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ARCHAEOMETALLURGICAL CHARACTERIZATION OF ANCIENT GOLD ARTIFACTS FROM ROMANIAN MUSEUMS USING XRF, MICRO-PIXE AND MICRO-SR-XRF METHODS

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Trace elements are more significant for provenance of archaeological metallic artifacts than the main components. For gold, the most promising elements are Platinum Group Elements (PGE), Sn, Te, Sb, Hg, Pb. To authenticate twelve Dacian gold bracelets and twenty Dacian gold coins (staters) type Koson was necessary to identify in their composition Transylvanian gold fingerprints Sn, Sb and Te. After an XRF examination of the artifacts, several small fragments from them and some natural Transylvanian native gold samples were studied using micro-PIXE at Legnaro National Laboratory, Italy and using micro-SR-XRF at ANKA Synchrotron, Karlsruhe, Germany.

Key words: XRF, micro-PIXE, micro-SR-XRF, ancient gold, archaeometallurgy.

1. INTRODUCTION

The study of trace elements in archaeological metallic artifacts can provide important clues about the metal provenance and the involved manufacturing procedures, leading to conclusions regarding the commercial, cultural and religious exchanges between the old populations and their way of life. Ancient metallic objects have been manufactured in a quite primitive manner, the metallurgy and techniques being developed over time; they are inhomogeneous on a micrometer scale, containing remains of imperfect smelting and inclusions (small areas with composition different from the surroundings) [1].

The elemental characterization (Au, Ag and Cu content and ratios) of representative Transylvanian gold deposits (alluvial-placers and mines) and their specific fingerprint (trace and minor element presence) can be alone a subject of paramount interest for the assignment of any archaeological artifact found on Romanian territory to one from these gold sources-deposits.

In the last years, the most important studies were performed on gold items recuperated by Romanian authorities coming from illegal excavation in Sarmizegetusa (capital of Dacian Kingdom) [2] area – spiraled bracelets (armbands) (Fig. 1) and gold coins (staters) type Koson (Figs. 2 and 3) [3, 4].

Fig. 1 – Dacian bracelets.

Fig. 2 – Dacian Koson with monogram.

Fig. 3 – Dacian Koson without monogram.

As a first step, we determine the basic elemental composition of the archaeological objects by XRF (X-Ray Fluorescence), as this allows the fast study of the finds as they are, without any damage or modification. The intervention on these objects is permitted for sample taking in the least damaging way, only when supported by the need for more accurate analysis to clear the details or controversies regarding the provenance. In such cases, more refined studies by micro-PIXE (Proton Induced X-ray Emission) and micro-SR-XRF (Synchrotron Radiation X-Ray Fluorescence) – point and scanning (elemental maps) spectra - are possible, e.g. at the spatially resolved set-ups like AN2000 accelerator microprobe of LNL-INFN in Legnaro [5] and ANKA/ISR FLUO beamline in Karlsruhe [6], where the accuracy and high excitation energy allows for the measurement of trace elements like Sb, Te, Pb – known fingerprints for the Carpathian mines, and Sn – characteristic for the panned alluvial gold. These elements have been identified in geological samples using the same techniques.

In this work, we synthesize compositional results on twelve gold Dacian braceles and on twenty Kosons and on some representative native gold samples (grains, nuggets, fine gold sand) from various Transylvanian mines and rivers obtained by XRF and, for very small (few-milligrams) fragments, by micro-PIXE and micro-SR-XRF point analysis and scanning.

