

Osmium isotopes as a provenance tracer? A case study from Cabrières

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La Capitelle du Broum, located in the chalcolithic copper mining district of Cabrières (Hérault, France), is the first chalcolithic copper smelting workshop known in France dating to the beginning of the 3rd millennium BC [1]. These fahlore mines are composed of tetrahedrite, and the secondary minerals malachite, azurite and cuprite [1]. The entire chain of production from ore to slags, droplets of copper, ingots and artefacts was located on the site [1].

To determine if Osmium (Os) isotopes can be used as a provenance tracer, primary and secondary minerals from different deposits around the archaeological copper smelting site as well as three ingots and six artefacts from within the excavation site, were analysed. That no additional flux agent had been added to the smelting process, which is important for a provenance tracer, was shown by the large variety of the slag compositions [2]. This proves that there was no intention to produce a liquid slag to separate the metal and/or matte from the host rock by adding a flux agent [2]. Beside the Os isotopes also the commonly used lead (Pb) isotopic composition for provenance tracing was applied.

The ore samples show a large spread in all the Pb/Pb isotope ratios, which is typical for fahlores, but no variation between primary and secondary minerals. The Pb isotopic variation of the ingots and artefacts are much smaller and plot within the large Pb/Pb ore field, which shows that during smelting the Pb isotopic composition homogenises and that high firing temperatures of the ore (1000-1200°C) [2] did not change the Pb isotopic composition. The artefacts are therefore most likely produced from those Cabrières ores.

This is different for the Os isotopes. The ¹⁸⁷Os/¹⁸⁶Os of the ores spread between 20 and 60, whereas the ingots have decreased ¹⁸⁷Os/¹⁸⁶Os ratios from 20 to 23 and the final artefacts show even lower ¹⁸⁷Os/¹⁸⁶Os values of around 12. Therefore Os isotopes cannot be used as a source tracer like Pb isotopes. Furthermore the [Os] decreases from around 90 pg/g for the ores down to 12 pg/g for the ingots and artefacts, due to the volatility of OsO₄, which must have been produced in the smelting process, indicating a primitive oxidising environment within the smelting process. The decrease in the isotopic composition and the [Os] from ore to ingots and artefacts shows that most of the Os was lost during smelting but that an ingrowth of the ¹⁸⁷Os by the decay of ¹⁸⁷Re had taken place. Rhenium concentration measurements on the ingots and artefacts will finally show if the Re/Os system can be used as a dating tool for metal artefacts.

References

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Mimetite formation from goethite adsorbed lead

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Immobilization of heavy metals widespread in contaminated soils is still an important issue in environmental research. High levels of arsenic are present as a contamination of agricultural soils where pesticides, herbicides, and fungicides were used (Comba et al. 1988; Bajda et al. 2007). These soils are often contaminated by lead as well. Bioavailability of arsenic in contaminated soils can be reduced to insignificant levels by precipitation of mimetite Pb₅(AsO₄)₃Cl. This results in conversion of bioavailable arsenate compounds into highly immobile mineral form resulting in neutralization of the toxicity without removal of As(V).

Goethite α-Fe(OH)₃ is a mineral widespread in soil environment. It can easily adsorb arsenates or lead ions. The adsorption of lead ion onto these surface is reversible and desorption increase with decreasing pH (Cornell and Schwertmann, 1996). The objective of this study was the reaction between arsenic ions in the solution and a synthetic goethite saturated with adsorbed Pb(II). The sorption of lead ions (initial [Pb] = 50 mg/L) onto goethite at pH=4.8 caused 99% decrease of Pb concentration in the solution in 24 hours. The subsequent reaction between goethite-adsorbed lead and aqueous arsenate in the presence of Cl⁻ results in crystallization of aggregates of mimetite crystals indicating homogeneous nucleation in the volume of the solution. Crystallization of mimetite is very rapid. The results suggest that the kinetics of lead desorption from goethite is fast, at least equal to the rate of diffusion and advection of AsO₄³⁻ ions in the solution and the crystallization of mimetite. The decrease of As concentration in the solution after 48 hours of reaction indicates that apart from mimetite crystallization, adsorption of goethite took place.

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