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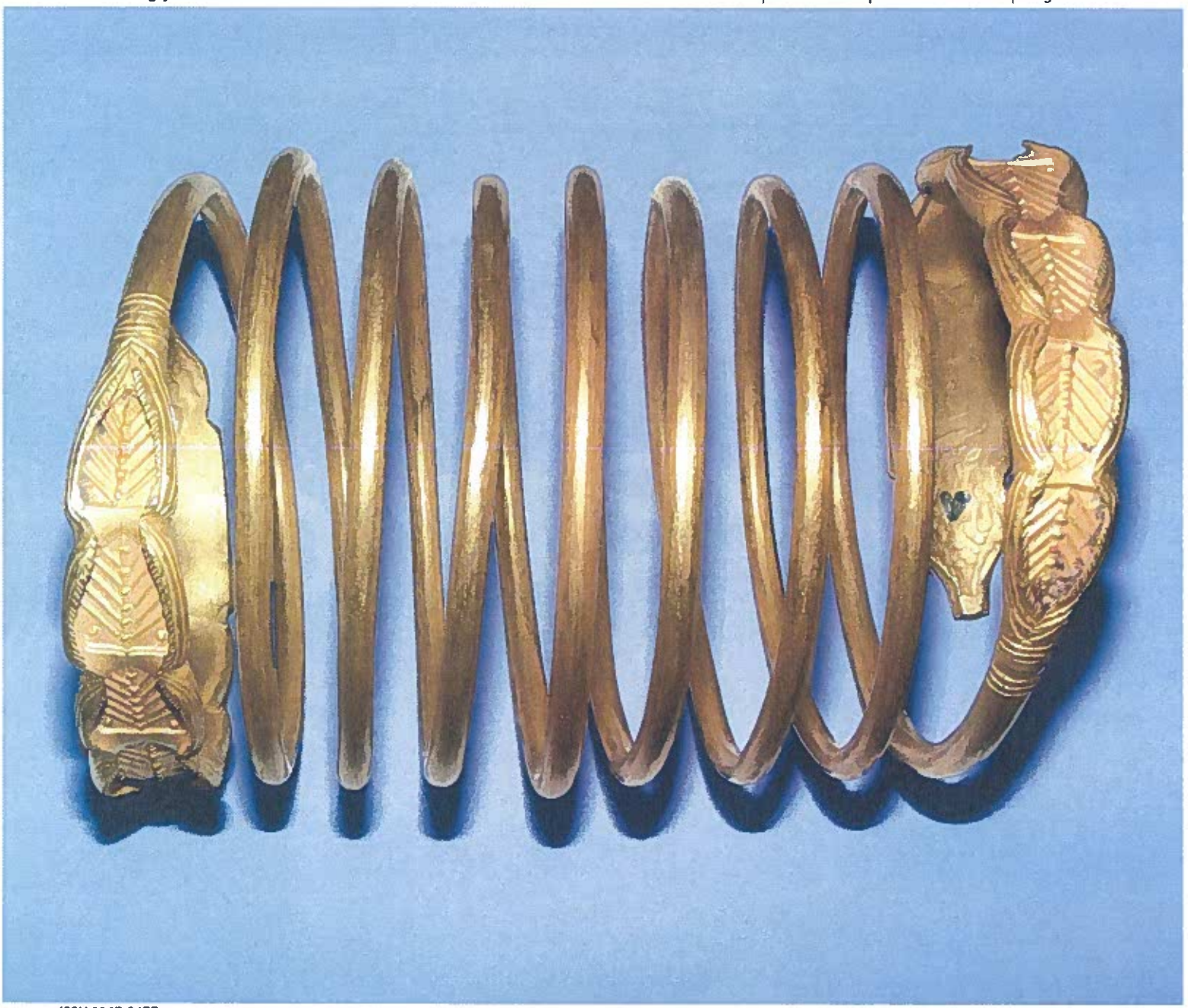

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PAPER

Studies on archaeological gold items found in Romanian territory using X-Ray-based analytical spectrometry

