Structures of the clean and hydroxylated α-Fe_2O_3 (0001) and ($1\bar{1}02$) surfaces: A density functional theory investigation

C.S. LO[1], A.M. CHAKA[1] AND T.P. TRAINOR[2]

[1]National Institute of Standards and Technology, Gaithersburg, MD 20899, USA (cynthia.lo@nist.gov, anne.chaka@nist.gov)
[2]Department of Chemistry, University of Alaska Fairbanks, Fairbanks, AK 99775, USA (fftpt@uaf.edu)

The structure and reactivity of metal oxides such as α-Fe_2O_3 depends on several factors, including the composition of the bulk material, crystallographic orientation, local coordination of the surface atoms, and topographic arrangement of the surface functional groups. In particular, the interaction of the surfaces with water is not well understood, because the majority of experimental and theoretical data has been on the corresponding UHV-prepared or clean surfaces. These interactions play major roles in environmental processes, including contaminant sequestration, mobility, and remediation, and biogeochemical cycling of contaminants and nutrients.

We have focused our studies on investigating the structure/reactivity relationship of iron oxide surfaces under conditions encountered in environmental settings. We present density functional theory studies of the structure of clean and hydroxylanted α-Fe_2O_3 (0001) and α-Fe_2O_3 ($1\bar{1}02$) surfaces, and the various H and metal coordinations leading to the lowest surface free energies. We also compare our theoretical results to those from crystal truncation rod diffraction data, and discuss the differences in structure between Fe_2O_3 and Al_2O_3 that may be responsible for the differences in surface reactivity.

References

X.-G. Wang, A.M. Chaka, M. Scheffler. (2000) Effect of the environment on α-Al_2O_3 (0001) surface structures. *Phys. Rev. Lett.* **84**, 3650–3653.

T.P. Trainor, P.J. Eng, G.E. Brown, Jr., I.K. Robinson, M.D. Santis. (2002). Crystal truncation rod diffraction study of the α-Al_2O_3 (1-102) surface. *Surf. Sci.* **496**, 238–250.

T.P. Trainor, A.M. Chaka, P.J. Eng, M. Newville, G.A. Waychunas, J.G. Catalano, G.E. Brown, Jr. (2004) Structure and reactivity of the hydrated hematite (0001) surface. *Surf. Sci.* **573**, 204–224.

Calcium oxalate surface interactions with lead

DAVID M. SINGER[1], JEFFEREY G. CATALANO[2] AND GORDON E. BROWN, JR.[1,3]

[1]Department of Geological and Environmental Scieces, Stanford University (dmsinger@stanford.edu, gordon@pangea.stanford.edu)
[2]Argonne National Laboratory (catalano@anl.gov)
[3]Stanford Synchrotron Radiation Laboratory

Calcium Oxalate (CaOx) is a significant biomineral produced by 2/3 of all plant families, and can comprise up to 80 weight percent of bulk plant tissue. Plants and fungi can also exude oxalate, which precipitates with Ca to form CaOx within the rhizosphere and in leaf litter. While CaOx has been shown to sequester lead (Pb), the nature and stability of these interactions is unclear, which is the focus of this model system study. Bulk uptake experiments have been conducted to determine the extent of Pb uptake by CaOx, and X-ray Absorption Spectroscopy has been used to determine the nature of the uptake reaction. Batch uptake experiments indicate that the uptake of Pb by CaOx is pH-independent over the pH range of 4 to 9, but increases as a step-function above pH 9. Regardless of the initial Pb concentration, 94 to 98% of the initial Pb in solution was removed below pH 9, and nearly 100% removed above. The removal of Pb in solution also corresponded to an increase in [Ca] in solution, but constant oxalate concentrations. Pb L_{III}-EXAFS indicated that the dominant Pb phase is the same at pH 4 and 6.5, but is different at pH 11. The spectra of the uptake samples at pH 4 and 6.5, can be fit well for a Pb-oxalate crystalline phase. We have used least-squares linear combination fitting to determine what phases are present in the high pH uptake sample, which is likely a combination of Pb-oxalate and Pb-hydroxide. We conclude that aqueous Pb exchanges for Ca at the CaOx surface, forming a Pb-oxalate coating. As Pb-oxalate is less soluble than CaOx, this is potentially a significant factor in the biogeochemical cycling of Pb in surface environments where CaOx is present. The formation of metal-oxalate precipitates in plants and soils versus the formation of less stable Pb surface complexes, could retard Pb mobility.