XRF AND MICRO-PIXE AS INVESTIGATION TOOLS FOR ANCIENT METALLURGY – THE CASES OF PRE-MONETARY SIGNS TYPE “ARROWHEAD” FROM HISTRIA AND OF AGIGHIOL HOARD

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Compositional analysis can identify alloys made by ancient people, help in the authentication of items with uncertain origin (*i.e.* not excavated from well-controlled archaeological environment) and bring information on the employed metallurgical procedures. The main metallurgical problem of ancient bronze alloys was to have a good homogeneous micro-structure at least in the range of few microns that means to avoid elemental segregation. If X-Ray Fluorescence (XRF) analysis gives the general elemental composition (approx. 30 mm^2 investigated area), micro-Proton Induced X-ray Emission (micro-PIXE) is an excellent tool to investigate the alloys microstructure, especially segregation phenomena. We investigated warfare Scythian-design arrowheads and pre-monetary signs type “arrowhead” found in Dobroudja, especially in Histria area, but also in Floriile (a Thracian settlement on Danube), both supposed produced by Histria and by its “barbarian” neighbors (Getae, Scythians). For comparison, we also present a preliminary study on two Geto-Thracian silver appliqués, part of Agighiol (Northern Dobroudja) hoard.

Key words: XRF, micro-PIXE, bronze, silver, archaeological artifacts, elemental maps.

1. INTRODUCTION

Compositional analysis can identify alloys made by ancient people, help in the authentication of items with uncertain origin (*i.e.* not excavated from well-controlled archaeological environment), bring information on the employed metallurgical procedures, and, in the case of very ancient artifacts (before re-melting procedure was wide-spread), provide hints about the raw materials provenance (metallic ores and geological deposits) [1, 2, 3].

X-Ray Fluorescence (XRF) and micro-Proton Induced X-ray Emission (micro-PIXE) are two widely used methods for such analyses due to their efficiency, accessibility and relatively low cost. In the first part of the paper we report on the investigation of bronze (copper) Scythian-design warfare arrowheads and pre-monetary signs type "arrowhead" – leaf or fish silhouette? – (VIIth–VIth centuries BC) found in Dobroudja, especially in Histria area and in Floriile (a Thracian settlement on Danube) – both supposed emitted by Histria and by its "barbarian" neighbors (Getae, Scythians) [4, 5].

Finally, for comparison, we present a preliminary study also performed using micro-PIXE on two Geto-Thracian silver appliqués, part of Agighiol (Northern Dobroudja) hoard [6].

Dobroudja during VII–VIth Centuries BC was the cradle of direct participation of its people – Greek colonists and "barbarians" (Getae, Thracians, Scythians) to a wide-ranging trade, economic and cultural relationships which are emblematic in the Black Sea region. Pre-monetary signs provide additional data on certain economic, social and political phenomena for this geographical area. Histria was often cited as a major issuer of such signs with monetary value, and their production was considered the first stage of city's monetary issues essential to maintain relations with local communities.

We investigated warfare Scythian-design arrowheads and pre-monetary signs type "arrowhead" found together in the same deposits in Dobroudja, in Histria area (Histria, Sinoe, Golovita, Cogealac) and in Floriile – Figure 1.

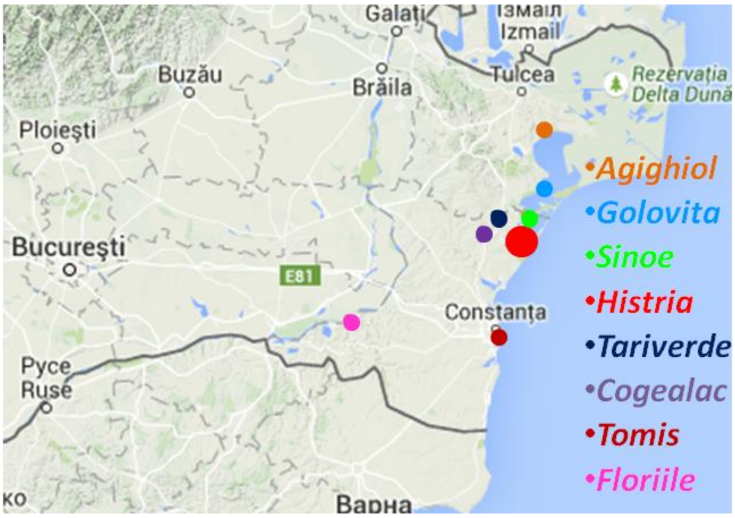


Fig. 1 – Investigation sites.