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This paper is an overview of the work developed by our group in the investigations of museum objects and alluvial gold, reflected in a series of studies published between 2000–2011, supplemented with new results, unpublished up-to-date. The X-ray based spectrometric techniques employed range from various X-Ray Fluorescence (XRF) investigations to ion beam analysis, including synchrotron radiation XRF and micro-Particle Induced X-ray Emission. The gold objects discussed are mainly part of the Sarmizegetusa Dacian hoards—spiraled bracelets (armbands) and coins. After obtaining in 2011 the permission of the Romanian authorities to take very small (1–2 mg) samples from the most "unimportant" areas of the Dacian bracelets and several Koson staters, to analyze them by micro-SR-XRF at BESSY, in February 2012, the investigation of several micro-areas of 17 stater and 28 bracelet samples revealed important micro-structural inhomogeneity, especially in Sn and Cu. The same inhomogeneous micro-structure has been seen in Transylvanian alluvial gold. The analyses revealed details on the fingerprint of geological gold deposits and also the main characteristics of ancient gold metallurgy procedures used by the Dacians: a relatively low temperature (lower than Au melting point) and hammering during heating to obtain an ingot through sintering. The use of the sintering procedure was proved for the spiraled bracelets and the Koson without monogram coins, a tradition starting in the Bronze Age in Transylvanian gold processing. The existence of micro-inclusions of Ta-minerals in alluvial gold was also detected, explaining Ta trace presence in the artifacts from the Pietroasa hoard.

Introduction

To illustrate the application of X-ray based spectrometric techniques to the study of metallic artifacts in art, archaeology and geology, we propose an overview of the work developed by our group in the investigations on museum objects and alluvial gold, reflected in a series of studies published between 2000–2011, supplemented with new results, unpublished up-to-date. The objects referred to in this paper are part of several gold treasures: the Sarmizegetusa Dacian hoards—spiraled bracelets (armbands) and staters,[1–3] the famous (21 kg gold!) Pietroasa Visigothic hoard,[4] but also other individual Bronze Age objects like gold rings, bracelets *etc.*[5,6] all unearthed on Romanian territory (Fig. 1).

The techniques employed range from various XRF (X-Ray Fluorescence) investigations to IBA (Ion Beam Analysis), with the micro-beam versions (micro-Synchrotron Radiation (SR)-XRF, micro-Particle Induced X-ray Emission (PIXE)) added for deeper level investigation on the micron scale.

The scientific literature comprises many studies on the provenance of metallic artifacts and mineral characterisation, to mention only a few,[7–10] presenting the use of various modern analytical spectrometric techniques in archaeology or geology.

Fig. 1 A Sarmizegetusa bracelet and a Koson stater with monogram (obverse and reverse).

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Dacian gold objects and alluvial gold—previous results and motivation

In the compositional studies of archaeological gold artifacts, besides the ratios between the three main components of gold alloys (Au–Ag–Cu) which can be used in their authentication, trace elements might bring significant clues. Trace-elements which can be found in native gold are the Platinum Group Elements (PGE): Pt, Ir, Os, Ru, Rh, Pd, but also Sn, Sb, Te, Hg, Ti, Zr, As, Bi, Fe.[7,8]

From Antiquity to the Middle Ages, the most important gold source consisted of placer deposits. Alluvial gold is derived from weathered rocks containing vein gold deposits. Gold is highly resistant to weathering; its particles along with the eroded rocks are washed down the mountains, and subsequently deposited in the sand and gravel of the rivers.

Naturally occurring gold contains several impurities, the most significant ones being silver and, in a much smaller proportion, copper.

During weathering and transport, silver and copper are more susceptible to dissolution or oxidation compared with gold, depending on the pH value of the surrounding environment. Thus, the overall silver and copper content of the alluvial gold is somewhat lower than that of the initial vein gold from which it had originated.[11]

In the case of the gold objects (jewellery, coins) found on Romanian territory, the most likely use of Transylvanian unrefined gold should be considered, especially for the earlier artifacts, when the manufacturing techniques were poorly developed. The use of alluvial gold in early historic times in Transylvania—one of the richest gold regions in Antiquity—was demonstrated in a series of elemental studies on Dacian gold artifacts performed from 2007 to-date.[1–3]

The context of these investigations is described in the following: according to later criminal investigations of Romanian authorities,[12] (several hoards containing at least twenty four gold spiral bracelets and a few thousand gold coins (staters) of pseudo-Lysimachus and Koson types (Koson with and without monogram, see ref. 13) have been unearthed in the time frame between 1999 and 2001, by organized gangs of illegal treasure hunters, in five different spots in the area of Sarmizegetusa Regia, in the Orastie Mountains, Romania. Sarmizegetusa Regia was the ancient capital of the Dacian Kingdom[14,15] and is a site on the UNESCO World Heritage List.