2. THE ARCHAEOLOGICAL PROBLEM

A spectacular application of our methods was the authentication of the twelve Dacian gold bracelets exhibited at the National History Museum of Romania, Bucharest. The Dacian multi-spiraled bracelets were made of gold (see figure 1); they belong to the classical period of the Dacian civilization (2nd century B.C. - 1st century A.D.). The bracelets were recovered from the international market of antiquities through a common effort undertaken by the Romanian authorities in collaboration with the German authorities. The artifacts were discovered by archaeological looting in the area of Sarmizegetusa Regia Dacian fortresses in the Orăştie Mountains (UNESCO World Heritage List site), and illegally exported. The bracelets are spiraled (5–7 spirals), weighting 800 to 1 200 g each. They are 10 to 12 cm diameter, being adorned with stylized palm leafs and with zoomorphic protomes at both ends. There are remarkable analogies with the Dacian

silver bracelets from Coada Malului (Prahova county), Senereuş (Hunedoara county), Orăştie (Hunedoara county) and Herăstrău-Bucureşti (near Bucharest) hoards [7]. These bracelets are the first gold bracelets of Dacian craftsmanship ever discovered on the Romanian territory, considering that up to this moment only silver bracelets of this type were found during archaeological excavations or by chance. The bracelets were probably insignia of power, if one take into account their dimensions and the context of their discovery.

The study of the origin of the Kosons treasures is of special interest to archaeologists and historians. The Kosons are considered as the only gold coins issued by the Dacians. The specific of these coins consists in their Roman iconography. One side (the obverse) shows an eagle standing left on a scepter, holding a wreath in the claw, inspired by the silver denarii issued by Pomponius Rufus. The reverse (figures 2a and 3a) represents three togate men advancing left, two of them holding an axe on the shoulder, possibly inspired by a silver denarius issued in 54 BC by Junius Brutus [8]. The meaning of the inscription (ΚΟΣΩΗ), the place of mint and the issuer are still under discussion. Two main types of Kosons - with and without a monogram (averse, left side) have been found (Figs. 2 and 3).

Our experiments intended to determine whether the gold used for these coins is native or refined, and as such, to give some insight into the workmanship of those days.

3. EXPERIMENTAL

3.1. The Set-ups

The XRF, micro-PIXE and micro-SR-XRF elemental analysis methods are completely nondestructive, requiring no sample preparation at all - the samples can be measured practically in any shape delivered, which is their major advantage in such studies.

For XRF, we used in our archaeometry laboratory from IFIN-HH a X-MET TX3000 portable spectrometer, were the exciting X-ray beam is generated by a 40 kV – Rh anode tube. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the K_α line of Mn (5.89 keV). The measurement spot size is about 30 mm^2. The spectrometer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage [9].

Micro-PIXE studies were performed at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy, using a 2 MeV proton microbeam (6 μm × 6 μm beam area) with a maximum beam current ~1 000 pA [10]. 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 [11].

Micro-SR-XRF studies were performed at the ANKA/ISR FLUO-line in Karlsruhe, where we performed 2-dimensional scans with the beam focused to 6×7-10 μm^2. The scan area could be visualized with an optical microscope and recorded with a camera. The detector used was a HPGe crystal. The maximum excitation energy of the X-rays was 32.5 keV. The gold samples were mounted in air on a dedicated frame, put on a motorized xyz stage and positioned at an angle of 45 degrees to the primary X-ray beam. The identification of the peaks and the off-line data analysis was performed with AXIL. Relative concentrations of minor and trace elements were determined using a procedure based on various standards and fundamental parameter calculations.

3.2. The Samples

The XRF analysis is performed directly on the objects, many times in situ in the museums treasure chambers.

For micro-PIXE and micro-SR-XRF studies, we must analyze both archaeological and geological gold micro-samples and to compare their composition. The archaeological samples were tiny fragments (~200÷500 μm chips) coming from coins or jewelry (the famous Dacian bracelets in our case), taken in the least destructive manner possible from parts of the objects with little relevance as to their shape and decoration.

The coins of interest in this work are with or without monogram Kosons (20 samples) belonging to a treasure discovered at Tarsa-Luncani, near Sarmizegetusa – the capital of Dacia [12].

The analyzed archaeological samples come from the National History Museum of Romania, Bucharest.

The native gold samples represent various deposits from Transilvania: primary gold (Rosia Montana and Musariu from Metaliferi Mountains) and alluvial gold coming from placer deposits (Valea Pianului and Valea Ariesului). These samples were obtained from the collections of the Department of Mineralogy, Faculty of Geology and Geophysics, University of Bucharest and of the Gold Museum Brad.

