COMPOSITIONAL STUDIES ON TRANSYLVANIAN GOLD NUGGETS: ADVANTAGES AND LIMITATIONS OF PIXE-PIGE ANALYSIS

Roxana Bugoi[1*], *Viorel Cojocaru*[1], *Bogdan Constantinescu*[1], *Thomas Calligaro*[2], *Laurent Pichon*[2], *Stefan Röhrs*[2], *Joseph Salomon*[2]

[1] *"Horia Hulubei" National Institute of Nuclear Physics and Engineering, Atomiştilor 407, Bucharest 077125, Romania*

[2] *Centre de Recherche et de Restauration des Musées de France (C2RMF), CNRS UMR 171, Palais du Louvre, 14 Quai François Mitterand, 75001, Paris CEDEX 01, France*

ABSTRACT

Minute fragments from nine gold nuggets from Transylvania - two belonging to placer deposits and seven to primary deposits - were analyzed by PIXE and PIGE at the AGLAE tandem accelerator of the Centre de Recherche et de Restauration des Musées de France (C2RMF) with 3 MeV proton beam extracted into air. This study was triggered by some archaeological provenance issues for which the elemental characterization of the Transylvanian gold source, exploited from the Antiquity, was required. All analyzed Transylvanian gold nuggets are characterized by a consistently high amount of Ag (18% on average). Au and Ag add up to roughly 99%, the other

[*]Corresponding author: Roxana Bugoi, Department of Applied Nuclear Physics, "Horia Hulubei" National Institute of Nuclear Physics and Engineering, Bucharest 077125, PO BOX MG-6, Romania, Phone: +40214042349, Fax: +40214574440, e-mail: bugoi@nipne.ro

elements - Cu, Fe, Te, Pb - being detected only at a trace level. The obtained results are in good agreement with the previous analyses of Transylvanian gold.

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INTRODUCTION

The minor and trace elements content of natural gold can be useful in defining the genesis of gold sediments; it can also shed some light on ancient gold artifact provenance studies.

However, the relationship between the elemental composition of a metalliferous ore and that of a metal object derived from it is complicated by factors such as different processing, mixing of ores from different sources, deliberate or accidental addition of metals to modify the mechanical or visual properties of the finished product, and the likely recycling of metal [1]. Ag, Sn, Sb, Te, Cu and Platinum Group Elements (PGE) - Pt, Ir, Os, Pd, Rh, Ru - were considered to be the best indicators for archaeological gold provenance considerations [2]. Although it is generally difficult to assign ancient gold artifacts to a certain gold deposit solely on the basis of the chemical composition, due to the recycling and/or mixing processes and to the limited knowledge on the geochemistry of ancient gold deposits, this type of approach has been successfully employed by Guerra [3, 4, 5], Cojocaru [6] and Bugoi [7].

Although lead isotope ratios in an archaeological metal object give indications regarding the ore source, being apparently unaffected by anthropogenic processing [8], this approach cannot be used for gold provenance issues, since lead is almost absent in ancient gold objects. Alternatively, Junk and Pernicka successfully used Os isotopic ratios used to provenance Celtic gold coins containing PGE inclusions [9].

In the last centuries, a relatively large number of ancient gold artifacts (mainly coins, but also jewelry) were unearthed in Transylvania. It was speculated that some of them were made out of unrefined Transylvanian gold [10]; in this case, the most likely gold source was the so-called Transylvanian "Golden Quadrangle", region in which gold was exploited since Antiquity [11, 12, 13].

The present study was undertaken due to the relative scarcity of the published data regarding Transylvanian gold composition [12, 13] and triggered by the interest in the above-mentioned archeological issues.

Although there is an inevitable difference in the composition of primary (mines) and secondary (placer) deposits of gold of the same origin, the variability is relatively reduced within the same deposit; therefore average concentrations might characterize gold ores from a certain geographical region [11].

Although geological gold is mostly found in native (elemental) form, the other encountered natural gold occurrence is *electrum* (from the Greek 'electron' = 'amber'), i.e. a natural alloy of gold and silver, with Ag up to 40%, Cu up to 1% and Fe up to 5% [3]. Other elements to be found in natural gold at trace level are Ni, Hg, Sb, Bi, Te, and Pt [11].