In order to confirm or disprove the authenticity of the bracelets and the coins, the compositional analysis of the gold alloy they were made of, has to be determined. The conditions imposed by the Romanian authorities were restrictive, implying the analyses to be performed locally (*i.e.*, on Romanian territory), non-destructive (*i.e.*, no sampling allowed) and such that no residual (radio)activity should be left in the objects (nuclear activation analysis methods were therefore excluded). The most suitable analytical method obeying all the above-mentioned conditions was Energy Dispersive X-Ray Fluorescence (ED-XRF).

Initially the compositional analysis of the bracelets and coins was performed using an experimental set-up based on a ^{241}Am (30 mCi) annular radioactive source excitation and a Si(Li) horizontal detector (with energy resolution of 180 eV FWHM at 5.9 keV), see details in ref. 16. A pure (99.99%) gold coin from the Royal Canadian Mint was used to evaluate the contribution of the γ-ray peaks emitted by the ^{241}Am source, particularly the 26.3 keV line, which overlaps with the SbK_α line. Several modern gold and silver coins and reference materials with certified composition were used to calibrate the set-up. The measurement times were of the order of thousands of seconds, to allow the detection of the possible trace elements.

The XRF elemental compositions for all twelve bracelets and for the Koson staters without monogram, show the presence of relatively large amounts of silver (10% on average) and small amounts of copper (1% on average), and fit the pattern of native gold, given in literature, as generally containing up to 40% silver and up to 1% copper.[17,18] Traces of tin were observed in all the ED-XRF spectra of these gold objects, and also antimony in some of them. These elements have also been detected in Transylvanian native gold samples. Transylvanian native gold samples (both alluvial/placer—sand and nuggets—and primary/mine) were analysed using micro-PIXE and micro-SR-XRF, in view of the identification of the probable sources of gold known in this geological area.[19–21] The investigation of a series of alluvial samples from the collection of the Brad Gold Museum (Brad, Romania) was especially focused on the presence of trace elements and their distribution and elemental correlations in natural gold.

Comparing the results from the archaeological and the geological gold studies, it looks like there was no intention of the manufacturer of the investigated items to refine the employed gold, nor that a modern gold alloy was used, thus supporting the authenticity of these finds. Without the possibility of a micron-scale investigation, one can conclude from the composition of these objects, that the recovered Dacian gold bracelets and the Koson without monogram staters were manufactured from a mixture of unrefined Transylvanian gold: dust and small nuggets panned from riverbeds and creeks, at most mixed with some primary gold from surface veins.[3]

A very interesting aspect revealed by our studies was that various gold "ingots" were used to manufacture each bracelet, since there are slight differences between the compositions of the twelve objects, and, moreover, each bracelet showed a rather inhomogeneous composition—this was noticed by comparing the results of the measurements in different regions of the same bracelet. Similar conclusions have been obtained, *e.g.*, from the compositional analysis of other Bronze- and Iron Age gold artifacts found in Transylvania, like a hair-ring and a bracelet found at Boarta, near Valea Pianului—the best known ancient area of gold placers from Transylvania (Fig. 2 and Table 1). Probably, different nuggets were put together, hammered and partially heated to obtain their "welding". In the visual inspection of the Boarta objects (Fig. 2), we notice two different types of gold used (one white and the other yellow), and the laboratory XRF results show different elemental compositional patterns (Table 1).

Traces of tin and, less frequently, antimony or even tellurium were also detected in various Bronze Age gold artifacts from the collection of the National Museum of History of Romania.[6]

Based on these observations, we decided to try to identify the metallurgical procedures used for the gold by the Dacians in the manufacture of the artifacts. We mainly concentrated on the microscopic distributions/variations in the gold mixture (of artifacts, but also of native "electrum") of trace elements as Sn,

Fig. 2 Gold bracelet Boarta P81613.

Table 1 Elemental composition of the Boarta gold bracelet by XRF; accuracy: ±(5–10)% for gold, and ±20% for Ag and Cu; MDL (minimum detection limit) is less than 200 mg kg^{-1}

Gold bracelet P81613	Au %	Ag %	Cu %	Sn
Central region	63	34	2	—
End region – white	55	44	2.6	—
End region – yellow	79	19	1	Traces

Sb, Te, Cu, Fe because it is directly related to the quality of the used metallurgy.