We also present the compositional analysis of two Geto-Thracian silver appliqués, part of the Agighiol hoard, performed by micro-PIXE in order to investigate aspects related to the metals and the metallurgy implied in their manufacture.

2. EXPERIMENTAL

We performed the analysis of 150 Scythian-type arrowheads and pre-monetary signs using XRF method and of 50 small fragments (approx. 100 microns diameter) of these bronze items-sampling being performed on previously corrosion-cleaned areas on the items surface, measured using micro-PIXE.

For XRF, a X-MET 3000TXR+ portable spectrometer was used, the exciting X-ray beam being generated by a 40 kV – Rh anode tube. The detection system is a PIN silicon diode detector with Peltier cooling, with 270 eV resolution for the Kα line of Mn (5.89 keV). The measurement spot size is about 30 mm^2. A Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage completes the spectrometer [7].

For micro-PIXE at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy, a 2 MeV proton microbeam (6 μm × 6 μm beam area), maximum beam current ~1000 pA was used [8]. The characteristic X-rays were measured with a Canberra HPGe detector (180 eV FWHM at 5.9 keV). An Al funny filter (80 μm thick and 8% hole) in front of the X-ray detector was used to reduce the intensity of the peaks in the low spectral region (below 4 keV). 2 mm × × 2 mm maps and point spectra were acquired. The quantitative analysis was performed using the GUPIXWIN software [9].

3. RESULTS AND DISCUSSION

The main metallurgical problem of ancient bronze alloys ("normal" Cu-Sn-Pb, but also Cu-As or Cu-Sb-Pb and other combinations) was to have a good homogeneous micro-structure at least in the range of few microns, that means to avoid elemental segregation – concentration of a specific element (*e.g.* Pb) in a micro-region. If XRF analysis gives the general elemental composition (approx. 30 mm diameter of investigated area), micro-PIXE is an excellent tool to investigate alloys microstructure, especially segregation phenomena.

Our XRF analysis on 150 Scythian-type arrowheads and pre-monetary signs suggested three types of alloys: Cu-Sn-Pb ("normal" bronze), Cu-Sn-Mn-Pb and Cu-Sn-Sb-Pb.

The most relevant for numismatists result is that for each finding place (see map from Fig. 1) the same type of alloy was used both for fighting arrowheads and for pre-monetary signs – Table 1. This aspect is illustrated in Figs. 2 and 3 for

Golovita and Sinoe Zmeica (the peak at energy about 16.1 keV is caused by the simultaneous reaching the detector of two quanta of radiations and it is associated with dual-energy photon). In the case of Sinoe Zmeica the pre-monetary sign is a stylized dolphin.

Table 1

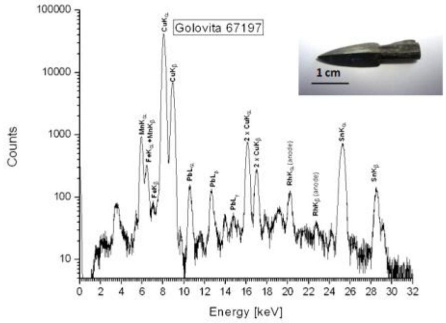
Elemental composition of Scythian-type arrowheads and pre-monetary signs obtained by XRF

Sample Name	Number	Cu%	Sn%	Mn%	Pb%	As%	Sb%	Ag%	Fe%
Cogelac-arrowhead	67196	84.2	11.8	2.5	0.75	0.15	–	–	0.3
Cogelac-pre-monetary sign	67195	86.6	8.9	4	0.1	–	–	–	0.4
Floriile-arrowhead	67157	89.6	6.2	3.1	0.2	–	–	–	0.4
Floriile-premonetary sign	67234	89.5	8.4	1.4	0.2	–	–	–	0.4
Golovita-arrowhead	67197	87.6	8	3.3	0.7	–	–	–	0.4
Golovita-premonetary sign	67232	90.5	5.2	1.6	1	0.7	–	–	0.4
Tariverde-arrowhead	80426	77.2	–	–	16.8	–	1.9	1.2	0.7
Tariverde-pre-monetary sign	80391	88.9	5.1	–	2.5	–	2.1	–	0.9
Histria-arrowhead	133-483	62.6	4	–	29.1	–	2.7	–	1.2
Histria-premonetary sign	58141	91.5	4.3	–	0.9	–	2.9	–	0.4
Sinoe Zmeica-arrowhead	42984	83.3	3.8	–	5.3	0.5	5.7	–	1.1
Sinoe Zmeica-premonetary sign –dolphin	66768	94.1	3.2	–	0.2	0.1	1.9	–	–

