



## **The attachment of aqueous organic species to oxide mineral surfaces: prediction of the surface speciation as a function of environmental parameters**

**D. A. Sverjensky** and K. Fukushi

Dept. Earth and Planetary Sciences, The Johns Hopkins University, Baltimore, MD 21218, USA

At a molecular scale, biomineralization and bioweathering processes all involve the interaction of organic species with mineral surfaces. Recent ATR-FTIR spectroscopic studies and molecular models have started to reveal the complexities of these interactions, which typically include the formation of inner- and outer-sphere surface complexes and multiple protonated or deprotonated complexes, and a variety of different coordination modes, such as binuclear-bidentate (bridging) or mononuclear-bidentate (chelating) forms. What has been missing is the incorporation of such information into quantitative surface complexation models which can predict the relative importance of different species on oxide surfaces as a function of environmental parameters such as pH, ionic strength, surface coverage and oxide type.

We developed an extended triple-layer surface complexation model (ETLM; Sverjensky & Fukushi 2006, *Env. Science & Technology*, Jan. 15) to better account for the process of inner-sphere surface complexation by ligand exchange. The ETLM treats a previously neglected phenomenon integral to ligand exchange reactions: the electrostatic work during desorption of water dipoles from a charged surface. The magnitude of this work is substantial and depends only on the stoichiometry of the surface reaction. When structures of adsorbed anions established in spectroscopic studies are used to calibrate an ETLM model of bulk adsorption data, the model then independently predicts proportions of inner- to outer-sphere surface complexes as functions of pH, ionic strength and surface coverage. The predicted proportions compare favorably with spectroscopic results. For example, ATR-FTIR measurements have established that oxalate forms mononuclear, bidentate inner-sphere and unprotonated

outer-sphere complexes on goethite (Persson & Axe 2005, *Geochim. et Cosmochim. Acta*, 69, 541). This information was used to infer reactions forming inner-sphere and outer-sphere complexes to fit bulk adsorption data. As an independent test of the model, the predicted abundances of the inner- and outer-sphere complexes as functions of pH and surface loading compare favorably with the speciation obtained experimentally by ATR-FTIR spectroscopy. In this way, the ETLM is useful as a tool for helping to unravel the way in which organic species adsorb to the oxide surface.