

# **ACS DIVISION OF GEOCHEMISTRY**

## **FALL 2003 NEWSLETTER**



**224<sup>th</sup> NATIONAL ACS MEETING**  
**September 7<sup>th</sup>-11<sup>th</sup>**  
**New York, New York**

### **In This Issue**

- Message from the Chairperson
- Upcoming Symposia and Message from the Program Chair
- New York Program
- New York Abstracts
- Division Officers and Contact Information

## Message from the Chair

Message from Bill Landing, 2003 Division Chair:

Greetings from the Division Executive Committee.

Our division continues to thrive, with tremendous turnout for the two national meetings this year. The March 2003 New Orleans meeting included 10 symposia (with an additional 7 co-sponsored symposia) and 198 abstracts. The meeting featured the Geochemistry Award Symposium honoring John Hayes, and the reception and banquet that followed on Tuesday evening 3/25/03. One of the advantages of being division chair is that I was in charge of booking the band for the reception, and I knew they would let me sit in with my tenor sax. I thank everyone who participated at the New Orleans meeting.

Our 2003 Program Chair, Susan Carroll, has arranged a strong line-up for the September 7-11, 2003 meeting in New York City featuring 147 abstracts distributed among symposia on arsenic geochemistry, interfacial biogeochemistry, molecular environmental surface chemistry, carbon dioxide sequestration, and a substantial poster session.

We are working on the March 28-April 1, 2004 meeting in Anaheim, CA and Philadelphia, PA meeting in August 22-26, 2004. If you have an idea for a symposium or would like to be involved in program planning, contact Susan (carroll6@lnl.gov). With electronic abstract submittal, organizing a symposium at a national meeting is easy. Remember that funds are available through the ACS Petroleum Research Fund (PRF) to support symposia at national meetings (up to \$3600). We are happy to assist all symposium organizers in submitting an application. This money can be used to pay expenses for invited European speakers or to support symposium-related activities. The division also supports each half-day session with \$300.

If you are getting this newsletter, then you are already a Geochemistry Division member. But our division needs more members. Please encourage your friends, colleagues, and students to join and support the Division. The Geochemistry Division exists to serve its members and the broader community of geochemists, and we are interested in your suggestions and support. Let us know if you want to run for an office, organize a symposium, or contribute in any way to the success of the Division. Check the GEOC web site frequently for up-to-date information: <http://membership.acs.org/g/geoc/>

## Planned Symposia for the Fall '03 and Spring '04 American Chemical Society Meetings

New York City 2003 and Anaheim 2004  
American Chemical Society Meetings  
Susan Carroll, Program Chair

We have an excellent program for the New York American Chemical Society meeting from September 7 - 11, 2003 with symposia on arsenic chemistry (Sunday - Tuesday AM), interfacial biogeochemistry (Tuesday PM), molecular environmental surface chemistry (Wednesday), CO<sub>2</sub> sequestration (Thursday), and a large poster session/social hour on Tuesday night. The poster session consists of over 40 presentations with contributions from most of our symposia and several additional presentations that were initially submitted to the symposium on the Geochemical and Environmental Applications of Nuclear Magnetic Resonance. The Geochemistry Division technical program and abstracts are also included in this newsletter for your review. Additionally, there are several symposia in the Environmental Chemistry Division (Biogeochemistry of Chelating Agents, Chemistry at the Watershed Level, Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface, Targeting Chemical and Biological Warfare Agents, Urban Aerosols and Their Impact: Lessons learned from the World Trade Center), the Fuel Chemistry Division (Environmental Issues in Fossil Fuel Utilization) and the Nuclear Chemistry Division Symposia (Environmental Management Science Program on Nuclear Waste Management, Environmental Radioactivity and Low-background radioactivity – Monitoring in Service to the Society) that are of interest to many of our members.

If you plan to attend the meeting in New York, I encourage you to sign up for the Geochemistry Division Dinner on Monday evening which has been organized and sponsored by the symposium on

**Advances in Arsenic Research.** This symposium is a joint effort by the Environmental Chemistry and Geochemistry Divisions and is open to interested conference attendees. You can sign up for the dinner when you register for the conference.

We continue to solicit symposia ideas for the spring 2004 meeting in Anaheim CA (March 28 – April 1, 2004). To-date we have several topics covering, aquatic and environmental geochemistry, microbial mediated chemistry, vibrational spectroscopy, fate and transport of colloids, and scaling issues important to the application of molecular mechanisms to field scale reactions. If you and your colleagues are interested in organizing a symposium for the Anaheim meetings please contact me as soon as possible ([carroll6@llnl.gov](mailto:carroll6@llnl.gov)).

Anaheim CA Spring Meeting, March 28-April1, 2004

#### Geochemistry Division Symposia

- Chemistry of Metals in Terrestrial and Aquatic Systems (Dr. Stephan M. Kraemer and Bernd Novack, Institute of Terrestrial Ecology, ETH [stephan.kraemer@ito.umnw.ethz.ch](mailto:stephan.kraemer@ito.umnw.ethz.ch))
- Microbially Mediated Manganese and Iron Oxidation in the Biosphere (John Bargar, [bargar@SLAC.stanford.edu](mailto:bargar@SLAC.stanford.edu), Stanford Synchrotron Radiation Laboratory, Brad Tebo, Scripps Institute of Oceanography, [btebo@ucsd.edu](mailto:btebo@ucsd.edu), Garrison Sposito, University of California, [gsposito@nature.berkeley.edu](mailto:gsposito@nature.berkeley.edu), Mario Villalobos, Ciudad Universitaria, Mexico, [marvilla@igiris.igeograf.unam.mx](mailto:marvilla@igiris.igeograf.unam.mx))
- Colloid-Facilitated Transport of Contaminants in the Subsurface: The Life and Death of a Colloid (Annie Kersting, Lawrence Livermore National Laboratory [kersting1@llnl.gov](mailto:kersting1@llnl.gov) and Edgar C. Buck, Pacific Northwest National Laboratory [edgar.buck@pnl.gov](mailto:edgar.buck@pnl.gov))
- Vibrational Spectroscopy in the Earth and Environmental Sciences (Derek Peak, University of Saskatchewan, Canada, [derek.peak@usask.ca](mailto:derek.peak@usask.ca), Michael J. Borda, University of Delaware, [mike@pbisotopes.ess.sunysb.edu](mailto:mike@pbisotopes.ess.sunysb.edu))
- Scaling Issues: Application of Molecular Geochemistry to Field Scale Transport (Bruce Honeyman, Colorado School of Mines [honeyman@mines.edu](mailto:honeyman@mines.edu))

Philadelphia 2004  
James Kubicki

James Farquhar - U of MD - Mass-independent isotope fractionation Aravind Asthagiri - Geophysical Laboratory - Astrobiology & the origin of life Dan Strongin - Temple

Surface Spectroscopy James Kubicki - PSU - Molecular Modeling in Environmental Chemistry

## New York National Meeting Program and Abstracts

### DIVISION OF GEOCHEMISTRY

Final Program, 226th ACS National Meeting, New York, NY, September 7-11, 2003

S. A. Carroll, *Program Chair*

#### **SOCIAL EVENTS:**

Executive Meeting: Sunday 6PM

Dinner: Monday, 6PM

Poster/Social Hour: Tuesday, 6PM

Business Meeting: Wed., 5:30 PM

#### **SUNDAY MORNING**

##### **Section A**

Javits Convention Center -- 1A25

**Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation**

##### **1. Speciation and Adsorption Studies**

Cosponsored with ENVR, and IEC

L. G. Benning, Organizer, *Presiding*

P. A. O'Day, X. Meng, and D. Vlassopoulos, *Organizers*

8:00 — Introductory Remarks.

8:05 —1. Arsenous acid deprotonation and stability from 25 to 300°C. V. P. Zakaznova-Iakovleva, T. M. Seward, O. M. Suleimenov

8:25 —2. Computed and observed redox chemistry of methyl arsenic species. P. M. Dombrowski, D. M. Di Toro, K. J. Farley, J. D. Mahony, L. Wei

8:45 —3. Effect of thioarsenite formation on As(III) toxicity. K. J. Rader, P. M. Dombrowski, K. J. Farley, J. D. Mahony, D. M. Di Toro

9:05 —4. Organoarsenic, the missing link? What happens when the Fe hydroxide model does not work? P. Louchouart, J. Brandenberger, B. Herbert, A. Patterson

9:25 —5. Arsenic transformation by algae: The role of phosphorus luxury uptake. F. L. Hellweger, K. J. Farley, U. Lall, D. M. Di Toro

9:45 — Intermission.

