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XRF-BASED COMPOSITIONAL MICROANALYSIS FOR PROVENANCE STUDIES OF METALLIC ARTIFACTS*

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Abstract. The origin and history of archaeological objects can be established based on the presence of specific elements proven e.g. as fingerprint of a given source of metal. Micro-PIXE and SR-XRF are adequate noninvasive tools for the detailed examination and mapping of inclusions of minor and trace elements in provenance studies in archaeometry. Such examples are the study of traces of Sn, Sb, Te in gold and of the presence of Ag or Co in bronze, in objects discovered on Romanian territory, aiming at establishing links of the found patterns to certain ancient manufacture habits/workshops or possible metal sources.

Key words: elemental analysis, micro-PIXE, SR-XRF, archaeometry, provenance.

1. INTRODUCTION

The origin and history of archaeological objects can be studied based on their elemental composition. Identification of specific proven fingerprints can give an indication on the sources of metal; the presence of certain inclusions can provide clues to the techniques used during their manufacture, and correlation with other information can lead to conclusions on commercial and cultural exchanges. The simultaneous presence of some elements in localized regions or in inclusions can provide more insight into the geology of the ores of origin; such information can be extracted from elemental maps of various regions in the samples.

Non-destructive techniques as micro-SR XRF (Synchrotron Radiation X-Ray Fluorescence) and micro-PIXE with protons (Particle-Induced X-ray Emission) are especially adequate for the study of small areas in both archaeological and geological samples, in order to establish the elemental composition for major, minor and trace elements and for mapping inclusions and profiling.

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For provenance studies one has to envisage two steps: firstly, to study the possible/ plausible sources of metal, based on existing historical knowledge on mining in various regions and historical times – analyzing geological samples from sites as close as possible to the hypothesis to be verified. Then, the archaeological objects are to be analyzed as well, and in the end, comparisons and correlation in the data have to be studied thoroughly, in order to verify the theoretical assumptions. Sometimes the conclusions of these studies have to be viewed in a critical manner, as the positive identification of the objects/metal sources is a rather difficult if not impossible task.

E.g., in the gold studies, it is worth evaluating the various elemental ratios like Au-Ag-Cu, searching for Pt group elements, traces of heavy elements like Sn, Sb, Pb, sometimes even of Te or Hg. In bronzes or copper objects, traces of As, Ag, Co, Se can be useful in the identification of old copper sources, especially for earlier times in the Bronze Age. Nevertheless one has to be always aware of the historical/archaeological context and connect the experimental results with the existing knowledge and theories from that field.

This paper intends to give a brief overview of our experience in establishing the provenance of archaeological metallic items using micro-beam facilities, with examples of gold and bronze studies performed by our group.

2. EXPERIMENTAL CONSIDERATIONS

2.1. Micro SR XRF

Our micro SR XRF experiments are performed in 2 laboratories: ANKA in Karlsruhe and BESSY in Berlin. This technique uses high-intensity bremsstrahlung radiation from an electron accelerator/ storage ring (synchrotron radiation) and it allows focussing of the beam to a very small area. Two orthogonal directions are available for scanning the surface of the sample: for each point a spectrum is recorded. Intensity profiles and maps can be extracted.

The facilities at BESSY (BAM-line) [1] and ANKA (FLUO beam-line) [2] work with maximum energies of 30-40 keV, with variable luminosity, according to the experimental choice. The samples are mounted on x-y-z stages, on holders, in air, ensuring the requested scanning capabilities for profiling and mapping. The fluorescent signal is measured using HPGe, Si(Li) or SDD spectrometers. The samples are fixed to the holder, usually by tape. Positioning is computer-controlled and the analyzed area of the sample is visualized with the aid of a microscope. Photographic registration is also possible. Material standards are also measured for reference for the quantitative measurements. Primary evaluation of the data is done during the beam-time by local software setups, and further analysis: fitting, mapping and quantitative evaluation, is done off-line, using computer packages as

AXIL-QXAS [3], PyMCA [4], fundamental parameter calculations, combined with SNRLXRF/evaluations of matrix effects and MC simulation [5].