4. RESULTS AND DISCUSSION

For the twelve Dacian bracelets, to confirm their authenticity the analysis of the gold alloy from which they were made was strongly requested. The conditions imposed by the Romanian authorities were: internal (in Romania) analyses, no sampling (even for LA-ICP-MS!), no nuclear activation. Therefore, between 2007 and 2010, the compositional analysis of the bracelets was performed by X-Ray Fluorescence (XRF) at "Horia Hulubei" National Institute for R&D in Physics and Nuclear Engineering, Bucharest. The compositional results (average of three measuring points) of XRF measurements are presented in Table 1.

Table 1

The composition of the twelve Dacian bracelets recovered up to March 2010
(the numbering of the bracelets is related to the succession in which they were recovered)

Bracelet no.	Weight (g)	Au (wt%)	Ag (wt%)	Cu (wt%)	Sn ($mg \cdot kg^{-1}$)
1	982.2	89.8	9.5	0.6	200
2	1076.72	78.2	20.3	1.5	60
3	1115.31	82.4	16.2	1.4	360
4	927.98	91.5	8.1	0.4	125
5	764.95	92.8	6.9	0.3	<MDL*
6	1062.55	92	7.1	0.9	230
7	1196.03	92.9	6.3	0.7	<MDL*
8	1136.06	85	12.8	2.1	1500
9	682.3	87.1	12.2	0.6	120
10	1047	88.7	10.3	0.9	425
11	825	86.1	12.6	0.7	400
12	884.37	83.5	14.3	1	500

*MDL – Minimum Detection Limits

Significant aspects are:

– the presence of tin traces – from cassiterite – fingerprint for placers/panned gold [13];

– the presence of antimony traces – probably from jamesonite ($Pb_4FeSb_6S_{14}$), stephanite (Ag_5SbS_4) – characteristic silver minerals in Metaliferi Mountains [14, 15];

– Ca-rich soil traces in cracks – probably due to the fact that the bracelets were buried for a long period of time;

– Relatively inhomogeneous composition of each bracelet.

In early 2011, we obtained the permission of the Romanian authorities to take very small (1-2 miligrams) samples from the extremities of the bracelets to analyze them by micro-SR-XRF to also verify their homogeneity. The study was performed at the ANKA/ISR FLUO-line in Karlsruhe. The relatively inhomogeneous composition of each bracelet was confirmed: e.g. for bracelet no.10 for head A (Fig. 6) we have 650 ppm Sn and 1.6% Cu as compare with head B (Fig. 7) – 275 ppm Sn and 0.7% Cu. Roughly, the composition obtained by XRF (Fig. 4 and Table 1) as average value on three approx. 30 mm diameter areas on the bracelet is confirmed: 425 ppm Sn and 0.9% Cu. Valability of XRF results is also confirmed by bracelet no. 2 head A measurement (Fig. 5): 45 ppm Sn and 1.45% Cu. Most likely, various gold ingots were

used to manufacture each bracelet. An explanation for the relative inhomogeneity of the ingot can be given through the fact that the manufacturers were not using an advanced technology; most likely, a mixture of gold nuggets and gold dust was melted down without being perfectly homogenized [16]. The original components of this mixture, having slightly different concentrations of Au-Ag-Cu, merged together, keeping their original structure. This lack of homogeneity of the gold nuggets and gold dust is also illustrated by the frequent cracks that appear of the bracelets' surface, cracks that appear despite gold alloy has remarkable mechanical properties. Both cold working and sintering of gold concentrates are also expected to conserve in the final product many mechanical impurities, like isolated minerals and inclusions [17].