9:55 —6. Arsenic speciation in porewaters of a freshwater sediment. S. Chow

10:15 —7. Calculation of the interaction of arsenites and arsenates with Al hydroxide surfaces. J. A. Tossell

10:35 —8. Modeling surface complexes of As(III) and As(V) with Al- and Fe-oxides. J. D. Kubicki

10:55 —9. Competitive sorption of Fe(II) and As(III) on goethite: Implications for arsenic mobilization in reducing environments. S. Dixit, J. G. Hering

11:15 —10. Arsenate and arsenite sorption and arsenite oxidation by Fe(II)-Fe(III) hydroxycarbonate green rust. C. Su, R. T. Wilkin

11:35 —11. Adsorption of Arsenic by Nanocrystalline Titanium Dioxide. X. Meng, C. Jing, M. E. Pena

## Biogeochemistry of Chelating Agents

### Speciation

Cosponsored with ENVR

## SUNDAY AFTERNOON

### Section A

Javits Convention Center -- 1A25

Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation

### 2. Occurrence, Cycling, and Natural Attenuation

Cosponsored with ENVR, and IEC

P. A. O'Day, Organizer, *Presiding*

X. Meng, D. Vlassopoulos, and L. G. Benning, *Organizers*

1:15 — Introductory Remarks.

1:20 —12. Arsenic adsorption on natural riverine suspended particulate material (SPM). J. G. Webster

1:40 —13. Arsenic cycling within surface and subsurface environments: Impact of iron mineralogy. S. Fendorf, M. Polizzotto, M. J. Herbel, B. C. Bostick, C. Harvey

2:00 —14. Bioavailability and sources of arsenic in reactive-iron limited sediments of the coastal plain of South Texas. B. Herbert, L. Lee, P. Louchouart, G. Moore, C. Markley, M. Roberts

2:20 —15. Spatial variability of arsenic concentrations and sediment properties in Bangladesh aquifers. A. van Geen, A. Horneman, Z. Aziz, M. A. Hoque, M. Shamsudduha, Z. Cheng, R. K. Dhar, R. Versteeg, M. Steckler, B. Mailloux, Y. Zheng, M. Stute, S. L. Goodbred, K. M. Ahmed

2:40 —16. Depth profiles of dissolved and particulate inorganic arsenic in Bangladesh aquifers. Y. Zheng, R. K. Dhar, Z. Mo, Z. Cheng, M. A. Hoque, M.

Shamsudduha, A. van Geen, M. Stute, K. M. Ahmed

3:00 —17. Geological controls on the occurrence and distribution of high arsenic in shallow groundwater: Araihasar, Bangladesh. S. L. Goodbred Jr., B. Weinman, A. van Geen, R. Versteeg, Y. Zheng, M. Stute, K. M. Ahmed

3:20 — Intermission.

3:30 —18. Pollution of groundwater by arsenic: a small-scale survey in West Bengal. J. M. McArthur, D. M. Banerjee, K. H. Hudson-Edwards, P. Ravenscroft

3:50 —19. Importance of mica surfaces in the propagation of a natural arsenic plume in West Bengal, India. L. Charlet, S. Chakraborty, D. Chatterjee, B. Mallik, T. Appello, S. Varma

4:10 —20. Occurrence, sources, mobilization and transport of arsenic in the Newark Basin in New Jersey. M. Serfes, S. Spayd, G. Herman

4:30 —21. Arsenic mobilization under reducing conditions beneath a landfill in Maine. A. R. Keimowitz, S. Datta, M. Stute, H. J. Simpson, S. N. Chillrud, M. Tsang, J. Ross

4:50 —22. Arsenic in groundwater in southeastern Wisconsin: Sources of arsenic and mechanisms of arsenic mobilization. T. L. Root, J. M. Bahr, M. Gotkowitz

## Biogeochemistry of Chelating Agents

### Reactions

Cosponsored with ENVR

## MONDAY MORNING

### Section A

Javits Convention Center -- 1A25

## Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation

### 3. Occurrence, Cycling, and Natural Attenuation

Cosponsored with ENVR, and IEC

A. Van Geen, *Presiding*

P. A. O'Day, D. Vlassopoulos, L. G. Benning, and X. Meng, *Organizers*

8:00 — Introductory Remarks.

8:05 —23. The molecular biology and biochemistry of bacterial respiratory arsenate reduction. C. W. Saltikov, D. Malasarn, D. K. Newman

8:25 —24. Anaerobic geochemistry and microbiology of arsenic in Holocene alluvial aquifers: Origin of natural contamination and remediation implications. J. A. Saunders, S. Mohammad, M. Lee, N. E. Korte

8:45 —25. Microbial mobilization of arsenic from mine tailings under aerobic conditions. J. Routh, A. Saraswathy

9:05 —26. Arsenic release coupled with biodegradation of organic compounds in contaminated groundwater plumes. J. L. deLemos, C. Renshaw, B. C. Bostick, S. Sturup, X. Feng

9:25 —27. Natural attenuation as a strategy for managing arsenic-contaminated groundwater. J. G. Hering

9:45 — Intermission.

9:55 —28. Natural attenuation of arsenic under fluctuating redox conditions in contaminated estuary sediments. R. Root, P. A. O'Day, N. A. Rivera Jr., D. Vlassopoulos

10:15 —29. A general biogeochemical model for arsenic cycling in shallow aquifers.

P. A. O'Day, D. Vlassopoulos

10:35 —30. Speciation and distribution of arsenic in the Mahomet Aquifer, Illinois.

T. R. Holm, W. R. Kelly, S. D. Wilson, G. S. Roadcap, J. L. Talbott, J. W. Scott

10:55 —31. Redistribution of arsenic in soils by natural hydrogeologic processes.

K. A. Doherty, R. Hon

11:15 —32. Vertical migration and speciation of smelter-ash arsenic in island soils of Puget Sound, Washington. B. T. Beaulieu, K. S. Savage

11:35 —33. Arsenic geochemical behavior in semiarid soils contaminated by mine processing wastes. F. Romero, M. Gutiérrez-Ruiz, P. Fernández-Lomelín, M. Villalobos

### Biogeochemistry of Chelating Agents

### Microbiology/Toxicology

Cosponsored with ENVR

## MONDAY AFTERNOON

### Section A

Javits Convention Center -- 1A25

## Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation

### 4. Treatment of Water and Soils

Cosponsored with ENVR, and IEC

X. Meng, *Organizer, Presiding*

P. A. O'Day, D. Vlassopoulos, and L. G. Benning, *Organizers*

1:25 — Introductory Remarks.

- 1:30 —34. Arsenic uptake processes in reducing environments: Implications for active remediation and natural attenuation. R. T. Wilkin
- 1:50 —35. Assessment of safe water options for villages in Bangladesh. P. T. Crisp, A. H. Chowdhury, A. Lau, Q. Quamruzzaman
- 2:10 —36. Characterization of arsenic containing water treatment residuals. H. Wee, T. A. Kramer
- 2:30 —37. Subsurface arsenic speciation analysis. N. Xu, C. Su, J. Hong, R. Wilkin
- 2:50 —38. Mechanisms of organic arsenic adsorption on nanocrystalline titanium dioxide. C. Jing, S. Baidas, X. Meng
- 3:10 — Intermission.
- 3:20 —39. In situ arsenic removal by zerovalent iron: An accelerated pilot test simulating long-term permeable reactive barrier performance. D. Vlassopoulos, C. B. Andrews, M. Rafferty, P. A. O'Day, N. A. Rivera Jr.
- 3:40 —40. Transport of As(III) and As(V) in experimental subsurface systems. M. O. Barnett, T. Radu, J. K. Yang, J. C. Hilliard
- 4:00 —41. Uptake of arsenic by *Pteris cretica*: in situ XANES study of living plants. M. A. Kissell, M. Fuhrmann, R. J. Reeder
- 4:20 —42. Arsenic uptake, hyperaccumulation, and detoxification in Chinese Brake fern: an mechanistic approach. Y. Cai, W. Zhang, J. Su, M. Feng, L. Q. Ma, K. Downum
- 4:40 —43. Phytofiltration of arsenic from drinking water. M. P. Elless, C. Y. Poynton, M. J. Blaylock

## Biogeochemistry of Chelating Agents

### Soils

Cosponsored with ENVR

## TUESDAY MORNING

### Section A

Javits Convention Center -- 1A25

Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation

## 5. Treatment of Water and Soils

Cosponsored with ENVR, and IEC

D. Vlassopoulos, Organizer, *Presiding*

P. A. O'Day, X. Meng, and L. G. Benning, *Organizers*

8:20 — Introductory Remarks.

