

Oxalate and Fe(II) adsorption onto the (010) goethite surface: A DFT investigation of ligand- and reduction-promoted dissolution

JAMES D. KUBICKI¹, DANIEL TUNEGA², AND
STEPHAN M. KRAEMER³

¹Dept. of Geological Sciences, University of Texas at
El Paso, El Paso TX 79968 USA

²Institute of Soil Research, University of Natural
Resources and Life Sciences, Peter-Jordan
Strasse 82, 1190 Vienna, Austria

³Dept. of Environmental Geosciences, University of
Vienna, Althanstrasse 14 UZAII, 1090 Vienna,
Austria

Oxalic acid is an important biologically-produced species in the natural environment. The deprotonated form, oxalate, is dominant in aqueous solutions under circumneutral pH conditions and is a strong ligand for Fe. The high affinity of oxalate for Fe means that Fe(III)-oxalate surface and aqueous complexes are common and can lead to ligand-enhanced dissolution. Fe(II) adsorption onto goethite (α -FeOOH) has been shown to enhance dissolution-recrystallization reactions. The goethite (010) face is one of the more common and reactive surfaces on this environmentally critical Fe-hydroxide phase. Hence, this study models both separate and coordinated adsorption of oxalate and Fe(II) onto the (010) face of goethite. Periodic and cluster DFT energy minimizations were performed to determine the structure, vibrational frequencies and energies of various surface complexes. The adsorption mechanism of oxalate was verified via comparison to observed IR spectra. The potential roles of oxalate and Fe(II) in ligand-enhanced reductive dissolution of goethite are discussed.