Quantifying the Enthalpy and Entropy of Europium-Hematite Surface Species using Variable Temperature Batch Experiments and EXAFS

Student Abstracts

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The environmental fate of actinides is greatly influenced by interfacial reactions, including sorption to solid surfaces where the sorption of trivalent and tetravalent actinides is generally a very strong and potentially irreversible reaction. We hypothesize that the strong interactions of actinides with mineral surfaces result from the formation of inner sphere complexes with a limited number of high-energy surface sites, and that displacement of solvating water molecules from the actinide and mineral surface during sorption is energetically favorable and results from a large increase in entropy. The goal of this research is to provide both a qualitative conceptual model and a quantitative thermodynamic speciation model describing plutonium partitioning to sediments, which is based upon a mechanistic understanding of sorption processes as determined from both molecular-, microscopic- and macro-scale experimental techniques.

Due to its strong hydration sphere and utility as a chemical analog of trivalent actinides, we selected trivalent europium (Eu) as a model case, and studied the sorption of Eu(III) to synthetic hematite (α-Fe_2O_3) using variable temperature batch sorption experiments and extended x-ray absorption fine structure spectroscopy (EXAFS) analysis. The variable temperature batch experiments, conducted at 15, 25, 35, and 50 °C, demonstrated increasing Eu(III) sorption with increasing temperature, and yielded Eu(III)-hematite sorption edge data over the pH range ~3–7.5. We modeled the sorption edge data at each temperature using FITEQL 4.0 and the equilibrium constants for dissociation of water, protonation of the hematite surface (derived from potentiometric titrations of a hematite suspension), and hydrolysis of Eu. Under the experimental conditions, several Eu(III) surface species were possible, and the FITEQL models for each species fit the experimental data equally well. EXAFS analysis indicated the presence of inner-sphere bidentate mononuclear hematite surface complexes with a decrease in the coordination number for the Eu-O shell from 8 to 5 after sorption and a radial distance of the Eu-Fe shell at ~3.1Å. Additionally, we observed no evidence of Eu surface/bulk precipitates in high-resolution transmission electron microscopy (HRTEM) and EXAFS analysis. In a separate experiment, there was no net pH change after reacting Eu(III) with hematite. Based on the results of multi-scale geochemical analyses, we postulate the following surface reaction:

$$2SOH + Eu^{3+} = (SOH)_2Eu^{3+}$$

Using a plot of the surface complexation constants versus T^{-1} (K^{-1}), we calculated sorption enthalpy and entropy values of 104.2 $kJ \cdot mol^{-1}$ and 705.3 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, for $(SOH)_2Eu^{3+}$. This implies that the entropy term ($-T\Delta S$) at 25 °C is -210 $kJ \cdot mol^{-1}$ and is the driving force behind this chemical reaction. This observation of the dominant entropy term is consistent with our experimental hypothesis that the energetic favorability of actinide surface complex formation is strongly influenced by positive sorption entropies, which are mechanistically driven by displacement of solvating water molecules from the actinide and mineral surface during sorption.