2.2. Micro-PIXE

The micro PIXE experiments are performed in 2 laboratories: at LNL-INFN, in Legnaro (Padova), Italy and at ATOMKI in Debrecen, Hungary. The two microprobes use both accelerated protons for X-ray excitation. The spot size is typically in the micrometer range. This method provides details for extremely small volumes, scanning of small areas of the sample, information on the presence and the nature of the inclusions (spectra, maps, elemental correlation). The LNL microprobe is an Oxford Instruments machine, based on a 2 MeV proton beam produced by the AN2000 Van de Graaff accelerator. Typical currents are ~1.2 nA. The areas investigated are divided into 256×256 pixels and can cover up to ~2×2 mm^2. The beam is filtered using Al foils or funny filters (in this case, Al foils with a hole of ~4–8 % of its surface). The results can be obtained as maps and point spectra. The detector used is HPGe, the samples are glued to a holder, positioned in vacuum, under a microscope [6].

No standards are measured; the beam conditions are checked with a reference copper grid. Data evaluation is done using MAPPIX [7] and GUPIX [8] software packages.

At ATOMKI (Debrecen, Hungary), the Oxford Instruments microprobe uses a proton beam of 3 MeV, from a 5MV van de Graaff accelerator [9]. Optional beams of 1–3.5 MeV, p, d, He^+ are available, and the beam diameter is about 1 μm, with typical current values of 300–400 pA. The spectrometer uses a Si(Li) detector. A state-of-art software package for evaluation has been used up to recently, but it is currently replaced by the GUPIX standard.

2.3. The samples

The geological samples are in general simpler to handle, and they can be smaller or somewhat larger objects, usually in the mm- to a few cm-range. The analyzed areas (one or several) are smaller than the whole object, as a rule. The samples are provided by our geologist collaborators, from various collections – either as nuggets, or bulk pieces, or as prepared sections, used previously in microscopy studies. The surface analyzed should be flat and clean, and we do not make any extra preparation of the samples.

The analysis of archaeological objects is usually more problematic, due to their special value and the restrictions in transportation and alteration as well. They are usually analyzed in a first study by in-situ or in-lab X-ray fluorescence (XRF), and only in a few cases some extremely tiny scraps are taken for more detailed investigations, and only when the objects cannot be transported/exported for testing. The interventions are allowed and especially chosen from spots with the least impact as to the shape and ornamentation of the artifact. If the whole object can be taken to the lab, this will be done preferably, and the analysis will be performed on its surface "as is".

Some examples of analyzed objects are: the Koson coin treasures (Tarsa-Luncani and Sarmizegetusa), the Dacian bracelets, the Tauteu gold hair rings, the Vulchitrun-type bronze disk with gold ornaments from Calarasi, bronze sickles, daggers and axes from Bronze Age deposits at Oinac, Gioseni, Straosti, Santana-Paulis, Spalnaca etc.

A selection of papers containing micro-SR XRF and micro-PIXE results obtained by our group in studies of archaeological objects is given in [10–14].

3. RESULTS AND DISCUSSION

In the following we will show results obtained on gold and bronze objects studied recently and some results from our geological studies.

3.1. Gold studies

The need for an extensive study on gold samples, including alluvial and native mined gold, coming especially from Transylvania, occurred during the years in the process of interpretation of the XRF data obtained on various artifacts. If these artifacts had been made locally and they were not modern fakes, a reasonable assumption is that there should be a way to link the compositional pattern of the gold in the objects to the one of the gold sources known in the region. The sources from the well-known "gold quadrangle" in the Metaliferi Mountains in the Western Carpathians are a point for a start, this region being known also in Roman times.

Other occurrences of gold minerals are known in the Eastern Carpathians (Baia Mare region) and in the Southern Carpathians, e.g. the Orastie region, the Olt Valley or in the Almajului Mountains [15, 16].