8:25 —44. Photoactive removal of As(III) from water using novel active material. M. A. Anderson, E. Lee, T. J. Lee, I. Tejedor, T. Holm

8:45 —45. Chemistry of a simple and effective groundwater arsenic filter Based on iron composites: A large scale Bangladesh experiment. A. Hussam, A. K. M. Munir, M. Alauddin, Z. A. Hossain, A. H. Khan, C. C. Chusuei

9:05 —46. Comparison of pilot and rapid small scale column tests (RSSCTs) for arsenic removal by porous iron oxides (GFH and E-33). P. Westerhoff, M. Badruzzaman

9:25 —47. Pilot scale study of polymer enhanced ultrafiltration process for the removal of arsenic from ground water. H. D. Gallo, E. J. Acosta, J. F. Scamehorn, D. A. Sabatini

9:45 — Intermission.

9:55 —48. Removal of arsenic anions from water using polyelectrolyte-enhanced ultrafiltration. J. F. Scamehorn, P. Pookrod, K. J. Haller

10:15 —49. Removal of arsenic(V) from drinking water by clay membranes. J. Fang, B. Deng

10:35 —50. Utility of Zeolites in arsenic removal from water. S. S. Shevade, R. Ford

**10:55 —51. A new highly selective resin for the removal of arsenate in groundwater. S. D. Alexandratos, L. Dambies**

**11:15 —52. Metals Remediation Compound (MRC™): A new slow release product for in situ metals remediation. A. Willett, S. S. Koenigsberg**

**11:35 —53. Evaluation of the effectiveness of quicklime-based stabilization/solidification (S/S) in arsenic (As) contaminated soils. D. H. Moon, D. Dermatas**

**Chemistry at the Watershed Level**

**Cosponsored with ENVR**

**Targeting Chemical and Biological Warfare Agents**

**Cosponsored with ENVR**

## TUESDAY AFTERNOON

### Section A

Javits Convention Center -- 1A25

**Interfacial Biogeochemistry: Biogeochemical Processes that Occur at Interfaces and Implications Toward Environmental Processes**

Cosponsored with BIOL, and ENVR

A. Neal and C. Cooper, *Organizers*

1:00 — Introductory Remarks.

1:05 —54. Consequences of disorder in biological reactions for chemical transport in unsaturated porous and fractured geologic media. R. A. LaViolette, D. L. Stoner

1:30 —55. Microbial biofilms: geochemically reactive environmental interfaces.

L. A. Warren, E. A. Haack

1:55 —56. Bacterial-silica interactions: Affinity or Fate? L. G. Benning, V. Phoenix,

N. Yee, O. Hammer

2:20 —57. Rapid oxidation of pyrite surfaces by *Thiobacillus ferrooxidans* and *T. thiooxidans*. B. C. Bostick, K. Lester, C. Doyle, T. Kendelewicz, G. E. Brown Jr.,

S. Fendorf, A. M. Spormann

2:40 —58. Accelerated calcite dissolution caused by alginic acid. T. D. Perry, O. W. Duckworth, C. J.

McNamara, S. T. Martin, R. Mitchell

3:00 —59. Interactions of polysaccharides and polypeptides with silica and Fe-oxide surfaces. J. D.

Kubicki, R. K. Campen, K. Kwon

3:20 —60. Modeling Reactive Ionic Diffusion within Bacterial Electrical Double-Layer. C. Liu, A. R. Felmy, J. M. Zachara

3:40 —61. Metal adsorption to kaolinite in the presence of siderophores. S. Hepinstall,

P. A. Maurice

4:00 —62. Reduction of ColIIEDTA Coupled with Microbially Mediated Goethite Reduction. A. Ito, F. Huang, B. Deng

4:20 —63. Transformation of RDX by biologically produced ferrous iron species. K. B. Gregory, A. G. B.

Williams, G. F. Parkin, M. M. Scherer

4:40 —64. Spatial comparison of sedimentary fatty acid profiles in the coastal mid-Atlantic (USA) Potomac River basin. G. D. Foster, C. L. Walls

5:00 — Concluding Remarks.

## Targeting Chemical and Biological Warfare Agents

Cosponsored with ENVR

## TUESDAY EVENING

### Section A

Javits Convention Center -- North Pavillion

### Poster Session

Cosponsored with ENVR

R. Maxwell, P. A. O'Day, R. J. Reeder, and C. Cooper, *Presiding*

S. Carroll, *Organizer*

6:00 - 8:00

65. Multinuclear NMR investigation of speciation in lead aluminoborosilicate glasses.

A. M. Sawvel, R. Maxwell, W. L. Bourcier

66. NMR detection of chemical weapons manufacturing byproducts in environmental media. S. C. Chinn, M. L. Davison, J. G. Reynolds, C. J. Koester, A. H. Love, R. Maxwell, A. L. Vance
67. NMR Investigation of Metal Complexation with Natural Organic Matter. X. Xu, R. J. Kirkpatrick
68. Possible Al-F bonding environments in F-bearing Na-aluminosilicate glasses from calculation of  $^{19}\text{F}$  NMR shifts. J. A. Tossell, Y. Liu
69. Solid state aluminum-27 NMR studies of the aluminum distribution in aluminosilicates. B. A. Gee
70. Adsorption of heavy metals on iron oxide coated silica. Y. Xu, L. Axe, S. Maeng, P. Trivedi, T. Boonfueng, T. A. Tyson, K. Pandya
71. Complexation and transport of contaminant uranium associated with corroding steel and stainless steel surfaces. G. P. Halada, C. Eng, A. J. Francis, C. J. Dodge
72. EXAFS investigation of Ni sorption to hydrologically conditioned amorphous Mn oxyhydroxides. E. A. Haack, T. P. Trainor, D. S. Smith, C. Kennedy, L. A. Warren
73. Formation and characterization of a ternary Fe(III)-U(VI)-citric acid complex with implications for uranium mobility. C. J. Dodge, A. J. Francis
74. Surface properties of manganese oxide coated montmorillonite. T. Boonfueng, L. Axe
75. Assessing the PAH sorption characteristics of glassy polymers as model NOM systems in contaminant binding studies. F. V. Schindler, F. J. Novotny, J. A. Rice
76. Uranium complexation with polyphosphates. G. J. Vazquez, C. J. Dodge, A. J. Francis
77. Biogeochemical processes controlling multi-element transport in vadose zone sediments. C. Kennedy, L. A. Warren, C. Cooper
78. Arsenic in groundwater at landfill sites in northern central Massachusetts. M. J. Mayo, R. Hon, W. C. Brandon, R. Ford
79. Measured Sticking Efficiencies of *Enterococcus faecalis* Using Atomic Force Microscopy. T. L. Cail, M. F. Hochella Jr.
80. Production and release of carbonyl sulfide from the rice paddies in the south area of the Yangtze River. J. Zhang, W. Qiao, Z. Yang
81. Arsenic speciation in reducing waters with specific attention to the roles of zero-valent sulfur and Pb(II). C. S. Neuberger, G. R. Helz
82. Volcanic ashes as source of As in Pampean sediments, Argentina. G. Roman-Ross, L. Charlet
83. Differential pulse cathodic stripping voltammetric speciation analysis of trace level inorganic arsenic compounds in natural water samples. Y. He, Y. Zheng, M. Ramnaraine, D. C. Locke
84. A rapid colorimetric method for measuring arsenic concentrations in groundwater. R. K. Dhar, Y. Zheng, J. Robenstone, A. van Geen
85. Preservation and stabilization of arsenic species during chemical extraction from soils. M. Georgiadis, Y. Cai, H. Solo-Gabriele
86. Determination of arsenic sorption characteristics in sediment porewater using an iron oxyhydroxide-doped gel probe. K. M. Campbell, J. G. Hering, S. Dixit
87. Preservation of sulfidic waters containing dissolved As(III). J. A. Smieja, R. Wilkin
88. Treatment of arsenic and organoarsenic compounds by ultrasound irradiation. K. O'Shea, S. Motamedi, Y. Cai, T. Xu
89. Speciation of arsenic sorbed on ferrihydrite determined by voltammetry in sodium phosphate and hydrochloric acid extracts. Z. Mo, Y. Zheng
90. Arsenic transport and transformation associated with MSMA application on a golf course green. J. Schrlau, M. Feng, Y. Cai, G. H. Snyder, M. Chen, J. L. Cisar
91. Binding of arsenic to dissolved colloidal materials derived from golf course soils. Z. Chen, Y. Cai
92. Spectroscopic studies of As(V) uptake by calcite. V. G. Alexandratos, E. J. Elzinga, R. J. Reeder, M. Schoonen
93. Characterization of a bimetal oxide adsorbent and its adsorption mechanism for Arsenic(V). Y. Zhang, M. Yang, H. He, X. Huang
94. Removal of arsenic from water by granular titanium dioxide. S. Bang, M. E. Pena, M. Patel, X. Meng
95. Adsorption technologies for small-scale treatment of arsenic. F. Brusciotti, P. Yadav, P. Duby, J. Kilduff, N. M. Assaf-Anid

