Romanian ancient gold objects provenance studies using micro-beam methods: the case of "Pietroasa" hoard

B. Constantinescu*[1], R. Bugoi[1], V. Cojocaru[1], D. Voiculescu[1]

D. Grambole[2], F. Herrmann[2], D. Ceccato[3]

[1]*National Institute for Nuclear Physics and Engineering "Horia Hulubei",*

PO BOX MG-6, Bucharest, Romania

[2]*Research Center Rossendorf Inc., Institute for Ion Beam Physics and Materials Research, PO BOX 510119, D-01314 Dresden, Germany*

[3]*Istituto Nazionali di Fisica Nucleare, Laboratori Nazionali di Legnaro, Padova, Italy*

Abstract

Five fragments of ancient gold objects belonging to Pietroasa "Cloşca cu Puii de Aur" ("The Golden Brood Hen with Its Chickens") Romanian hoard were analyzed using the micro-PIXE (Particle Induced X-ray Emission) technique. The purpose of the study was to gain some more knowledge regarding the metal provenance by determining the presence of PGE (Platinum Group Elements) and other high-temperature melting point trace elements (Ta, Nb, Cr) at a micrometric scale. Ta and Nb inclusions (micrometric areas of composition different from the surroundings) on three samples and Pd inclusions on one sample were found. The measurements led to some conclusions for the possible gold ore sources of Pietroasa treasury: the South-Ural Mountains, Nubia (Sudan) and/or Anatolian deposits and Roman imperial coins.

* Corresponding author: Tel: 4021.404.23.49, Fax: 4021.457.44.40, e-mail: bconst@ifin.nipne.ro

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1. Introduction

The study of trace-elements in archaeological metallic objects can provide indications about the metal provenance and the involved manufacturing procedures, leading to important conclusions regarding the commercial, cultural and religious exchanges between the antique populations. Ancient metallic materials are usually inhomogeneous on a micrometric scale, the imperfect smelting being revealed by the presence of segregated phases in alloys and inclusions [1].

Inclusions of Platinum Group Elements (PGE) - Ru, Rh, Pd, Os, Ir and Pt - in gold were released into rivers by the decomposition of rocks and occur in placer deposits in the form of grains and nuggets of complex alloys. The melting point of PGE is higher than that of gold; thus, PGE grains remain unchanged during the metallurgical processing of the gold ore. The presence of PGE as inclusions in gold objects can constitute a fingerprint for the ore that the object was manufactured from, indicating that a placer deposit was the precious metal source. Apart from PGE inclusions, gold alloys can contain low amounts of high-temperature melting point trace elements, such as Ta, Nb, Cr etc, other potential fingerprints for base metal deposits.

The purpose of this Pietroasa hoard study was to obtain relevant information about the metal provenance. Trace elements – such as PGE, correlated with known mines fingerprints can help to identify the ore source. The gold provenance of the objects can lead to further historical conclusions.

A set of nuclear activation analyses - Neutron Activation Analysis (NAA) and Proton Activation Analysis (PAA) - on fragments from artefacts from Pietroasa hoard was performed some years ago, trying to clarify which of the different historian hypotheses regarding the origin of the gold is the correct one [2]. However, PAA has the disadvantage of sample activation – e.g. ^{109}Cd ($T_{1/2}$ = 463 d) – obtained through proton activation of ^{109}Ag, or ^{65}Zn ($T_{1/2}$ = 244 d) – obtained from ^{65}Cu activation (practically, the PAA analysed samples cannot be re-analysed approximately for three years). The disadvantage of NAA consists in the necessity of using a radiochemical preparation in order to detect platinum and iridium - the HCl digestion - implying the destruction of the neutron activated sample. The NAA and PAA results are relevant for the major components (Au, Ag, Cu) concentrations and also for the Pt content.

In the present work, *non-destructive* micro-PIXE (Particle Induced X-ray Emission) analysis on fragments from the original objects was used for micro-inclusions detection in order to refine the knowledge on this hoard.

2. Materials and methods

2.1. Sample description

The hoard discovered in 1837 at Pietroasa, Buzău county, Romania by two peasants is known in the literature and the history of arts as “Cloşca cu Puii de Aur” (“The Golden Brood Hen with its Chickens”). This hoard is one of the most famous collections of archaeological objects ever found in Romania, due to its fine artistic quality and to the myths created around it. It is largely accepted today that this hoard belonged to the Visigoths –a Germanic population who lived on the actual Romanian territory in the period of the IVth-Vth Century A.D.