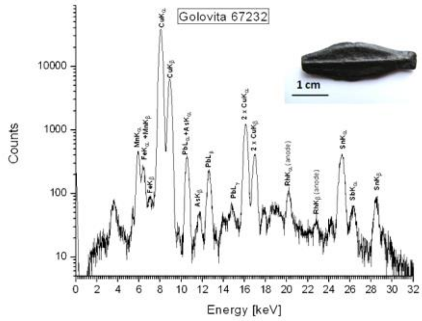
– : under minimum detection limit (MDL)

To study elemental segregation, we realized elemental maps using micro-PIXE, cases of Cu-Mn-Pb being illustrated in Figs. 4, 5(a,b) and 6 respectively.

As concerning the metals provenance, the presence of manganese and of antimony suggests the use of fahlore-type poly-metals deposits (mainly metallic oxides), having an important copper concentration and manganese, antimony, silver, arsenic as important impurities. The most relevant geological region for such poly-metallic deposits is Caucasus Mountains (closed to Scythian areas). For antimony-rich copper minerals, Slovakia-North Hungary region (with a Scythian presence in VII–V Centuries BC) must be also considered [10, 11], but to definitely conclude it is necessary a complex geological investigation. We must outline that copper minerals from North Bulgaria and Serbia don’t contain manganese or antimony [12].

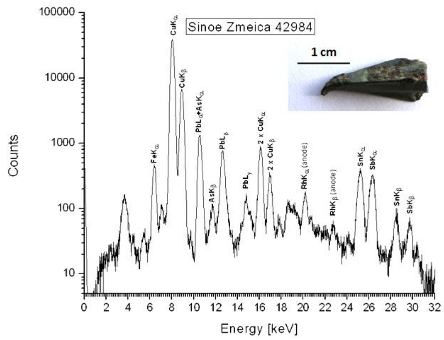


a)



b)

Fig. 2 – Golovita arrowhead (a) and pre-monetary sign (b) – photos and XRF spectra.



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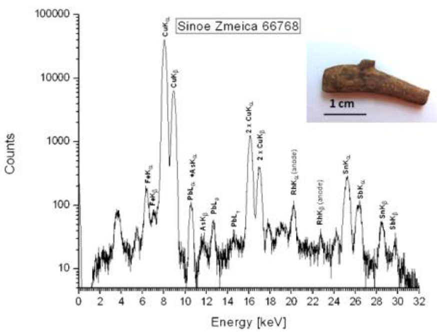

b)

Fig. 3 – Sinoe Zmeica arrowhead (a) and pre-monetary sign (b) – photos and XRF spectra.

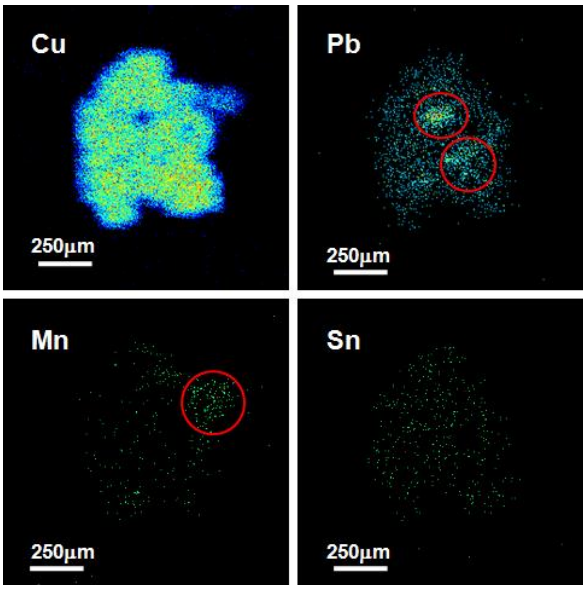

Fig. 4a.

b.

