Enhanced radionuclide capture by bioreduced biotite and chlorite

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Background and methodology

Management and geological disposal of our nuclear waste legacy requires an in-depth understanding of biogeochemical processes that occur in the subsurface and their influence on radionuclide speciation and mobility. Here, we explore molecular-scale processes involved in radionuclide immobilisation at the solution-mineral interface and the indirect, but potentially crucial role which microorganisms play in such reactions. The research focuses on two common rock-forming minerals, biotite and chlorite that contain both ferric (Fe(III)) and ferrous (Fe(II)) iron within their octahedral layers. The experimental systems were focussed around "unaltered" or as-sampled biotite and chlorite, and "bioreduced" biotite and chlorite. For the bioreduced minerals, biotite and chlorite were exposed to the model Fe(III)-reducing subsurface microorganism *Geobacter sulfurreducens* in the presence of an electron shuttle (AQDS) to promote reduction of bioavailable Fe(III) within the mineral moeity to Fe(II). After this, unaltered or bioreduced biotite and chlorite were suspended in solutions containing undersaturated Tc(VII), U(VI) or Np(V). The solubility of the redox active radionuclides was then monitored and the variations in the solid phase speciation of the radionuclides was characterised by X-ray absorption spectroscopy (XAS).

Results and implications

G. sulfurreducens was able to reduce Fe(III) associated with biotite and chlorite thus priming the minerals with Fe(II) for “indirect” reductive transformations. However, the interactions of the different radionuclides with the mineral systems differed. There was evidence for reductive transformation of Tc(VII) to Tc(IV) in the bioreduced biotite and chlorite, presumably mediated by labile Fe(II) associated with the bioreduced minerals [1,2]. By contrast, there was poor reactivity towards Tc(VII) in the unaltered samples. Ongoing work with the actinides shows some selectivity for the different mineral surfaces with both sorption and potentially reductive precipitation pathways possible.

Overall, these results show that relatively small increases in Fe(II) content (up to 0.12 mmoles per gram) in the bioreduced minerals can have a profound effect on mineral reactivity and radionuclide behaviour compared to bacterial-free systems. This suggests that indirect reduction of microbially reduced minerals may be an important pathway to immobilisation in rock environments typical of geological disposal sites for radioactive wastes.

[1] Lloyd et al (2000) *Appl. Environ. Microbiol* **66,** 3740-3749, [2] Morris et al (2008) *App. Geochem.* **23**, 603-617.

Effects of pore fluid chemistry on diagenesis.

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Sediment compaction by dissolution – precipitation creep

Sediment compaction occurs largely through dissolution-precipitation creep, also called pressure solution, a process that is driven by gradients in stress. Grains dissolve at grain contacts that support the load of overlying sediments, and solutes precipitate at pore walls, leading to a decrease in permeability. Pore fluid chemistry can be expected to significantly affect sediment compaction behavior and therefore how permeability changes with time. However, not much research has been done to study such chemical effects. Recently, [1] studied the effect of additives on calcite compaction. We investigate the influence of trace elements in solution that affect dissolution and precipitation rates, and the effect of mineral replacement on compaction behavior.

Experiments

We present results of uniaxial compaction experiments on cylindrical (10 mm. length, ø 2.3 mm.) aggregates of various alkali halides. A stress of 1.2 MPa is applied and compaction monitored using a simple set-up after [2]. We show that certain trace metals in solution may affect compaction rates of NaCl, but not of KCl. We investigate the effect of mineral replacement during compaction in the solid-solution system $K(Br_xCl_{1-x})$. A reservoir containing a saturated solution of KCl or KBr is placed on top of the cylindrical aggregate of KBr resp. KCl. The results show that reaction leads to enhancement and localization of compaction, leading to fast reduction in permeability. The change in permeability with time, and therefore fluid infiltration and reaction progress, is not only influenced by the compaction rate, but also by solid volume changes related to the reaction.

Conclusion

Mineral and pore fluid chemistry is an important factor in sediment compaction behavior. Chemical disequilibrium leading to mineral reaction during compaction leads to enhancement and localization of compaction.

[1] Zhang et al. (2011) *Geofluids* **11**, 108-122. [2] De Meer and Spiers (1997) *J. Geophys. Res.* **102**, B1 875-891.