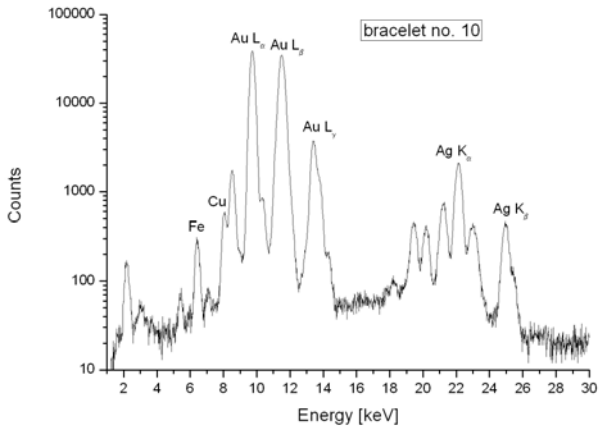

Fig. 4 – Dacian bracelet no.10 – XRF spectrum.

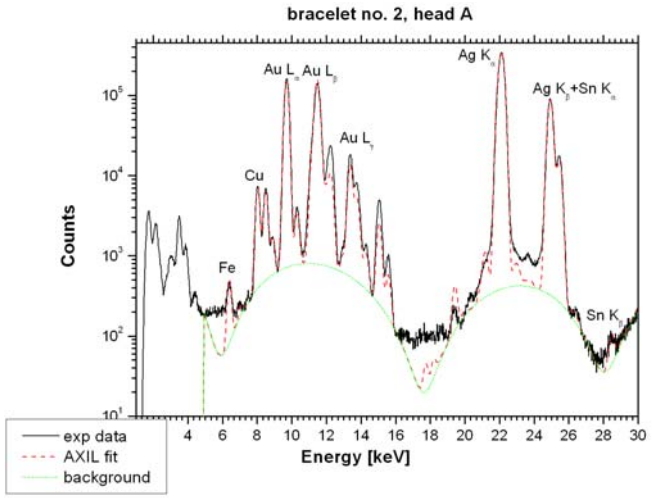

Fig. 5 – Dacian bracelet no. 2, head A – micro-SR-XRF spectrum.

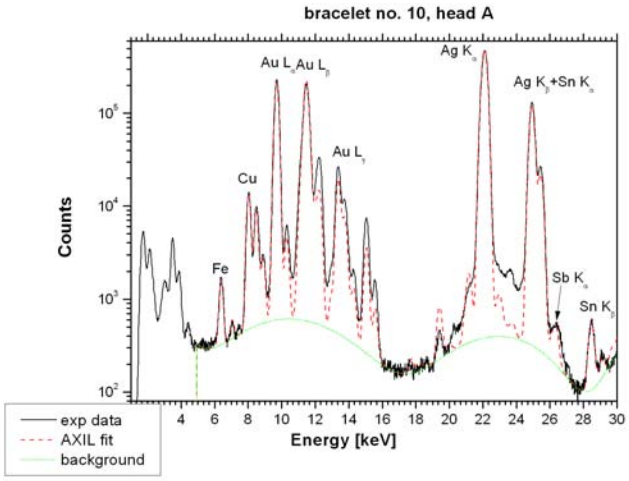

Fig. 6 – Dacian bracelet no. 10, head A – micro-SR-XRF spectrum.

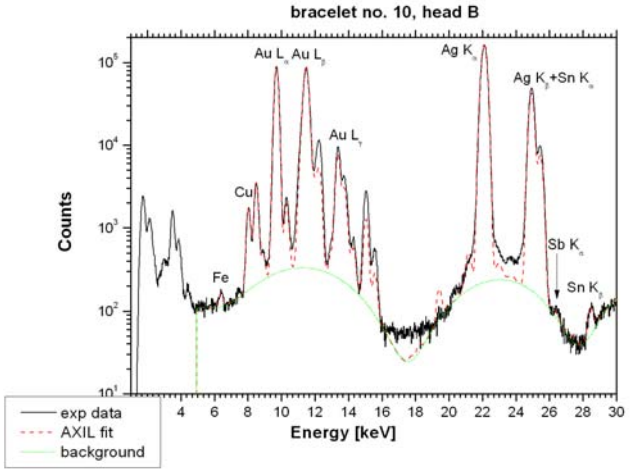

Fig. 7 – Dacian bracelet no. 10, head B – micro-SR-XRF spectrum.