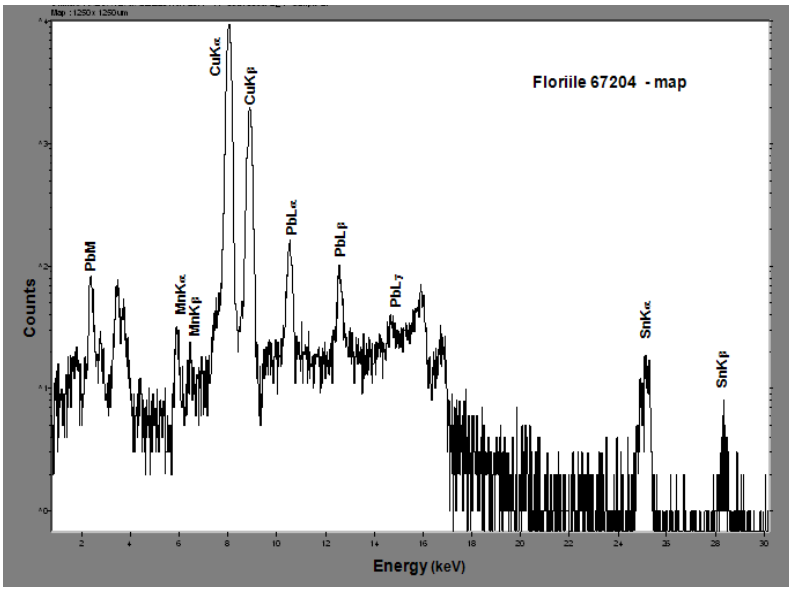

Fig. 4 (continued) – Floriile 67204 sample – micro-PIXE elemental maps and spectrum; Pb and Mn segregation – non-homogeneous composition.

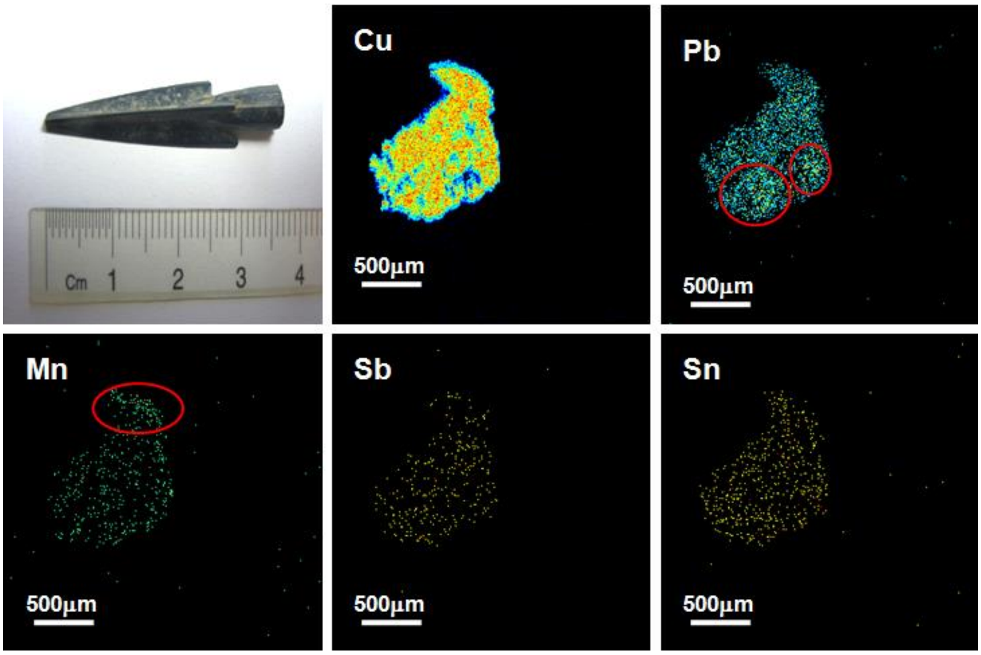

Fig. 5a – Floriile 67207 sample – photo and micro-PIXE elemental maps; small areas with Pb and Mn concentrations.