Experimental aspects

The first method applied in the gold investigations was laboratory ED-XRF, using ^{241}Am source excitation, as already mentioned,[16] and later, X-ray tube excitation.[21] The results obtained thus for the artifacts were global compositions, but soon it became clear that the sensitivity was not enough for a better quantification and the study of heavy trace elements, while Proton Activation Analysis (PAA)[13] ensured the access to the mg kg^{-1} level, however, with the disadvantage of very long exposure times and possible activation of the object. To circumvent the problem, the micro-elemental investigations were performed onwards, mainly by micro-SR-XRF at BESSY and micro-PIXE at LNL.

The experimental conditions at the BAM line at the BESSY storage ring in Berlin have been described in several publications (*e.g.*, ref. 22). Micro SR-XRF beams of various sizes, ranging from a few micrometers to 100–300 micrometers and maximum excitation energies of 32.5–34 keV, and a Si(Li) detector for the measurement of the fluorescent signal have been used. The samples were mounted in air, on a dedicated frame on an *XYZ*-stage, at 45° to the primary beam. The evaluation of the spectra was done using the QXAS AXIL standard package[23] and a combination of measurements of pure elemental standards and an iterative method of convergence described in ref. 24.

For micro-PIXE at the AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy,[25] a 2 MeV proton microbeam (typically of 6 × 6 μm^2 beam area), with maximum beam current ~1000 pA was used. 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 × 2 mm^2 maps and point spectra were acquired.

The quantitative analysis was performed using the GUPIX-WIN[26] and MAPPIX[27] software packages.

As mentioned in ref. 28 surface depletion in Cu and Ag in the analysis of gold artifacts can be an issue of discussion. In our case, due to the low content in copper, only silver corrosion could be considered. The penetration depth of the probing beams is in the range of 20–30 μm, larger than the immediate surface layer for which such depletion was measured, *e.g.*, in ref. 28 by SEM-EDX. The corresponding depth for the emission of the Ag-lines is about 10 μm. Secondary effects, absorption and enhancement are included in the analysis program. At present, it is not possible to make "layered" measurements with sufficient resolution at the BAM-line, in order to get more detailed information on the corrosion of the surface.

New results and discussion

In 2011, we obtained the permission of the Romanian authorities to take very small (1–2 mg) samples from the most "unimportant" areas of the Dacian bracelets and several Koson staters—*e.g.*, the extremities of the bracelets and the edges of the coins—to analyze them by micro-SR-XRF at BESSY.

In February 2012, we analysed 2–3 microareas of 17 Koson and 28 bracelet samples in a 32.5 keV maximum energy X-Ray beam of 108 × 170 μm^2 of the BAM-line. The method of the quantitative QXAS evaluation used was described in ref. 24. The relative uncertainty estimate for Au and the geochemical paragenesis (minor and major elements) is ~1% and <10% for Sn. As no standards were available for Sb and Te, a limit of 20% could be a reasonable estimate from the extrapolation.

The results obtained in the homogeneity analysis of the Koson stater samples are given in Table 2.

Evidently, the two categories of staters have been minted using two different metallurgical "recipes" and, consequently, represent two types of gold "alloy".

The Koson staters with monogram have a high gold percentage (Au: 94.4–99.2%) and are rather homogeneous, with a reduced content of copper (0.10–0.30%) and tin (0–67 mg kg^{-1}). On the contrary, the Koson staters without monogram have a higher content of silver (8.31–16.0%) and copper (0.96–2.9%), and a significant presence of tin (149–1066 mg kg^{-1}), coupled with an evident inhomogeneity in all metallic elements, but especially in tin, copper and iron.

These aspects indicate the use of refined gold (advanced "real" metallurgy) for the Koson staters with monogram and the use of native (mainly alluvial) gold in a primitive metallurgy for the Koson staters without monogram. A most trustful hypothesis is that the Koson staters with monogram, the primary coins, were minted somewhere in the neighbouring Roman provinces (in the Balkans) from refined, "coined" gold and the Koson staters without monogram are "Barbarian" copies made in Dacia (Transylvania) from native gold using a primitive metallurgy incapable of completely melting the small pieces of alluvial gold.