By comparing the amount of copper determined in the Transylvanian gold samples and the ones obtained for the analyzed bracelets, one can notice that cooper concentration in artifacts is higher than in native gold. This increased copper content in the artifacts might be related to the presence of accompanying gold minerals in gold dust and nuggets – e.g. chalcopyrite ($CuFeS_2$) – "foolish gold", with a shinny aspect similar to real gold [17] and to the primitive processing of the raw material.

A confirmation of the dual presence of copper in ancient gold artifacts (from the electrum Au-Ag-Cu natural alloy and from chalcopyrite) was obtained when we performed Au, Ag and Cu elemental maps on two polished samples from Rosia Montana and Musariu (Metaliferi Mountains) using micro-PIXE at AN2000 accelerator of Laboratori Nazionali di Legnaro. If in Musariu sample (Fig. 8) copper is present in electrum area, in Rosia Montana sample (Fig. 9) copper presence is out of electrum (Au-Ag) area, very probably as chalcopyrite.

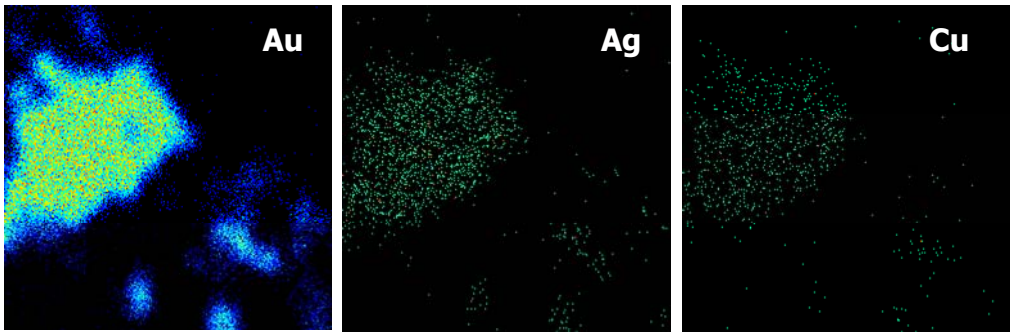

Fig. 8 – Elemental maps of Musariu gold sample.

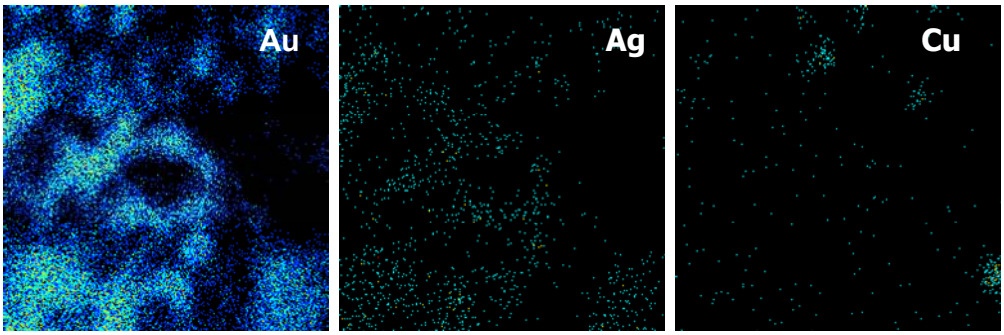

Fig. 9 – Elemental maps of Rosia Montana gold sample.

