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Molecular-Level Process Governing the Interaction of Contaminants with Iron and Manganese Oxides

Scott A. Chambers
Pacific Northwest National Laboratory
MS K8-93
P.O. Box 999
Richland, Washington 99352
Phone: 509-376-1766
E-mail: sa.chambers@pnl.gov

Gordon E. Brown
Stanford University
Mail Stop 2115
Stanford, California 94305
Phone: 650-723-9168
E-mail: gordon@Pangea.stanford.edu

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Scott A. Chambers, Pacific Northwest National Laboratory

Gordon E. Brown, Stanford University

Research Objective

We are carrying out a program of research that focuses on the fundamental mechanisms of redox chemistry of contaminants on mineral surfaces. As much of this chemistry in sediments involves the Fe(III)/Fe(II) and Mn(IV)/Mn(II) couples, we are focusing on mineral phases containing these species. We are using a variety of experimental probes, along with molecular modeling theory, to determine clean mineral surface structure and morphology, details of the chemisorption and decomposition of water, and the interface structure and redox chemistry of important contaminants such as CrO_4^{-2} on these surfaces. Insight gained in this project will aid in the formulation of more accurate and realistic contaminant-surface complexation and contaminant transport models, and may suggest improved remediation strategies for certain kinds of contaminated soil and groundwater.

Research Progress and Implications

In what follows, we highlight the most important results obtained from June 1, 1997 to June 1, 1998, the second year of this three-year project. Detailed comparison of scanned-angle photoelectron diffraction (PED) measurements taken at the Advanced Light Source (ALS) with simulations employing quantum mechanical scattering theory reveal that a-Fe_2O_3(0001) (hematite) is terminated with a single layer of Fe atoms, and that the percentage relaxations of the first four layers are -41%, +18%, -8% and +47% of the respective bulk values. These rather large surface relaxations, which are similar in both magnitude and sign to those determined to exist on a-Al_2O_3(0001), are driven by the associated decrease in surface energy. We have calculated the surface energies of relaxed and bulk-terminated (unrelaxed) a- Fe_2O_3(0001) to be 1.64 and 4.24 J m^{-2}, respectively. An implication of this finding is that it is an outer layer of Fe(III) on basal-plane hematite that interacts with water, toxic anions and organics, rather than oxygen, as expected based on conventional wisdom. Scanning tunneling microscopy (STM) reveals that the Fe_3O_4(001) (magnetite) surface is terminated exclusively by either a tetrahedral iron or an octahedral iron layer with lattice oxygen, but not by both. Given that both the coordination number and the charge states of the iron in these layers are different, significant differences in the surface chemistry are expected depending upon the terminating layer. Determining which atomic layer constitutes the surface is the focus of both PED and STM experiments in the immediate future. Dramatic differences in the surface step density of Fe_3O_4 (001) can be achieved by using different MBE growth conditions. The resulting step densities (defined as the ratio of the number of atoms at a step edge to the total number in the surface) can vary from as high ~0.20 to lower than 0.05. The ability to systematically vary the step density is crucial to ultimately understanding the role of steps in the redox chemistry that occurs between magnetite and toxic anions and chlorinated organics. The measured threshold water vapor pressure s for the hydroxylation of a-Al_2O_3(0001) and a-Fe_2O_3(0001) surfaces have been measured by soft x-ray photoemission at the Stanford Synchrotron Radiation Laboratory (SSRL) to be 1 torr and 10E-4 torr, respectively. While the measured threshold pressure for a-Al_2O_3 is similar to the calculated threshold pressure for the conversion of a-Al_2O_3 to $Al(OH)_3$ based on an equilibrium thermodynamic model, the measured threshold pressure for a-Fe_2O_3 is more than five orders of magnitude lower than the calculated threshold pressure for the conversion of a-Fe_2O_3 to FeOOH or Fe(OH)3. This result is most likely due to the higher acidity of surface Fe(III) on a-Fe_2O_3(0001) relative to that of surface Al(III) on a-Al_2O_3(0001), which is corroborated by our molecular mechanics calculations. The reaction of water with (001) and (111)