Our studies on gold minerals have begun in 2007 with the aim to establish the fingerprint of various sources. We considered some mines and alluvial sites: e.g. Rosia Montana, Bucium, Valcoi, and Baia de Aries, in the Rosia Montana district; Brad, Hondol, Ruda Barza, Musariu, Fizesti, Sacaramb and Trestia in the Brad - Sacaramb district, Hunedoara county; Magura, Techereu and Stanija from the Zlatna - Stanija district, Alba county; Valiug, Valea Oltului, Valea lui Stan, Rahau, Valea Pianului, Lipova etc. Most of them are relatively closely situated from the ancient capital of Dacia, Sarmizegetusa Regia. In Transylvania, primary gold occurs typically as (free) native gold, tellurides or lamprites (heavy metal + antimony compounds), with variable concentrations of Au, Ag and Cu, but also containing a host of other elements like Sn, Sb, etc. Native gold is present as nuggets, veins etc embedded in volcanic minerals, along with quartz or pyrite.

According to present knowledge, gold was known and used on the territory of present Romania already in the Bronze Age, mostly from panned alluvial origin. Recent archaeological finds suggest that mining might have started already before the Roman era, in the 3rd–2nd centuries BC [17]. A reasonable guess is that most of the gold used by the Dacian population was of alluvial origin, coming from the nearby rivers, either from the Ampoi, Aries, Cris basins or from Pianu de Sus (Pianu valley, Alba county), which is one of the best known alluvial gold sources.

Some illustration of typical results obtained by micro-beam techniques on gold is given below.

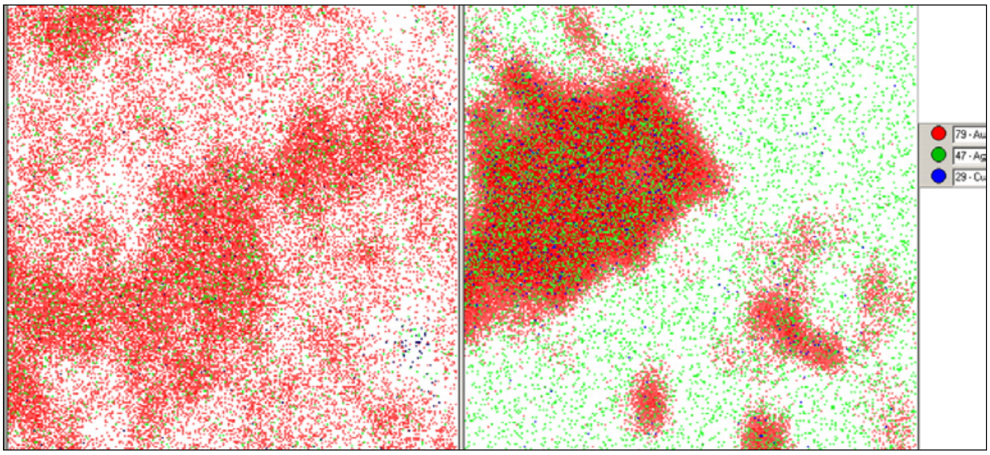

Fig. 1 – Micro-PIXE mapping of gold – elemental correlation in Rosia Montana (left) and Musariu (right) samples @ LNL