This paper presents the results obtained on nine minute (several mm^2) Transylvanian gold samples through a combination of PIXE (Particle Induced X-ray Emission) and

PIGE (Particle Induced Gamma-ray Emission) with an external 3 MeV proton micro-beam at the AGLAE accelerator of the C2RMF, Paris, France. Some comments on the performances of the employed analytical approach will be made.

EXPERIMENTAL

Small fragments from several Transylvanian gold nuggets - two belonging to placer deposits (Valea Arieşului and Valea Pianului) and the rest to primary deposits (Roşia Montana, Bucium Izbița, Baia de Arieş, Zlatna and Muşariu Brad mines) were provided for analysis by the Gold Museum located in Brad, Romania. The nugget from Baia de Arieş was divided into three smaller sub-samples, in order to check the homogeneity within the same nugget.

PIXE and PIGE measurements on fragments from these nuggets were performed at the AGLAE tandem accelerator of the C2RMF, located in the basement of the Louvre Museum [15, 16], with a 3 MeV proton beam, extracted into air. 200×200 μm^2 areas on each samples were scanned in front of the micro-beam (~ 100 μm in diameter), in order to obtain average concentrations, and to avoid any odd result due to the eventual inclusions or sample inhomogeneity. The beam-current was 50 nA on average, and the acquisition time was around 5 minutes for each sample. For PIXE signals detection, a low-energy detector with a pinhole filter (ϕ = 1 mm) and a high-energy Si(Li) detector with a 75 μm Cu filter were used. The Cu filter was used to absorb Au L lines and to reduce the sum peaks interfering with the signals of the elements neighboring Ag, optimizing the detection limits for Sn, Sb, Te, trace-elements of potential interest for this study. The quantitative analysis of the PIXE spectra was carried out using the

GUPIX software [17]. 6917 gold standard (76% gold, 17% silver and 6% copper) and FAU8 natural gold standard from the Royal Canadian Mint were used was used for calibration purposes and to asses the Minimum Detection Limits (MDL). The overall uncertainties were of the order of less than 1% for major elements, and of the order of 20% for trace-elements. The MDL for the employed PIXE set-up were around 100 μg/g for elements with atomic number between 20 and 60, and drastically increasing for PGE and for other trace-elements neighboring Au, such as Hg and Pt, in which case they reached some 1000 μg/g.

PIGE measurements were simultaneously performed with the PIXE ones, by using a HPGe detector [4]. 279 keV, 311 keV and 152 keV peaks, the most intense gamma-ray lines produced in the (p, p'γ) reactions at this energy [18], were sought in the PIGE spectra, in order to evaluate the Au, Ag, and Cu contents. From the PIGE spectra, only the Au and Ag concentrations were determined following the procedure described in [18], the amounts of Cu in the analyzed gold samples being too low to be detected by PIGE. The MDL for PIGE were estimated to be around 1% for Au and Pb and between 0.1% and 1% for Ag, Sn, Ti, Pt and Cu [18].

RESULTS AND DISCUSSIONS

Table 1 presents the results obtained by PIXE and PIGE measurements. The analyzed samples are characterized by a consistently high amount of Ag, the average being around 18%. Au and Ag add up to roughly 99%. Ag content in the placer samples is considerably lower than for the primary deposits samples. The other determined

elements detected at a trace level were Fe, Cu, Te, and Pb. Figure 1 illustrates the good agreement between the PIXE and PIGE results for Ag and Au.

The low content of European gold - below 1% [13] - was also confirmed by the analyses reported in this paper - Cu was either detected at a level of hundreds of μg/g, or it was below the MDLs. Similar results were obtained both by INAA or by PAA – see [6] and [14].

The chemical element tellurium was originally discovered in 1782 in Transylvanian gold ores, and there are several mineral species that are to be found only in Transylvanian gold. Te traces were found by PIXE, only in one of the sample analyzed in this paper, but similar findings are reported in [19]. Unfortunately, this element has a very low melting point (449°C), therefore it ´´disappears´´ during gold ore processing, and it cannot be further used for provenance issues.

