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Studies on ancient silver metallurgy using SR XRF and micro-PIXE

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HIGHLIGHTS

- SR XRF and μPIXE were used to investigate the composition and structure of ancient silver.
- Au and Bi are fingerprint elements, useful to identify metal sources.
- A Geto-Thracian silver sample is linked to the Laurion mine in Greece, by the Au/Ag and Bi/Ag ratio.
- Microstructure was correlated with metal-working techniques.
- Corrosion related traces of Br and Cl was identified by characteristic X-ray mapping.

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ABSTRACT

This work presents a complex evaluation of a series of Geto-Thracian silver adornments found on Romanian territory, part of the 4th century BC Agighiol (Northern Dobruja) hoard and of an ingot from the 1st century BC Geto-Dacian Surcea (Transylvania) hoard, using Synchrotron Radiation X-Ray Fluorescence and micro- Proton Induced X-ray Emission analysis and mapping in order to investigate aspects related to the elemental composition of the metal and the metallurgy implied in their manufacture. One of the samples can be linked to Laurion as the source of metal, and several items contain silver probably originated in Macedonia. The set of silver items was found to be heteregenous as composition and microstructure, and corrosion-related elements could be also identified in the X-Ray maps.

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1. Introduction

Synchrotron Radiation X-Ray Fluorescence (SR XRF) and micro-Particle (proton) Induced X-ray Emission (PIXE) have been used with great success in the microscopic investigation of various archaeological and art objects, as proven by a host of publications, including review articles (Bertrand et al., 2012, 2013; Guerra and Calligaro, 2003).

The information extracted from the quantitative X-ray micro-analysis of archaeological silver can possibly answer questions about their provenance, the metallurgical techniques used in their manufacture and their corrosion-status. The study of the metallurgical aspects of old silver adornments can lead to conclusions on mining, metalworking, crafts and trades, commercial routes.

Based on the experience of previous studies for ancient gold objects (e.g. the case of the famous Dacian gold bracelets (Constantinescu et al., 2002, 2012), where the presence of certain trace elements like Sn, Sb, Te etc. proved to be useful in order to identify the most probable sources of metal for their manufacture within the historical background, and even help to authenticate the respective items, a similar approach is applied here to archaeological silver. Both the minerals and the metallurgy of gold and silver have their specificities, but, keeping this in mind, one can try to correlate their chemical composition and the presence of certain trace elements in the material with geological and historical knowledge.

The goal of the study was to evaluate the homogeneity of the material in relation to the metallurgical process to obtain information on the silver mineral probably used (presence of Au, Bi, Zn, Sb – provenance of the mineral?), whether there were elements added intentionally in the metallurgical process (Cu, Pb?) and to check the presence of corrosion-related elements (Br, Cl,

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