

DOM complexation of Fe(II) and its effect on Fe(II) stability under oxic conditions

THOMAS BORCH^{1,2*}, ELLEN DAUGHERTY², PETER
NICO³, AND BENJAMIN GILBERT³

¹Department of Soil and Crop Sciences, Colorado
State University, Fort Collins, CO, U.S.,
(*correspondence: thomas.borch@colostate.edu)

²Department of Chemistry, Colorado State
University, Fort Collins, CO, U.S.

³Energy Geoscience Division, Lawrence Berkeley
National Laboratory, Berkeley, CA, U.S.

Iron is an essential element for most living organisms, but the low solubility of Fe(III) limits its bioavailability in most natural environments. Fe(II) is more soluble, but oxidizes and precipitates readily in the presence of oxygen. In the past decade, several reports of organic-matter-associated Fe(II) found in oxic conditions have suggested that dissolved organic matter (DOM) can preserve Fe(II). However, little is known about how Fe(II) complexes DOM. We used X-ray absorption spectroscopy (XAS) to determine the coordination environment of Fe(II) added to as-received and chemically reduced DOM at pH 4-7, and investigated the effect of DOM complexation on Fe(II) redox stability.

Fe K-edge X-ray absorption near edge structure (XANES) spectra indicated that Fe(II) added to anoxic solutions of as-received DOM oxidized to Fe(III) and complexed in the same way as Fe(III) added to DOM. Linear combination fitting analysis of XAS data using reference organic ligands demonstrated that Fe(II) complexed primarily with citrate-like and catechol-like functional groups in DOM chemically reduced with H₂ and Pd. Although studies of pure organic compounds have shown that complexation with citrate enhances Fe(II) oxidation, our experiments revealed that association with reduced DOM slowed iron oxidation, with up to 15% of the initial Fe(II) concentration remaining after 10 hours. We conclude that reduced DOM is capable of acting as a redox buffer and decelerating the net rate of Fe(II) oxidation.