2.2. Micro-PIXE measurements

Five small pieces from five different objects belonging to the Pietroasa treasury were analyzed: the large, the middle and the small fibulae, the dodecagonal basket and a piece of the patera - to be more specific, from the central figure representing Cybele. Small fragments (a few square millimetres area) of the original objects were taken by mechanically cutting the artefacts, operation performed during a restoration of the hoard. Cautions were taken in order to obtain the samples from the unimportant zones of the objects, to avoid a visible deterioration of these precious museum artefacts.

The micro-PIXE scan measurements and point analyses were done at the Nuclear Microprobe Facility of the Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Germany, using the 3 MV Tandetron accelerator [3] and at the Oxford microprobe facility of the Legnaro National Laboratory (LNL), Italy [4].

At Rossendorf, a 3 MeV proton beam was used and the beam current intensity was about 400 pA. A focused beam of 6×6 μm^2 was rastered on 800×800 μm^2 areas (128×128 pixels elemental maps). The X-rays were detected using a Si(Li) detector - FWHM of 190 eV at 5.9 keV - positioned at 120° with respect to the incident beam, and mylar absorbers of different thicknesses were employed to reduce the soft X-ray region of the spectra. The total accumulated charge for the scanned areas was of the order of 3 μC.

At Laboratori Nazionali di Legnaro, a 2 MeV proton beam generated from the AN 2000 Van de Graaff accelerator was used. The beam was focused to 5×5 μm^2. The maximum beam current was around 1 nA. To reduce the intensity of the peaks in the low spectral region (below 4 keV), a mylar funny filter (171 μm thickness, 3.3% hole) was employed. The maps were scanned on areas of 250 × 250 μm^2. The Legnaro Si(Li) detector had a resolution (FWHM) of 170 eV at 5.9 keV.

Since one of the Pietroasa samples was cracked, spectra for the sample holder and the carbon tape on which the samples were stuck were also acquired in both experiments, in order to subtract the eventual spurious signals coming from the backing.

PIXE data analysis was done using the GUPIX code [5].

It must be mentioned that using micro-PIXE for this kind of samples, it is practically impossible to detect Pt traces due to the presence of a massive Au signal. This is mainly due to the Si(Li) detector resolution(s) and to the high differences in the expected Pt and Au concentrations (Pt at trace level, and Au major component).

3. Results and discussions

Table 1 presents some point concentrations for the five analysed samples. The points were chosen in the following way: for the three fibulae, the points were characterized by high concentrations of Ta, while for the dodecagonal basket and the central figure of the patera, the points featured a relatively high content in PGE (Pd, respectively Rh).

A first conclusion of these microprobe experiments was that the elemental composition for the five pieces is strongly different, which is in good agreement with the classification made for the objects taking into account only the stylistic aspects [6]. Thus, the patera is of Greek-Roman style, the dodecagonal basket combines Sassanide (Persian) and Greek-Roman characteristics while the fibulae are of

Germanic style (the bird motif). The microscopic concentrations are rather different from the ones obtained using NAA [2]. This fact is not surprising at all, since it is not expected an agreement between the point (the present measurements) and the bulk concentrations of an ancient inhomogeneous alloy [2].

Combining the NAA [2] and the results from table 1, for the central figura of the patera – Pt determined through NAA and a Rh – Ir inclusion (Pt cannot be detected from any X-ray spectrum due to the massive presence of Au) found using micro-PIXE – we can assume that gold ore from Ural mountains was used to manufacture this object. However, in the patera itself (the plate) Pt was not detected [2], so, a re-melting procedure is more credible. Due to the high fineness of gold (~95%), it is likely that gold used to create this object has been obtained by melting some existing jewellery and Roman imperial coins of Mediterranean origin, as Romans were mastering very well the gold processing technique.

Analyzing the elemental maps for the three fibulae, inclusions of Ta (see figure 1, showing a Ta map for the small fibula) were found. Another finding for these samples is the presence of Nb at trace level (see figure 2, presenting a point spectrum on the large fibula). These metals have high melting points, and the Ta and Nb grains did not dissolve during the gold processing. As stated in [7], the Ta and Nb are found in tantalite - columbite type minerals, e.g. in samarskite, mineral which is found in gold ores from the Ural Mountains (Southern region around Samara). These findings confirm the fact that the Germanic 'owners' of the hoard were coming from the region between Caucasus and Ural Mountains in the second half of the IIIrd Century A.D., bringing along their precious jewellery [8], and that some of the Pietroasa hoard artefacts – i.e. the fibulae – were manufactured using Ural mountains gold. The Ural mountains hypothesis is also supported by the Pt content in the large and small fibulae– see [2] – and the Ru - Os (for small fibula) and Ru - Ir (for middle fibula) inclusions – see table 1.

