## 4.2.61

# Metal sorption to iron(III) (hydr)oxides: The first surface complexation models consistent with spectroscopy and quantum chemistry

D.M. SHERMAN[1] AND C.L. PEACOCK

[1] Dept. of Earth Sciences, University of Bristol, Bristol BS8 1RJ UK (dave.sherman@bris.ac.uk)

The aqueous concentrations of many trace metals in the environment are controlled by sorption onto iron(III) (hydr)oxides. When we have thermodynamic data for these reactions, we can predict the equilibrium concentrations of metals in aquatic environments. However, before we can derive thermodynamic data from laboratory sorption experiments, we need a molecular-level understanding of metal-sorption reactions. Sorption to iron (hydr) oxides can occur by surface precipitation, outer-sphere complexation and a variety of inner-sphere surface complexes. Using EXAFS spectroscopy and first-principles (quantum mechanical) calculations based on density functional theory, we have determined the surface complexation mechanisms for As(V), V(V), Cu(II) and U(VI) on iron (hydr)oxides as a function of surface and aqueous concentration.

EXAFS spectra show that all of these metals sorb to iron(III) (hydr)oxides by forming inner-sphere surface complexes; next nearest neighbor distances are interpreted as resulting from bidentate corner- or edge-sharing with surface $Fe(O,OH)_6$ polyhedra. The EXAFS spectra for all systems are complicated by multiple scattering, however. Quantum mechanical calculations on clusters show that bidentate corner-sharing is the only energetically stable complex for the oxyanions $(H_nVO_4)^{3-n}$ and $(H_nAsO_4)^{3-n}$. On goethite, such complexes can form on the dominant crystal faces ({100} and {101} in space group setting Pnma). Uranium(VI) as the hydrated $UO_2^{++}$ ion sorbs via both bidentate corner- and edge-sharing complexes; the bidentate-edge complex is predicted to be 25 kJ/mole more stable. Copper(II) forms bidentate corner-sharing complexes but also sorbs as binuclear clusters.

Currently used surface complexation models (e.g., Dzombak and Morel, 1991) are at odds with the spectroscopic and quantum mechanical results obtained here. However, we can closely model the sorption isotherms measured in our laboratory (Peacock and Sherman, GCA, 2004a,b) and elsewhere (e.g., Hsi and Langmuir, GCA, 1985) to our observed surface complexes with the diffuse layer approximation to the surface electrostatics. The application of our surface complexation models to field (and planetary) scale reactive transport will be discussed.

## 4.2.62

# Chromate binding to organic adlayers at silica/water interfaces studied by second harmonic generation

C. KONEK, H. AL-ABADLEH, A. MIFFLIN AND F. GEIGER

Northwestern University Department of Chemistry, Evanston, IL, 60208 (geigerf@chem.northwestern.edu)

Hexavalent chromium in ground water has received much attention in the past decades. While much research has focused on the interaction of hexavalent chromium with geosorbents, little is known about how organic adlayers, originating for instance from biosurfactants, can impact chromium binding under environmentally representative chromium concentration conditions.

Using the nonlinear optical laser spectroscopy surface second harmonic generation (SHG), we have studied chromate adsorption and desorption at silica/water interfaces in the presence of acid-terminated carbon-11 silanes diluted in methyl-terminated carbon-8 silanes. The chromate surface coverage is measured directly at the interface, in real time, at room temperature and at chromate concentrations ranging from 1x10-6 to 2x10-4 M. The experiments show reversible chromate binding, are consistent with interfacial pKa measurements, and are applied to a simple chemical transport model. Our experimental approach is highly flexible through structural and chemical control of the surface-bound silanes and is applicable for studying more complex organic adlayers.