monetary signs were issued for trade, from remelting arrowheads.

CONCLUSIONS

Micro-PIXE investigations of ancient bronze can bring useful insight into the microstructure of archaeological items, and elemental mapping of the samples can help in the discussion of various hypotheses related to the skills/technological know-how available to the populations living in the geographical area of interest.

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