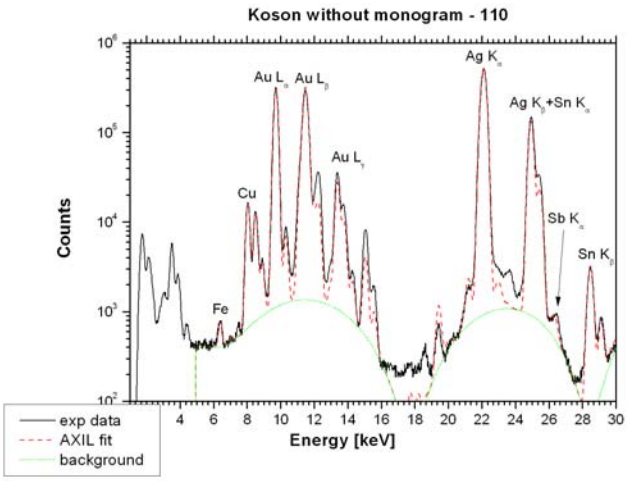

Fig. 10 – Koson without monogram – micro-SR-XRF spectrum.

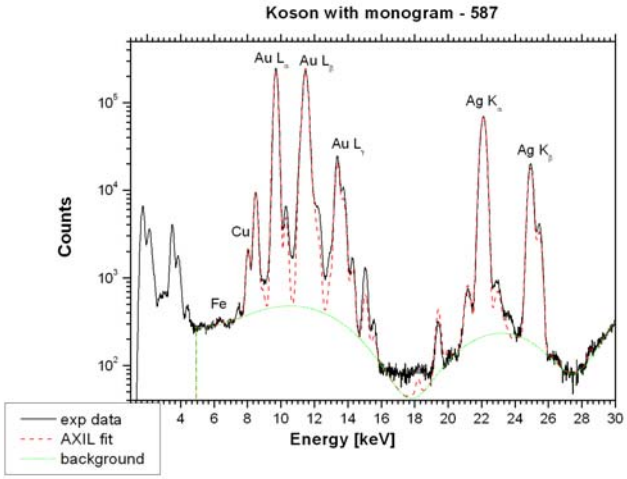

Fig. 11 – Koson with monogram – micro-SR-XRF spectrum.

Comparing the XRF results on bracelets with the micro-PIXE and micro SR-XRF results on Transylvanian gold samples, the conclusion was that the bracelets were made from native Carpathian (Transylvanian) gold (panned mixed with primary) and realized using a primitive metallurgy (no intention to refine the native gold). In this way, XRF results strongly support the stylistic arguments regarding the authenticity of the bracelets. Meantime, we received from Pieter Meyers [Los Angeles Metropolitan Museum, private communication] his LA-ICP-MS results (fall 2006) for bracelet no. 5, which are similar with ours, including, besides Sn and Sb presence, the detection of Pd and Pt, relevant micro-elements for placers. His conclusion was: genuine ancient bracelet, mainly from panned gold.

As concerning the Kosons, using micro-SR-XRF at ANKA/ISR-FLUO-line in Karlsruhe, we identified clearly that the Kosons without monogram contain Sn and sometimes Sb (Fig. 10), while the ones with monogram do not (Fig. 11). We have also found a micro-inclusion of Sb in one Koson without monogram sample, which could point at the possible use of Transylvanian primary gold associated with alluvial in the manufacture of these coins.

We illustrate the presence of Sn as fingerprint for Transylvanian alluvial gold in figures 12 and 13: Lupsa, Valea Ariesului and Pianu de Sus samples. Tellurium can not be found in artifacts because during the ingots melting it is lost through evaporation.

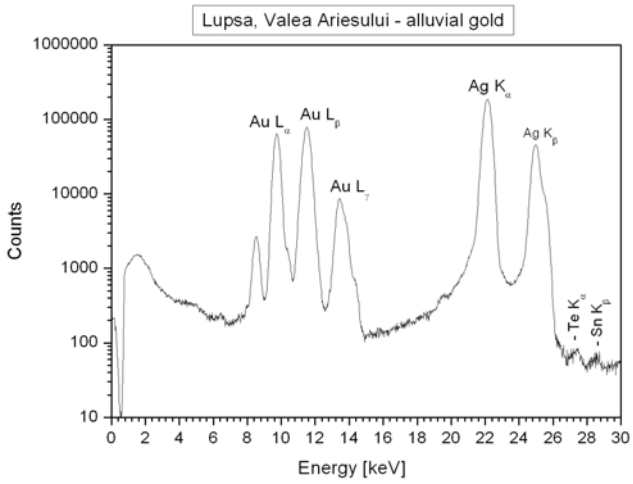

Fig. 12 –Alluvial gold, Lupsa, Valea Ariesului- micro-SR-XRF spectrum.

