AGLAE User Report

Project: Micro-PIXE studies on Visigothic “Pietroasa”gold hoard objects.
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The study of trace elements in archaeological metallic objects 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. Ancient metallic objects are inhomogeneous on a micrometric scale, containing remains of imperfect smelting and inclusions (small areas with composition different from the surroundings) [1].

In the frame of this project, several small fragments of ancient gold objects from Pietroasa “Closca cu Puii de Aur” (“The Golden Brood Hen with Its Chickens”) hoard exhibited in the National Museum of Romania’ History in Bucharest, are intended to be studied with the external microprobe of the AGLAE accelerator. The Pietroasa treasury (approx. 19 kg of gold), the most famous in Romania, was discovered in 1837 in the ruins of a Roman castrum (fortress) and is generally considered as a collection of sacred (religious) objects belonging to the Visigothic king Athanaric, probably buried in 386 A.D. during the Huns invasion led by the famous Attila. The origin of the objects must be heterogeneous, because three styles are evident: Germanic (fibulae with eagle aspect covered with gemstones), Roman (e.g. a patera with mythological figures) and Persian-Sassanide (decorated cups for libations) [2].

The goal of this project is to clarify the metal provenance using trace elements information and Platinum Group Elements (PGE) – Ru, Rh, Pd, Os, Ir, Pt or any other high temperature melting point metals inclusions, such as Ta or Nb.

Some fragments from nuggets coming Transylvania mines are also intended to be studied, to gain information about their elemental composition and to check whether the hypothesis of local (Carpathian Mountains) gold holds.

During this first experiment - May 2005, the optimal conditions to detect trace elements, expected to be found as micro-inclusions of Platinum Group Elements (PGE) or high-temperature melting point elements (Ta, Nb) were established. These elements are particularly interesting, since they can be used as fingerprints for natural gold sources.

When dealing with trace elements in gold, there are two “regions of interest”: the one of the elements neighboring gold, such as: Ta, Os, Ir, Pt, Hg (they belong to the sixth period of the Periodic Table of Elements) and another one of elements neighboring silver, such as: Nb, Ru, Rh, Pd, Sn, Sb, Te (the fifth period of the Periodic Table of Elements). It is obvious that due to the high contribution of gold L lines in PIXE spectra, we should look for two kind of experimental solutions in order to determine these trace elements.

During the 3 days of beam-time performed in May 2005 (10^{th}, 11^{th} and 12^{th} of May), micro and mili – PIXE measurements were performed at the AGLAE accelerator of the Centre de Recherche et de Restauration des Musees de France, located in the basement of the Louvre Museum. For this experiment, a 3.2 MeV proton beam, extracted into helium atmosphere was used. The micro-beam (roughly 30 microns diameter) was used to scan different size areas on the samples (usually 300×300

μm^2 in size, but larger areas were scanned as well), while the milli-beam (approximately 100 microns in diameter) was employed in order to make some point measurements using beams of higher current intensity (I ~ 40 nA). For PIXE signals acquisition, both low - and high-energy Si(Li) detectors were used. All the measurements were performed using a pinhole filter in front of the low energy PIXE (LE-PIXE) detector. For the high-energy PIXE detector (HE-PIXE) sometimes a 50 microns Al filter was used, while in other measurements a 75 microns Cu filter was chosen, in order to reduce the high contribution of gold L lines and to diminish the sum peaks of Au L lines which interfere with the signals of elements neighboring silver. 6917 gold standard (75% gold, 17% silver and 7% copper) was used for calibration purposes. To check the detection limits of the experimental set-up, a natural gold standard – FAU8, containing some trace elements at level of tens of ppm, was analyzed as well.
The gold samples - archaeological and mineralogical - were put on tape holders. We took caution in order to avoid the cracks present in some samples, by making the measurements in areas that were not affected by the sampling or by other previous manipulation. An optical examination of the samples with a microscope was also performed, in order to check if the inclusions in the archaeological samples were visible as grains of color different from the surroundings.
After the acquisition of the point spectra, the quantitative analysis was carried out using the GUPIX software at AGLAE, with the support of the local experts.
Prior to this experiment, on some of these archaeological samples we performed micro-PIXE measurements at the Rossendorf TANDETRON and at the Legnaro AN2000 accelerator, in the frame of some EU 5th Framework Programme ARI (Access to Research Infrastructure) missions [3, 4]. Those measurements revealed the presence of some Ta inclusions on three samples from Pietroasa hoard, i.e. the Germanic style fibulae. To test the performances of the AGLAE micro-beam system, the first measurements were performed on a sample from Pietroasa gold hoard - a fragment from the small fibula, a Germanic style jewelry – known to exhibit Ta inclusions. To demonstrate the existence of Ta inclusions, the samples were mapped ($600\times600\ \mu m^2$) using a 30 μm beam and a sample-detectors distance of several mm. The presence of Ta grains with diameter of the order of some tens of micrometers was revealed in the small fibula fragment only by using a 50 μm Al filter in front of the HE-PIXE detector. Two point spectra were acquired, roughly corresponding to the two detected inclusions, and a spectrum in a region in between these points was acquired as well. The corresponding spectra were analyzed to prove that Ta grains presence was certain. The Ta inclusions suggest that gold was used for the first time when manufacturing these objects. Since Ta minerals are characteristic for the Ural Mountains gold ores, it can be concluded that the Germanic style small fibula was manufactured by using gold from this source in workshops situated in the North of the Black Sea.
The sample from the patera was analyzed by scanning a $300\times300\ \mu m^2$ area, and an Ir inclusion was put into evidence – this conclusion was obtained by analyzing the point spectrum. A literature search has to be made, in order to find out possible the possible sources of gold containing Ir as micro-inclusions.
The above results turned out to be a successful application of the AGLAE micro-beam facility for the detection of micro-inclusions. It is worthwhile mentioning that the accelerator and the acquisition software - specially designed for micro-beam measurements - worked in very good conditions.
Due to the short remaining time, the samples taken from the tray, the dodecagonal basket, the oenohoe cup, the middle fibula, the simple girdle and the girdle with runic inscriptions were analyzed by acquiring only average spectra. The acquisition was done using a beam with 100 μm diameter, which was slightly scanning sample (a square with $100\times100\ \mu m^2$ area), and of higher intensity (tens of nA). Sn was detected as trace elements in the following samples: middle fibula, girdle with runic inscriptions, oenohoe cup, and patera.
Total spectra for four natural gold samples from Transylvania were also acquired. Te turned out to be an element which is characteristic to the native gold of Transylvania.
There is a theory [5, 6] that Sn is a trace element characteristic for gold coming from Carpathian Basin (i.e. Transylvanian Carpathian Mountains). The reason for studying at AGLAE the native gold samples of Transylvania was to check if Sn is present in these samples at a level of hundreds of ppm.
The conclusions of this preliminary experiment are the following:

