Final Summary Report: DE-FG02-00ER15063
In-situ Evaluation of Soil Organic Molecules: Functional Group Chemistry Aggregate Structures, Metal & Surface Complexation Using Soft X-Ray

Satish C. B. Myneni
Department of Geosciences, Princeton University, Princeton, NJ 08544

1.0 Project Overview

Organic molecules are common in all Earth surface environments, and their composition and chemistry play an important role in a variety of biogeochemical reactions, such as mineral weathering, nutrient cycling and the solubility and transport of contaminants. However, most of what we know about the chemistry of these molecules comes from spectroscopy and microscopy studies of organic molecules extracted from different natural systems using either inorganic or organic solvents. Although all these methods gave us clues about the composition of these molecules, their composition and structure change with the extraction and the type of ex-situ analysis, their true behavior is less well understood. The goal of this project is to develop synchrotron instrumentation for studying natural organics, and to apply these recently developed synchrotron X-ray spectroscopy and microscopy techniques for understanding the:

- functional group composition of naturally occurring organic molecules
- macromolecular structures of organic molecules, and
- the nature of interactions of organic molecules with mineral surfaces in different environmental conditions.

2.0 Research Accomplished

Fabrication of the Synchrotron Endstation. Our group built a synchrotron endstation to examine the functional group composition of organic molecules in aqueous solutions and at particle-water interfaces. This endstation enables researchers to conduct XAS studies of light elements, such as C, N, in aqueous systems under realistic solution chemical conditions. The sample chamber is separated from the UHV part of the endstation, which is connected to the synchrotron beamline, by a 1600 A thick Si_3N_4 window. The sample chamber is maintained at 1 atm pressure of He during sample analysis. The solution and suspension samples are either sealed in a cell made with Si_3N_4 windows, or a flow through cell. The solids are examined by preparing thin smears either on C tape or on In foil. Using this endstation, we examined i) the functional group composition of several small and long chain synthetic organic molecules and the naturally occurring organic macromolecules from fluvial and soil systems and their metal complexes, ii) H-bonding networks in liquid water, and iii) the solvation of metal ions in water.

Functional group composition. Our X-ray spectroscopy studies, in combination with 2-D NMR and IR spectroscopy, have provided new evidence for certain functional groups and their dynamics in naturally occurring organic molecules.

Information obtained from the C X-ray spectra is not novel for the C- functional groups (e.g. carboxyls), since the same groups were also identified using the NMR and IR spectroscopy before. However, the X-ray methods allowed in-situ studies of these molecules directly when they are present in soil or sediment samples while the other

methods could not. Using the NMR and IR spectroscopy, we focused on the nature of carboxylic acid structures in fluvial and soil humic substances. Our studies suggest that a significant fraction of carboxyls contain substituents, such as OH and COOH, on the α-carbon, which makes these carboxyls highly reactive, and can assist in metal chelation by carboxyls. Our X-ray studies on N, P, and S groups indicated unique functional group information and we identified aromatic N in addition to aliphatic moieties (identified by previous NMR studies), phosphate esters and phosphonates, and reduced and oxidized S moieties.

We also examined the Cl moieties in the natural organics and the detailed molecular structure and composition of naturally formed organohalogens. We found that Cl^- in plants and other biological systems convert to organo-Cl during weathering. Although we could not identify the organisms or the reactions responsible for these reactions, we successfully halogenated plant material using haloperoxidase enzymes isolated from *Caldaiomyces fumago*. We also developed X-ray based techniques for the quantification of natural organohalogens, and these techniques helped in the evaluation of rates of organohalogen formation in forest ecosystems. We also found the brominated and iodinated compounds in marine and terrestrial systems, and we are in the process of publishing these results.

Macromolecular structure. Our X-ray microscopy studies of fluvial and soil humic substances showed that humic substances change their aggregate structures based on the solution pH, ionic strength of solution and the type of metal ions, and the presence of minerals. We could also identify the organo-mineral interactions in soil aggregates under different solution chemical conditions.

Structure of water and solvation of metal ions in water. Since our new synchrotron endstation also allowed the examination of O-XAS, we also examined the nature of H-bonding networks in liquid water, and the nature of solvated water around metal ions. Our studies revealed new information on H-bonding in liquid water, which indicated that the tetrahedral structure of water is disturbed for a significant fraction of water molecules. Studies on ice and gas phase water and complementary DFT studies on water supported these observations. Ion solvation studies on different mono-, di-, and tri-valent ions indicate that these ions disturb the water structure and, especially in the case of transition metal ions, covalent bonds are also observed with solvated water molecules.

3.0 Future Directions

The future studies of our group will focus on the understanding the details of the functional groups of N, P and S, and their cycling/transformation during weathering reactions in soils and aquatic systems, and the reactions of organic molecules with different mineral surfaces and how this influences the structure and stability of different classes of organic molecules. We are also interested in identifying of the molecular structures of organohalogens and in examining the processes involved in the formation of organohalogens and their ultimate fate.

