



## **Fluid speciation controls of low-temperature copper isotope fractionation**

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The classic study of Ohmoto (1972) on the sulfur isotope system demonstrated that mass-balance among reduced and oxidized solution species can exert a strong control on the isotopic composition of sulphide ore minerals. Recent experimental studies on copper isotope fractionation also reveal that fluid speciation among reduced and oxidized species can be an important control of the Cu-isotopic composition of copper sulfide minerals. We explore this issue for sedimentary copper sulfide deposits through fluid speciation-isotopic Eh-pH calculations based on the thermodynamic stability of copper aqueous solutions species and experimentally measured copper isotope fractionation factors. Chemical speciation calculations were made using The Geochemists Workbench v4.03, Cu isotopic fractionation data were taken from experimental calibrations and the diagrams were calculated by Matlab programming. The calculations show that isotopically-light Cu-sulfide minerals (with respect to the bulk  $\delta^{65}\text{Cu}$  value of the solution) will only form in Eh-pH conditions where oxidized species dominate, whereas more reducing conditions will give Cu-sulfide minerals with  $\delta^{65}\text{Cu}$  values similar to the bulk solution value.

The contrasting geological characteristics of the stratiform sedimentary hosted deposits of the Kupferschiefer of SW Poland and Timna Valley in Israel provide excellent case-studies for examining the fluid speciation-isotopic model. Applying these

speciation diagrams to new MC-ICP-MS copper isotope data points to notable differences between the two deposits in terms of the ore formation conditions. The Timna valley copper sulfides have light Cu-isotopic compositions of  $\delta^{65}\text{Cu} = -2.04 \pm 0.4 \text{ ‰}$ , which corresponds to Eh values of 0.45 to 0.75 for chloride activities in the range of 0.5 to 5 at  $\text{pH} < 6$ . These values indicate that copper sulphide precipitation occurred at relatively oxidized conditions where most of the copper in solution was as Cu(II) complexes ( $\sim 90\%$ ). In contrast, the Kupferschiefer Cu-sulfides show significantly higher  $\delta^{65}\text{Cu}$  values =  $-0.42 \pm 0.38 \text{ ‰}$ , corresponding to Eh values of 0.35 to 0.55 for chloride activities in the range of 0.5 to 5 at  $\text{pH} < 6$ . At these pH conditions, most of the copper in the solution occurs as Cu(I) complexes ( $\sim 90\%$ ). These observations are in accord with field relations showing that Cu(II) minerals dominate the Timna system but that Cu-sulfides are the major minerals of the Kupferschiefer deposits.

The fluid speciation-isotopic calculations made in this study show that copper isotopes can be used as effective tracers of redox conditions during sulphide ore deposition. Although, the calculations are made at sedimentary conditions, this approach can potentially be applied to hydrothermal ore deposits, such as black smokers and volcanic-hosted massive sulphide deposits.