96. Chemical factors affecting arsenic removal at water treatment plants. T. R. Holm, S. D. Wilson, J. L. Talbott, W. R. Kelly
97. Colloidal transport of As from smelter sites in Cornwall, UK. S. Shaw, B. Hull-Bailey
98. Influence of phosphate on arsenic accumulation in *Pteris vittata*. W. Zhang, Y. Cai, L. Q. Ma, K. Downum
99. Mechanisms of arsenic removal by zero valent iron reactive barriers. N. A. Rivera Jr., P. A. O'Day, D. Vlassopoulos, R. Root
100. Remediation of an arsenic contaminated site. M. Rafferty, C. B. Andrews, D. Vlassopoulos, K. M. Binard
101. Arsenic removal by zero-valent iron: Field tests in rural Bangladesh and at the Vineland Chemical, NJ, Superfund Site. Z. Cheng, N. P. Nikolaidis, A. Van Geen, R. C. Bailey, M. Westgate
102. Microcosm studies examining the release of arsenic from Bangladesh aquifer sediments. B. J. Mailloux, A. Van Geen, Z. Cheng, S. Datta
103. Molecular characterization of novel arsenic oxidizing or reducing isolates. E. D. Rhine, E. Garcia-Dominguez, L. Y. Young
104. Two-year operation of an air/iron treatment system for the removal of arsenic from simulated Bangladeshi tubewell water. A. H. Chowdhury, P. T. Crisp
105. Arsenic distribution in underground aquifer water in Bangladesh and potential source of arsenic-free water. B. K. Biswas, G. K. Basu, D. Chakraborti, R. H. Loeppert

## WEDNESDAY MORNING

### Section A

Javits Convention Center -- 1A25

Molecular Environmental Surface Chemistry: Techniques and Methods for Determining Structural Role of Adsorbed and Coprecipitated Contaminants

#### 1. Sorbate Structure

Cosponsored with ENVR

R. J. Reeder and B. Phillips, *Organizers*

8:00 — Introductory Remarks.

8:05 —106. Atomic-scale x-ray analysis of ion adsorption at the rutile-water interface.

Z. Zhang, P. Fenter, L. Cheng, N. C. Sturchio, M. J. Bedzyk

8:25 —107. Periodic density functional theory calculations of Sr(II) and Zn(II) adsorption onto the (110) face of rutile. J. D. Kubicki, A. V. Bandura

8:45 —108. Long-Period X-ray Standing Wave (XSW) studies of Pb(II) ion distributions at organic thin film – mineral interfaces. T. H. Yoon, T. P. Trainor, P. Eng, J. R. Bargar, G. E. Brown Jr.

9:05 —109. Fourier reconstruction of adsorbate crystallographic distributions using X-ray standing waves. L. Cheng, M. J. Bedzyk, N. C. Sturchio, P. Fenter

9:25 —110. Structure of Chromate Bound to Quartz-Water Interfaces from Second Harmonic Generation Studies. F. M. Geiger, A. L. Mifflin, K. A. Gerth

9:45 —111. A spectroscopic investigation of ferrous iron adsorbed on oxides. A. G. B. Williams, M. M. Scherer

10:05 — Intermission.

10:15 —112. Using variable angle ATR FT-IR spectroscopy to probe the mineral-water interface. M. J. Borda, M. A. Schoonen

10:35 —113. Computer modelling of cation segregation to oxide and mineral surfaces in the presence of water. S. C. Parker, D. C. Cooke, S. Kerisit, A. S. Marmier

10:55 —114. X-ray absorption spectroscopy (XAS) study of mercury(II) adsorption in mercaptan-functionalized mesostructured silicas with a wormhole framework structure. C. Chen, K. F. Hayes, E. McKimmy, T. J. Pinnavaia

11:15 —115. Spectroscopic characterization of U(VI) sorption at the calcite-water interface. E. J. Elzinga, C. D. Tait, R. J. Reeder, K. D. Rector, R. J. Donohoe, D. E. Morris

11:35 —116. Computer simulation studies of aqueous uranyl interactions with clay mineral surfaces. J. A. Greathouse, R. T. Pabalan

## Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface

Sorption to Clays and Metal Oxides: Applications of Spectroscopy

Cosponsored with NIEHS/EPA Superfund Basic Research Program, and ENVR

## Urban Aerosols and Their Impact: Lessons Learned from the World Trade Center Tragedy

Cosponsored with ENVR

## WEDNESDAY AFTERNOON

### Section A

Javits Convention Center -- 1A25

Molecular Environmental Surface Chemistry: Techniques and Methods for Determining Structural Role of Adsorbed and Coprecipitated Contaminants

### 2. Surface Properties and Sorption

Cosponsored with ENVR

R. J. Reeder and B. Phillips, *Organizers*

1:30 —117. Molecular dynamics modeling of confined water. J. Wang, A. G. Kalinichev, R. J. Kirkpatrick

1:50 —118. Molecular models of interlayer adsorption of water and halocarbons by clay minerals. L. J. Criscenti, R. T. Cygan

2:10 —119. Effect of lipids on sorption/desorption hysteresis of hydrophobic organic compounds in natural organic matter. G. Ding, J. A. Rice

2:30 —120. Creating mixed planar Fe/Al oxide surfaces for metal-ion sorption studies. C. F. Conrad, C. J. Chisholm-Brause, M. J. Kelley

2:50 —121. Effect of oxygen on siderite and rhodochrosite dissolution. O. W. Duckworth, S. T. Martin

3:10 —122. Chromium Speciation in Soils: A Selective Extraction and Coprecipitation Study. B. Hua, B. Deng, J. E. Amonette, E. C. Thornton, J. yang

3:30 — Intermission.

3:40 —123. Mechanisms of Cobalt Adsorption and Co-Precipitation with Manganese Oxide using Microscopic Techniques. Y. Jun, S. T. Martin

4:00 —124. Lipid coatings on pyrite surface – an AFM study. X. Zhang, D. R. Strongin, M. A. A. Schoonen

4:20 —125. Interrogating microbe/mineral interactions and contaminant speciation using laser-based optical and chemical imager (LOCI). J. R. Scott, P. L. Tremblay, T. R. McJunkin

4:40 —126. Agent-based simulation of biocomplexity: Effects of adsorption on natural organic mobility through soils. L. Arthurs, P. A. Maurice, G. Madey, X. Xiang, Y. Huang

5:00 —127. Arsenic removal by gypsum and calcite: the continuum between sorption and solid-solution phenomenon. G. J. Cuello, G. Roman-Ross, L. Charlet

**Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface**

**Sorption of Pharmaceutical Compounds to Soils and Pure Phase Minerals**

**Cosponsored with NIEHS/EPA Superfund Basic Research Program, and ENVR**

**Urban Aerosols and Their Impact: Lessons Learned from the World Trade Center Tragedy**

**Cosponsored with ENVR**

### **WEDNESDAY EVENING**

**Targeting Chemical and Biological Warfare Agents**

**Poster Session**

**Cosponsored with ENVR**

**Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface  
Poster Session**

**Cosponsored with NIEHS/EPA Superfund Basic Research Program, and ENVR**

**Biogeochemistry of Chelating Agents**

**Poster Session**

**Cosponsored with ENVR**

**Urban Aerosols and Their Impact: Lessons Learned from the World Trade Center Tragedy**

**Poster Session**

**Cosponsored with ENVR**

### **THURSDAY MORNING**

**Section A**

**Javits Convention Center -- 1A25**

**CO<sub>2</sub> Sequestration: Advanced Technologies for Predicting and Monitoring Isolation Performance**

**Cosponsored with FUEL, IEC, and PETR**

**J. W. Johnson, J. Friedmann, and K. Caldeira, *Organizers***

8:00 — Introductory Remarks.

8:05 —128. Kinetic data for CO<sub>2</sub> sequestration in geological deposits. R. W. Breault, M. Malik

8:25 —129. Experimental CO<sub>2</sub> –saturated brine-rock interactions at elevated temperature and pressure: Implications for CO<sub>2</sub> sequestration in deep-saline aquifers.

R. J. Rosenbauer, T. Koksalan

8:45 —130. Density change of underground water due to CO<sub>2</sub> dissolution. Y. Song,

B. Chen, M. Nishio, M. Akai, T. Oshumi

9:05 —131. A two-step mechanism model of Anorthite dissolution in CO<sub>2</sub> solution.

B. Chen, Y. Song, M. Nishio, M. Akai, T. Oshumi

9:25 —132. Reducing uncertainty of geochemical modeling for a better prediction of CO<sub>2</sub> fate after geological sequestration. E. Brosse, C. Magnier, C. Noiriél, D. Bernard

9:45 — Intermission.

