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# Mineral-scale control on Cu isotope variability in ore-slag systems (North Sudetic Basin, SW Poland)

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This study integrates bulk $\delta^{65}Cu$, bulk $\delta^{56}Fe$, in-situ $\delta^{65}Cu$ (fs-LA-ICP-MS) and reference Pb isotope data to evaluate isotope redistribution during the smelting of oxidized Cu ores from the North Sudetic Basin (SW Poland), representing the Zechstein Limestone (Ca1) formation, a distal segment of the Kupferschiefer system.

Bulk oxidized ores display consistently light $\delta^{65}Cu$ values (-0.60 to -0.40‰; mean approx. -0.49‰), whereas historical slags span a broader interval (-0.42 to +0.59‰; mean approx. +0.05‰). In contrast, bulk $\delta^{56}Fe$ values overlap between ores (0.02-0.30‰) and slags (0.06-0.25‰), with comparable means (~0.15‰), indicating limited net Fe isotope modification during high-temperature technological process.

In-situ $\delta^{65}Cu$ analyses reveal substantially larger intra-sample variability than observed at bulk scale. Oxidized ores show extreme heterogeneity (malachite: -1.92 to +0.97‰; covellite: -2.84 to -1.55‰), while slag phases (bornite-like, pyrite-like, metallic Cu and Cu-Fe assemblages) range from -0.41 to +1.09‰. These mineral-scale ranges exceed bulk ore-slag offsets and demonstrate that isotopic redistribution is strongly phase-dependent.

No systematic relationship is observed between slag $\delta^{65}Cu$ and Cu concentration or estimated liquidus temperature, arguing against simple Rayleigh-type fractionation during smelting. Instead, the combined Cu-Fe dataset suggests that bulk slag compositions reflect (i) inheritance of heterogeneous ore signatures and (ii) selective redistribution of Cu among coexisting metallic and sulfide phases.

Bulk Pb isotope ratios in slags span a relatively broad range ($^{206}Pb/^{207}Pb$ = 1.15-1.24; $^{208}Pb/^{206}Pb$ = 1.97-2.09), comparable to the variability observed in the associated oxidized mineralization. This spread exceeds the narrow fields typically reported for single industrial ore systems, yet does not indicate the presence of an additional external Pb source. Instead, the data suggest internal heterogeneity within the basin-scale mineralization.

To our knowledge, this represents the first coupled Cu-Fe isotope dataset from the Zechstein Limestone (Ca1) mineralization genetically linked to the Kupferschiefer system, extending isotope constraints beyond the central Fore-Sudetic Monocline domain. By explicitly quantifying isotopic variability across mineral, ore and slag scales, this study clarifies the strengths and limitations of Cu and Fe isotopes in archaeological provenance studies.