

Modeling actinide interactions with minerals and microbes

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Actinide geochemistry is extremely complicated primarily due to the presence of multiple oxidation states, and actinides' varying tendency to form ligand complexes, sorb to sediments, and precipitate from solution. This work describes ongoing efforts to develop simplified models of actinide interactions with environmentally relevant surfaces such as mineral and microbial surfaces. Our goal is to capture the inherent complexity of actinide interfacial reactions in simplified thermochemically based models which can be easily incorporated into speciation and transport calculations.

Previous work has demonstrated that redox sensitive actinides like Pu undergo surface mediated reduction from the highly mobile pentavalent state to the relatively immobile tetravalent states [1, 2]. Modeling these interfacial processes requires consideration of redox chemistry, surface complexation, and ion exchange processes. This has been demonstrated through modeling studies of Np (V) and Pu (V) sorption to montmorillonite and metal oxides. Further experiments examining Pu sorption in the presence of dissolved organic ligands indicate that highly functionalized ligands such as citric acid and humic acid may increase sorption of Pu relative to a binary (Pu-mineral) system. To aid in quantitative modeling of ternary Pu-ligand-mineral systems, a discrete pK_a model of Pu binding with humic acid has been developed.

Recent experiments indicate that similar reduction of Pu (V) may occur in the presence of microorganisms. Sorption of Np (V) to *Pseudomonas putida* cells increased with increasing pH and was quantified using the discrete pK_a, ligand binding approach described previously [3]. However, similar sorption trends between initially Pu (V) and Np (V) systems were not observed. Sequential filtration steps (200-nm followed by 4-nm filtration) indicate that sorption of Pu is drastically influenced by exuded organic ligands. Reduction of Pu (V) to Pu (IV) is inferred from this behavior.

[1] Powell *et al.*, (2005) *Env. Sci. Technol.*, **39**, 2107-2114. [2] Powell *et al.*, (2006) *Env. Sci. Technol.*, **40**, 3508-3514. [3] Gorman-Lewis *et al.*, (2005) *Geochim. Cosmochim. Acta*, **69**, 4837-4844.

Modern thrombolites from an asbestos open pit pond

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Modern thrombolites were discovered in an open pit pond at an abandoned asbestos mine near Clinton Creek, Yukon, Canada. These thrombolites are extremely young given that they presumably began forming soon after the mine closed in 1978. Detailed characterization of the periphyton and thrombolites using light and scanning electron microscopy (SEM) were coupled with mineralogical and isotopic analyses. The thrombolites have a columnar morphology (cm-scale), internal clotted fabric (mm-scale), and are almost entirely made of aragonite, which is supersaturated in the sub-saline pond water. The maximum accretion rate was determined to be ~5.2 mm per year. Initial precipitation is seen as acicular crystals nucleating onto microbial biomass and detrital particles. Continued precipitation entombs benthic diatom species (e.g. *Brachysira vitrea*) that are particularly abundant and well preserved, but also filamentous algae (e.g. *Oedogonium* sp.) and dinoflagellates are easily recognizable. Acid-etching to expose biomass followed by traditional preparation for examination of microbes using SEM was particularly effective for imaging cyanobacteria trapped in the aragonite. The presence of phototrophic microbes at clot centers strongly suggests that these microbes play an important role in aragonite precipitation and thrombolite formation. Clots continue to grow abiotically through periodic precipitation of aragonite that forms concentric laminations around clot centres. Pauses in clot growth allow for recolonization of the clot surface by microbes. Aragonite more closely associated with microbial biomass has an average $\delta^{13}\text{C}$ composition of -4.6‰ or 0.8‰ enriched relative to milky white aragonite that has no microbial biomass (-5.4‰), suggesting a modest removal of isotopically light dissolved inorganic carbon by phototrophs. The low sedimentation rate, high calcification rate, and noticeably low microbial growth rate appear to result in the formation of microbialites with a thrombolitic texture. The formation of thrombolites in a mining environment demonstrates that an anthropogenically formed environment can foster microbialite formation.