

Cu isotope fractionation between Cu-bearing phases and hydrothermal fluids: Insights from ex situ and in situ experiments

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ABSTRACT

Cu isotope ratios have been widely applied to fingerprinting metal sources, tracking fluid pathways, and tracing mineralization processes, for which knowledge of isotope fractionation is required. This paper presents new experimental calibration data of Cu isotope fractionation between Cu-bearing minerals (native Cu and cuprite) and Cl-bearing hydrothermal fluids at 25–800 °C and 0.1–200 MPa. The experiments were performed either using a polytetrafluoroethylene (Teflon) beaker on a hotplate, a rapid heat/rapid quench argon cold seal pressure vessel (RH/RQ Ar-CSPV), or a large volume fluid reactor, which enabled fluid sampling ex situ (the former two) and in situ (the latter). Three setups were designed to investigate Cu isotope fractionation ($\Delta^{65}\text{Cu}_{\text{fluid-mineral}}$): (1) associated with Cu(I) dissolution, Cu(I) disproportionation as well as oxidation of Cu(0) (native copper) and Cu(I) in $\text{Cu} \pm \text{Cu}_2\text{O} + \text{HCl}$ systems at temperatures of up to 800 °C and pressures of up to 200 MPa; (2) related to Cu-Au alloying processes in the $\text{Cu} + \text{NaCl/HCl}$ system at 600 °C and 150 MPa; (3) to evaluate the influences of different sampling techniques (ex situ vs. in situ) and superimposed cooling processes. The selected system is $\text{Cu}_2\text{O} + \text{NaCl} + 0.2 \text{ m HAc/NaAc}$ (pH-buffer), and runs were conducted at 200–250 °C and 20 MPa.

$\Delta^{65}\text{Cu}_{\text{fluid-mineral}}$ shows the least variation during solid separation from source fluids, generally $<0.16 \pm 0.03\text{‰}$. Positive $\Delta^{65}\text{Cu}_{\text{fluid-mineral}}$ values are found in most runs, excluding cuprite dissolution in NaCl/HCl solutions at 200–250 °C, 20 MPa, and 800 °C, 200 MPa. Cu oxidative leaching into Cu(I) results in decreasing $\Delta^{65}\text{Cu}_{\text{Cu(I)-Cu(0)}}$ values from $0.12 \pm 0.05\text{‰}$ to $0.07 \pm 0.05\text{‰}$, and $-0.30 \pm 0.03\text{‰}$ at 25, 50, and 200 °C, respectively. In contrast, Cu dissolution at high temperatures (600–800 °C) leads to Cu(I)-containing quench fluids and subsequent native Cu precipitates. Both products are enriched in heavy isotopes by up to 5‰, caused by preferential enrichment of ^{65}Cu at the surface layer during the alloying-induced diffusion transport process. Cuprite oxidative leaching in HCl leads to fluids enriched in Cu(II), and the corresponding $\Delta^{65}\text{Cu}_{\text{Cu(II)-Cu(I)}}$ increases from $0.52 \pm 0.04\text{‰}$ at 25 °C to $0.89 \pm 0.02\text{‰}$ at 50 °C. Fluids are enriched with light isotopes (^{63}Cu) during cuprite dissolution at 200, 250, and 800 °C, i.e., $0-0.55 \pm 0.04\text{‰}$ lower than the precursor. At 250–300 °C, Cu(I) disproportionation into Cu(II) and Cu(0) dominates the observed isotope fractionation, yielding $\Delta^{65}\text{Cu}_{\text{fluid-Cu}_2\text{O}}$ up to $0.59 \pm 0.03\text{‰}$ and $\Delta^{65}\text{Cu}_{\text{Cu(0)-Cu}_2\text{O}}$ up to $-0.28 \pm 0.02\text{‰}$.

Rapid cooling ($3-25 \text{ K s}^{-1}$) relative to slow cooling (0.014 K s^{-1}) can cause phase separation as well as significant isotope fractionation, particularly if fluids cool from an intermediate high temperature to ambient temperature (e.g., from 200–300 to 25 °C), which highlights the importance of kinetic processes that may potentially alter the isotope composition of natural ore-forming fluids.

Keywords: Cu isotope fractionation, redox reaction, cooling, Cu-Au alloying, diffusion, in situ fluid sampling; Isotopes, Minerals, and Petrology; Honoring John Valley