4.0 Participated Researchers

Post-doctoral Scholars

Timothy Strathmann (Assistant Professor at University of Illinois, Urbana-Champaign)
Ashish Deshmukh (Research Scientist at ENVIRON International Corp., Columbus, OH)

Graduate Students

Rachel Reina (M. Eng, Fall 2003)
David Edwards (Ph. D, Fall 2005)
Michael B. Hay (Ph. D, Spring 2007)
Alessandra Leri (Ph. D, Spring 2007)
Hay and Leri also received NSF Graduate Student Fellowships ad EPA STAR fellowships in addition to this support.

Undergraduate Students

Jacqueline A. Hakala (Completed Ph.D at Ohio State University)
Rachel Zwillinger (completed Environmental Law at Stanford University)

5.0 Publications

1) Hay M. B., Myneni SCB. Structural environments of carboxyl groups in organic molecules from terrestrial systems: Part I: Infrared spectroscopy, ***Geochim. Cosmochim. Acta*** 71: 3518-3532 (2007).
2) Deshmukh, Hay M. B., Myneni SCB. Structural environments of carboxyl groups in organic molecules from terrestrial systems: Part II: NMR spectroscopy, ***Geochim. Cosmochim. Acta*** 71: 3533-3544 (2007).
3) Edwards D. C., Myneni S. C. B. Near Edge X-ray Absorption Fine Structure Spectroscopy of bacterial hydroxamate siderophores in aqueous solutions. ***J. Phys. Chem. A*** 110: 11809-11818 (2006).
4) Cavalleri M., Naslund L. A., Edwards D. C., Wernet P., Ogasawara H., Myneni SCB., Ojamae L., Odelius M., Nilsson A., Pettersson LGM. The local structure of protonated water from X-ray absorption and density functional theory. ***J. Chem. Phys.*** **124** (19) 194508 (2006).
5) Leri A. C., Hay M. B., Lanzirotti A., Rao W., Myneni S. C. B. Quatitative speciation of absolute organohalogens concentrations in environmental samples by X-ray absorption spectroscopy. ***Anal. Chem***. **78**: 5711-5718 (2006).
6) 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).
7) Edwards D. C., Myneni S. C. B. Hard and soft X-ray absorption spectroscopic investigation of aqueous Fe(III)-hydroxamate siderophore complexes ***J. Phys. Chem. A*** **109**: 10249-10256. (2005).
8) Strathmann T. J., Myneni S. C. B. Effect if soil fulvic acid on nickel (II) sorption and bonding at the aqueous-boehmite (γ-AlOOH) interface. ***Environ. Sci. Technol. 39***: 4027-4034 (2005).
9) Naslund L., Edwards D. C., Wernet P., Bergmann U., Ogasawara H., Pettersson L. G. M., Myneni S. C. B., Nilsson A. X-ray absorption spectroscopy study of the hydrogen bond network in the bulk water of aqueous solutions. ***J. Phys. Chem. A*** **109**: 5995-6002 (2005).

10) Strathmann T., Myneni SCB. Speciation of aqueous Ni(II)-Carboxylate and Ni(II)-Fulvic Acid Solutions: Combined ATR-FTIR and XAFS Analysis. ***Geochim. Cosmochim. Acta*** **68**: 3441-1458, (2004).
11) Reina R., Leri A, Myneni SCB. Cl K-edge X-ray spectroscopic investigation of enzymatic formation of organochlorines in weathering plant material. ***Env. Sci. Technol***. **38**: 783-789 (10.1021/es0347336), (2004).
12) Maria S, Russell LM, Gilles MK, Myneni SCB. Organic aerosol growth mechanisms and their climate forcing implications. ***Science*** **306**: 1921-1924 (2004).
13) Naslund LA, Cavalleri M, Ogasawara H, Nilsson A, Pettersson LGM, Wernet P, Edwards DC, Sandstrom M, Myneni SCB. Direct evidence of orbital mixing between solvated transition-metal ions: An Oxygen 1s XAS and DFT study of aqueous systems. ***J. Phys. Chem*** *A*, **107**: 6869-6876 (Cover page article), (2003).
14) Myneni SCB. Soft X-ray spectroscopy and spectromicroscopy studies of organic molecules in the environment. In ***Rev. Mineral. Geochem***. Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science, Ed P. Fenter, M. Rivers, N. Sturchio, S. Sutton, **49**: 485-579, (2002)
15) Myneni SCB. Formation of stable chlorinated hydrocarbons in weathering plant material. ***Science***, **295**, 1039-1041 (Science Express, published online 17 January 2002; 10.1126/science.1067153), (2002).
16) Myneni SCB, Luo Y, Naslund LA, Ojamae L, Ogasawara H, Pelmenshikov A, Vaterlain P, Heske C, Pettersson LGM, Nilsson A. Spectroscopic evidence for unique hydrogen bonding structures in water. ***J. Phys****.: Condens. Matter*, **14**, L213-L219, (2002).
17) Myneni SCB.. X-ray and vibrational spectroscopy of sulfate in earth materials. In: ***Rev. Mineral.*** Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance, ed. C. N. Alpers, J. L. Jambor, and D. K. Nordstrom, Vol 40: 113-172, (2000).
18) Myneni SCB., Brown J., Martinez GA., and Meyer-Ilse. W. Imaging of Humic Substance Macromolecular Structures in Water and Soils, ***Science***, **286**, 1335-1337, (1999).