The same aspects were revealed after the analyses of similar small fragments (less than 100 microns in diameter) from 13 Dacian gold bracelets. We illustrate with bracelet no. 2, where

Table 2 Elemental concentration variations in Koson staters[a]

Sample	Meas.	Au (%)	Ag (%)	Cu (%)	Fe (%)	Sn (mg kg^{-1})	Other elements
K 73	1	82.2	15.2	2.44	0.22	522	
K 73	2	82.0	15.5	2.25	0.17	496	
K 73	3	81.8	16.0	2.90	0.20	1066	Sb 2 mg kg^{-1}
K135	1	83.1	14.4	2.29	0.17	532	
K135	2	84.1	13.7	2.08	0.106	426	
K118	1	87.5	8.69	1.49	2.31	149	Te 17 mg kg^{-1}
K118	2	85.5	12.2	1.60	0.67	291	
K 54	1	88.6	9.71	1.49	0.19	365	
K 54	2	85.6	12.4	1.49	0.41	1036	
K131	1	88.0	10.7	0.98	0.26	338	
K131	2	87.3	11.4	1.04	0.24	361	
K132	1	88.1	10.9	0.18	0.75	553	
K132	2	90.6	8.31	0.96	0.14	268	
K 40	1	89.0	9.07	1.75	0.13	388	
K 40	2	86.8	11.3	1.71	0.09	772	
K 38	1	88.8	9.93	0.92	0.31	439	
K 38	2	88.1	10.3	1.48	0.06	412	
K 65	1	87.8	11.0	1.17	0.04	318	
K 65	2	86.2	12.7	1.07	0.034	428	
K 92	1	85.8	12.1	1.93	0.09	677	
K 92	2	85.6	12.7	1.31	0.38	309	
K 43	1	87.0	11.2	1.63	0.053	1031	
K 43	2	87.1	11.1	1.69	0.055	667	
KM 23	1	95.7	4.03	0.25	0.056	10	
KM 23	2	95.2	4.43	0.27	0.045	15	
KM 53	1	94.5	5.19	0.25	0.05	37	
KM 53	2	94.4	5.20	0.28	0.09	10	
KM 10	1	97.0	2.76	0.18	0.07	10	
KM 10	2	96.7	2.80	0.15	0.34	—	
KM 8	1	95.1	4.50	0.30	0.06	19	
KM 8	2	94.8	4.84	0.27	0.04	31	
KM719	1	99.2	0.64	0.10	0.03	62	
KM719	2	99.2	0.67	0.11	0.04	35	
KM321	1	98.4	1.28	0.16	0.06	67	
KM321	2	98.5	1.32	0.15	0.04	48	
KM321	3	98.4	1.38	0.15	0.05	42	

[a] K = Koson without monogram; KM = Koson with monogram.

the XRF measurement in three areas (approx. 2 cm^2 each) gave the average composition of Au 81.2% Ag 16.2% Cu 1.6% Sn 60 mg kg^{-1}. The gold used for the manufacture of this bracelet was mainly extracted by panning from the local rivers or from placer deposits near Sarmizegetusa: Valea Pianului (a famous placer deposit), and was mixed with surface vein gold from, *e.g.*, Baia de Aries.[29]

Table 3 presents results of the SR-XRF measurements on 2 microsamples of the same bracelet, head A and B.

The differences are significant not only between the two "heads" (ends) of the bracelet (a "huge" item for gold jewellery: weight 1076.72 g, length 2.69 m, external diameter 112 mm, 8 spires), but also for the same fragment in the case of "head" A, indicating the use of small grains ("gold sand") of alluvial gold melted partly or not at all.

Table 3 SR-XRF results on bracelet #2

Measurement	Au (%)	Ag (%)	Cu (%)	Fe (%)	Sn (mg kg^{-1})
Head A					
1	77.8	19.5	2.43	0.25	52
2	80.8	17.1	1.46	0.68	109
3	81.0	16.9	1.45	0.65	88
Head B					
1	77.7	18.5	3.71	0.030	52
2	78.2	18.7	3.11	0.039	49

Comparing the gold percentage obtained in XRF measurements with the microscopic investigation results given in Table 3, we see that on average the concentration of major elements is roughly the same, but only micro SR XRF can reveal the details on the inhomogeneous structure of the gold present in the object.

The same inhomogeneous micro-structure was seen by micro-SR XRF for alluvial gold (several small samples, less than 2 mm in diameter).