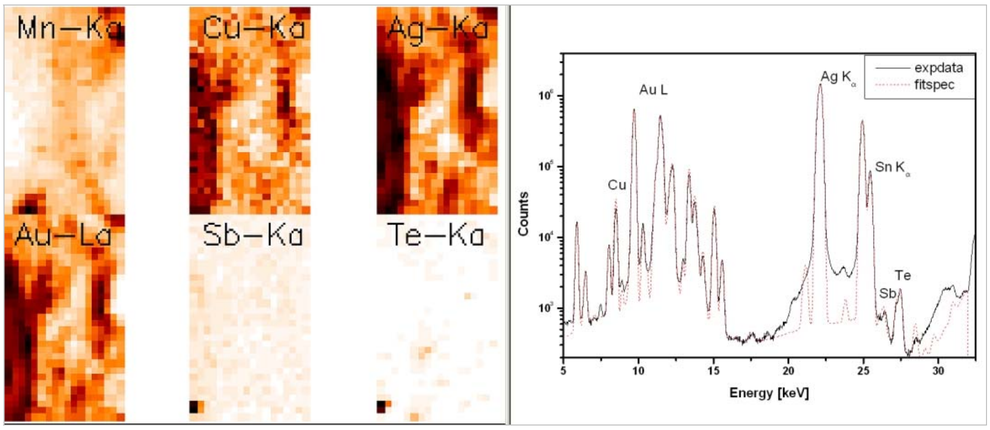

Fig. 2 – Rosia Montana polished section: X-ray signal intensity map (left; dark = high value): Au-Ag-Cu apparently (!) correlated, Mn complementary (in matrix), and sum spectrum of the scan area (right; dotted = QXAS-AXIL fit) – @ ANKA 2010.

Figure 1 shows comparative compositional maps obtained by micro-PIXE for gold samples from Rosia Montana and Musariu plotted with MAPPIX.

Figure 2 presents an extended X-ray intensity map of an area and the corresponding spectrum obtained at ANKA in the summer of 2010 in the gold vein region of a Rosia Montana section. Figure 3 is a profile output for column 7 of the map presented in Fig. 2, enabling more insight into details of the compositional map and better local correlation.

In the gold studies, it is worth evaluating the various elemental ratios like Au-Ag-Cu, searching for Pt group elements, traces of heavy elements like Sn, Sb, Pb, sometimes even of Te or Hg.

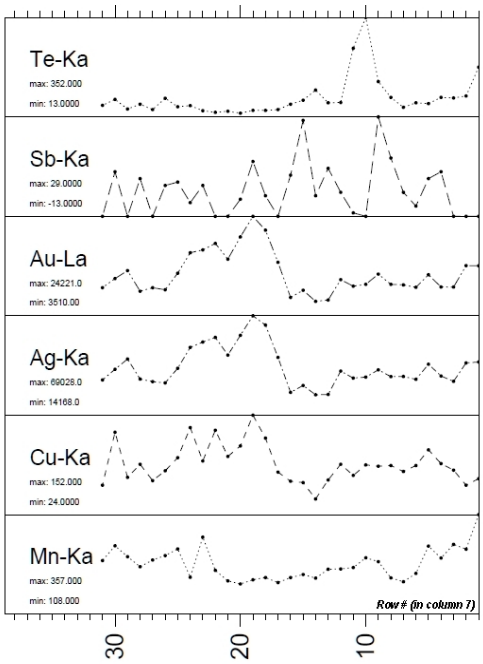

Fig. 3 – Normalized intensity profile in column 7 of Rosia Montana map as in Fig. 2.
(This detailed view shows that Cu is ONLY partly correlated with the Ag and Au profiles!).

We consider that we have established beyond doubt the fingerprint of Transylvanian gold, enabling us to offer valuable archaeometrical support in the study of gold objects, by X-ray based micro-beam tests.

Most of the results obtained in our mineral studies are part of provenance studies [10–14], but a few dedicated papers have also been published [18–20].

Gold coming from Transylvanian sources is known to have a high silver content and little copper. The Au-Ag ratio and Au-Ag-Cu ratio cover a wide range of values. Au and Ag are always present together in native gold, coming from sources like Rosia Montana and Musariu. Cu presence can be connected or not to Au and Ag, and partly or completely may follow the same localized geometrical pattern. E.g. in the Musariu ore sample, the three elements were found perfectly correlated, while in the Rosia Montana such a correlation is only partial (see figure 3). This might be related to a different structure and possibly to a different geological history. As to the fingerprint, we determined that typical trace elements are Sn, Sb, Pb, Te, of which Te will be lost during thermal treatment, due to its volatility. Alluvial gold contains traces of Sn 100–300 ppm from cassiterite. Traces of antimony are also present in some sources: 50–500 ppm from jamesonite ($Pb_4FeSb_6S_{14}$), stephanite (Ag_5SbS_4).

