

Experimental investigation of copper transport in fluids: Cu solubility and isotopic fractionation

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In order to understand processes during mineral dissolution and metal transport of Cu in hydrothermal fluids, we performed experiments in the system $\text{Cu}_2\text{O} - \text{H}_2\text{O} \pm \text{HCl} \pm \text{NaCl}$ and determined the isotopic fractionation of Cu between fluid and solid phases. Two different approaches were applied: (i) rapid quench of Au capsules filled with cuprite pellets and fluid components after annealing in cold seal pressure vessels at T up to 300°C and P up to 120 MPa; (ii) *in situ* sampling of fluids at T up to 250°C and 20 MPa pressure using a large volume Parr autoclave. In some cases acetic acid/sodium acetate mixtures (HAc/NaAc) were added to buffer pH.

After an experiment of type (i) at 300 °C, 100 MPa with cuprite in 1.5m HCl, quenched fluid was extracted by a 0.30 ml metal syringe and two types of solid were retrieved by cutting through the capsule, i.e. residual cuprite pellet and white CuCl powder. During experiment 7% of pellet weight loss was observed. The experimental products were measured by both *in situ*-LA-MC-ICP-MS ($2\sigma \pm 0.1 \text{ ‰}$) and solution based MC-ICP-MS ($2\sigma \pm 0.05 \text{ ‰}$). The pH of the quenched fluid was almost neutral, i.e. 4.87, and $\delta^{65}\text{Cu}$ was 1.10 ‰. *In situ* solid analyses indicated that the rim of the pellet was severely altered due to formation of copper chloride ($\text{Cu}_2\text{O} + 2 \text{HCl} = 2 \text{CuCl} + \text{H}_2\text{O}$) while the core was rather intact. The $\delta^{65}\text{Cu}$ of unaltered core and starting pellet was similar, $\sim 0.5 \text{ ‰}$, while $\delta^{65}\text{Cu}$ in the altered rim increased up to 0.8 ‰ near the surface. This indicates transfer of lighter Cu isotope into the solution at high T. The precipitated CuCl yielded the lowest $\delta^{65}\text{Cu}$, $\sim 0.25 \text{ ‰}$, suggesting strong fractionation of Cu isotopes between fluid (1.10 ‰) and CuCl upon quenching. Experiments at 200°C, 20MPa with Cu_2O pellets in 1.0m NaCl solutions demonstrated the importance of buffering pH. Cu content in the quenched fluid was higher by a factor of 7 in the non-buffered system than the buffered system.

In situ sampling was used to avoid retrograde modifications of the fluid. In a run of type (ii) using cuprite pellet, 1.0m NaCl solution and 0.2m HAc/NaAc pH buffer, Cu concentrations increased with increasing temperature and reached maximum values of $\sim 3000 \text{ ppm}$ within 5 h at 250°C. Analyses of copper isotopes for these experiments are in progress.