Neptunium biogeochemistry and the manganese cycle

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Neptunium is a key risk-driving radionuclide in geological disposal and is predicted to be the most mobile transuranic in the subsurface at nuclear contaminated sites. However there is a lack of information concerning Np environmental behavior; notably in relation to manganese, a ubiquitous element in any geological setting that has been implicated in actinide beogeochemical cycling [1]. To explore this relationship further, we have characterised Np biogeochemical behaviour in: (i) a ^{237}Np(V) amended δMnO$_2$-rich sediment treatment where we have poised the system at Mn-reducing conditions; and (ii) a range of ^{237}Np(V) amended synthetic Mn mineral systems (pure-phase δMnO$_2$, tri-clinic and acid birnessite, todokrokite, hausmennite and rhodochrosite).

In the sediment system, acetate addition stimulated microbially-mediated bioreduction and the rate of Np sorption to sediment increased during both Mn-reduction and Fe(III) reduction. By the onset of sulfate reduction, all (>99 %) of the added Np(V) (~0.3 μM) had been removed from solution. Parallel XAS experiments (Np(V) ~ 0.3 mM) underwent a similar biogeochemical evolution and data collection is ongoing. In the pure-mineral systems, Np(V) (0.3 μM – 0.3 mM) rapidly (minutes – hours) sorbed to each mineral phase except rhodochrosite, which showed more limited Np sorptive potential. XAS analysis of each mineral phase is ongoing and we expect a range of Np speciation and co-ordination environments related to the Mn-mineral structure and average oxidation state.

[1] Law et al. (2010) *Environmental Science and Technology* **44**, 8924-8929.

Modeling the influence of organic acids on soil weathering

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The potential infuences of low molecular weight organic acids (LMWOA) on the dissolution of soil minerals and, conversly, the stabilization of organic compounds by complexation with minerals or weathering products are well characterized. Mineral weathering is enhanced through several processes including: ligand promoted dissolution; the influence of organic-metal comlexation on dissolution reaction affinity; and/or the changes in soil pH resulting from organic acid dissociation and the production of CO$_2$ through the decomposition of organics [1]. Protection of organic matter occurs through adsorption of organics on mineral surfaces, complexation of organics with metals in solution, the formation of soil aggregates and/or other processes that limit the microbes access to organic compounds or increase the energy required to initiate decomposition [2]. Although these processes are well documented, the net influence of these interactions in a natural soil weathering system has yet to be quantified.

Reactive transport modeling of soils provides a viable framework for examining the organic-mineral interactions at the field scale. The inclusion of LMWOA in simulations of soil development at the Santa Cruz Marine Terrace Chronosequence yields supprising results with regard to mineral weathering. Our work suggests that inclusion of reactions describing the complexation of organic acids and aqueous Al species does not dramatically alter the spatial extent of primary mineral dissolution (and hence the overall weathering rate), but has a comparativly greater influence on seondary mineral precipiation (e.g. kaolinite). In our model system, complexation of organic acids with trace metals competes with kaolinite precipitation as a sink of Al^{3+}; effectively reducing precipiation in the top 0.5 m of the study soils but not leading to large enough changes in the saturation state of albite or K-feldspar to increase the dissolution rate of those minerals. Furthermore, our results show how the spatial extent of weathering fronts may control the distribution of organic substrates. Several other processes linking organic acids to mineral weathering still need to be encorporated into this model framework, but these results demonstrate that our understanding of organic-mineral interactions in soils may be advanced through consideration of these processes in natural systems.

[1] Ganor (2009) *Reviews in Mineralogy & Geochemistry* **Volume 70**, 259-369. [2] v. Lützow (2006) *European Journal of Soil Science* **Volume 57**, 426-445.