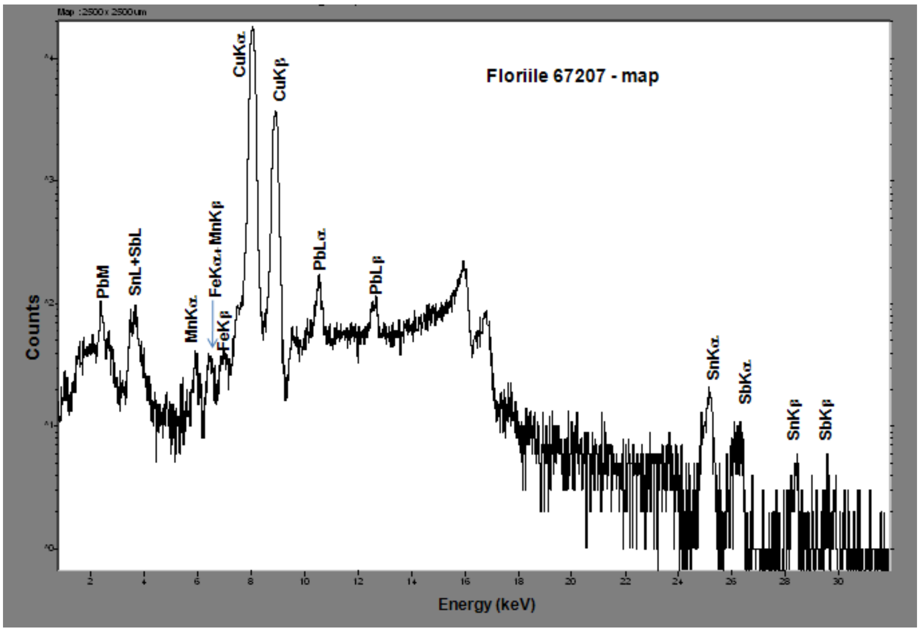

Fig. 5b – Floriile 67207 sample – micro-PIXE spectrum.

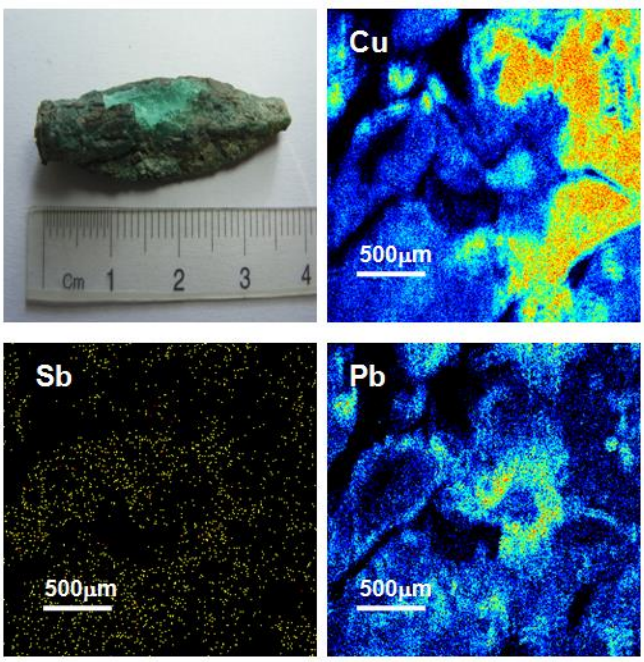

Fig. 6

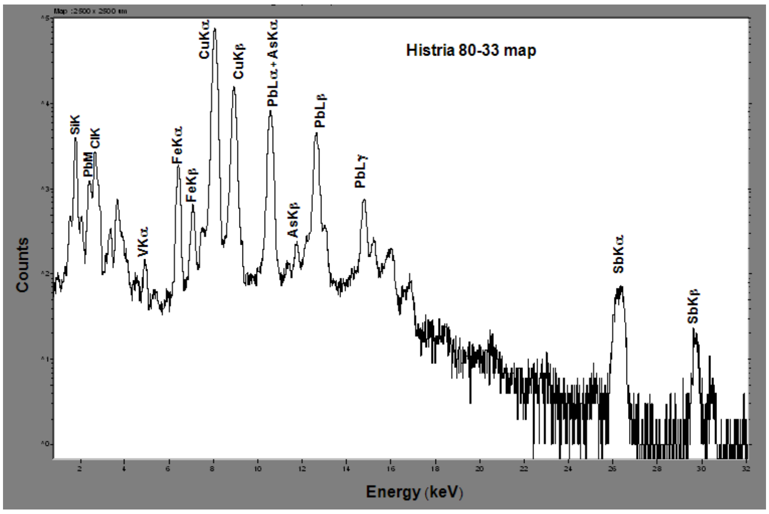

Fig. 6 (continued) – Histria 80-33 arrowhead-photo, elemental maps and micro-PIXE spectrum; strong lead segregation.

