Archaeometallurgical studies on Dacian Gold and Dacian Silver using advanced X-Ray spectrometric techniques
Project PN-2-ID-PCE-2011-3-0078, Contract 48

The purpose of this project is to perform, using some of the most advanced spectrometric techniques, compositional analyses – elemental, layers structure (e.g. gilding, silvering, tinning), micro-inclusions (PGE elements, Sn, Sb, Te, Pb etc in gold samples) – on ancient (Geto-Dacian, Geto-Thracian, Greek – classical, Hellenistic, Roman) gold and silver objects (coins included) from Romanian Museums. From these informations, we obtaine essential clues for provenance-authentication of the objects:

- gold origin (alluvial, primary, geological deposits), refining and alloying
- silver origin (mines, metallurgical obtaining), alloying
- gilding and silvering procedures
- modern and contemporary forgeries

Political, commercial, military aspects - goldsmiths and minting workshops, trade routes, payments, looting and significance (spiritual or material) of gold and silver objects can be also cleared by such compositional analyses.

From October 2011 to December 2012 our studies were concentrated on archaeo-metallurgical characterization of the Dacian (from Transylvania) gold objects.

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-in-gold region in Antiquity – was demonstrated by our microscopic elemental studies on Dacian gold artifacts.

The context of these investigations is described in the following: According to later criminal investigations of Romanian Authorities (several hoards containing at least twenty four gold spiral bracelets and few thousands of gold coins (staters) of pseudo-Lysimachus and Koson types (Koson with and without monogram) 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 to the ancient capital of the Dacian Kingdom 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, was 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). The elemental compositions for all the 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 containing up to 40% silver and up to 1% copper. 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 also analysed using micro-PIXE (Proton Induced X-ray Emission) and micro-SR-XRF (Synchrotron Radiation induced X-Ray Fluorescence), in view of the identification of the probable sources of gold known in this geological area. The investigation of a series of alluvial samples from the collection of the Brad Gold Museum (Brad, Romania) by SR-XRF and micro-PIXE 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 that 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 a microscopical investigation possible, from the composition of these objects one can conclude is 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. 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 armband.

In 2011, we obtained the permission of the Romanian authorities to take very small (1-2 mg) samples from the most “non-important” 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 108x170μm^2 of the BAM-line, confirming these strong in-homogeneity from sample to sample not only from bracelet to bracelet, but also from one head to the other head of the same bracelet and even between samples from the same head of a bracelet. An explanation 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 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. The explanation for this phenomenon is the following: cassiterite (SnO_2) and gold can simultaneously occur in the same vein or placer deposit. Despite all possible precautions taken during gold panning in ancient times, some cassiterite grains could still be found in gold-rich concentrates. When such a naturally occurring gold-rich concentrate was melted in a reducing atmosphere, the cassiterite was reduced to metallic tin, which entered into the liquid phase of the primary gold. However, if the melting was not complete, it is possible that micro-inclusions of cassiterite still remain in the matrix, which is consistent of our previous observation of both uniformly distributed Sn in gold and localized micro-inclusions 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 minerals in gold dust and nuggets - e.g.

chalcopyrite ($CuFeS_2$) - “fool’s gold” and pyrite (FeS) – due to the probable confusion made by Dacian “miners” and to the primitive processing of the raw material.

The results were published in:
Bogdan Constantinescu, Angela Vasilescu, Martin Radtke, Uwe Reinholz, Claire Pacheco, Laurent Pichon, Ernest Oberlaender-Tarnoveanu, *SR XRF and micro-PIXE studies on ancient metallurgy of thirteen Dacian gold bracelets,* Appl. Phys. A (2012) 109, p. 395-402.
Bogdan Constantinescu, Angela Vasilescu, Daniela Stan, Martin Radtke, Uwe Reinholz, Guenter Buzanich, Daniele Ceccato and Ernest Oberlaender-Tarnoveanu, *Studies on archaeological gold items found in Romanian territory using X-Ray-based analytical spectrometry,* Journal of Analytical Atomic Spectrometry, Vol. 27. No. 12, (2012), p. 2076-2081.
Bogdan Constantinescu, Daniela Cristea-Stan, Angela Vasilescu, Rolf Simon, Daniele Ceccato, *Archaeometallurgical Characterization of Ancient Gold Artifacts from Romanian Museums Using XRF, Micro-PIXE and Micro-SR-XRF Methods,* The Publishing House of the Romanian Academy – Proceedings of the Romanian Academy, Series A, 13(1), (2012) 19-26.
Daniela Cristea-Stan, B. Constantinescu, Catalina Chiojdeanu, D. Ceccato, Claire Pacheco, L. Pichon, *Micro-PIXE and XRF Studies on Native Gold from Cavnic Ore Deposit (Baia Mare District),* Romanian Journal of Physics 57(3-4), (2012), p. 594-606.