As concerning the dodecagonal basket, the most important result of these experiments is the finding of small Pd inclusions. The only accessible gold sources with Pd in the IVth Century A.D. were Nubia (Sudan) and Anatolia (Turkey) deposits, intensively used in Egypt (Alexandria) and Syria (Antiochia) workshops - see [9], where Pd was determined in Alexander the Great coins, minted after the Persian Empire conquest (however, we did not find Pt and/or Sn traces) and in early Alexandria Byzantine coins. The average composition of this sample - Au = 98%, Ag = 1%, Cu = 0.5% - also suggests a re-melting procedure, probably using Roman imperial coins struck in Oriental provinces – see [10].

Summarizing the results, we can conclude for the analyzed objects of Pietroasa hoard we have at least four possible gold sources: Southern region of Ural Mountains, Nubia (Sudan) deposits or a Persian source (most likely Pactolus river in Anatolia) and/or various emissions of Roman imperial coins.

4. Conclusions

The results obtained by micro-PIXE experiments on gold ancient artefacts, especially the inclusions findings, provided some useful hints regarding the possible provenance of the manufacturing metal. The Pietroasa hoard artefacts were again proved to be of different origins, confirming the stylistic arguments by the different possible gold sources identified: Southern region of Ural Mountains, Nubia (Sudan) deposits, Pactolus river and Roman imperial coins emissions. Further analyses on other artefacts belonging to the same hoard are to be done. However, a correct answer to the question of the native metal provenance used for each artefact remains a difficult task, taking into account that a complete data bank for the composition of Euro-Asian native gold is not yet available.

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References

1. R. F. Tylecote, The early history of metallurgy in Europe, Longman, London and New York, 1987.

2. V. Cojocaru, C. Besliu, C. A. Manea, J.of Radioanal. and Nucl. Chem. 240 (3) (1996) 897.

3. F. Herrmann, D. Grambole, Nucl. Instr. and Meth. in Phys. Res. B 104 (1995) 26.

4. P. Boccaccio, D. Bollini, D. Ceccato, G. P. Egeni, P. Rossi, V. Rudello and M. Viviani, Nucl. Instr. and Meth. in Phys. Res. B 109/110 (1996) 94.

5. J. A. Maxwell, L. A. Campbell, W. Teesdale, Nucl. Instr. and Meth. in Phys. Res. B 43 (1989) 218.

6. Al. Odobescu, Le tresor de Petrossa: Etude sur l’orfevrerie antique, Paris-Leipzig, 1889 (in French).

7. N. Lupei, C. Barna, Zestrea de minerale a lumii, Ed. Stiintifica, Bucuresti, 1971 (in Romanian).

8. Ammianus Marcellinus, Rerum gestarum libri qui supersunt, C. U. Clark, Berlin, 1963.

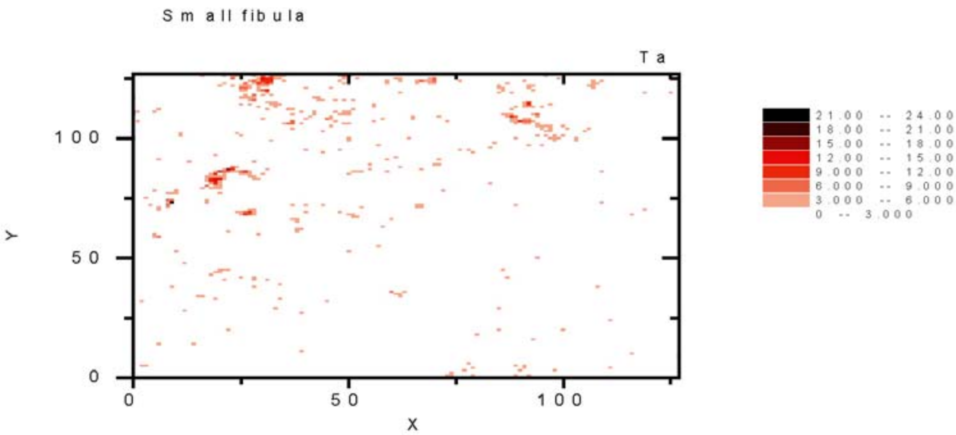
9. M. F. Guerra, C.–O. Sarthre, A. Gondonneau, J.-N. Barrandon, J. of Arch. Sci. 26 (1999) 1101.

