

## Mechanisms of Cd sorption to montmorillonite (Na-SWy-2) clay affected by ionic strength and microbial ligand

Z. SONG<sup>1</sup>, B.A. BUNKER<sup>1</sup> AND P.A. MAURICE<sup>2</sup>

<sup>1</sup>Department of Physics, University of Notre Dame, Notre Dame, IN 46556, USA (\*correspondence: zsong@nd.edu)

<sup>2</sup>Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA

Many microorganisms exude low molecular weight organic ligands known as siderophores to acquire nutrient Fe; these ligands may also affect the fate and transport of other metals. In this study, we investigated the effects of pH, ionic strength, and the siderophore desferrioxamine B (DFOB) on Cd sorption to montmorillonite using batch experiments, Extended X-ray Absorption Fine Structure (EXAFS) analysis, and X-ray Diffraction (XRD) measurements to monitor changes in montmorillonite 001 d-spacing upon sorption.

The extent of Cd sorption to montmorillonite increased with increasing pH and decreasing ionic strength. The presence of DFOB inhibited Cd sorption at pH < ~7 and enhanced Cd sorption at pH > ~7. Sorption densities ranged from 1.1 (11% sorption) to 10.0 (100% sorption)  $\mu\text{mol}$  sorbed/gram of clay. EXAFS analysis showed that the detailed sorption mechanism varied as a function of pH, ionic strength and DFOB concentration (0 or 1.0 mM). In the absence of DFOB, at low pH (~5.0 for samples in 0.1M NaNO<sub>3</sub> and ~5.0 and ~7.5 for samples in 0.01M NaNO<sub>3</sub>), EXAFS showed that Cd sorbed outer-spherically; at higher pH (~7.5 and ~8.5 for samples in 0.1M NaNO<sub>3</sub> and 8.5 for samples in 0.01M NaNO<sub>3</sub>), Cd sorbed as a mixture of inner-sphere and outer-sphere complexes. In the presence of DFOB, at pH ~5.0, Cd sorbed outer-spherically; at pH ~7.5 and 8.5, Cd sorbed as a mixture of inner-sphere and outer-sphere Cd-DFOB complexes. Furthermore, the ratio between inner-sphere and outer-sphere sorption increased with both pH and ionic strength. XRD measurements indicate that layer spacing did not vary substantially as a function of Cd concentration, ionic strength, or pH. However, in the presence of DFOB, the d-spacing expanded by ~2Å, which is consistent DFOB absorption. This study demonstrates that Cd sorption to swelling clay can involve a complex interplay of mechanisms depending upon environmental conditions.

## Experimental fluid-rock interaction simulating brine reinjection in greywacke-hosted reservoirs of the Taupo Volcanic Zone, New Zealand

R. SONNEY AND B.W. MOUNTAIN\*

GNS Science, Wairakei Research Centre, 114 Karetoto Rd, Taupo 3377, New Zealand

(\*correspondence: b.mountain@gns.cri.nz)

A high temperature-pressure fluid-rock interaction apparatus has been used to simulate greywacke - brine interaction at 154°C and 27 bars using a continuously-flowing fluid. The experiment was designed to reproduce the scenario where reinjection brine is disposed in a fractured greywacke aquifer; a typical lithology at New Zealand geothermal power plants. The fluid used was an actual reinjection brine from an operating plant, containing ~3400 mg/kg of total dissolved solids including SiO<sub>2</sub> (960 mg/kg), Na (799 mg/kg), K (131 mg/kg), Cl (1027 mg/kg) and SO<sub>4</sub> (423 mg/kg). In order to remove atmospheric oxygen contamination, the fluid was degassed first with ultrapure N<sub>2</sub> followed by a H<sub>2</sub>S:N<sub>2</sub> mixture (1:100) for 20 minutes. The final pH of the fluid was 6.8 at room temperature. For the simulation, 24 g of crushed, sieved and ultrasonically-cleaned greywacke (1-2 mm) was placed in the core holder of the flow-through apparatus. At room temperature and 1 ml/hr of brine flow (one week duration), the reacted fluid attained a pH of 7.8 and contained elevated concentrations of Ca and Mg (77 and 6 mg/kg, respectively). This is attributed to calcite dissolution. After a temperature increase to 154°C, the reacted fluid remained oversaturated with respect to amorphous silica but a loss of 240 mg/kg of SiO<sub>2</sub> was observed. Of the other dissolved species: Mg, Ca, Sr, Al, Mn, and Fe showed a significant decrease; while Li, Na, K, As, and the anions showed no measurable change. Variation of flow rate (0.5 ml/hr) showed little change in effluent chemistry suggesting partial equilibrium with some mineral phases. SEM examination of the run products at the entry point of the brine showed a complete overgrowth of amorphous silica on all mineral surfaces. Reacted material at the exit point of the fluid did not show extensive silica overgrowths indicating removal of polymerised silica nanospherules early during water-rock interaction. Partial equilibrium with a secondary phase containing Ca-Mg-Fe suggests a possible control on fluid composition by calcite and/or clay minerals. This was observed in previous experiments using distilled water. These results show that the silica phase precipitating at these conditions in the geothermal aquifer is amorphous silica.