Atomic-scale distribution of uranium during iron oxide mineral growth

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Iron oxide nanominerals are common throughout the environment. Their redox-active surfaces provide many opportunitites for interaction with heavy metals and other environmental contaminants. Naturally-occuring and anthropogenic distribution of uranium in the environment poses a public health risk through uranium contanimation of groundwater and bioaccumulation in edible plants and animals. The association of uranium with iron oxide nanoparticles through incorporation or adsorption has significant influence on the availability of soluble uranium species and their mobility in the environment. Although iron oxide minerals frequently immobilizie uranium through incorporation or adsorption, they can also serve as a source from which uranium re-mobilizes, e.g. by dissolution of a uranium-doped iron oxide. Understanding the fundamental mechanisms governing uranium-iron oxide interactions will increase the predictive capability of uranium transport models.

In this work we probe the bonding dynamics and atomic-scale distribution of uranium ions associated with iron oxide nanoparticles. The transformation of ferrihydrite (Fh; $Fe_5HO_8 \cdot 9H_2O$) into goethite (Gt; α-FeOOH) and lepidocrocite (Lp; β-FeOOH) is used as a model system for understanding the fate of uranium ions during iron oxide phase transformation and growth. Extended X-ray absorption fine structure spectra were interpreted using *ab initio* molecular dynamics simulations to determine the coordination state and bonding dynamics of U atoms embedded in the iron oxide matrix. High angle annular dark field scanning transmission electron microscopy was used to image the locations of individual uranium atoms and characterize heterogeneous distribution of uranium association with iron oxide mineral phases. Inductively coupled plasma optical emission spectroscopy showed changes in the concentration of uranium in the solution phase of our iron oxide suspensions. We find that uranium uptake and association with iron oxide particles strongly depends on uranium oxidation state and iron oxide mineral phase.