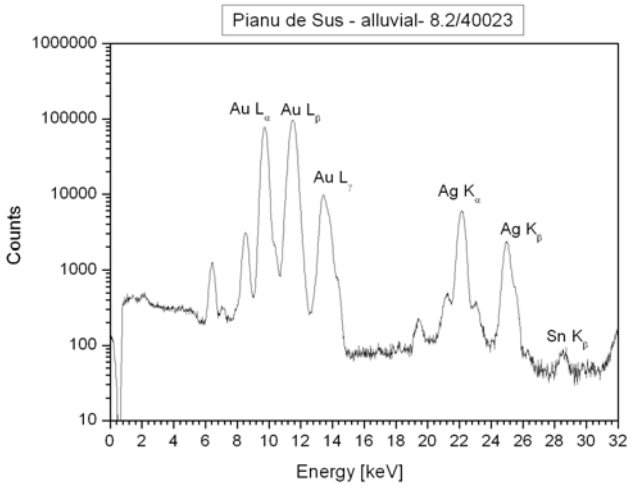

Fig. 13 –Alluvial gold, Pianul de Sus- micro-SR-XRF spectrum.

5. CONCLUSIONS

Our studies demonstrate that XRF, micro-PIXE and micro-SR-XRF are useful tools in establishing the authenticity and the provenance of gold ancient artifacts. If micro-sampling is possible during restoration (e.g. from the edges of the objects), micro-PIXE and micro-SR-XRF are the perfect choice for analysis, due to their high sensitivity and ability to non-destructively analyze minute samples. However, one has to keep in mind that in general, there are tough regulations regarding gold museum objects, and that is very difficult to take the artifacts out of the museum for investigations. In such cases, in-situ XRF measurements might be a good alternative to answer elemental composition-related questions, even if under these conditions they only give semi-quantitative results for trace elements.

The XRF measurements on the Dacian gold bracelets determined compositions that were consistent with the ones of natural panned gold that has not been deliberately alloyed or purified, mixed with primary gold. The traces of tin in the bracelets composition were connected with the presence of cassiterite grains in the alluvial gold, the corresponding tin being not removed during the relatively primitive metallurgical processing of the gold used to produce the artefacts. The micro-SR-XRF analyses on a set of native Transylvanian gold samples showed similarities with the composition of the recovered spiralled bracelets. Most likely, the recovered gold Dacian bracelets were manufactured from a mixture of unrefined Transylvanian gold: dust and small nuggets panned from riverbeds and creeks and primary gold from surface veins. Concerning the provenance of the Dacian gold coins, our study shows that the Kosons with monogram are made from refined (more than 97%) gold with no Sb, Te or Sn traces, and the ones without monogram are manufactured mainly from native alluvial gold (Sn traces detected). Contemporary with the Kosons, the Greek pseudo-Lysimachus staters are made of refined gold (no Sn, Sb, Te).

