

Reaction between Cu-bearing minerals and hydrothermal fluids at 800 °C and 200 MPa: Constraints from synthetic fluid inclusions

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ABSTRACT

Transport and deposition of copper in the Earth's crust are mainly controlled by the solubility of Cu-bearing phases and the speciation of Cu in magmatic-hydrothermal fluids. To improve our understanding of copper mobilization by hydrothermal fluids, we conducted an experimental study on the interaction between Cu-bearing phases (metallic copper, Cu₂O, CuCl) and aqueous chloride solutions (H₂O ± NaCl ± HCl; with Cl concentrations of 0 to 4.3 mol kg⁻¹). The experiments were run in rapid heat/rapid quench cold-seal pressure vessels at 800 °C, 200 MPa, and log_f_{O₂} ~ NNO+2.3. Either Cu or Au capsules were used as containers. The reaction products were sampled in situ by the entrapment of synthetic fluid inclusions in quartz. Fluid composition was subsequently determined by analyzing individual fluid inclusions using a freezing cell and laser ablation inductively coupled plasma-mass spectrometry. Our results show that large isolated and isometric inclusions, free of late-stage modifications, can be preserved after the experiment even when using a high cooling rate of 25 K s⁻¹.

The obtained results demonstrate that: (1) reaction between native Cu, NaCl solution, and quartz (± silica gel) leads to the coexistence of fluid inclusions and Na-bearing silicate melt inclusions. Micrometer- to submicrometer-sized cuprite (Cu₂O) crystals have been observed in both types of the inclusions, and they are formed most probably due to the dissociation of CuOH. (2) When Cu⁰ reacts with HCl and CuCl solutions, or Cu⁺ reacts with NaCl solution, nantokite (CuCl) formed due to oversaturation has been found in fluid inclusion. Copper concentration in the fluid shows a strong positive dependence on the initial chlorine content, with Cu/Cl molal ratios varying from 1:9 to 1:1 in case 1 and case 2, respectively. When Cl is fixed to 1.5 m, initial fluid acidity has a major control on the Cu content, i.e., 0.17 ± 0.09 and 1.29 ± 0.57 m Cu were measured in fluids of case 1 and case 2, respectively. Cu solubility in pure water and in 1.5 m NaCl solutions are 0.004 ± 0.002 and 0.16 ± 0.07 m, respectively. The main responsible Cu-bearing complexes are CuOH(H₂O)_x in water, NaCuCl₂ in NaCl solutions and HCuCl₂ in alkali-free solutions. These results provide quantitative constraints on the mobility of Cu in hydrothermal solutions and confirm that Cl is a very important ligand responsible for Cu transport. The first observation that silicate melt can be generated in the fluid-dominated and native-copper-bearing system implies that transitional thermosilicate liquids can coexist with metal-rich fluids and may enhance Cu mobility in magmatic-hydrothermal systems. This may have important implications for the formation of Cu deposits in the systems with low S activities.

Keywords: Synthetic fluid inclusions, silicate melt inclusions, native copper, cuprite, nantokite, quench rate, proper sealing; Applications of Fluid, Mineral, and Melt Inclusions