Chemical and isotopic provenance tracers in ancient copper and bronze artifacts: a geochemical database of copper mines


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The provenance of ore minerals used in prehistoric and historic times for copper smelting and extraction is one of the basic questions that archaeologists pose to modern analytical archaeometry [1]. To aid metal provenancing studies, a database of fully characterized Alpine copper mineralisations is being developed as the fundamental reference frame for metal extraction and diffusion in the past. In the early stages of the project, some of the most well known copper deposits in the Western Alps were selected and compared with very different minerogenetic deposits from the French Queyras (Saint Veran) and the Ligurian Apennines (Libiola, Monte Loreto).

The fully characterized samples were then analysed by ICP-QMS (inductively coupled plasma-quadrupolar mass spectrometry). The abundances of about 60 minor and trace elements, including most transition metals and chalcophile elements, and the rare earths were measured in all samples. Furthermore, the feasibility of the routine reliable measurement of the 65Cu/63Cu isotope ratio [2] and its eventual use as a possible ore tracer was tested. Multicollector ICP-Mass Spectrometry was used to determine precise Pb isotopic ratios (206Pb/204Pb, 207Pb/204Pb, 208Pb/204Pb) and is being used for 65Cu/63Cu ratios as well.

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 [3] and PLS-DA [4,5] 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.

Application of PCA and PLS-DA to the geochemical and isotopic database proved to be a very powerful tool to discriminate the ore source areas with very little ambiguity. The applications to archaeometallurgical copper specimens from the Agordo area (Veneto) and the recently found prehistoric slags from Millan (Alto Adige) indicate that the approach is successful in provenance and trade route investigations. Future efforts are directed towards (1) completion of the mine database, (2) investigation of archaeological copper slags, (3) deeper interpretation of the geochemical tracers and their behaviour during the smelting processes.