10:05 —133. CO<sub>2</sub> fixation by rock-water interactions. J. L. Krumhansl, C. Jove-Colon

10:25 —134. Kinetic modeling of CO<sub>2</sub> sequestration reactions in a deep saline aquifer. B. Zerai, B. Saylor, G. Matisoff

10:45 —135. Accessing the risks of geological storage of CO<sub>2</sub> in mature oil fields: What can we learn from numerical modeling of the Forties Field, North Sea? J. M. Ketzer,

B. Carpentier, Y. Le Gallo, P. Le Thiez

11:05 —136. CO<sub>2</sub> Sequestration in Faulted Sandstone Aquifers. S. M. Pasala, C. B. Forster, M. D. Deo

11:25 —137. Reactive transport modeling of cap rock integrity during natural and engineered CO<sub>2</sub> sequestration. J. W. Johnson, J. J. Nitao, J. P. Morris

Issues of Homeland Security: What Can Chemists Do?

Cosponsored with PRES

Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface

Surface Transformation and Redox Processes

Cosponsored with NIEHS/EPA Superfund Basic Research Program, and ENVR

**THURSDAY AFTERNOON**

Section A

Javits Convention Center -- 1A25

CO<sub>2</sub> Sequestration: Advanced Technologies for Predicting and Monitoring Isolation Performance

Cosponsored with FUEL, IEC, and PETR

J. W. Johnson, J. Friedmann, and K. Caldeira, *Organizers*

1:15 —138. Soil gas surveys and autonomous geochemical stations for the monitoring of geologically sequestered CO<sub>2</sub>: Results from a leaking natural CO<sub>2</sub> reservoir below the San Vittorino Plain (central Italy).

G. Ciotoli, S. Lombardi, S. E. Beaubien, A. Annunziatellis

1:35 —139. Soil gas as a monitoring tool of deep geological storage of carbon dioxide: Results from the Encana EOR project in Weyburn, Saskatchewan

(Canada). D. G. Jones, M. H. Strutt, S. E. Beaubien, S. Lombardi, N. Voltatoni, J. Baubron, C. Cardellini, F. Quattrocchi, D. Granieri, L. Penner

1:55 —140. High CO<sub>2</sub> gas fields: Natural analogs to the chemical evolution of CO<sub>2</sub> storage in depleted gas fields. J. Friedmann, R. C. Burruss, S. T. Brennan, A. Hughes, D. Nummedal

2:15 —141. Carbon sequestration in aquifers associated with ultramafic to mafic rocks.

J. M. Matter, T. Takahashi, D. S. Goldberg

2:35 —142. Geologic Sequestration of CO<sub>2</sub> in a Depleted Oil Reservoir. R. J. Pawar, N. R. Warpinski, B. Stubbs, R. B. Grigg, J. C. Lorenz, S. P. Cooper, J. L. Krumhansl, R. D. Benson, J. T. Rutledge  
2:55 — Intermission.  
3:15 —143. An overview of ocean carbon storage options. K. Caldeira  
3:35 —144. Numerical experiments on the behavior of the sequestered CO<sub>2</sub> in the mid-depths ocean using eddy-resolving OGCM. S. Aoki, T. Doi  
3:55 —145. Non-invasive, in-situ quantification of soil carbon sequestration. G. R. Hendrey, L. Wielopolski, S. Mitra  
4:15 —146. Sequestration of CO<sub>2</sub> in peat and soil organic matter. Sorption and diffusion controlled hysteresis model. P. I. Ravikovitch, A. V. Neimark, J. J. Pignatello  
4:35 —147. Chemical extraction of carbon dioxide from air to sustain fossil energy by avoiding climate change. M. K. Dubey, H. Ziock, J. Colman, T. Rahn, K. Lackner  
4:55 — Concluding Remarks.

**Chemistry of Polar and Ionic Organic Compounds at the Mineral-Water Interface**

**Characterization, Cycling and Transport**

**Cosponsored with NIEHS/EPA Superfund Basic Research Program, and ENVR**

## New York National Meeting Abstract Listing

### **GEOC 1 [674836]: Arsenous acid deprotonation and stability from 25 to 300°C**

**Valentina P. Zakaznova-Iakovleva**, Terry M. Seward, and Oleg M. Suleimenov, Geochemistry Group, Institut für Mineralogie und Petrographie,  
**ETH-Zentrum, Sonneggstrasse 5, Zürich CH-8092, Switzerland, Fax: +411-632-10-88,**  
**iakovleva@erdw.ethz.ch**

#### **Abstract**

Thermodynamic data on aqueous arsenic species are very important in understanding of the behavior of arsenic both in hydrothermal systems and in toxic waste environments. Using a high temperature-high pressure optical cell, we have measured the ultraviolet spectra of arsenous acid species from 25 to 300°C at equilibrium saturated vapour pressures. The first deprotonation constant of arsenous acid ( $\text{HAsO}_2$ ) was obtained by a mathematical treatment of the spectra using factor analysis together with a MATLAB platform.  $\text{pK}_1$  for the equilibrium  $\text{HAsO}_2 = \text{AsO}_2^- + \text{H}^+$ , was found to change from 9.25 to 7.11 over the temperature range from 25 to 300°C. We have also calculated the ionisation constant using quantum chemical methods (i.e. ab initio with extrapolation to aqueous solutions using the Polarised Continuum Model) and obtained  $\text{pK}_1 = 8.88$ . In addition, the reaction of arsenous acid to form thioarsenite species has been studied and these data will also be discussed.

### **GEOC 2 [675351]: Computed and observed redox chemistry of methyl arsenic species**

Paul M. Dombrowski<sup>1</sup>, **Dominic M. Di Toro**<sup>2</sup>, Kevin J. Farley<sup>1</sup>, John D. Mahony<sup>1</sup>, and Long Wei<sup>1</sup>. (1) Department of Environmental Engineering, Manhattan College, Riverdale, NY 10471, Fax: 718-862-8018, pauleluv@yahoo.com, (2) Department of Civil and Environmental Engineering, University of Delaware, 356 DuPont Hall, Newark, DE 19716, Fax: 302 831-3640, dditoro@ce.udel.edu

#### **Abstract**

Methylated arsenic species are present in many biological media. The arsenic methylation reactions are reported to be a sequence of alternating reductions of pentavalent arsenic, As(V), to trivalent arsenic, As(III), followed by an oxidation to As(V) during methylation. The sequence repeats as methylation proceeds. This unusual oxidation-reduction sequence prompted an examination of the equilibrium speciation as redox potential decreases. Quantum chemical methods are employed to estimate the Gibbs free energy for monomethyl, MMA(V), MMA(III), dimethyl, DMA(V), DMA(III), and trimethyl, TMA(V), TMA(III) species. In order to reproduce the observed succession, the TMA species had to be prevented from forming, and the free energy of DMA(V) had to be significantly lowered, by 15 kcal/mol. Bond energy computations confirm the need to make the correction. This is an unusual failure of the Gaussian2 method. The computed thermodynamics were further adjusted within the known accuracy of the methods (+/- 2 kcal) to reproduce observed arsenic speciation in human urine.

### **GEOC 3 [675339]: Effect of thioarsenite formation on As(III) toxicity**

**Kevin J. Rader**<sup>1</sup>, Paul M. Dombrowski<sup>1</sup>, Kevin J. Farley<sup>1</sup>, John D. Mahony<sup>1</sup>, and Dominic M. Di Toro<sup>2</sup>. (1) Department of Environmental Engineering, Manhattan College, Manhattan College Parkway, Riverdale, NY 10471, Fax: 718-862-8018, krader02@yahoo.com, (2) Department of Civil and Environmental Engineering, University of Delaware

## Abstract

Soluble arsenite-sulfide complexes (thioarsenites) play a significant role in the chemistry of arsenic in reducing, sulfidic environments at circumneutral pH. Chemical equilibrium calculations using thioarsenite thermodynamic data from the literature indicate that the formation of a dithioarsenite complex,  $\text{AsS(OH)(SH)}^{-1}$ , reduces the concentration of all uncomplexed As(III) species present (defined as  $\text{S H}_x\text{AsO}_3^{x-3}$ ), usually dominated by  $\text{H}_3\text{AsO}_3^0$  at neutral pH. The Microtox® acute toxicity test was used to assess the effect of thioarsenite formation on As(III) toxicity. Tests performed on solutions with varying S:As ratios provide strong evidence that As(III) toxicity is primarily a function of the  $\text{S H}_x\text{AsO}_3^{x-3}$  concentration rather than the total soluble arsenite concentration. This suggests that the formation of thioarsenites mitigates As(III) toxicity. The potential for thioarsenite formation to reduce arsenite toxicity in sediment is evaluated using chemical equilibrium calculations and sediment pore water field data from various sources.

