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Using lanthanides to probe the interfacial chemistry of nano-scale pores

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Spatial confinement of mineral-water interfaces leads to changes in the kinetics and equilibrium interfacial reactions when compared to non-confined systems. We use lanthanides to test how nano-scale confinement affects the kinetics of adsorption, overall uptake, and coordination environment. Lanthanides have similar chemical behaviors and typically exist as trivalent cations. However, the ionic radii decrease with increasing atomic number from 1.032 Å for La to 0.861 Å for Lu, in contrast with the hydration energy, which increases across the series. We use this systematic variation in the ionic radii and hydration energies to probe the reactivity of nano-scale confined surfaces as a function of pore size. We tested mesoporous silicas with 4 nm and 8 nm pores (SBA-15), and mesoporous alumina with 4 nm pores (MSU-X). These mesoporous substrates were reacted in single adsorbate experiments as well as with aqueous mixtures of lanthanides in a competitive study.

Measured uptake of lanthanides on mesoporous silica indicates that the adsorption capacity increases with decreasing ionic radii in both competitive and single adsorbate experiments. The uptake capacity of lutetium (Lu^{3+}) and thulium (Tm^{3+}) was independent of pore size, but the adsorption kinetics were pore-size –dependent, as Tm^{3+} exhibited enhanced adsorption kinetics on mesoporous silica with 4 nm pores compared to 8 nm. This result is analogous to the earlier reported results for copper (Cu^{2+}). Europium (Eu^{3+}) uptake was higher on mesoporous silica with 4 nm compared to 8 nm pores. However, the kinetics of Eu^{3+} adsorption was about the same for these two pore sizes.

To determine the adsorption pathway and to explain the observed differences in the macroscopic adsorption behavior, we performed *ab initio* molecular dynamics (AIMD) simulations for Eu^{3+} and Lu^{3+} adsorption on the surface of β-cristobalite. Our preliminary results indicate that both lanthanides adsorb as inner-sphere complexes, and each hydrolyzes one water molecule after adsorption takes place.

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