Matrix and laser energy effects during in-situ determination of Cu isotope ratios by UV-fsLA-MC-ICP-MS

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Copper isotope compositions in Cu-bearing metals and Cu-rich minerals (chalcopyrite, enargite, covellite, malachite and cuprite) have been measured by deep UV-fsLA-MC-ICP-MS. A long-term reproducibility of better than 0.08‰ (2SD) on the NIST SRM 976 Cu-metal standard has been achieved with this technique. The δ^{65}Cu values for all samples have been determined relative to NIST SRM 976. For correction of instrumental mass bias, a Ni NIST SRM 986 standard solution has been introduced simultaneously to LA analyses. Potential effects from matrix-induced mass interferences, such as $(^{32}S^{33}S)^+$, $(^{32}S\text{-}^{16}O^{17}O)^+$ and Zn-H on the measured copper isotope ratio of minerals, have not been observed.

Copper isotope measurements are, independent of the matrix analysed, sensitive to the applied laser energy density (fluence). A positive correlation between the energy density and the magnitude of the isotope ratio shift has been observed in the energy density range from 0.2-1.3 J/cm^2. When using an energy density of ~2 J/cm^2 for laser ablation, artificial shifts in the δ^{65}Cu values on the order of ~3‰ for Cu-metal, ~0.5‰ for brass and ~0.3‰ for malachite were obtained.

The results demonstrate that it is possible to measure Cu isotopic ratios in native copper and Cu-bearing sulfides, carbonates and oxides in-situ with a precision of better than 0.1‰ (2SD) without using a matrix-matched standard during laser ablation analyses.