In 2013 our studies were concentrated on archaeo-metallurgical characterization of the Extra-Carpathian Geto-Dacian (Thracian) gold and gilded silver objects – princely hoards and remarkable isolated discoveries.

Gold alloy analyses on Cotofenesti helmet, Cucuteni-Baiceni helmet and appliqués (Geto-Dacian artifacts), zoomorphic artifacts from Stancesti (probably Scythian), Bunesti-Averesti diadem (provenance from Greek cities around Black Sea) were performed. A comparison with similar gold artifacts found in Transylvania, especially the spiraled bracelets (armbands), demonstrated a totally different gold metallurgy. Extra-Carpathian gold artifacts are produced by an advanced metallurgy (Greek or Scythian type) from refined gold and the artifacts from Sarmizegetusa by a relatively primitive metallurgy using alluvial gold. Analyses were performed using an X-Ray Portable Spectrometer.
The results are published as Daniela Stan, Bogdan Constantinescu, “Compositional analysis of some Geto-Dacian artifacts found in Muntenia and Moldova”, Proceedings Symposium "ArheoVest" - Inter-disciplinarity in Archaeology, 2nd edition: In Honorem Prof. Univ. Dr. Gheorghe Lazarovici, JATEPress Kiadó, Szeged (2014) 667-676.

Compositional analyses of Geto-Dacian silver artifacts from National History Museum of Romania belonging to Agighiol (helmet, beakers, appliqués, various vases), Peretu (helmet, human head artifact appliqués, various vases) and Craiova (various appliqués) treasures were performed. The treasures are heterogeneous, issued from different workshops and masters, including itinerants persons. Analyses were performed using an X-Ray Portable Spectrometer. One of the main results is a comparative technical analysis (elemental composition and method of manufacture) for four famous examples of Thracian art – a silver cup (beaker) and a silver (partially gilded) helmet from Agighiol hoard, a silver cup (beaker) in The Metropolitan Museum of Art New York and a silver helmet in the Detroit Institutes of Arts. A stylistic comparison was included in “Style and Subject Matter in Native Thracian Art” by Ann E. Farkas, and the

technical examination of USA museum artifacts in "Three Silver Objects from Thrace: A Technical Examination" by Pieter Meyers, papers published in Metropolitan Museum Journal 16, 1982. The princely tomb at Agighiol, near the delta of the Danube River in Eastern Romania, was partly robbed by local inhabitants in late 1930-1931 before being investigated and excavated by Ioan Andriesescu. The USA items are described as discovered in 1913-1914 near Danube border between Romania and Serbia, arriving in USA after WW2 from a collection in Vienna, Austria. Our analysis was performed "in-situ" (in the museum) using a portable X-Ray Spectrometer. We also carefully examined the hammering marks, especially those by chasing tools. We observed the thin (approx 30 microns – from Ag K-alpha/K-beta ratio) gold foil used for partial gilding of the helmet was attached after hammering was finished. The silver is very pure – approx 99%, with traces of gold, copper, lead and bismuth from the silver initial mineral. Bismuth is a fingerprint for South Bulgaria and Greece silver minerals (argentiferous galena). The compositional analysis and chasing tools fingerprints demonstrated the common provenance (same workshop and probably same silver-"master") of these four valorous Thracian silver artifacts from USA and from Romania.
Some results were published as Bogdan Constantinescu, Daniela Stan, Mircea Babeş, Catalin Nicolae, "Compositional analysis of Geto-Dacian silver hoards from Agighiol, Peretu, Craiova and Poroina", Proceedings Symposium "ArheoVest", 2nd edition: In Honorem Prof. Univ. Dr. Gheorghe Lazarovici, JATEPress Kiadó, Szeged (2014) 645-666.

