

# Cu and Ni solubility in high-temperature aqueous fluids

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Sulphide ore deposits are the most important primary sources of copper and nickel. While some deposits have formed at magmatic conditions because of the immiscibility of sulphide and silicate melts [1], hydrothermal ore deposits stem from the precipitation of metal sulphides from aqueous fluids. Among those of hydrothermal origin, huge Cu porphyry-type deposits such as Butte, Montana, USA, have formed at high temperatures to about 700 °C, whereas other Cu and Ni sulphide and arsenide deposits originated at lower temperatures of about 200 to 400 °C [2]. Because of geochemical similarities, Cu and Ni are often associated in various geological settings. However, no Ni porphyry deposits are found in nature, which points to different mobilization and transport properties in high-temperature fluids. This study aims to investigate the solubility of Cu and Ni in aqueous fluids by in-situ studies at high temperatures and pressures.

Synthetic CuS or NiS crystals or natural covellite [CuS] + chalcopyrite [CuFeS<sub>2</sub>] + pyrite [FeS<sub>2</sub>] crystals were equilibrated in aqueous NaCl ± HCl or CaCl<sub>2</sub> solutions at temperatures between 400 and 700 °C and pressures up to 900 MPa using modified hydrothermal diamond-anvil cells [3]. The experiments were carried out at beamlines P06 at Petra III and at 13-ID-E at APS. A confocal X-ray fluorescence spectrometry (XRF) setup [4] was used to collect consecutive spectra of the fluid excluding signal contributions from the crystals in the sample chamber. The dissolved Cu and Ni concentrations were determined at equilibrium conditions indicated by a steady state of the dissolved metal concentrations. The minimum detection limit for both elements was ~4 ppm.

The dissolved Cu concentrations ranged between 25 ppm at 500 °C, 320 MPa and 338 ppm at 600 °C, 445 MPa (Fig. 1). We observed an increase in the Cu solubility with temperature along an isochore and a decrease with pressure at constant temperature.

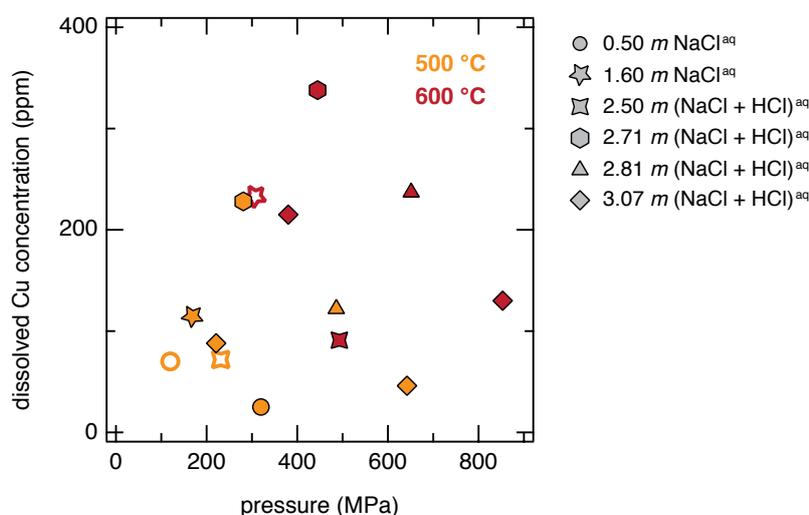


Figure 1: Pressure and temperature dependence of Cu concentrations in the fluid from dissolution of CuS. Symbol shape denotes fluid composition; HCl additions range from 0 to 0.0015 molal. Errors are mostly within symbol sizes. Open symbols depict data points with higher uncertainties.

The dissolved Ni concentrations were significantly lower and ranged from 3 ppm at 500 °C, 200 MPa in a 1 molal NaCl solution to 33 ppm at 500 °C, 411 MPa in a 0.75 molal CaCl<sub>2</sub> solution (Fig. 2). In the studied temperature region, we observed a solubility maximum around 500 °C along an isochore for both solutions. The experiments with aqueous CaCl<sub>2</sub> solutions resulted in significantly higher dissolved Ni contents compared to the NaCl solutions at similar pressure and temperature conditions. This points to a Ni mobilization via aqueous Ni–Cl complexes.

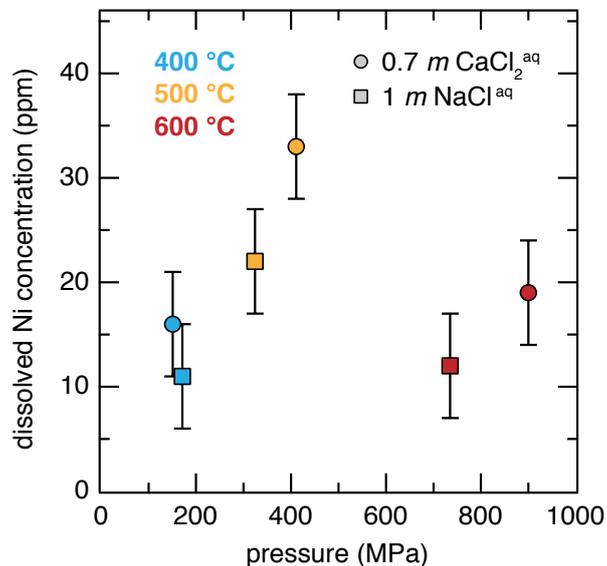


Figure 2: Pressure and temperature dependence of dissolved Ni concentrations in 0.7 molal CaCl<sub>2</sub> solution (circles) and in 1 molal NaCl solution (squares) along an isochore.

The assemblage covellite + chalcopyrite + pyrite was not stable at high temperatures and pressures, but reacted to form an intermediate Cu–Fe sulphide solid solution (approximately CuFe<sub>2</sub>S<sub>3</sub>). Once this reaction was finished, dissolved Cu and also Fe concentrations were determined. They range from 32 ppm Cu and 4 ppm Fe at 400 °C, 49 MPa to 283 ppm Cu and 73 ppm Fe at 600 °C, 611 MPa. Both solubilities showed an increase with temperature along an isochore as well as an increase with pressure at constant temperature. With respect to pressure and temperature, Cu solubilities in the Fe-free and Fe-bearing system are in good agreement and can, thus, be studied based on the simpler Fe-free system.

Our experiments suggest that pressure and temperature have a much larger effect on the Cu solubility than the pH of the solution (within the range from near neutral to pH=3 in the starting solutions). Thus, in hydrothermal ore deposits Cu mobilization is more efficient at low-pressure conditions and Cu ore precipitation should often simply be due to cooling as the metal-bearing fluid rises towards the surface [2]. Ni solubility showed a pronounced dependence on the chlorinity of the fluid.

## References

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