Zinc and cadmium behavior in low-density fluids

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Low-density fluids and vapors (density $\leq$ 0.5-0.3 g/cm^3) are ubiquitous in the Earth crust from moderate depth (vapor-brine immiscibity) to the surface (volcanic degassing). Quantitative understanding the transport capacity of such fluids for metals is, however, weak owing to both experimental difficulties and imperfections of classical thermodynamic models (e.g., HKF) when applied to the low-density aqueous phase. Our study is aimed at quantifying the transport of Zn and Cd, typical base metals, in such phases. We combined solubility measurements of ZnO and CdO in H_2O and H_2O-NaCl-HCl fluids and vapors and Zn and Cd vapor-liquid partitioning experiments in water-salt systems across a wide range of temperature, pressure and density (T = 350-450°C, P = 150-600 bar, d = 0.01-0.5 g/cm^3) with physical-chemical modeling.

Results reveal significant differences in the behavior of Zn versus Cd in low-density fluids in the presence of chloride. For example, the Cd/Zn ratio in the H_2O-NaCl-HCl vapor in equilibrium with CdO and ZnO increases with increasing Cl content, which demonstrates a stronger stability of Cd-Cl complexes compared with their Zn analogs. Our thermodynamic model [1] allow accurate description of the obtained solubility data using the neutral chloride and hydroxide species of Zn and Cd. These findings in homogenous fluids are in agreement with our data in dense aqueous solution [2], and vapor-liquid distribution measurements, which demonstrate that although both Zn and Cd partition in favor of the dense Cl-rich brine, vapor-liquid partition coefficients ($K = m_{vapor}/m_{liquid}$) for Cd are much lower than for Zn (e.g., log K ~ -5.5 and -3.3 at 450°C/280 bar for Cd and Zn, respectively). The different stabilities of Cd- and Zn-Cl complexes may play a key role in Cd fractionation by low density fluids, and explain the elevated Cd/Zn ratios in volcanic gases compared to the mean Earth crust value.

[1] Akinfiev and Diamond (2003) *GCA* **67,** 613–627. [2] Bazarkina *et al*. (2010) *Chem. Geol*. **276**, 1-17.

Reactive transport modelling of natural carbon sequestration in ultramafic tailings

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Anthropogenic CO_2 is naturally sequestered in ultramafic mine tailings as a result of the weathering of serpentine minerals [$Mg_3Si_2O_5(OH)_4$] and brucite, and subsequent mineralization of CO_2 in hydrated magnesium carbonates such as hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ [1]. Understanding the CO_2 trapping mechanisms is key to evaluating the capacity of such tailings for carbon sequestration.

Natural CO_2 sequestration in ultramafic tailings at a mine site near Mount Keith, Australia is assessed with a modified version of the process-based reactive transport code MIN3P [2]. The model formulation includes energy and vapor transport fully coupled with fluid conservation in the aqueous phase and geochemical reactions. Atmospheric boundary conditions accounting for the effect of climate variations are also included. Kinetic dissolution of chrysotile, dissolution-precipitation of brucite [$Mg(OH)_2$] and primary carbonates [i.e. calcite, $CaCO_3$; dolomite, $MgCa(CO_3)_2$; magnesite, $MgCO_3$] as well as the formation of hydromagnesite, halite (NaCl), gypsum ($CaSO_4 \cdot 2H_2O$), blödite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) are considered.

Simulation results at ten years are consistent with field observations. Precipitation of hydromagnesite is predicted, and is mainly controlled by the dissolution of chrysotile (the source of Mg) and the equilibrium with the $CO_2(g)$ ingressing from the atmosphere. The predicted rate for CO_2 entrapment in these tailings is 1.2 kg m^{-2} year^{-1}. Modeling results suggest that this rate is sensitive to CO_2 fluxes through the mineral waste and may be enhanced by several mechanisms, for instance by atmospheric pumping.

[1] Wilson, S. A., Dipple, G. M., Power, I. M., Thom, J. M., Anderson, R. G., Raudsepp, M., Gabites, J. E., Southam, G., (2009). *Economic Geology*, **104**, 95–112. [2] Mayer, K. U., Frind, E. O., Blowes, D. W., (2002). *Water Resources Research*, **38**, 1174.