Sulfidation mechanism of iron-oxide nanoparticles

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Although many studies have examined the role played by natural nanoparticles in contaminant transport and remediation, increasing emphasis is now being placed on studying the transformation of nanoparticles in natural environments. The physical, chemical, and biological transformations of nanoparticles can affect their surface properties, and thus their reactivities in the environment. Colloidal or nanoparticulate Fe-(hydr)oxides are major consituents of soil and sediment and known scavengers of heavy metals and other contaminants. The sulfidation of Fe-(hydr)oxides is an important process in Fe geochemical cycling and is the starting point of a complex reaction sequence that results in the production of sedimentary pyrite. Electron transfer between surface-complexed sulfide and solid phase Fe^{III} results in the oxidation of dissolved sulfide to elemental sulfur, and subsequent dissolution of the surface-reduced Fe. Sulfidation of Fe-(hydr)oxides is a heterogeneous reaction that is difficult to study kinetically because physical and chemical processes usually happen simultaneously.

In this study, lab-synthesized nano-Fe-(hydr)oxides (goethite, ferrihydrite, and hematite) were reacted with varying sulfide concentrations at room temperature to understand the mechanism of sulfidation with major focus on structural changes at molecular level. Formed as intermediates, poorly crystalline Fe-sulfides exhibit weak diffraction patterns that can be masked by other minerals and thus are hard to detect. We used x-ray absorption spectroscopy (XAS) and XRD at the Stanford Synchrotron Radiation Lightsource (SSRL) to characterise these Fe-S species associated with the three nano-Fe-(hydr)oxides. Nanomaterials with lower crystallinity (e.g., ferrihydrite) are highly reactive and completely transformed to Fe-S, whereas more ordered solids like goethite and hematite underwent transformation to Fe sulfides more slowly. By analysing XAS data collected at the Fe-K-edge and S K-edge, coupled with linear combination fitting, we were able to identify the sulfidation products of these nanoparticles. Results will be reported and discussed.