FTIR, XAS and XPS studies on the stability & reactivity of ferrihydrite and nano-goethite

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Amorphous phases of Fe, Al and Si are common, and influence contaminant and nutrient cycling in the Earth surface environments. Using different molecular probes, we examined the stability and surface chemistry of ferrihydrite made in the presence of Cl^-, NO_3^-, SO_4^{2-} and Al^{3+} at 25 ºC.

The FTIR spectroscopy studies suggest that ferrihydrite is stable for a longer time, and convert to goethite as a function of associated ligand and pH (rapid appearance in the presence of SO_4^{2-} at pH 5.5, and in the presence of NO_3^- and Cl^- at pH 8.0). However, the rate of goethite formation from ferrihydrite was the slowest in the presence of SO_4^{2-} irrespective of pH. In addition, ferrihydrite synthesized in the presence of different levels of Al did not exhibit any goethite in 4 years. Enthalpies of dissolution for ferrihydrite also varied significantly with the associated ligand, suggesting that ferrihydrite samples made in the presence of different ligands are not the same. The Fe-XAS of ferrihydrite, together with the FTIR spectroscopy of ligands associated with ferrihydrite suggest that the loss of ligand and the coordination environment of ligands in ferrihydrite influenced ferrihydrite transition to goethite. The Fe-XAS studies also indicate that progressive formation of corner-sharing Fe-neghbors promoted the formation of goethite. Whereas the associated ligands and cations inhibited this process.

The O 1s binding energies of surface hydroxyls, examined using XPS and ambient pressure-XPS, differ significantly with the particle size of goethite. In addition, the O 1s binding energies of surface hydroxyls of ferrihydrite differ from those of goethite, but are in the proximity of coarse goethite. We also found that these surface hydroxyls interact differently with CO, a probe molecule used to evaluate the reactivity of surface hydroxyls. A majority of CO adsorbed on nano-goethite converted to formate, while this conversion was partial on coarse goethite and on ferrihydrite. A detailed discussion of these results will be presented.