Redox reactions on mineral surfaces: Spectroscopic and imaging studies at the molecular level

GORDON E. BROWN, JR.^{1,2,3}*, GUILLAUME MORIN⁴, GEORGES ONA-NGUEMA⁴, FARID JUILLOT⁴, YUHENG WANG⁴, DIK FANDEUR⁴, KARIM BENZERARA⁴, GEORGES CALAS⁴, YINGGE WANG¹, JU YOUNG HA¹, SARP KAYA², TOM KENDELEWICZ¹, ALFRED M. SPORMANN³, AND ANDERS NILSSON²

¹Dept. of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA (*gordon.brown@stanford.edu)

²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, USA.

³Dept. of Chemical Engineering, Stanford University, Stanford, CA, USA.

⁴Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UPMC; Université Paris 7; CNRS; 4, Place Jussieu, 75252 Paris Cedex 05, France.

Electron transfer at mineral-water and mineral-microbe interfaces is a major biogeochemical process that can result in transformation of redox-sensitive minerals and adsorbed pollutant ions, capture (through adsorption and precipitation reactions) or release (through reductive transformation of the sorbent and desorption of surface complexes) of pollutant species, and major controls on element cycling. Over the past decade, a growing number of spectroscopic and imaging studies of the products of electron transfer reactions in model mineral-water systems have advanced our understanding of these reactions and their kinetics in the laboratory. Here, we will review a number of these studies, including abiotic reduction of As(V), Cr(VI), and Se(VI) on metal oxide surfaces, photocatalyzed As(III) oxidation on kaolinite and anatase surfaces, the role of reactive oxygen species and Fe²⁺ on the oxidation kinetics of As(III) on iron oxides, microbially mediated redox reactions of arsenic at iron oxide-water interfaces, and the role of exopolysaccharides in the reduction of nanoparticulate hematite by Shewanella oneidensis MR-1, and microbially mediated oxidation of metal sulfides. We will also present the results of several studies of complex environmental samples that illustrate the effects of electron transfer reactions in natural settings, including chromium reduction by magnetite, the effect of electrically insulating coatings on the Cr(VI) to Cr(III) reduction at the magnetitewater interface, Cr(III) oxidation by Mn-oxides, and arsenic redox reactions, including As(III,V) biomineral formation in an acid mine drainage environment.

Interfacial area measurements for robust models of multiphase flow in porous media

KENDRA I. BROWN¹, DORTHE WILDENSCHILD¹, WILLIAM G. GRAY² AND CASS T. MILLER²

¹School of Chem/Bio/Env Eng, Oregon State University, Corvallis, OR 97331; (brownke@engr.orst.edu, dorthe@engr.oregonstate.edu)

²Dept of Env Science and Engineering, University of North Carolina, Chapel Hill, NC; (graywg@unc.edu, casey_miller@unc.edu)

Understanding the physics of natural flow systems that include *three* immiscible fluid phases in porous media is important to applications such as remediation of NAPL from the vadose zone, oil and gas recovery, and CO_2 sequestration.

Flow and transport in such systems are strongly influenced by the presence of fluid-fluid interfaces. Theoretical work based on conservation laws and the second law of thermodynamics has demonstrated the advantage of a different approach to modeling multiphase flow, accounting not only for traditional variables such as saturation and porosity, but that also incorporate specific interfacial areas, specific common curve lengths, and average curvatures, that are measures of the morphology and topology of the phase distributions.

This research expands previous work on two-fluid-phase systems to three-fluid-phase systems, and the particular focus is the generation of a pore-scale experimental data set that expresses the dependency of capillary pressures in the system on two saturations, as well as interfacial areas per volume. Synchrotron-based X-ray computed microtomography (CMT) is used to generate high-resolution images during drainage and imbibition, which are analyzed to measure the saturations and interfacial areas, and to calculate capillary pressures via meniscus curvature.

Mineralogical Magazine