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REFERENCES

1. E. PERNICKA, *Provenance determination of metal artifacts: Methodological considerations*, Nucl. Instrum. Meth. Phys. Res., **B14**, pp. 24–29, 1986.
2. C. DAICOVICIU, H. DAICOVICIU, *Sarmizegethusa: les citadelles et les agglomerations daciques des Monts d'Orastie* (in French), Editura Meridiane, Bucureşti, 1963.
3. B. CONSTANTINESCU, E. OBERLÄNDER-TÂRNOVEANU, R. BUGOI, V. COJOCARU, M. RADTKE, *The Sarmizegetusa Bracelets,* Antiquity Journal, London, **84**, *326*, pp. 1028–1042, 2010.
4. A. VILCU, B. CONSTANTINESCU, R. BUGOI, C. PAUNA, *Some considerations on Dacian gold coins of Koson type in the light of compositional analyses,* Revue Numismatique, **166**, pp. 295–308, 2010.
5. B. CONSTANTINESCU, R. BUGOI, V. COJOCARU, D. VOICULESCU, D. GRAMBOLE, F. HERRMANN, D. CECCATO, *Romanian ancient gold objects provenance studies using micro-beam methods: the case of "Pietroasa" hoard*, Nucl. Instrum. Meth. Phys. Res., **B 231**, pp. 541–545, 2005.
6. B. CONSTANTINESCU, R. BUGOI, V. COJOCARU, R. SIMON, D. GRAMBOLE, F. MUNNIK, E. OBERLÄNDER-TÂRNOVEANU, *Elemental analysis through X-ray techniques applied in archaeological gold authentication – the case of Transylvanian gold and of the Dacian bracelets*, Spectrochimica Acta Part B: Atomic Spectroscopy, **64**, *11*, pp. 1198–1203, 2009.
7. V. PÂRVAN, *Getica. O protoistorie a Daciei* (in Romanian), Editura Meridiane, Bucharest, 1982.
8. C. M. PETOLESCU, *The treasure of King Koson* (Booklet), Romanian National History Museum, Bucharest, 2000.
9. B. CONSTANTINESCU, C. PAUNA, A. VASILESCU, F. CONSTANTIN, D. STAN, GH. C. POPESCU, A. NEACSU, *Some applications of X-ray based elemental analysis methods for Romanian gold minerals studies*, Romanian Reports in Physics, **62**, 1, pp. 47–56, 2010.
   C. CHIOJDEANU, D. C. STAN, B. CONSTANTINESCU, *Gold and silver coating characterization using an X-ray fluorescence based method-The case of archaelogical artifacts*, Romanian Reports in Physics, **63**, *3*, pp. 685–692, 2011.
10. B. CONSTANTINESCU, R. BUGOI, V. COJOCARU, M. RADTKE, T. CALLIGARO, J. SALOMON, L. PICHON, S. ROEHRS, D. CECCATO, E. OBERLAENDER-TARNOVEANU, *Micro SR-XRF and micro-PIXE studies for archaeological gold identification – the case of Carpathian (Transylvanian) gold and of Dacian bracelets,* Nuclear Instruments and Methods in Phys Research B, **266**, *10*, pp. 2325–2328, 2008.
11. G. C. WILSON, J. C. RUCKLIDGE, J. L. CAMPBELL, Z. NEJEDLY AND W. J. TEESDALE, *Applications of PIXE to mineral characterization,* Nucl. Instr. Meth. B, **189**, pp. 387–393, 2002.
12. V. COJOCARU, B. CONSTANTINESCU, I. STEFANESCU, C.M. PETOLESCU, J. Radioanal. Nucl. Chem.**, 246**, *1*, pp. 185–190, 2000.
13. MARIA FILOMENA GUERRA, *Fingerprinting ancient gold with proton beams of different energies*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, **226**, *1–2*, pp. 185–198, 2004.
14. GH.C. POPESCU, *Metalogenie aplicată şi prognoză geologică. Partea a II a* (in Romanian), Editura Universităţii, Bucharest, 1986.
15. G. UDUBASA, S. SZAKALL, R. DUDA, V. KVASNYTSYA, E. KOSZOWSKA, M. NOVAK, *Minerals of the Carpathians,* Granit, Prague, 2002.
16. CH. J. RAUB, *The metallurgy of gold and silver in prehistoric times*, in: G. Morteani, J. P. Northover (eds.). Prehistoric Gold in Europe – Mines, Metallurgy and Manufacture, **243–59**, Springer Verlag, Berlin, 1995.
17. A. HAUPTMANN, TH. REHREN, E. PERNICKA, *The composition of gold from the ancient mining district of Verespatak/Roşia Montană, România,* in: G. Morteani, J. P. Northover (eds.), *Prehistoric Gold in Europe – Mines, Metallurgy and Manufacture*, **369–81**, Springer Verlag, Berlin, 1995.

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