6.0 Invited Presentations

2007

- Department of Civil Engineering & Geological Sciences, University of Notre Dame
- User's Conference, Stanford Linear Accelerator Center, Stanford
- Workshop on spectromicroscopy studies in the soft X-ray region, Stanford Linear Accelerator Center, Stanford
- Advanced Photon Source, Argonne National Laboratory, Chicago
- Workshop on Tender X-ray Spectroscopy, National Synchrotron Light Source, Brookhaven National Laboratory

2006

- European Mineralogical Society Meetings (Bath, UK)
- Keynote, World Congress of Soil Science, Philadelphia
- Keynote, Frontiers in Geochemistry. American Chemical Society National Meetings, San Francisco.
- Workshop on Spectromicroscopy, Advanced Photon Source, Argonne National Laboratory, Chicago.
- National Synchrotron Light Source, Brookhaven National Laboratory

2005

- United Kingdom Synchrotron Research User's Conference (had to be cancelled in the last minute because of health problem)
- BES Workshop on Surface and Interfacial Sciences
- Goldschmidt Conference, Moscow, Idaho
- Pacifichem Conference, Hawaii

2004

- State University of New York, Stony Brook
- Canadian Light Source, University of Saskatchewan
- Soil Science Society of America, Symposium on Biogeochemical Cycling of Elements in Soils, Seattle
- Stanford Synchrotron Radiation Laboratory
- Workshop on Frontiers in Soft X-ray, VUV, and Infrared Research; Synchrotron Research Center, University of Wisconsin, Madison, WI
- Gordon Research Conference, Organic Geochemistry
- Gordon Research Conference, Environmental Chemistry (Water)
- Scientific Advisory Committee, Advanced Light Source, Berkeley
- Clay Minerals Society Symposium on Microbe-Mineral Interactions, Richland
- DOE/NSF Workshop on Research Facilities in Geosciences, Washington DC
- Future Directions in Actinide Chemistry, NSF/DOE Workshop, May (Could not attend)
- Department of Geosciences, University of Chicago, May (Could not accept)
- Key Note Speaker, International Humic Substance Society Conference, Boston

2003

- Turner Lecture, Department of Geological Sciences, University of Michigan, MI
- Environmental Research Division, Argonne National Laboratory, Argonne, IL
- Telluride Conference on Aqueous Geochemistry, Telluride, CO
- NABIR(DOE)/ Stanford Synchrotron Radiation Laboratory Workshop (could not attend)
- American Chemical Society, Princeton Chapter
- Guest Lecture, Center for Environmental Molecular Science, State University of New York, Stony Brook
- Mesilla Conference on Interfacial Phenomena, Mesilla de Mesilla, NM
- Arogonne National Laboratory/DOE Workshop, Argonne, IL

2002

- Goldschmidt Conference, Switzerland
- Mineralogical Society of America, Monterey, CA
- National Synchrotron Light Source, Brookhaven National Laboratory, Brookhaven, NY

2001

- Department of Soil & Environmental Sciences, University of Delaware
- Goldschmidt Conference, VA
- Department of Civil & Environmental Engineering, Johns Hopkins University, Baltimore, MD

2000

- International Conference on Electron Spectroscopy, Berkeley, CA
- Mineralogical Society of America, Geochemistry of Sulfate, Lake Tahoe, CA

- ETH, Switzerland (could not attend because of VISA related issues and teaching duties)
- DOE (Basic Energy Sciences) Workshop on Surface Chemical Processes, Washington, DC
- XAS Workshop on sulfur containing systems, Stanford Synchrotron Radiation Laboratory, Stanford, CA
- Advanced Photon Source, User's Conference, Chicago
- American Chemical Society, Washington, DC.

1999

- International Conference on X-ray Microscopy, Berkeley
- Department of Geological and Environmental Sciences, Stanford University, Stanford, CA
- Department of Civil and Environmental Engineering, Stanford University
- User's Conference, Advanced Light Source
- User's Conference, Stanford Synchrotron Radiation Laboratory, Stanford, CA

1998

- Department of Geological and Environmental Sciences, Stanford University, Stanford, CA
- Department of Earth Sciences, Pennsylvania State University, PA
- Department of Geosciences, Princeton University, Princeton, NJ
- DOE/ NABIR workshop on biogeochemistry of contaminated systems, Washington DC
- DOE (Basic Energy Sciences) Workshop on Aqueous Geochemistry & Interfacial Phenomena, Pascoe, WA
- Department of Environmental Science, Policy and Management, University of California, Berkeley
- American Chemical Society National Meetings