- To detect Ta or PGE inclusions of elements from the sixth period (Os, Ir, Pt), a Cu filter is not suitable; in the case of Ta because of the interferences between the K_α line of Cu and the L_α line of Ta; while in the case of PGE, the intensity of the L lines of Pt, Ir, Os is also cut-off together with the high intensity L lines of Au (the samples contain on average more than 90% of Au); the solution in this case turned out to be to use an Al filter in front of the HE-PIXE detector;

- In the future experiments we intend to use AGLAE accelerator and an Al filter in front of the HE-PIXE detector to acquire some micro-PIXE maps on larger area with a better statistics, in order to detect eventual micro-inclusions of the elements with Z just below the one of gold (Pt, Ir, Os, Ta);

- To detect the fifth period PGE trace-elements (Ru, Rh, Pd) and Sn, Sb, Te, maps of the archaeological samples using a Cu filter in front of the HE-PIXE detector in order to reduce the contribution of gold sum peaks are to be acquired.

Taking into account that the acquisition time for a micro-PIXE map with a good statistics is usually very long (several hours), we could not establish in this experiment if there are any other PGE inclusions in all the archaeological samples we analyzed. Therefore, we intend to apply again for beam-time at AGLAE - in the frame of EU-ARTECH project, having as a goal the clarification of the structure of all these gold samples, with the particular hope of finding PGE and/or any other high melting point elements inclusions in Pietroasa archaeological samples, as well as Sn, Sb, Te as trace elements in the native Transyvanian gold ones.

We can complete this report with the conclusion that the results of this preliminary experiment are extremely promising. Having as a starting point the practical knowledge we gained regarding the experimental set-up available at AGLAE and what can be done in order to solve our particular problems, we hope that the future micro-PIXE measurements will lead to the clarification of the microstructure of these precious archaeological artefacts.

References

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

[2] "Nuclear analysis of the Pietroasa gold hoard" - V. Cojocaru, C. Besliu, C. A. Manea, Journal of Radioanalytical and Nuclear Chemistry, vol. 240, no.3 (1999), pp. 897-908.

[3] "Micro-PIXE study of gold archaeological objects" - R. Bugoi, V. Cojocaru, B. Constantinescu, F. Constantin, D. Grambole, F. Herrmann, Journal of Radioanalytical and Nuclear Chemistry, vol. 257, no. 2 (2003), pp. 375-383.

[4] "Romanian ancient gold objects provenance studies using micro-beam methods: the case of "Pietroasa" hoard" - B. Constantinescu, R. Bugoi, V. Cojocaru, D. Voiculescu, D. Grambole, F. Herrmann, D. Ceccato, Nuclear Instruments and Methods in Physics Research B 231 (2005) pp. 541-545.

[5] "European Network of Competence at 1600 BC" - E. Pernicka, M. Radtke, H. Riesemeier, C.-H. Wunderlich, Bessy Highlights 2003 – Scientific Highlights, 8-9.

[6] Axel Hartmann, "Prehistorische Goldfunden in Europa" I und II – Studien zu den Anfängen der Metallurgie 3 (Berlin 1970) und 5 (Berlin 1982).