GEOCHEMICAL TRACERS IN COPPER DEPOSITS AND ANCIENT ARTEFACTS: A DATABASE FOR PROVENANCE
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Abstract
A database of Alpine copper mineralisations is being developed as a reference frame for metal extraction and diffusion in the past. This point is one of the most crucial that archaeologists wish to discover, mainly for a better understanding of the ancient trade courses and technology knowledge of Prehistoric culture. Here database protocol changes and improvements are presented, together with several statistical techniques used to inquire the database and discriminate the ore mineral provenance. Geochemical and minerogenetic informations of copper deposits are also treated. Archaeometric applications such as the Monte Cavanero (Chiusa di Pesio, CN) and Millan case are reported. Finally the Agordo case is described: besides copper ores, recent copper fragments and slags, and also archaeological metal finds found in this area were analyzed.

Introduction
The provenance of metal artifacts in the early history of metallurgy has been a major question in archaeology for many decades. Pb isotope ratios ($^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, $^{208}$Pb/$^{204}$Pb) are commonly used for provenancing in archaeometry (Gale & Stos-Gale, 2000; Hauptman, 2007), but the interpretation is hardly debated (see Pollard, 2009 and Gale, 2009) and it can sometimes be ambiguous because natural ore deposits frequently have overlapping Pb isotopic compositions. So, besides lead isotopes, the database is based on abundances of about 60 minor and trace elements, including most transition metals and chalcophile elements, and the REE (Iser, 1999; Pernicka, 1999). Moreover, the feasibility of the routine reliable measurement of the $^{65}$Cu/$^{63}$Cu isotope ratio (Ciceri et al., 2005) and its use as a possible ore tracer is tested.

Several statistical methods are used for correlating these data; mainly the treatment of the chemical/isotopic datasets of the mines was carried out with PCA (Principal Component Analysis) and PLS-DA (Partial least Square-Discriminant Analysis) with the purpose of discriminating the ore minerals. Sampling is much more considerable, since we have samples from about 40 mining areas, in all more than 300 samples, and almost 100 prehistoric artifacts included both metal objects and slags. Actually about 180 samples were analyzed.

Some of the most well known copper deposits in the Eastern Alps (Agordo area in Veneto, Valsugana, Val dei Mocheni, Valle Aurina e Val Venosta in Trentino-Alto Adige) were selected and compared with very different minerogenetic deposits from the French Queiras (Saint Veran), the Western Alps and the Ligurian Apennines (Libiola, Monte Loreto). More than 40 archeological samples were also analyzed, then compared to the copper based minerals, and projected into the statistical mine models.

Experimental methods
The samples were first characterized mineralogically and petrologically (XRD, RL-OM), and then they were analysed by ICP-QMS (Inductively Coupled Plasma-Quadrupolar Mass Spectrometry), to investigate trace elements and Rare Earth Elements.

Multicollector ICP mass spectrometry (MC-ICP-MS) was used to determine precise Pb isotopic ratios ($^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, $^{208}$Pb/$^{204}$Pb) and is being used for $^{65}$Cu/$^{63}$Cu ratios as well; the instrument is at the Institut für Geologie, in Bern where I spent a large extent of the year.

A very interesting part of my work in this year consisted in developing a new separation method that let us to analyze copper isotopes by means of MC-ICP-MS and testing the feasibility of this measurement. Several proofs were realized using different exchange ionic resins, different conditioning agents and eluents to separate copper isotopes from their isobars and to avoid isotopic fractionation; we had only a few good results but work is still in progress.

Advanced strategies based on multivariate analysis were then used to discriminate the ore mineral provenance. Data were treated with the chemometric software “The Unscrambler Version 9.5” (CAMO AS, Trondheim, Norway). Data pre-treatment, PCA (Wold et al., 1987) and PLS-DA (Geladi &
Kowalski, 1986) models were performed as implemented in the software. The availability of such unprecedented and complete amount of data of Alpine copper deposits also yields information relevant for the geochemical and minerogenetic interpretation of the deposits themselves.

Applications and results

Sampling, lead isotopes analyses and experimental tests on copper isotopes extraction were the main activities for this second year.

Pb data are almost finished and gave very interesting results if we consider them geologically; instead if we use lead isotopes only for establish the provenance of copper artifacts, they often seem to be very ambiguous because natural ore deposits frequently have overlapping Pb isotopic compositions.

The discriminating power of the database was applied to the provenancing of copper metals and slags from the Agordo area and the recently found prehistoric copper fragment and slags from Millan (Bressanone, BZ). The same thing was made with the only Pb isotopes data about the Western Alps, Ligurian Appennines and copper artefacts from Monte Cavanero (Chiusa di Pesio, CN).

Data of metal artifacts and slags, found in Agordo area, show that the discriminant model selected to identify the Agordo ores, is perfectly applicable to the copper samples, clearly indicating that the metal was extracted from the local ores.

For the Millan case, the discriminating model of the deposits that best describes the copper fragment is the one that identify the Val Venosta area (Oris, Val Martello, Stelvio mines), located 80 km to the West of the archaeometallurgical site of Millan. This result suggests that the copper sample is genetically unrelated to the large amount of associated slags produced during the smelting of copper from a sphalerite/galena-rich chalcopyrite ore, since Val Venosta ores have a rather different mineralogical character. Lead isotopes data about the Western Alps, Ligurian Appennines and copper artefacts from Monte Cavanero, show that minerals employed for copper smelting are primary sulfides (chalcopyrite, bornite). Copper objects have a similar isotopic compositions of Western Alps ores, and so we can exclude ophiolitic ores of the Appenninic area (Libiola mine). Probably the presence of Sn in artifacts causes the $^{207}\text{Pb}/^{204}\text{Pb}$ enrichment. The availability of such unprecedented and complete amount of data of Alpine copper deposits also yield interesting information concerning the geochemical and minerogenetic interpretation of the deposits themselves.

Conclusions

Application of PCA to the geochemical and isotopic data proved to be a very powerful tool to discriminate the ore source areas and geochemical character. The presented preliminary applications to copper metal samples and slags seem to indicate that the analysis can be successfully performed on archaeometallurgical specimens for provenancing and diffusion investigations. Future efforts are directed towards (1) completion of the mine database with the inclusion of Pb data, (2) investigation of archaeological copper slags, (3) interpretation of the geochemical tracers, and (4) their behaviour during the copper smelting processes.
References


SUMMARY of LAST YEAR'S ACTIVITY

Courses:
BOESSO S.: Corso introduzione alla biblioteca, Dipartimento di Geoscienze, Università degli Studi di Padova
OMENETTO P.: “Mediterranean tectonics and metallogenesis”, Dipartimento di Geoscienze, Università degli Studi di Padova
SCOTT D.A.: Summer course on “Ancient and historic metals: technology, microstructure and corrosion”, 5-12 Luglio 2009, UCLA-University College of Los Angeles, Los Angeles (CA)

Communications:


Publications:


Other:
SUMMER SCHOOL: “SILS: X school on synchrotron radiation: fundamentals, methods and applications”, 7-18 Settembre 2009, Duino, Trieste
Experimental activities:

Mines sampling activity

ICP-Q-MS samples preparation and analysis of trace and REE elements, at Insubria University, Como

HR-ICP-MC-MS samples preparation and analysis of Lead and Copper Isotopes, at Institut fur Geologie in Bern University, Bern (CH)

Experimental tests for Copper isotopes separation, with several ionic exchange resins and eluents at the Clean Lab of the Institut fur Geologie in Bern University, Bern (CH)