For comparison, we present a preliminary study also performed using micro-PIXE at LNL Legnaro on ancient silver from Agighiol hoard (same period).

From our in-situ (Treasure room of National History Museum of Romania) XRF measurements of the silver objects from Agighiol hoard, it was already seen that it contains silver items of quite different types and also made from different alloys, probably including “import” ingots [13]. So, it was likely that not only the detailed elemental composition is heterogeneous, but also there could be significant differences in the metallurgical structure, depending on the craft mastered by the workshop where the objects were made.

For Agighiol hoard we discuss two relevant cases.

Fig. 7 – Button-type applique 8468.

First case: Agighiol applique 8468

The button-type appliques are made of silver and have a soldered “handle” made of bronze. For item 8468, this handle was broken (Fig. 7). Soldering on old silver was done typically with a material containing high amounts of Cu and Pb. A sample from the solder material was mapped by micro-PIXE. The size of the map is 1250 × 1250 μm^2, and it covers the whole sample (Fig. 8).

The map shows a uniform mixing of the material and some corrosion by Br and Cl (see spectrum) – unfortunately, no Cl map was performed. Probably the Ag corrosion products are bromianchlorargyrite or embolite. As concerning the soldering procedure of the bronze handle on the silver button our results indicate the use of a quite strange alloy consisting in silver plus bronze instead of the largely used lead-silver alloy.

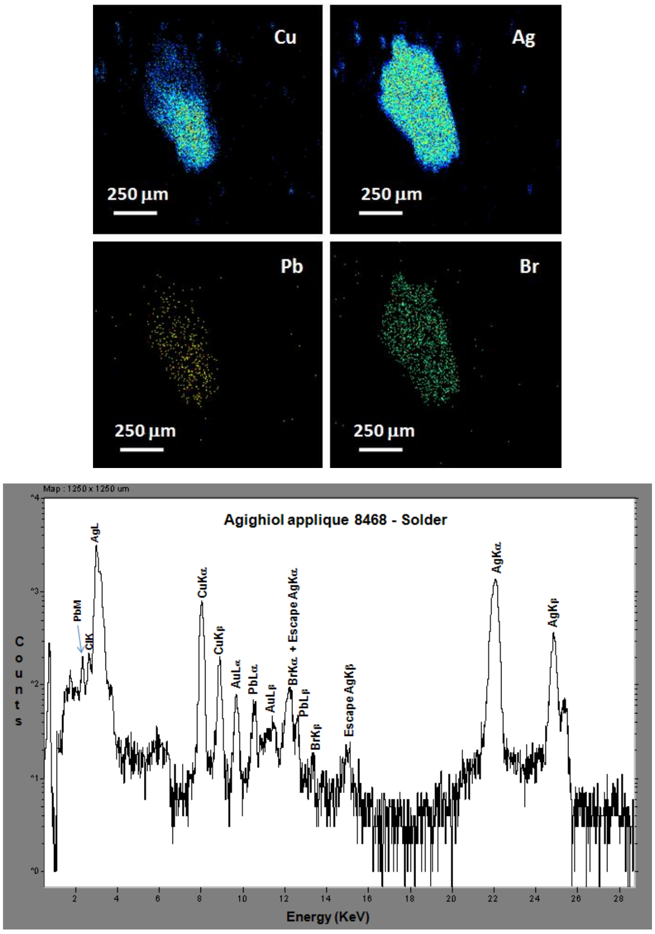

Fig. 8 – Agighiol applique 8468 – micro-PIXE elemental maps and spectrum.

Second case: Agighiol applique 8470

The Agighiol applique 8470 sample illustrates the case of strong presence of silver corrosion products induced by S, Cl, Br (see spectrum in Fig. 9). In elemental maps, an inclusion with high Ca content has been identified (probably a concretion-mixture of organic and inorganic calcite and aragonite).

