

Coordination and redox chemistry of aqueous Fe(II) and dissolved organic matter

ELLEN DAUGHERTY¹, BENJAMIN GILBERT²,
PETER NICO² AND THOMAS BORCH^{1,3,*}

¹Department of Chemistry, Colorado State University, Fort Collins, CO, U.S (ellen.daugherty@colostate.edu)

²Earth Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, U.S
(bgilbert@lbl.gov; psnico@lbl.gov)

^{3*}Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO, U.S (borch@colostate.edu)

Biogeochemical cycling of iron and carbon is dependent upon the molecular-level interactions between iron (Fe) and natural organic matter (NOM) in soil and water. Several studies have found evidence for strong Fe(III) complexation via carboxylic functional groups. Less is known about the coordination and reduction-oxidation chemistry of Fe(II) in the presence of NOM. In particular, the extent to which NOM inhibits or enhances Fe(II) oxidation is still under debate. Resolving these questions is crucial to understanding the chemistry that determines the solubility, mobility, and bioavailability of iron in terrestrial and aquatic systems.

We studied the interactions of Fe(II) with various types of NOM, including Suwannee River fulvic acid and Leonardite at pH 5–7. Oxidation of Fe(II) in anaerobic solutions of NOM indicated the presence of oxidizing functional groups that could be reduced by H₂(g) in the presence of palladium. X-ray absorption spectroscopy (XAS) was used to investigate the molecular structure of iron complexes formed upon reaction of Fe(II) with reduced NOM. For the reference NOM types, Fe(II) complexation was dominated by carboxylic acid groups. Complexed Fe(II) exhibited faster kinetics of oxidation by O₂. For one hydrophilic fraction of subsurface pore-water NOM, extensive Fe(II)–thiol coordination was detected. These results demonstrate one mechanism for the enhanced rate of Fe(II) oxidation, and show that Fe(II)-NOM interactions are dependent upon the type of NOM.