10. E. Oberländer-Târnoveanu, V. Zoran, G. Poenaru-Bordea, L.Trache, E. Iacob, I. Lukanc, C. Ciortea, Revue Numismatique 151 (1996) 141.

Figure captions

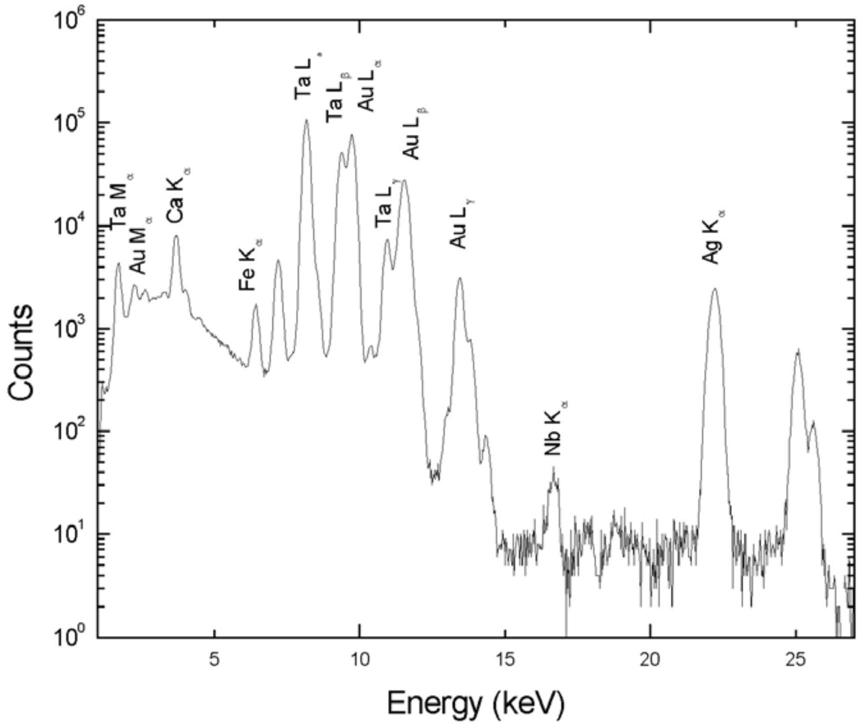
Figure 1 - Ta map on the Pietroasa small fibula sample; scanned area: $800 \times 800\ \mu m^2$ (128×128 pixels).

Figure 2 - Point spectrum on the Pietroasa large fibula sample - high content in Ta and Nb at trace level.



Small fibula
Ta
100
50
0
0
50
100
X
Y
21.00 -- 24.00
18.00 -- 21.00
15.00 -- 18.00
12.00 -- 15.00
9.000 -- 12.00
6.000 -- 9.000
3.000 -- 6.000
0 -- 3.000

Figure 1



Counts
Energy (keV)
Ta M_α
Au M_α
Ca K_α
Fe K_α
Ta L_α
Ta L_β
Au L_α
Ta L_γ
Au L_β
Au L_γ
Nb K_α
Ag K_α

Figure 2

Table 1 – Pietroasa hoard samples point concentrations

Object	Cu	Ru	Rh	Pd	Ag	Te	Ta	Os	Ir	Au
Central figure of patera	Traces	nd	0.12 %	nd	4.48 %	0.13 %	nd	nd	Traces	95.14 %
Dodecagonal basket	1.25 %	nd	nd	0.35 %	4.95 %	nd	nd	nd	nd	93.35 %
Large fibula*	0.13 %	nd	nd	nd	15.35 %	0.31 %	4.93 %	nd	nd	78.82 %
Middle fibula	0.05 %	0.44 %	nd	nd	16.85 %	0.29 %	0.16 %	nd	0.04 %	82.17 %
Small fibula	Traces	1.88 %	nd	nd	8.73 %	nd	39.14 %	0.45 %	nd	49.30 %

nd - not detected

Traces – concentrations less than 100 ppm.

* Nb traces were also detected in this sample – see the spectrum presented in figure 2.