MINING AND DIFFUSION OF ALPINE COPPER IN THE BRONZE AGE

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Cycle: XXVIII

Abstract

The provenance of Late Bronze Age metal artifacts has been a major question in archaeology for many decades. The study of copper and bronze objects from well-dated protohistoric contexts in Friuli Venezia Giulia is aimed to reconstruct the exploitation areas of raw copper, through the interpretation of the mineral origins, and intends to trace the diffusion and the subsequent circulation paths of the metal.

This first year of the doctoral project has involved the selection of the set of samples that could be considered representative for the metal tracing, reducing the possibility of mixing and recycling. The definition of efficient investigation protocols and data-treatments (multivariate analysis) is required and the achievement of such procedures has been developed on similar samples from others ongoing projects. The clean laboratory of chromatographic separation in the Department of Geosciences was equipped for samples preparation and blanks were tested in order to carry out the Pb-isotopes analysis in Bern University by means of MC-ICP-MS.

1. Research aims.

In the Late Bronze Age the metallurgical processes devoted to copper extraction usually started by mining Cu-rich ore, followed by several technological steps including smelting, production of raw metal, refinement and, finally, the creation of artifacts in pure copper or bronze alloys. This research, which focuses on the study of "stock-in-trade" hoards of Friuli Venezia Giulia, outlines not only the techniques involved in copper production, but also the diffusion of Alpine Copper in North-Eastern Italy and its relationship with the Central Europe.

The hypothesis on which this research is based stems from the scarce data available in the literature and from the idea that there is an apparent change in the exploitation areas of copper between the Middle Bronze Age (MBA) and the Recent Bronze Age (RBA), possibly moving from the Balkans to the Eastern Alps. Therefore, the study of sealed and well-dated archaeological complexes embracing the time period under investigation – from the Middle Bronze Age to the Final Bronze Age (FBA) – is needed. In this regard, the hoards of Cervignano (RBA), Muscoli (RBA-FBA1), Castions di Strada (FBA1), Celò (FBA1/2), Verzegnis (FBA1/2), Galleriano and Porpetto (FBA2) were identified and selected, in collaboration with archaeologists, including Dr. Elisabetta Borgna, University of Udine.

From each of these complexes ingots and pick-ingots obtained from primary processes of extraction will be characterized, together with other distinctive types of dated artifacts, in order compare with the available literature data or to analyze similar specimens found in the Veneto area. The analyses therefore will be performed on different types of objects (ingots, pick-ingots, axes and little shovels) found in the above listed hoards and which are presently preserved to the National Archaeological Museums of Aquileia, Cividale and Udine.

One other aspect of the present research deals with the extension of such analysis also to swords (4 of them have been already sampled), since these artifacts possess distinctive features that can be related to specific time periods and well defined geographical distribution.

2. Samples and Methods.

The whole set of selected archaeological samples is composed by 63 ingots (of various shapes) and 28 artifacts, specifically weapons. After the Soprintendenza's authorization, received in September 2013, the sampling activity has been divided into three stages and the first one has been carried out in October 2013 at the National Archaeological Museum in Aquileia. Now 36 samples are ready to be analysed, while the remaining will be taken into account no later than next December.
In order to perform an efficient archaeometallurgical study, it is necessary to plan a strategy of analysis which must consider not only the information provided by each technique, but also important issues such as the state of conservation of the finds. The investigation protocol, tested on others ongoing projects, is split in different phases, characterized by specific study methodologies:

- Macro- and microscopical observations of the finds.
- Detailed recording of the archaeological samples, photographic documentation and preparation of sampling data-sheets containing physical characteristics and conservation statuses (weight, size, presence of corrosion products, use-wear patterns, etc.). This step is not only useful for the purpose of the research but was also required by the Soprintendenza.
- Investigation by reflected-light optical microscopy (RL-OM) of the microsamples taken from the artifacts (cross-sections, about 1 mm² of fresh metal).
- Carry out, in sequence, chemical analyses by means of Scanning Electron Microscopy (SEM) with Energy-Dispersive Microprobe (EDS) and Electron Probe MicroAnalysis (EMPA), and metallographic observations. These techniques are employed in order to identify the technology of metallurgical processes and then reconstruct the life-cycle of each object (Scott, 2011).
- Based on the results of the analyses listed above and the archaeological relevance of the finds, the most relevant objects will be selected for the Pb-isotopic analysis. These kind of measurements are based on the isotopic ratios of Pb and are usually employed for the provenance studies. In case of ambiguity – because natural ore deposits frequently show overlapping Pb isotopic compositions – the lead isotopic signature can be combined with other geochemical indicators, like minor and trace elements (Pernicka, 1999; Artioli et al. 2008).

By combining these analytical techniques, the relationship between the ores deposits and the metal found in the archaeological objects will be investigated. In fact, the set of mineralogical, metallurgical, chemical and isotopic analyses, through a comparison with a database of mineralogical source of the raw metal, enables to suggest the provenance of the metal, the reconstruction of the network of the metal trade, and eventually the interpretation of metal hoarding in the Late Bronze Age in North-Eastern Italy, which is a period of profound societal changes.