For archaeologists the metallurgical aspects of silver adornments give important information about the provenance of such items – mines, metal production workshops, jewelry makers, commercial relations. In the case of silver - gold, bismuth, zinc and antimony can be used as fingerprints from East European geological deposits (e.g. bismuth for South Thracian and Greek silver). The presence of copper and lead is directly related to silver metallurgy – e.g. copper is used to increase the mechanical properties of silver. Some Thracian-Dacian adornments found on Romanian territory from Agighiol treasure (4th Century B.C.) and Poiana Galati (1st Century A.D.) were investigated. Initially, to determine the composition of major (Ag) and minor (Cu, Au, Pb) elements, in-museum XRF analysis was performed Afterwards, obtaining a special museum's permission, two series of small samples (less one millimeter diameter) from some artefacts belonging to above mentioned treasures (various appliqués, beads and small bracelets) were analyzed using 32.5 keV micro-SR-XRF, respectively measured using 2 MeV proton micro-PIXE, obtaining maps and point spectra. As main results, we mention the identification of bismuth in Agighiol samples, suggesting their provenance from Southern Thrace or Northern Greece, a homogeneous distribution of silver, copper and lead, indicating an advanced (for Antiquity) metallurgy and the presence of bromine and chlorine (well-known silver corrosion agents) giving information on soil characteristics for discovering place. For some bracelets from Poiana Galati Dacian hoard we identified as metallurgical procedure the use of copper, zinc and tin (most probably from bronze and brass) as components of the silver alloy. This alloying procedure increased the mechanical resistance of adornments, silver being a "soft" metal. In the case of one bracelet, the elemental maps for the analysed area (1 mm x 1 mm) revealed a strong in-homogeneity of copper presence and a good compatibility (superposition) of silver, gold and lead. Copper in-homogeneity reflects a quite primitive alloying procedure, while gold and lead accompany the silver from its minerals.

In 2014 our studies were concentrated on archaeo-metallurgical characterization of the Dacian staters type "Koson" - old collections, Tarsa-Luncani hoard, September 2009 hoard, new recoveries.

In the last years, hoards consisting of massive gold, multiply coiled bracelets, pseudo-Lysimachus type staters, gold and silver Dacian "Koson" coins were found during illegal detection activities around Sarmizegetusa Regia, nearby the sacred precincts. The "Kosons" have Roman iconography and Greek inscription. In 2009, Romanian Police recuperated a hoard of 143 Koson coins (37 with monogram and 106 without monogram) and in May 2011 from USA 163 silver "Kosons" and 27 pseudo-Lysimachus staters. From our X Rays-based compositional study on these coins, we concluded the coins without monogram are made of native Transylvanian gold - a similar composition with the gold bracelets. The monogram samples are similar to the alloy used in the Balkan workshops for the pseudo-Lysimachus - type staters.

We propose the following in-time evolution for "kosons" emissions:

- Silver "Kosons" type Macedonia Prima (drachms) inscripted KOSON DROUEIS - two different alloys
- Silver "Kosons" inscripted KOSON with monogram BRU – the second alloy from Macedonia Prima emission
- Pseudo-Lysimachus-staters type Callatis and Tomis – refined gold used for regional coinage
- Gold "Kosons" with monogram BRU – refined gold for jewelry

The minting was performed in a workshop somewhere in Macedonia, ordered by Brutus as payment for his allies Koson and Droueis.

- Gold "Kosons" without monogram – alluvial Transylvanian gold, "Barbarian" copies of Brutus's coins minted in Sarmizegetusa region.

After the defeat of Brutus, Koson offered his silver-gold payment and the supplementary without monogram emission to Dacian God – votive deposits around main sanctuary in Sarmizegetusa.

These results will be presented at XV International Numismatic Congress– Taormina, September 2015.