## **GEOC 4 [675474]: Organoarsenic, the missing link? What happens when the Fe hydroxide model does not work?**

**Patrick Louchouart**, Department of Earth and Environmental Sciences, Columbia University, Lamont-Doherty Earth Observatory, P.O. Box 1000; 61 Route 9W, Palisades, NY 10964-8000, Fax: (845) 365-8163, pl2065@columbia.edu, Jill Brandenberger, Batelle MSL, Pacific Northwest Laboratories, Bruce Herbert, Department of Geology and Geophysics, Texas A&M University, and April Patterson, School of International and Public Affairs, Columbia University

## Abstract

Iron (and manganese) oxi-hydroxides (i.e.  $\text{FeOOH}$ ) have been often recognized in the past to act as predominant reactive components of solid-phases in aquatic systems. Empirical and experimental data have demonstrated that iron oxi-hydroxides can exert a significant control on the dissolved/particulate partition of metals and nutrients in both surface aquatic and groundwater systems and their sediments. Although many studies point to a critical role these compounds play in controlling the aqueous mobility of arsenic in surface and groundwater systems, we present data that suggest the “Fe hydroxide” model is not always appropriate to generalize sequestration of this metal in oxic sediments. Other phenomena can be substantially more important in environments where reactive iron oxi-hydroxides are absent (or depleted), and where phytoplankton production is blooming. We suggest that, under the latter condition, organoarsenicals can constitute a substantial and predominant sediment sink of As.

## **GEOC 5 [675714]: Arsenic transformation by algae: The role of phosphorus luxury uptake**

**Ferdi L. Hellweger**<sup>1</sup>, Kevin J. Farley<sup>2</sup>, Upmanu Lall<sup>1</sup>, and Dominic M. Di Toro<sup>3</sup>. (1) Earth and Environmental Engineering Department, Columbia University, 918 Seeley Mudd Building, 500 West 120th St, New York City, NY 10027, ferdi@hydroqual.com, (2) Department of Environmental Engineering, Manhattan College, (3) Civil and Environmental Engineering Department, University of Delaware

## Abstract

Algae reduce and methylate arsenate. The end-product of the transformation reaction is a function of the growth rate of the algae. At high growth rates arsenite (As(III)) is produced and at low growth rates dimethylarsinic acid (DMA) is produced. In lakes this leads to high As(III) concentrations in the early stages of spring and fall blooms and high DMA concentrations in the summer. We hypothesize that this phenomenon is linked to the phosphorus luxury uptake of algae and propose the following mechanism. Under P-limited conditions, which usually exist in the summer, algae take up  $\text{PO}_4$  and, because of similar chemical characteristics, As(V) as well. Inside the cell As(V) is reduced to As(III), methylated to monomethylarsonic acid (MMA) and DMA, and then excreted. However, under non P-limited conditions, which exist in the early stages of blooms, algae up-regulate their  $\text{PO}_4$  transport system to take up excess P, a phenomenon known as luxury uptake. Since As(V) is taken up by the  $\text{PO}_4$  transport system, As(V) uptake also increases at this time. Within the cell, reduction of As(V) to As(III) is fast,

but methylation is slower causing As(III) to build up in the cell and be excreted causing an increase in extracellular As(III). This mechanism allows for synergistic (luxury uptake) and antagonistic (competition) effects of PO<sub>4</sub> on As(V) uptake and can therefore explain the seemingly contradictory results found in the literature. A mathematical model is constructed, based on existing established algal-nutrient interaction models, and is used to simulate As transformation in a laboratory batch experiment.

### **GEOC 6 [677151]: Arsenic speciation in porewaters of a freshwater sediment**

**Stephanie Chow**, Earth and Atmospheric Science Department, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332,  
schow@eas.gatech.edu

#### **Abstract**

The toxicity and biogeochemical behavior of arsenic depends on its chemical form. Both As(III) and As(V) are highly mobile, though reduced As (As(III)) is more toxic. Thus, it is important to investigate arsenic speciation under reducing conditions. A major removal process for As(V) is the interaction with solid phases. However, reduction and re-mobilization may occur rapidly below the sediment-water interface. In this study, the biogeochemical processes regulating the cycling of arsenic in the sediment of a freshwater lake in Georgia are investigated using a combination of Au/Hg voltammetric microelectrodes (O<sub>2</sub>, Fe(II), Mn(II), H<sub>2</sub>S), voltammetry with Hanging Mercury Drop Electrode (HMDE), and Inductively Coupled Plasma-Mass Spectrometer with Hydride Generation (HG-ICP-MS). The influence of iron, manganese, and sulfur cycling on the mobilization of arsenic will be discussed.

### **GEOC 7 [674173]: Calculation of the interaction of arsenites and arsenates with Al hydroxide surfaces**

**John A. Tossell**, Chemistry and Biochemistry, Univ. of Maryland, College Park, MD 20742, tossell@chem.umd.edu

#### **Abstract**

The importance of mineral surfaces in determining the bioavailability of heavy metals has been discussed by many researchers. Recently there has been substantial interest in understanding the mechanism for solubilization of As in well water in Bangladesh. Although field studies of this phenomenon, involving both observation and experimentation, will certainly be necessary to fully understand it, laboratory and computational studies on the microscopic mechanisms involved in the interaction of arsenites and arsenates with surfaces may also be valuable. For example, one of the newest of the suggested mechanisms for As mobilization involves competition of HCO<sub>3</sub><sup>-</sup> ion with AsO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> for sites on mineral surfaces. Conflicting experimental data has been presented on the strength of HCO<sub>3</sub><sup>-</sup> - mineral surface interactions. We have initiated a series of calculations of HCO<sub>3</sub><sup>-</sup>, AsO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> and AsO(OH)<sub>2</sub><sup>-</sup> interaction with models for unsaturated sites on the surfaces of aluminate and Fe oxyhydroxide minerals, starting with Al<sub>2</sub>(OH)<sub>2</sub>(OH<sub>2</sub>)<sub>6+4</sub> as a simple model for a coordinatively unsaturated Al site. This is similar to the computational model employed by Ladeira, and coworkers for arsenate adsorption on gibbsite. The calculated geometry of this complex has been obtained at the polarized SBK Hartree-Fock level. In evaluating reaction energies for such a process when the mineral is in contact with aqueous solution, it is important to properly incorporate solvation effects upon reactants and products. Our preliminary results indicate that HCO<sub>3</sub><sup>-</sup> complexation is much less favorable (by about 15 orders of magnitude in equilibrium constant) than complexation by AsO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>. This result will have to be refined by evaluating energetics for different charge states of the substrates and for different surface models, but it illustrates the constraints that such calculations can place upon modeling approaches. Vibrational spectra and other properties of the absorbed species have also been calculated to compare with emerging experimental data.

**GEOC 8 [675169]: Modeling surface complexes of As(III) and As(V) with Al- and Fe-oxides**

**J. D. Kubicki**, Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, Fax: 814-863-8724, [kubicki@geosc.psu.edu](mailto:kubicki@geosc.psu.edu)

**Abstract**

Adsorption of arsenic to Al- and Fe-oxides surfaces can be important in the transport of As in the environment and in water treatment. Recent studies have observed strong adsorption of As(V) onto Al- and Fe-oxides, but As(III) has been observed to adsorb less to Al-oxides than Fe-oxides. This work focuses on molecular orbital calculations of previously proposed surface complexes for As(III) and As(V) onto Al- and Fe-oxides. Comparison of the calculated and observed vibrational frequencies for the aqueous As species suggests that the molecular orbital approach can describe As bonding. Vibrational frequencies of the model surface complexes will be compared to the observed spectra of As adsorbed onto these oxides. Models of the bridging bidentate surface complexes of As(III) and As(V) with Al- and Fe-oxides are consistent with the hypothesis of stronger As(III) bonding to the Fe-oxide.

**GEOC 9 [675059]: Competitive sorption of Fe(II) and As(III) on goethite: Implications for arsenic mobilization in reducing environments**

**Suvasis Dixit**, Environmental Science and Engineering, California Institute of Technology, 1200 E. California Blvd., MS 138-78, Pasadena, CA 91125, Fax: 626-395-2940, [sdixit@caltech.edu](mailto:sdixit@caltech.edu), and Janet G. Hering, Environmental Science and Engineering, California Institute of Technology

**Abstract**

In reducing environments, elevated concentrations of arsenic in the porewaters and groundwaters are often associated with higher Fe(II) levels. Fe(II), which has previously been shown to sorb onto iron oxides, is often present in concentration tens to hundreds of times higher than those of arsenic. In this study, the competitive sorption of Fe(II) and As(III) for sorption sites on goethite is investigated. Single ion sorption edges were obtained at various solid-to-solution ratios and modeled with a diffuse double layer model. The competitive effect was investigated by simultaneous addition of As(III) and Fe(II) to goethite suspensions maintained at a fixed pH. Fe(II) concentrations in the experiments varied from 0 to 1.5 mM and the pH ranged from 6.5 to 7.5. Experimental data are compared with the model results, which were constrained with parameters obtained from fitting single ion sorption edges. The results from this study show that Fe(II) sorption onto iron oxides may play a relatively minor role in As(III) mobilization.