Fig. 3 and 4 show two point-spectra of a sample from Pianu de Sus (Sn and Sb inclusions, Fig. 3) and a sample from a river at the state border between Yugoslavia (now Serbia) and Romania (Sn and Te inclusions, Fig. 4).

An explanation for the relative inhomogeneity of the ingots could be determined by the fact that the manufacturers were not using an advanced technology: most likely, a mixture of gold nuggets and gold dust was melted together, without being perfectly homogenized. Both cold working and sintering of the gold concentrates are expected to conserve in the final product many mechanical impurities like isolated minerals and inclusions. Traces of tin were observed in practically all the items. One explanation for this phenomenon is the following: cassiterite

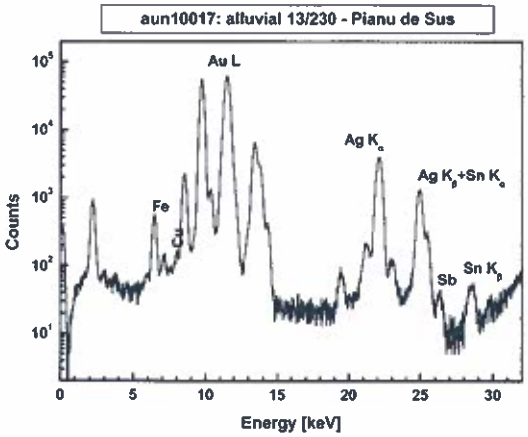

Fig. 3 Alluvial gold from the Pianu basin.

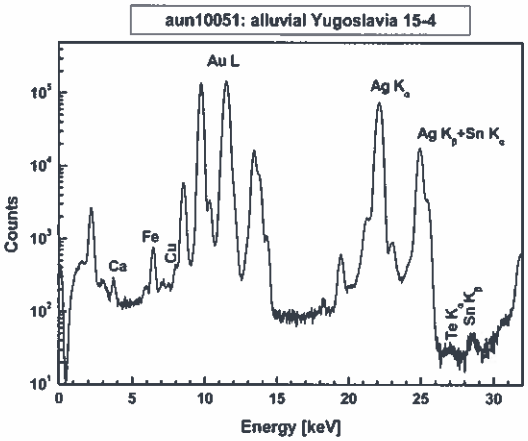

Fig. 4 Serbian (Yugoslavia) alluvial gold.

Fig. 5 Danube gold maps (2 mm × 2 mm; the darker colour, the higher the intensity of the fluorescence signal): Fe K_α, Au L_α, Sn K_α; micro-inclusions containing Fe (1–) or Sn (2–).

(SnO_2) and gold can simultaneously occur in the same vein or placer deposit.[30] Despite all the possible precautions taken during gold panning in ancient times, some cassiterite grains could still be found in gold-rich concentrates. If the melting was not complete, it is possible that microinclusions of cassiterite still remain in the matrix, which is consistent with our previous observation of both uniformly distributed Sn in gold and localized microinclusions containing Sn in the gold area.

The copper concentration found in the artifacts is higher than the one in Transylvanian native gold, related to the presence of accompanying gold coloured minerals in gold dust and nuggets—*e.g.*, chalcopyrite ($CuFeS_2$), "fool's gold" and pyrite

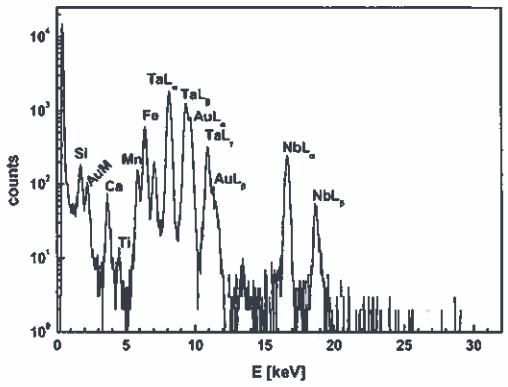

Fig. 6 Ta–Nb presence in Danube alluvial gold (1).