3. Chromatographic separation activity in Geosciences Lab.

The ultra-clean laboratory in Geosciences Department was equipped and tested in order to produce reliable lead isotopic samples (slag, mineral or metal). The purity of nitric and hydrochloric acids, necessary to dissolve the samples, and the room level of pollution were tested producing blanks, according to the standard procedure developed in Bern (Villa, 2009). The analysis by Multicollector ICP-MS to determine lead isotopic ratios will be performed at the University of Bern.

In July 2013, the analysis carried out on two blanks obtained in Geosciences's Laboratory following the standard procedure recorded high intensities: 250 mV (blank PD1) and 350 mV (blank PD2). These values were unacceptable because in the same measurement session, the lower recorded signal of a sample was 20 mV. To resolve this problem the quality of acids and cleaning of equipment were checked again, therefore the procedure was divided into 3 steps: a Savillex with only water exposed to air for 5 hours (B1), a Savillex with Aqua Regia evaporated (B2) and a blank obtained by the complete flow in column, with resin (B3). The results, received in September 2013, were the following: B1 marked 1.7 mV, B2 marked 0.3 and B3 marked 0.8 mV. These values ensure that now there is no contribution from the environment which could affect the samples.

4. Multivariate statistical analysis

The Principal Component Analysis (PCA) provides a transform in a linear way the original variables into new variables that describe differences between samples. It is an exploratory method that allows the samples study without imposing any prior knowledge on the model. The objective is to reduce the dimensionality of the data through the matrix calculation: the first component PC1 reproduces most of the
variance of the matrix in question, the second component PC2 reproduces the second share of the residual variance after the first component, and so on the third and subsequent components. The constraint is that the extracted components are not correlated with each other.

The new set of coordinates has several advantages compared to the original variables: they are orthogonal to each other, ordered in function of the amount of information that allows a graphical representation. In this way the interpretation of the structure of the data is almost intuitive.

As a test the statistical analysis, both descriptive and multivariate, was performed on available XRF data of copper and bronze objects from the Veneto area. These are 152 artifacts from several archaeological sites of the Verona side of Lake Garda and they are dated from the Copper Age to the Late Bronze Age. The artifacts are kept in the Civic Museum of Natural History of Verona (Aspes, 2011). This statistical analysis is carried out as a preliminary step to evaluate the metal groups and alloys circulating in the area in prehistoric times, and to form a basis for comparison with the objects analysed in the present work.

5. Plan for second year

In the second year the work will complete chemical and metallographic analyses of the retrieved samples to achieve more information about ancient metallurgists’ know-how. According to the described methodology, each sample will undergo chemical, microstructural, metallurgical and isotopic characterization. The Pb-isotope data will be included and compared with other results from a major project already in progress, which aims to study and interpret the deposits of the Alps through the study of primary and secondary mineralization of copper ores. The existing data on minerals form the reference database for Alpine copper mineral deposits (Nimis et al. 2012) and together with isotopic data from other metal-producing areas from the literature (Balkans, Austria, central Europe, etc.) will serve as the basis to interpret the provenance of the copper used to produce the archaeological artifacts. The starting models for the interpretation should be developed in the second part of the year.

References


SUMMARY OF FIRST YEAR ACTIVITY

Courses:
L. SALMASO, L. CORAIN: Corso di statistica applicata alla Sperimentazione Scientifica, Università degli Studi di Padova.
M. CUPITO': Protostoria Europea, Dip. Scienze Archeologiche, Università degli Studi di Padova.
S. BOESSO: Introduzione all'uso della biblioteca, servizi di biblioteca e del sistema bibliotecario, cataloghi e portale AIRE, gestionale bibliografie RefWorks
E. CALANDRUCCIO: Corso di inglese parlato, Dip. Geoscienze, Università degli Studi di Padova.
L. GULIK: Corso avanzato di inglese scientifico, Dip. Geoscienze, Università degli Studi di Padova.
A. ROSS, Scientific Communication, Dip. Geoscienze, Università degli Studi di Padova.
L. PERUZZO, Corso introduttivo SEM, Dip. Geoscienze, Università degli Studi di Padova

Schools, workshops and congresses:
XLVIII Riunione Scientifica dell’Istituto Italiano di Preistoria e Protostoria, PREISTORIA E PROTOSTORIA DEL VENETO, Padova, 5-9 November 2013

Teaching activities:

Field and experimental activities:
Metallographic characterization of samples by means of RL- microscope and SEM-EDS analyses performed at the Geosciences Department, Università degli Studi di Padova.

Isotopes separation (clean laboratory) and ICP-MC-MS analysis at Institute of Geology in Bern University: 14 – 19 March 2013, 3 – 6 July 2013 and 25-27 November 2013.