**GEOC 10 [672542]: Arsenate and arsenite sorption and arsenite oxidation by Fe(II)-Fe(III) hydroxycarbonate green rust**

**Chunming Su**, and Richard T. Wilkin, Office of Research and Development, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, 919 Kerr Research Drive, Ada, OK 74820, Fax: 580-436-8703, [su.chunming@epa.gov](mailto:su.chunming@epa.gov)

**Abstract**

Ferrous ferric hydroxycarbonate green rust is a major corrosion product of zerovalent iron that is being used in permeable reactive barriers to remediate groundwater arsenic contamination. To optimize the design of iron barriers, it is important to evaluate the influence of geochemical parameters such as arsenic concentration, pH, and time on the interactions of arsenic with iron corrosion products. We synthesized Fe(II)-Fe(III) hydroxycarbonate green rust in the laboratory by neutralizing ferrous sulfate solution with sodium hydroxide and sodium carbonate or sodium bicarbonate followed by air sparging. The synthetic products were characterized with X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, and wet chemical analysis. We conducted batch arsenic sorption experiments with arsenate and arsenite in an anaerobic glovebox. The pH ranged from 8 to 10.5. Both arsenate and arsenite sorption increased

with increasing time up to 30 days. Arsenite showed much higher sorption than arsenate. Adsorbed arsenite (up to 90 mg kg<sup>-1</sup>) was partially oxidized on solid surface at pH near 10.5. Oxidation of sorbed arsenite could be advantageous because arsenate is generally less toxic and less mobile than arsenite.

### **GEOC 11 [676092]: Adsorption of Arsenic by Nanocrystalline Titanium Dioxide**

**Xiaoguang Meng**, Chuanyong Jing, and Maria E Pena, Center for Environmental Systems, Stevens Institute of Technology, 1 Castle Point on Hudson, Hoboken, NJ 07030, Fax: 201-216-8303, xmeng@stevens-tech.edu

#### **Abstract**

The adsorption of arsenate [As(V)] and arsenite [As(III)] by a novel nanocrystalline titanium dioxide were studied. The adsorbent had a high specific surface area and high content of surface sites. Batch adsorption results demonstrated that the adsorbent had high adsorption capacity for As(V) and As(III) in a circumneutral pH range. Electrophoretic mobility measurements and Fourier transform infrared (FTIR) spectroscopy were employed to determine the adsorbed As(V) and As(III) species on the TiO<sub>2</sub>. It seemed that both As(V) and As(III) formed anionic complexes on the adsorbent surface. Speciation analysis indicated that titanium dioxide catalyzed oxidation of As(III) to As(V) in the presence of dissolved oxygen.

### **GEOC 12 [679099]: Arsenic adsorption on natural riverine suspended particulate material (SPM)**

**Jenny G. Webster**, SGES Environmental Science, University of Auckland, Tamaki Campus, P.O. Box 92019, Auckland, New Zealand, Fax: 94-9-373-7042, j.webster@auckland.ac.nz

#### **Abstract**

Consistent seasonal variations in As concentration in a major lowland river in New Zealand has prompted closer examination of factors controlling As adsorption and desorption processes in this environment. In this river, As is predominantly dissolved inorganic AsV. Experimental adsorption studies using SPM showed AsV adsorption to be unaffected by river water temperature, but influenced by the biological component of the SPM, specifically the presence of certain diatom species. The SPM was characterized, adsorbent surfaces identified and adsorption properties (site density, PZC and surface complexation constants) determined, in order to predict the degree of As adsorption using a diffuse layer model. Modeling results were compared to field observations, and to predictions made assuming hydrous ferric oxide to be the only adsorbing surface present in the SPM (an assumption often made when surface complexation modeling is used to predict the contaminant-SPM associations in aquatic environments).

### **GEOC 13 [673239]: Arsenic cycling within surface and subsurface environments: Impact of iron mineralogy**

Scott Fendorf<sup>1</sup>, Matthew Polizzotto<sup>2</sup>, Mitchell J. Herbel<sup>2</sup>, Benjamin C. Bostick<sup>3</sup>, and Charlie Harvey<sup>4</sup>. (1) Department of Geological & Environmental

Sciences, Stanford University, Braun Hall, Bld. 320, Room 118, Stanford, CA 94305, Fax: 650-725-2199,

fendorf@stanford.edu, (2) Department of Geological

and Environmental Sciences, Stanford University, (3) Department of Earth Sciences, Dartmouth College, (4) Department of Civil and Environmental

Engineering, Massachusetts Institute of Technology

#### **Abstract**

Arsenic is a toxic trace element that is rather ubiquitously distributed throughout the world. While geographically limited, there are areas where arsenic is having a devastating impact to human health. The question arises as to why arsenic is partitioned in the solution and not in the solid phase within specific locations. The most common factor leading to the release of arsenic from

the solid phase appears to be a transition from an aerobic to anaerobic state. Here we describe the impact of iron mineralogy on arsenic retention, emphasizing the importance of biologically driven mineralogical transformations. Reductive biomineralization dramatically modifies the retention of arsenic, typically decreasing the binding capacity nearly 50-fold in sulfide limited systems. Sulfogenesis, however, can lead to arsenic sequestration but is dependent principally on iron to sulfur ratios. Dissolved concentrations of arsenic are thus largely controlled by the cycling of iron within many surface and subsurface environments.

**GEOC 14 [675921]: Bioavailability and sources of arsenic in reactive-iron limited sediments of the coastal plain of South Texas**

**Bruce Herbert**<sup>1</sup>, Laiman Lee<sup>1</sup>, Patrick Louchouart<sup>2</sup>, Graciela Moore<sup>3</sup>, Chris Markley<sup>1</sup>, and Melissa Roberts<sup>1</sup>. (1) Department of Geology and Geophysics, Texas A&M University, MS 3115, College Station, TX 77843-3115, Fax: 979-845-6162, herbert@geo.tamu.edu, (2) Department of Earth and Environmental Sciences, Columbia University, (3) ENTRIX, Inc

**Abstract**

Geogenic sources control the occurrences of arsenic and associated trace metals in Texas groundwater systems, with arsenic concentrations as high as 560 ppb. In the San Antonio and Nueces watersheds along the South Texas Coasts, arsenic and associated trace metals have been released to the environment through the leaching of volcanic ash-rich formations, including the Catahoula Formation, and extensive U mining. Low concentrations of reactive iron in South Texas sediments suggest that iron oxyhydroxides are not controlling arsenic sequestration and bioavailability. Laboratory and field experiments using a newly developed chelating resin (DOWEX M4195) technique estimated potential arsenic bioavailability in sediment in six geologic environments (i.e. lake, river, perennial stream, ephemeral stream, pond, and wetland) in the watersheds over a twenty-eight day period. Observational and modeling results suggest that arsenic and other trace metals are highly bioavailable and may pose a significant human and ecological health risk.

**GEOC 15 [674190]: Spatial variability of arsenic concentrations and sediment properties in Bangladesh aquifers**

**Alexander van Geen**<sup>1</sup>, Allan Horneman<sup>1</sup>, Zahid Aziz<sup>1</sup>, M. A. Hoque<sup>2</sup>, M. Shamsudduha<sup>2</sup>, Zhongqi Cheng<sup>1</sup>, Ratan K. Dhar<sup>3</sup>, Roelof Versteeg<sup>1</sup>, Michael

Steckler<sup>1</sup>, Brian Mailloux<sup>1</sup>, Yan Zheng<sup>4</sup>, Martin Stute<sup>1</sup>, Steven L. Goodbred<sup>5</sup>, and Kazi Matin Ahmed<sup>2</sup>. (1) Lamont-Doherty Earth Observatory of Columbia University, Route 9W, Palisades, NY 10964, Fax: 845-365-8154, avangeen@ldeo.columbia.edu, (2) Geology Department, University of Dhaka, (3) School of Earth and Environmental Sciences, Queens College and Graduate School & University Center, City University of New York. New York, USA, (4) School of Earth and Environmental Science, Graduate Center and Queens College of The City University of New York; Lamont-Doherty Earth Observatory of Columbia University, (5) Marine Sciences Research Center, State University of New York

**Abstract**

A bewildering aspect of the current arsenic crisis in Bangladesh is the extreme degree of spatial variability of arsenic concentrations. This presentation focuses on the origin of this variability in shallow (<20 m) aquifers by combining surface geophysical measurements with a detailed section of groundwater and sediment properties. The samples were obtained by modifying a local manual drilling method. Our observations suggest that groundwater As concentrations are linked to the redox state of the aquifers, as determined from sediment reflectance and the Fe(II) content of acid-leachable Fe oxyhydroxides. The less reducing aquifers that are low in arsenic are associated with sandy deposits that extend to the surface and, therefore, are presumably recharged locally with oxic surface water. In contrast, the more reducing aquifers that are high in arsenic frequently appear to be covered with less permeable clay or silt layers that inhibit local recharge and may increase groundwater residence times.