In the studies of gold objects we have obtained the following results:

– Referring to the provenance of the Koson treasures: Koson coins with monogram (KCM) contain > 97% Au, so they are made most likely from remelted gold; Koson coins without monogram (KFM) are made of alluvial gold (containing Sn and some also Sb).

– On the provenance of the Dacian bracelets – They made of alluvial gold, similar to the KFM coins. No micro-beam studies have been performed up to now on these objects. (Only micro-beam data on the gold minerals has been used in the interpretation of XRF measurements.)

– About the manufacture of Dacian gold objects: rather primitive, many objects were produced by using alluvial gold as is, resulting non-uniform bulk and surfaces with inclusions, conglomerates with different composition. Some objects have been manufactured reusing older gold objects, while later technologies implied thermal treatment as well.

3.2. Copper and bronze studies

Our studies on bronze and copper artifacts are of recent date [14]. Part of the data is still preliminary and needs further investigation, especially due to the complexity of the task. The difficulties in establishing the provenance of bronze objects are far more than in the case of gold, due to the more complicated composition pattern, due to alloying, and also due to corrosion which affects these objects, compared to gold which is practically inert to environmental influence.

We base our discussion of the measurement results on data found in the literature, obtained by groups working on compositional studies of various bronze objects [21–23]. Correlation has to be done also with historical knowledge, sometimes quite scarce, due to the fact that the history of bronzes goes far back in time and often the finds are not well documented. The technology was developed and refined earlier, and the composition of the artifacts is by far presenting a great variability of patterns. Nevertheless a few clues can be found looking for plausible fingerprint elements for the native copper, like Sb, Co, Ag, Se, which could have been used in the manufacture of the objects. Little is known on the availability of copper in Bronze Age Romania (Altin Tepe, Sasca, Deva), so the hypothesis go towards the historical mines situated in the Balkans, e.g. Majdanpek and Rudna Glava in Serbia or Ai Bunar, in Bulgaria. The respective fingerprints are considered to be: large Sb for Hungarian mines, high As with Ag and Sb traces for Bulgaria and no Co, Ag+Sb for Transylvania. The copper originating in the Serbia is characterized by the presence of As+Ni+Ag+Sb and possibly Se and Co [21].

The copper content in the ores is quite variable, and so is the Fe concentration. The differences measured for various trace elements grouped on samples coming from regional mines are also quite spread.

Thus we note for Bulgarian mine ores Cu concentration between < 3 to about 53% wt, compared to about 1% at Altin Tepe (Romania, in Dobrudja), or 93–100% in SW Romanian mines (Sasca, Moldova Noua). Rudna Glava (RG) and Majdanpek (M) (Serbia) measurements showed ranges of 1–42% (RG) or higher levels 20–84% (M) of Cu. The Fe content is also highly variable: 1–11% in Bulgaria, 1–39% (RG) and 0–27% (M) in Serbia, traces only in SW Romanian copper, but 23% at Altin Tepe [21–22].

The metallurgy also evolved already in the Bronze Age – from rather primitive and non-uniform metal to more elaborate smelting and later, very likely, re-melting previous objects to produce new artifacts. Siderophile and chalcophile elements (As, Sb, Ag, Co, Ni) are concentrated in the metal, so they are likely to be present in the artifact too. These elements are considered as most adequate indicators of the ore sources [21]. According to the same authors, it is possible that Ag and Sb content increased due to the manufacturing process.

We have studied objects mainly from the Late Bronze Age and Iron Age, sickles, daggers, sun disks, axes and Celt axes. Some objects are pure copper, tin-bronzes, and some have probably Pb added, or are antimony-bronzes.

For illustration, we show a set of element profiles for a blade sample found in western Transylvania, in a Hallstatt-A deposit in Arad County, at Santana (see Fig. 4). We note the presence of Sb and Ag, but no other significant trace elements (Co, Ni, Se) were identified.

Further investigation of various native copper samples is necessary, for as many samples as possible coming from various sources. Then, a critical analysis and a statistical evaluation of the results both for different artifacts and native copper samples are mandatory. All these should be correlated to information on the finds. One should address with special care the specificity of the bronze alloys, the early manufacturing techniques and the impact of corrosion during time.