Lead was detected by PIXE only in Bucium-Izbita sample, which is of primary origin (gold from mine). Its presence can be due to the jamesonite ($Pb_4FeSb_6S_{14}$) mineral that accompanies Transylvanian gold [11]. However, because Pb is present in very low amounts (below 100 μg/g) in alluvial gold, the most often employed type of gold in the antiquity [3], and in even smaller amounts in manufactured gold artifacts, due to its low melting point (327 °C), this element does not present much interest for archaeological gold provenance issues.

There is still some debate about the assumption that the presence of PGE inclusions in gold objects indicates a placer deposit provenance [6, 12, 13]. The MDL for PGE turned out to be too high for the employed set-up. INAA and PAA were able to detect Pt and Ir (by radiochemical separation!) at μg/g level – see [6] and [14].

The compositional results are consistent with other previous analyses on Transylvanian gold [6, 12, 13, 14]. In particular, in figure 2, the gold concentrations of the nugget fragments are compared with the corresponding concentrations previously obtained by Instrumental Neutron Activation Analysis (INAA) [6] and Proton Activation Analysis (PAA) [14]. From this figure, it can be seen that Au concentrations obtained through activation methods are in general 10% higher than those obtained through PIXE and PIGE, and that PIGE results are slightly higher than the PIXE ones. The opposite effect takes place for Ag. Obviously, every of the above analytical technique probe different sample depths: PIXE and PIGE provides results representative only for the surface of the analyzed samples (28 μm for PIGE, and between 5 and 20 μm for PIXE, depending on the analyzed element), while PAA probes 200 μm in depth, and INAA provides bulk results. However, the likely depletion of the less noble metals - in this case, Ag and Cu - from the samples surface would have led to a different result (PIXE and PIGE Au concentrations higher than the PAA and INAA ones). Therefore, a systematic uncertainty in the PIXE and PIGE results cannot be excluded.

Although through the previously employed activation techniques (PAA, INAA) one can determine the content of a larger number of trace-elements in gold matrices with a better sensitivity (PGE including!), they have the following disadvantages: radioactivity induced in the samples, and reduced availability (for INAA). Simultaneous PIXE and PIGE might be employed as an alternative method determine in a fast and non-destructive manner the elemental composition (the major, the minor and some trace-elements) of geological and/or archaeological minute gold samples. These advantages - plus the one of high lateral resolution, which, unfortunately, was not exploited during

this experiment! - have to be taken into account when gold archaeological samples/artefacts are to be analyzed and compared with geological ones.

CONCLUSIONS

The compositional results on fragments from Transylvanian gold nuggets obtained through PIXE and PIGE at the AGLAE accelerator revealed that Transylvanian natural gold is characterized by low concentrations of Cu (hundreds of μg/g) and high concentrations of Ag (18% on average). The results are in good agreement with the previous analyses on natural Transylvanian gold, especially regarding the major element (Au-Ag-Cu) content. Through non-destructive PIXE and PIGE, the elemental characterization of natural gold samples can be obtained in just a few minutes of proton bombardment, approach that might be used for further investigations and comparisons with gold archaeological artifacts.

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FIGURE CAPTIONS

Figure 1 – Au and Ag contents (in %) obtained by PIXE and PIGE for the analyzed samples.

Figure 2 – Comparison of the Au concentrations (%) determined by PIXE and PIGE (the experiment described in this paper) and previously by INAA [6] and PAA [14].