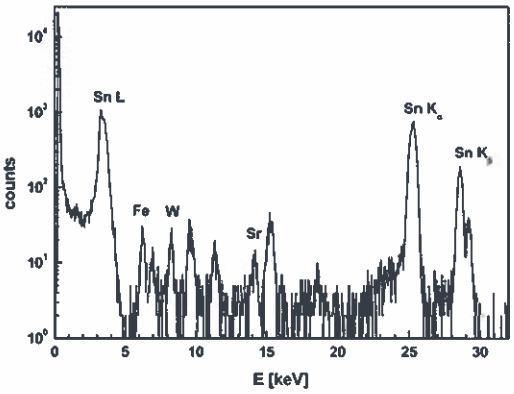

Fig. 7 A W–Sn inclusion in Danube alluvial gold (2).

(FeS)—due to the probable confusion made by Dacian "miners" and to the primitive processing of the raw material.

During 2002–2004, our archaeometry group analyzed by micro-PIXE small (less than one millimeter diameter) samples from several objects from the famous Visigothic Pietroasa treasure "The Golden Brood Hen with its Chicken" supposedly dated 4th to 5th century AD.[4]

The most spectacular finding was the presence of Ta–Nb inclusions in two brooches (fibulae) with a typically Germanic bird design. The hypothesis for Ta provenance was that the gold used in the fibulae had been extracted from the Southern Ural Mountains, where Ta minerals are known to be present (*e.g.*, samarskite, found for the first time near the Ural town of Samara).

Last year, analyzing by micro-PIXE small grains of alluvial gold from the Danube river (between Bratislava and Budapest), we obtained several elemental concentration maps (characteristic X-Ray intensity) revealing Fe and Sn inclusions, see Fig. 5.

In one of the iron inclusions (1 in Fig. 5), a "point" ($3 \times 3\ \mu m^2$) spectrum proves the presence of a Ta–Nb micro-inclusion (Fig. 6). The GUPIX analysis gives (relative error in parantheses): 5.9% Mn (±6.14%), 12.7 % Fe (±3.45%), 16.6 % Nb (±2.35%), 64.8% Ta (±1.32%).

Similarly, in one Sn-rich area (2, in Fig. 5), we found a Sn–W micro-inclusion (Fig. 7). The analysis gives: Fe 1405 mg kg^{-1} (rel. err. ±11%, MDL = 95 mg kg^{-1}), Sr 218 mg kg^{-1} (±45%, MDL = 207 mg kg^{-1}), Sn 78.44% (±1%, MDL = 3319 mg kg^{-1}),

W 1642 mg kg^{-1} (±8.5%, MDL = 100 mg kg^{-1}). The geological explanation for the presence of such microinclusions is the substitution of tin in cassiterite by Ta, Nb, W, Fe and Mn.[31] We can mention ref. 32 and 33, where the authors present the list of minerals which have been found in the alluvial placer deposits from the Sinecne Valley, Pezinok near Bratislava, associating native gold and columbite—$(Mn,Fe)(Nb,Ta)O_6$,[34] and on the presence of Sn–W–Mo mineralization in specific areas in Central Slovakia, a probable source, reaching the Danube *via* local rivers.

Thus, we demonstrated for the first time—as far as we know—the existence of Ta-mineral inclusions in alluvial gold, the higher melting temperature of Ta (T_m[Ta] = 2980 °C; T_m[Au] = 1063 °C) allowing for its preservation in the final product, even after the gold refining procedure.

The presence of Si, Ca, and Sr in the spectra (Fig. 6 and 7) is connected to the sand of the riverbed from which the placer samples were collected.

Conclusions

Our studies demonstrated that micro-SR-XRF and micro-PIXE are efficient tools both in the authentication and provenance of ancient gold artifacts and for the characterization of the oldest metallurgical processing of gold.

Micro-structural investigations revealed details regarding the fingerprint of the geological gold deposits and also the main characteristics of the ancient gold metallurgy processes used: a relatively low temperature (lower than the melting point of Au) and hammering during heating to obtain an ingot through sintering. The sintering procedure was proven in the case of the analyzed Dacian items–spiraled bracelets and Koson without monogram coins—a tradition starting in the Bronze Age for Transylvanian gold processing. The existence in gold of micro-inclusions containing Ta-minerals was also detected, a possible source for the presence of the Ta traces in artifacts like the "Pietroasa" hoard items.

We also demonstrated that micro-SR-XRF and micro-PIXE are useful in the micro-geochemistry investigation of native (both alluvial and primary) gold samples. As a continuation, we intend to complete the study of Transylvanian gold using X-Ray based analytical methods together with geologically focused Electron Micro-Probe Analysis.

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