

Silicate sorption on Fe oxyhydroxides: Reactive sites and complexation topology

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Dissolved silicate is ubiquitous in natural waters with near millimolar concentrations and may sorb strongly onto natural Fe oxyhydroxides under a wide range of conditions, altering their sorption potential for contaminants, affecting Fe cycling and availability, and slowing phase transformation in the case of ferrihydrite. However the nature of the surface complexation, and whether it involves surface polymerization is not well established. Our initial surface diffraction study indicated that monomeric silicate bound in a monodentate topology to the reactive Fe-OH sites on the hematite R-plane, and could also form bridging structures by linkup of these sorbed silicate tetrahedra. We have now extended this study to examine sorption on lepidocrocite and goethite nanoparticles by examining ATR-FTIR spectra of surface hydroxyls and their attenuation and frequency shifts when exposed to monomeric silicate solutions. Results verify the expected ratio of exposed hydroxyl types as a function of nanoparticle habit, and also confirm that the most reactive hydroxyl is that coordinated to a single surface Fe. With increased silicate sorption other hydroxyls are affected suggesting a range of surface interactions depending on silicate concentration and surface plane termination. Changes in hydrogen bonding can also be deduced from analysis of the frequency shifts of surface hydroxyls involved in the silicate binding. At high loadings spectral changes indicative of surface polymerization occur.