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Project Title: Contaminant Organic Complexes: Their Structure and Energetics in Surface Decontamination Processes

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Project Overview:

Siderophores are biological macromolecules (400-2000 Da) released by bacteria in iron limiting situations to sequester Fe from iron oxyhydroxides and silicates in the natural environment. These molecules contain hydroxamate and phenolate functional groups, and exhibit very high affinity for Fe³⁺. While several studies were conducted to understand the behavior of siderophores and their application to the metal sequestration and mineral dissolution, only a few of them have examined the molecular structure of siderophores and their interactions with metals and mineral surfaces in aqueous solutions. Improved understanding of the chemical state of different functional moieties in siderophores can assist in the application of these biological molecules in actinide separation, sequestration and decontamination processes. The focus of our research group is to evaluate the a) functional group chemistry of selected siderophores and their metal complexes in aqueous solutions, and b) the nature of siderophore interactions at the mineral-water interfaces.

We selected desferrioxamine B (desB), a hydroxamate siderophore, and its small structural analogue, acetohydroxamic acid (aHa), for this investigation. We examined the functional group chemistry of these molecules as a function of pH, and their complexation with aqueous and solid phase Fe(III). For solid phase Fe, we synthesized all naturally occurring Fe(III)-oxyhydroxides (goethite, lepidocrocite, akaganeite, ferroxylite) and hematite. We also synthesized Fe-oxides (goethite and hematite) of different sizes to evaluate the influence of particle size on mineral dissolution kinetics. We used a series of molecular techniques to explore the functional group chemistry of these molecules and their complexes. Infrared spectroscopy is used to specifically identify the variations in oxime group as a function of pH and Fe(III) complexation. Resonance Raman spectroscopy was used to evaluate the nature of hydroxamate binding in the case of Fe(III)-siderophore complexes and model ligands. Soft and hard X-ray spectroscopy techniques were used to examine the electronic structure of binding groups, and their local structural environment. The synchrotron X-ray studies were conducted at the Stanford Synchrotron Radiation Laboratory and at the Advanced Light Source (Lawrence Berkeley National Laboratory). These experimental vibrational and X-ray spectroscopy studies were complemented

with density functional theory calculations. The highlight of this study is the evaluation of the fundamental electronic state information of the hydroxamate moiety in siderophores during deprotonation and Fe(III) complexation. The applications of soft X-ray studies are also new, and were applied, for the first time, to examine the chemistry of organic macromolecules in aqueous solutions.

Accomplishments:

Vibrational Spectroscopy Studies of aHa, desB and their Fe(III) Complexes.

The vibrational spectroscopy studies focused on the vibrations of the C-O and N-O groups, and their changes with solution conditions. Our experimental and theoretical studies indicate that cis-keto-aHa is the dominant form of aHa in aqueous solutions, deprotonation occurs at O, and forms Fe(aHa)₃ complex in a wide range of pH conditions than previously assumed. Using the vibrational spectra, the amide and oxime groups can also be identified in desB. Based on amide group spectral changes, the conformational changes in desB are considered small. Enhanced delocalization in the oxime group of the Fe(desB)⁺ when compared to Fe(aHa)₃ may be responsible for higher stability constant of the former.

Soft, and Hard X-ray Spectroscopy of Siderophores and their Fe(III) Complexes.

Soft X-ray spectroscopy studies focused on the electronic transitions from C, N, and O 1s orbitals to empty molecular orbitals to identify the electronic states of different moieties in desB and aHa. These studies clearly indicate that the electronic state of the ligand changes significantly with deprotonation at the reactive group. This is primarily indicated by the electronic transitions of C, N, and O $1s \rightarrow \pi^*_{(C=O)NO}$ transition. These studies document that the functional groups of macromolecules can be studied using soft XAS studies.

Hard X-ray absorption spectroscopy (XAS) studies indicate that Fe(III) forms hexadentate complex with hydroxamate siderophore and a bidentate complex with acetohydroxamic acid. The coordination environment of Fe(III) is similar in these two complexes, however, the octahedron is more symmetric in the case of siderophore. Although Fe(aHa)₃ and Fe(desB)⁺ are stable complexes in the pH ranges of 2.8-10.1, and 1.4-11.4, respectively, soft X-ray spectroscopy studies indicate that the electronic structure of the ligand changes with changes in pH in the case of Fe(aHa)₃. These variations are attributed to the further deprotonation of aHa in alkaline solutions. Our studies also indicate that Fe 3d orbitals exhibit significant overlap with the molecular orbitals of the hydroxamate group.

Dissolution kinetics of Fe-Oxyhydroxides in the Presence of Hydroxamate Siderophores.

Surface area normalized dissolution rates of synthetic Fe-oxyhydroxides in the presence of aHa and desB indicated that the rate of Fe(III) release was highest in fine grained minerals than the coarse grained minerals. The rate of dissolution was greater for aHa than desB in the case of goethite while the opposite was true for hematite. All disordered iron oxides (ferrihydrite, akaganeite, ferroxhyte and fine grained goethite) also exhibit higher dissolution rates than coarse goethite. We are using this information to explore Fe(III) dissolution rates from Fe-coated sand in soils (Pine Barrens, NJ). Surface spectroscopy studies could not be conducted for aHa and desB on the surfaces of these minerals in aqueous solutions because of poor adsorption. Although we conducted such

studies on dried mineral suspensions, it was not possible to distinguish contributions from mineral adsorbed molecules from dried aqueous molecules.

Publications:

- (1) Edwards D. C. *Molecular Studies of Hydroxamate Siderophore Interactions with Aqueous and Solid Phase Iron*. Ph.D Thesis. Princeton University, Princeton, NJ (2005)
- (2) Edwards, D. C., Nielsen S. B., Jarzecki A. A., Spiro T. G., Myneni S. C. B. Experimental and theoretical vibrational spectroscopy studies of acetohydroxamic acid and desferrioxamine B in aqueous solutions: Effects of pH and iron complexation. *Geochim. Cosmochim. Acta* **69**: 3237-3248 (2005).
- (3) Edwards D. C., Myneni S. C. B. Hard and soft X-ray absorption spectroscopic investigation of aqueous Fe(III)-hydroxamate siderophore complexes (2005) *J. Phys. Chem. A* **109**: 10249-10256.
- (4) Edwards D. C., Myneni S. C. B. NEXAFS spectroscopy of bacterial hydroxamate siderophores in aqueous solutions. To be submitted shortly to *J. Phys. Chem. A*.
- (5) Edwards D. C., Cervini-Silva J., Nachimuthu P., Myneni S. C. B., Sposito G. The structure of aluminum substituted goethite. To be submitted shortly to *Environ. Sci. Technol.*
- (6) Edwards D. C., Myneni S. C. B. Dissolution of iron oxy hydroxides by acetohydroxamic acid and desferrioxamine B. In preparation and will be submitted to *Environ. Sci. Technol.*