surfaces of natural Fe_3O_4 prepared in ultrahigh vacuum was monitored using chemical shifts of O 1s and Fe 2p core-level photoemission spectra. We found that the initial reactions of water with these surfaces are quite similar to those for the a-Fe_2O_3(0001) and (1-102) surfaces and involve dissociation of water, indicating almost identical and small sticking coefficients. However, while hydroxyl coverages for a-Fe_2O_3 remain in the submonolayer range for water doses as high as 10E9 Langmuir, the Fe_3O_4(001) and (111) surfaces react very strongly with water, resulting in hydroxylation extending several layers deep. Cr L2,3-edge and O K-edge x-ray absorption fine structure (XAFS) studies, also carried out at SSRL, of the reaction of aqueous CrO_4^{-2} with Fe_3O_4(111) reveal that Cr(VI) in chemisorbed CrO_4^{-2} is very quickly reduced to Cr(III), and that the surface converts into a goethite-like phase. Grazing-incidence x-ray absorption fine structure (GI-XAFS) studies of CrO_4^{-2} on partially reduced a-Fe_2O_3(0001) reveal that substantial reduction of Cr(VI) to Cr(III) occurs. An implication of this result is that both magnetite and partially reduced hematite are effective at converting toxic, bioavailable Cr(VI) into less toxic and less bioavailable Cr(III). We have developed pulsed-laser photoacoustic spectrosc copy at the Environmental Molecular Sciences Laboratory (EMSL) to nondestructively monitor the levels of Cr(VI) in solutions contacting iron oxides. Initial experiments reveal that the technique can be used to: (i) measure adsorption affinity of anions on hematite surfaces, (ii) monitor the rate of Cr(VI) adsorption on hematite powder in real time, and, (iii) study the effect of competing anions, specifically phosphate, sulfate, and carbonate, on Cr(VI) uptake. Significantly, we now have a new tool to determine the effect of nontoxic, naturally occurring anions in blocking sorption sites for Cr(VI) on iron oxide surfaces.

We have developed a molecular mechanics model to predict the protonation/deprotonation energetics of the adsorption of oxoacids on solvated Fe oxide surfaces with realistic proton stoichiometries. This model was tested against hydrated Fe(II)- Fe(III)-(Cr,P,Si)O_4-H_2O crystal structures with generally good results, yielding lattice constants within 5% of experiment. The ability of this model to account for both the structure and protonation energetics in the tetrahedral oxyanions is remarkable and makes the ionic model a feasible option for future investigation of surface complexation reactions using molecular dynamics techniques. We have conducted exploratory work on the synthesis of thin-film pyrolusite (beta-MnO_2) on TiO_2(110) at the EMSL. Well-ordered, pseudomorphic overlayers form for substrate temperatures between 400°C and 500°C for coverages of up to 6 bilayers. Thicker films rapidly disorder due to the simultaneous formation of pyrolusite and ramsdellite, which is orthorhombic and not lattice matched to TiO_2(110). However, thin films of rutile pyrolusite are preferentially stabilized by the TiO_2 substrate. Being able to prepare these well-defined surfaces allows us to begin experiments to determine their redox potential compared to that of the Fe oxides.

Planned Activities

Immediate future activities will focus on high-resolution STM imaging at EMSL, PED at the ALS, and crystal truncation rod (CRT) x-ray scattering studies at the Advanced Photon Source (APS) of clean and water-exposed hematite and magnetite surfaces to determine the structural modifications caused by the hydroxylation process. We plan to fully analyze our GI-XAFS data on the interaction of Cr(VI) on synthetic thin-film hematite samples (reduced and unreduced) collected in March 1998, and to extend these studies to Cr(VI) interactions with thin-film magnetite. This work should lead to a model of Cr(III) surface complexes on reduced hematite and magnetite. We also plan to initiate a study of the reaction of TCE in solution with magnetite surfaces using C K-edge and Cl L-edge measurements. Our future LPAS experiments will focus sorption kinetics and equilibria measurements for Cr(VI) sorption on the MBE-synthesized hematite and magnetite thin films at ultra-trace levels of Cr(VI). Using our Fe(II,III)-(Cr,Si,P)O_4 potentials, which have now been rather rigorously tested on crystalline solids, in conjunction with our iron oxide-water potential models, we will conduct molecular dynamics investigations of chromate sorption to solvated hematite and magnetite surfaces. We plan to grow a-Fe_2O_3(0001) with substitutional Al by MBE, in order to determine the effect of this geochemically important impurity on redox chemistry.

Other Access To Information

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