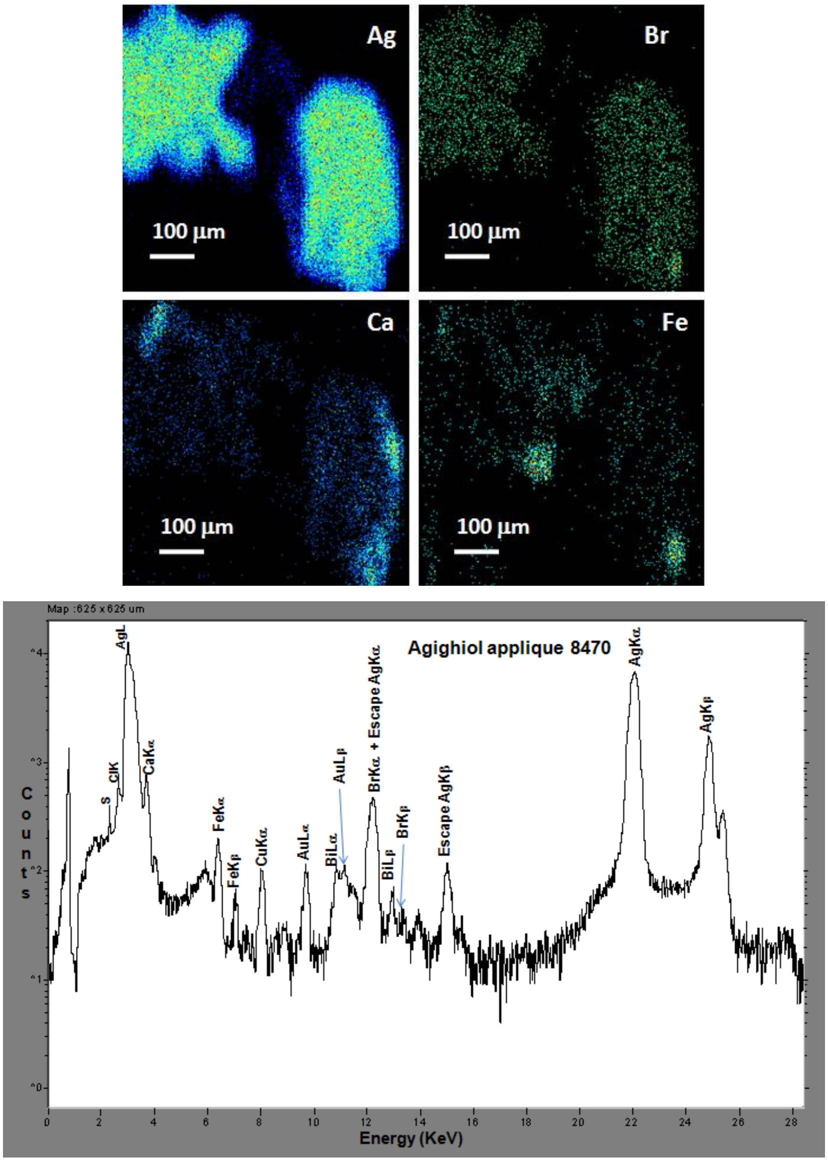

Fig. 9 – Agighiol applique 8470 – micro-PIXE elemental maps and spectrum.

From the micro-PIXE spectrum we observed the presence of Bi traces, suggesting the South Balkans provenance (Macedonia or Southern Bulgaria mines) of the silver, but a definite geological provenance requires supplementary investigation.

4. CONCLUSIONS

In the case of Histria pre-monetary signs, based on our compositional analyses, we propose the following time-evolution scenario:

• Warfare Scythian design arrowheads used for trade between Greek colonies and "barbarian" neighbors (mainly Scythians);

• Mechanically modified (without killing capability) arrowheads "safely" used as pre-coins;

• Dedicated cast monetary signs issued by Histria Greeks for trade with "barbarians" from re-melting of the real arrowheads.

As concerning the metals provenance, the presence of manganese and of antimony suggests the use of fahlore-type poly-metals deposits, most probably from Caucasus Mountains, but to definitely conclude it is necessary a complex geological investigation including on mineralogical samples from this region.

As concerning Agighiol hoard, basically, all silver is of high purity, with little added elements. Nevertheless various traces and minor elements are present, which would induce the idea of silver imported possibly from Greece, the Aegean and/or Macedonia, as ready ingots maybe, obtained by cupellation from argentiferous galena ores. Agighiol is situated in Dobroudja, and the ancient Greek had colonized the nearby Black Sea coast. We could identify a significant amount of Bi, but also some Pb in the silver, the presence of Bismuth indicating the Balkans origin. Micro-PIXE proved to be an adequate tool to study the corrosion of ancient silver artifacts.

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