Table 1 – PIXE and PIGE concentrations*

Gold source	Au (%) PIXE	Au (%) PIGE	Ag (%) PIXE	Ag (%) PIGE	Cu (μg/g) PIXE	Other (μg/g) PIXE
Valea Arieşului - placer	89.3	91.8	7.0	8.1	≤ MDL	Fe: 34418
Valea Pianului - placer	99.7	99.9	0.1	≤ MDL	597	Fe: 296
Roşia Montană - primary	65.3	67.9	34.3	32.1	237	Fe: 2776
Bucium Izbița - primary	73.9	78.1	23.6	21.9	≤ MDL	Fe: 22618; Pb: 1733
Baia de Arieş - primary	81.7	82.7	18.1	17.3	≤ MDL	Fe: 92
Baia de Arieş - primary	81.3	80.3	18.5	19.7	≤ MDL	Fe: 223
Baia de Arieş - primary	78.6	82.2	21.3	17.8	≤ MDL	Fe: 159
Zlatna - primary	68.6	70.8	31.2	29.2	199	Fe: 277
Muşariu Brad - primary	88.9	90.5	10.8	9.5	338	Fe: 392; Te: 734

* < MDL – below the Minimum Detection Limits

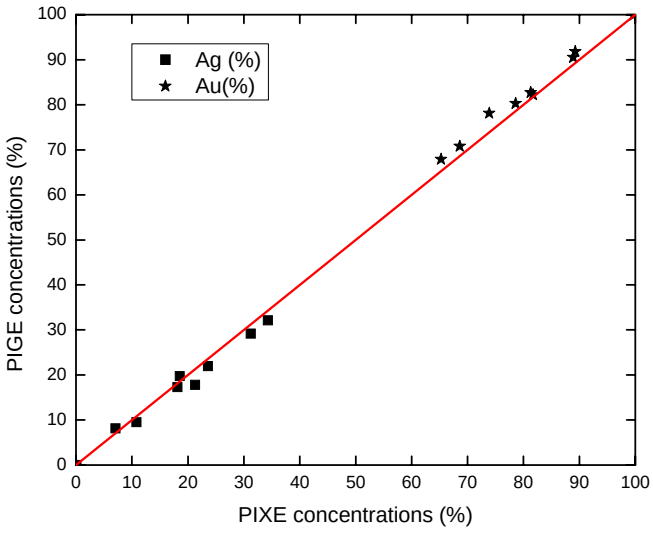

Figure 1

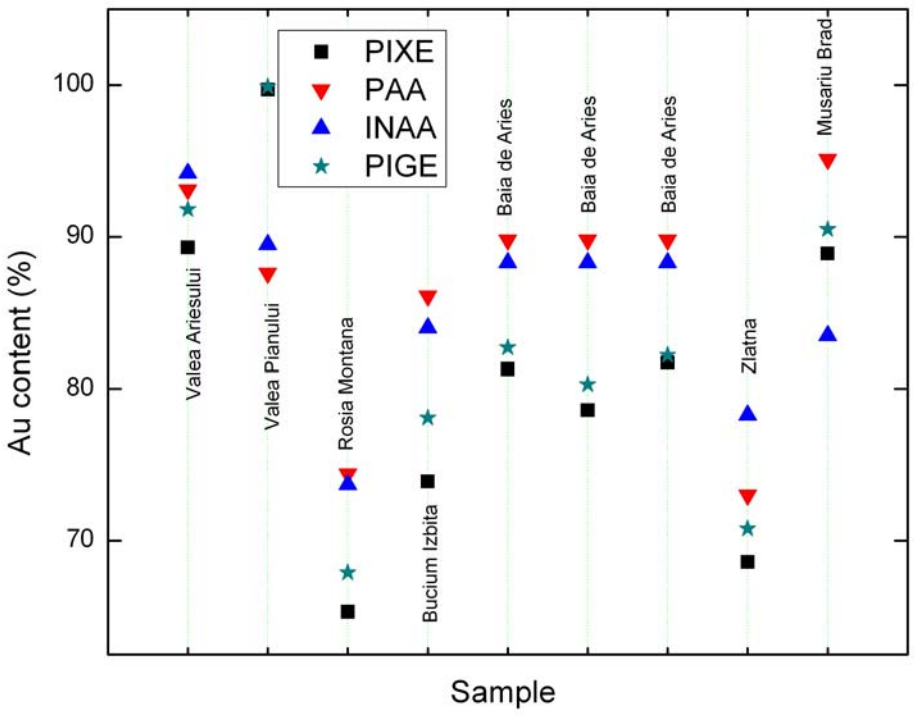

Figure 2