New insights into cadmium and zinc transport and fractionation by hydrothermal fluids

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Cadmium and zinc are geochemical "brothers" displaying very similar Cd/Zn ratios among different magmatic rocks. By contrast, in hydrothermal systems, the Cd/Zn ratio may vary by several orders of magnitude. Knowledge of Zn and Cd aqueous speciation is thus necessary to explain such variations. Chloride and hydrosulfide are believed to be the main ligands controlling Cd and Zn mobility. Here we combined different experimental (solubility, XAS spectroscopy) and theoretical (thermodynamic models) approaches to quantify the speciation of Cd and Zn in aqueous Cl^-- and S- bearing ore-forming fluids.

Our new XAS data on Zn aqueous complexes in Cl-bearing solutions at 25-500°C are compared with those reported recently [1]. Significant disargeements are found for $ZnCl_4^{2-}$ above 300°C, our data indicating a much lower stability for this complex. Zn K-edge XANES and EXAFS spectra obtained in our study in SO_4-H_2S solutions in equilibrium with sphalerite ZnS(s) at 350°C and 450°C and 600 bar are also very different from those reported recently [1], suggesting different Zn complexation depending on acidity, redox and S content and dominant ligands.

Our new solubility measurements of greenockite CdS(s) at 25-80°C allow revision of the standard thermodynamic properties of CdS(s) ($\Delta_f G^0_{298.15,\ 1bar}$ = -151.5±0.3 kJ/mol) and quantification, for the first time, of the stability of Cd-HS complexes in hydrothermal fluids. In view of these results, we do not recommend the use of common thermodynamic handbooks (e.g., [2]) for CdS(s) thermodynamic properties.

These new data, complemented by our previous results [3], demonstrate that in ore forming systems the Cd/Zn ratio is primarily controlled by the temperature and H_2S content of the fluid, whereas variations of pressure, salinity or pH are less important. Thus the Cd/Zn ratio may be used as a tracer of some fluid properties, which are not accessible by other methods.

[1] Mei *et al.* (2016) GCA, in press. [2] Robie and Hemingway (1995) U. S. Geol. Surv. Bull. 2131. [3] Bazarkina *et al.* (2010) Chem. Geol. 276, 1-17.