

# Copper and iron stable isotopes as tracers of non-ferrous historical metal objects - validation to the metal provenance studies

## Popular science abstract

One of the key questions of modern archaeometallurgy is how to determine the origin of a metal artefact that has been moved from a place of its manufacture. The latest and promising method is a verification of ore and artefact isotopic composition on the base of the stable copper (Cu) and iron (Fe) isotope ratios. This is because stable Cu and Fe isotopes do not fractionate at high temperatures, and the risk of contamination from other components used in the metallurgical process, such as fuel or flux, is insignificant. In addition, copper and iron are two metals that are commonly found in copper deposits, most often in the form of sulphides such as e.g. bornite ( $\text{Cu}_5\text{FeS}_4$ ), chalcopyrite ( $\text{CuFeS}_2$ ) or chalcocite ( $\text{Cu}_2\text{S}$ ). During metal smelting, Cu and Fe are deposited in metal concentrate (future artefact), as well as in metallurgical slag, together with silicate remains of ore and flux.

The main goal of the project is to determine whether the study of Cu and Fe stable isotopes ratios is a reliable method for recognizing the provenance of non-ferrous (copper) metal artefacts. In the study, we address the validity of this methodology due to the possible influence of additional elements of the metal smelting process, such as cooling conditions and redox-sensitive flux additives. According to the current state of knowledge, these components should result in the fractionation of Cu and Fe isotopes but have not been verified by the previous studies. The study will also discuss the problem of isotopic homogeneity of copper deposits on the example of the Zechstein Kupferschiefer deposit. Primary mineralization (massive and dispersed) currently exploited in the Fore-Sudetic Monocline and the secondary (oxidized) mineralization of the North Sudetic Basin will be examined.

The first stage of the project will focus on the analyses of copper ores and metallurgical slags formed as a secondary product of metal smelting. Slags are a valuable research material because they allow determining changes occurring in artefacts, without the need to destroy the cultural heritage. At the same time, slags are preserved in large quantities in the former (North Sudetic Basin) and modern (Fore-Sudetic Monocline) copper smelting centres. In the second stage we will execute a series of low- and high-temperature laboratory experiments carried with the addition of fluxes changing redox conditions during simulated smelting. The tests will be carried under various cooling conditions - quenching and slow crystallization. Results will allow determining whether, with changes in the smelting process, Cu and Fe isotopes fractionation could have been intensified. Anticipated results and conclusions are expected to have a substantial value due to a modest number of similar studies. Equally important will be an implementation of additional elements of the metallurgical process (varied in time and location) into the research.

In the project, we will use methods commonly adopted for geochemical and petrological studies, such as total chemical composition (bulk-chemistry) and the chemical composition of minerals and metallic phases (scanning-electron microscopy (SEM-EDS), electron microprobe (EMPA)). We will also apply more sophisticated techniques such as multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS) and high-resolution sector field inductively coupled plasma-mass spectrometer (ICP-MS) coupled with femtosecond laser ablation (fs-LA) to determine Cu and Fe isotopic compositions.

The project will confirm the possibility of using copper and iron stable isotopes ratios as indicators of the origin of non-ferrous metal artefacts. The study will contribute to the detailed isotopic recognition (Cu and Fe) of two zones of the most important copper deposit in Poland. Depending on the results, the project has an opportunity to create additional conclusions on the genesis of the studied copper deposits as well as on the isotope fractionation in the supergene zone.