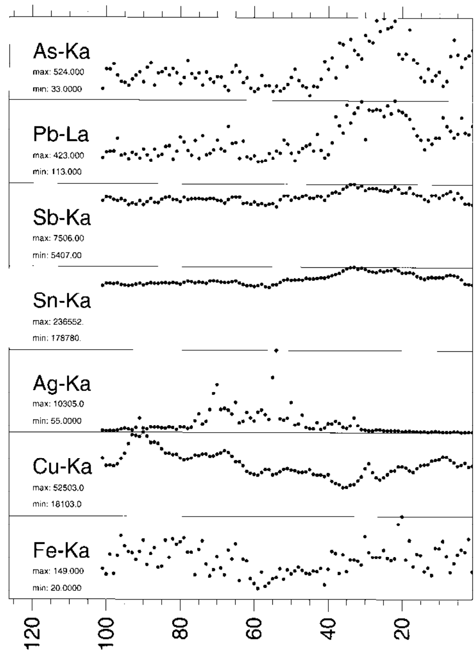

Fig. 4 – Ag inclusions in a profile of a sample of a bronze blade (dagger) – Santana, Arad County.

4. CONCLUSIONS

Micro-PIXE and -SR XRF are adequate tools for establishing the provenance of metallic archaeological objects, in correlation with mineralogical studies of various metal samples coming from historically known sources. These techniques are especially useful in identification of minor and trace elements and for looking for fingerprint elements in extremely small samples, but also for scanning larger areas or objects with apparently variable surface composition. They are well suited for the detailed analysis of inclusions, for the elemental mapping and identification of certain compounds suggested by the elements present in the global X-ray spectrum previously measured.

The most important studies where these methods have been applied and their conclusions are:

– In establishing the fingerprint of Transylvanian gold: Typical trace elements are Sn, Sb, Pb,Te; alluvial gold contains traces of Sn 100-300 ppm from cassiterite, traces of antimony are also present in some sources: 50-500 ppm from jamesonite ($Pb_4FeSb_6S_{14}$), stephanite (Ag_5SbS_4).

– The provenance of the Koson treasures: Koson coins with monogram (KCM) > 97% Au, so they are made most likely from re-melted gold; Koson coins without monogram (KFM) are made of alluvial gold (containing Sn and some also Sb).

– The provenance of the Dacian bracelets: They are made of alluvial gold, similar to the KFM coins.

– The studies of the primitive gold manufacture of Dacian objects: Many objects were produced from alluvial gold as is, by hammering and minimal or no thermal treatment, resulting non-uniform bulk and surfaces. It is also possible that some mining existed already in the pre-Roman era, based on recent archaeological finds of some tools dedicated to such activities.

– The Bronze Age Vulchitrun – type disk: It is made of alluvial gold. Its bronze part suggests a Serbian source. It is possible that auriferous gold from Anatolia or some gold from the Balkans has been used for its manufacture.

– The gold hair rings of the Tauteu hoard: these objects are made of alluvial gold.

– The bronze objects (axes, disks, daggers, sickles): These objects are the subject of a new study started in 2010, and only preliminary results are available up to now. These lead to a classification to several compositional patterns, which can be connected to the possible use of the objects (cult objects, weapons, etc.) [14]. Again, the presence of Ag in the Santana blade suggests a Bulgarian or Transylvanian source. Co content in the order of hundreds to thousands of ppm [23] would point more likely to a Serbian mine, e.g. Rudna Glava. On the contrary, in a set of extra-Carpathian Bronze Age objects (celt axes and sickles,[14]) we found one with a Co content corresponding to the fingerprint of Rudna Glava, and different patterns for all the other objects. The large spread of the results shows the difficulties in bronze provenance studies, and only by increase of the statistics we can hope to identify trends and limit the number of patterns. Only thus we will be able to know how adequate the method is for the copper-bronze studies. Up to now we can make only limited comments on the analysed archaeological objects.

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