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First insights into Cr^{3+} solubility in aqueous fluids at elevated P and T by μ-XRF

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The mobility of chromium in aqueous fluids and melts strongly depends on its oxidation state. In contrast to Cr^{6+} species, Cr^{3+} is considered to be relatively immobile. However, there are numerous counterexamples in nature that indicate Cr^{3+} mobilization, e.g. from serpentinites or black shales by aqueous fluids during metamorphism or by pegmatite melts [e.g. 1,2]. However, there are very few studies on the solubility at relevant conditions, and the Cr^{3+} speciation in such fluids is still unsettled. Here, we report first results on the Cr^{3+} concentration in aqueous fluids at high pressures and temperatures determined by in-situ synchrotron radiation μ-X-ray fluorescence spectroscopy (μ-XRF).

Synthetic eskolaite (Cr_2O_3) crystals were partly dissolved in aqueous HCl solutions (1.4 – 4.4 molal HCl) at temperatures up to 600 °C and pressures up to 900 MPa using a modified Bassett-type hydrothermal diamond-anvil cell with a recess in one diamond [3]. A confocal setup was used including a single-bounce capillary focussing the incoming X-rays and a polycapillary in front of the detector [4] to collect only the fluorescence signal from the fluid in the recess and to exclude possible contributions from the eskolaite grain to the measured Cr signal. The minimum detection limit for chromium was 400 ppm by weight for 1000 s acquisition time and was calculated from measurements of a standard solution (H_2O + 10 wt% NaCl doped with 1 wt% Cr by addition of $Na_2CrO_4 \cdot 4H_2O$).

In each run, the eskolaite grain and the fluid were heated to the first experimental temperature. Then, consecutive fluorescence spectra of the fluid were taken during crystal dissolution until the Cr signal indicated that steady state was attained. Subsequently, the liquid-vapour homogenization temperature was measured for calculation of the sample pressure and fluid density during spectra acquisition. Then, the sample was heated to the next experimental temperature, and the data collection procedure was repeated.

The concentration of dissolved Cr in the fluid shows strong temperature and pressure dependencies. Independent of the fluid acidity, it appears to reach a maximum of about 14000 ppm at temperatures near 400 °C and decrease significantly by several 1000 ppm at 500 °C and even more at 600 °C. At a constant temperature of 500 °C, a pressure increase from about 170 to about 910 MPa resulted in a twofold increase in the concentration of dissolved Cr from 9200 to 18100 ppm.

Our data for HCl solutions indicate that temperatures around 400 °C and high pressures enhance the mobility of Cr^{3+} in aqueous fluids. Preliminary results suggest that carbonate fluids are less efficient agents for Cr^{3+} transport, because the Cr concentration in the fluid was below the detection limit in an additional eskolaite dissolution experiment with an aqueous Na_2CO_3 solution at 600 °C.

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