**GEOC 16 [675130]: Depth profiles of dissolved and particulate inorganic arsenic in Bangladesh aquifers**

**Yan Zheng**<sup>1</sup>, Ratan K. Dhar<sup>1</sup>, Zheng Mo<sup>2</sup>, Zhongqi Cheng<sup>3</sup>, M. A. Hoque<sup>4</sup>, M. Shamsudduha<sup>4</sup>, Alexander van Geen<sup>5</sup>, Martin Stute<sup>3</sup>, and Kazi Matin Ahmed<sup>4</sup>. (1) School of Earth and Environmental Sciences, Queens College and Graduate School and University Center, City University of New York, 65-30 Kissena Blvd., Flushing, NY 11367, Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, Fax: 718-997-3299, yzheng@ldeo.columbia.edu, (2) School of Earth and Environmental Sciences, Queens College and Graduate School and University Center, City University of New York, (3) Lamont-Doherty Earth Observatory of Columbia University, (4) Geology Department, University of Dhaka, (5) Lamont-Doherty Earth Observatory, Columbia University

**Abstract**

Seven nests of monitoring wells were installed at sites selected to represent different spatial patterns of dissolved arsenic in shallow aquifers based on a detailed study of 6000 tubewells in a 25 km<sup>2</sup> area of Araihaazar, Bangladesh. At all sites, deep water associated with orange-brown Pleistocene sands contained < 1 ug/l dissolved As and the concentration of phosphate-extractable As from the sediment was low (< 1 mg/kg). In shallower aquifers, dissolved As concentrations increased with depths, ranging from a few ug/l to maximum levels ranging between 50 and 600 ug/l at different sites. At two sites where the sediment phase was also analyzed, maxima in phosphate-extractable As concentrations of 5 mg/kg corresponded to maxima in dissolved As. Field determinations using differential pulse cathodic stripping voltammetry indicates that most of the dissolved arsenic in the shallow aquifer is arsenite. Dissolved arsenic appears to mobilize from a local source of sedimentary arsenic.

**GEOC 17 [674683]: Geological controls on the occurrence and distribution of high arsenic in shallow groundwater: Araihaazar, Bangladesh**

**Steven L. Goodbred Jr.**<sup>1</sup>, Beth Weinman<sup>1</sup>, Alexander van Geen<sup>2</sup>, Roelof Versteeg<sup>2</sup>, Yan Zheng<sup>3</sup>, Martin Stute<sup>2</sup>, and Kazi Matin Ahmed<sup>4</sup>. (1) Marine Sciences Research Center, State University of New York, Stony Brook, NY 11794-5000, sgoodbred@notes.cc.sunysb.edu, (2) Lamont-Doherty Earth Observatory of Columbia University, (3) School of Earth and Environmental Sciences, City University of New York and Columbia University, New York, USA, (4) Geology Department, University of Dhaka

**Abstract**

High As concentrations are widespread across more than half of the 100,000 km<sup>2</sup> Ganges-Brahmaputra (G-B) delta plain, yet the distribution of groundwater As at a local scale (101-103 m) is extremely heterogeneous. These heterogeneities suggest that a set of very specific conditions is needed for elevated As concentrations to develop. We report here initial findings about the nature of sediments linked with high As and develop a framework for the history and processes of floodplain evolution leading to these conditions. Our geophysical and coring data reveal a strong correlation between As levels in shallow wells and the sediment texture of near-surface (< 6 m) floodplain deposits. These observations indicate that near-surface floodplain geology is an overarching control of these conditions. The implication is that, ultimately, a better understanding of the controls on groundwater As will arise from the integration of geology, geochemistry, and hydrology.

**GEOC 18 [674617]: Pollution of groundwater by arsenic: a small-scale survey in West Bengal**

**John M McArthur**, Earth Sciences, UCL, Gower Street, London WC1E 6BT, United Kingdom, Fax: 020 7387 1612, j.mcarthur@ucl.ac.uk, Dhiraj M Banerjee, Geology, Delhi University, Karen H Hudson-Edwards, Geology, Birkbeck College, and Peter Ravenscroft, Arcadis Geraghty and Miller Inc

**Abstract**

In order to provide comparisons to Bangladesh aquifers, and data with which to understand arsenic pollution in groundwater, we provide the first small-scale water-quality survey of an arsenic polluted aquifer (10-30m) in West Bengal that has reasonably complete analysis. Our area is 500m by 200m in extent and we have analysed waters from 56 wells within it.

Groundwaters have high concentrations of iron (up to 13.7 mg/L), manganese (up to 5.3 mg/L), phosphate (up to 4.1 mg/L), ammonium (up to 3.5 mg/L) and arsenic (up to 1190 µg/L). The waters vary spatially in redox state: those in the northwest of our area are rich in iron and arsenic, whilst those from the southeast of the area are rich in manganese and sulfate but contain less than 50 µg/L of arsenic.

A core from the arsenic-rich northwest of the area recovered organic-rich sediment at 7m and 29m (7.2% TOC). A well sited 6 m from the core is polluted with 360 µg/L of arsenic: the well screen is at a depth of 30.5 to 36.5 m, so the top of the screen is at a depth just below that of the lower organic-rich unit. Our findings are consistent with the authors' current model of arsenic pollution in the Bengal Basin, whereby arsenic is released to groundwater by reductive dissolution of hydrous ferric oxides that is driven by buried peat.

**GEOC 19 [675700]: Importance of micas surfaces in the propagation of a natural arsenic plume in West Bengal, India**  
**Laurent Charlet**<sup>1</sup>, Sudipta Chakraborty<sup>2</sup>, Debashi Chatterjee<sup>2</sup>, Basu Mallik<sup>3</sup>, Tony Appello<sup>4</sup>, and Shikha Varma<sup>5</sup>. (1) Environmental Geochemistry Group, LGIT, OSUG, Université Joseph Fourier, BP 53, F-38041 Grenoble Cedex 9, France, Fax: +33 4 76828101, Laurent.Charlet@obs.ujf-grenoble.fr, (2) Department of Chemistry, University of Kalyani, (3) Department of Geology, University of Javlapur, (4) Hydrochemical Consultant, (5) Institute of Physics

#### **Abstract**

A reaction transport model is proposed to explain the propagation of a contaminated plume originating in the Ganges delta from a paleo-meander and moving along water flow lines. Measured Eh values are close to equilibrium with both Fe(II)/Fe(III) and As(III)/As(V) couples. An arsenic distribution of 42% As(III) and 58% As(V) is observed in average at the Chadkha site, India. Micaceous minerals form up to 30% of the aquifer solid material, and their contribution to the observed arsenic speciation has been studied in details. XPS spectra of As species sorbed on micas show that an electron transfer occurs between sorbed arsenic atoms and surface oxygen atoms. As products of the reaction between As(V) and Fe(II), in presence of phlogopite, small surface hydroxy polymers were observed with in situ AFM microscopy. The role of micas basal plane and edge surfaces will be further discussed at the light of PIXE measurements.

**GEOC 20 [672337]: Occurrence, sources, mobilization and transport of arsenic in the Newark Basin in New Jersey**  
**Michael Serfes**, Steven Spayd, and Gregory Herman, Bureau of Water Resources\Geoscience Research and Support, New Jersey Geological Survey, PO 427, Trenton, NJ 08625, mserfes@dep.state.nj.us

#### **Abstract**

Data from the Ambient Ground Water Quality Network, public water supplies and other studies reveal that arsenic concentrations in ground water are highest in certain bedrock aquifers of the Newark Basin than other aquifers in New Jersey. The Newark Basin is mainly comprised of red, gray and black (organic rich) shale and sandstone that are inter-layered and intruded by basic igneous rock. Random sampling of 94 domestic wells in a 200 square mile study area within the basin indicate that 15 percent of the wells have arsenic concentrations exceeding 10 parts per billion with a maximum of 57 ppb. Well water with arsenic concentrations greater than 10 ppb are characterized by having low dissolved oxygen concentrations (DO < 3 mg/L) and have pH values ranging from 7.5 to 8.0. Arsenic concentrations greater than 40 ppb are associated with anoxic (DO < 1.0 mg/L) or nearly anoxic ground water.

Initial whole rock geochemical analysis of red (maximum: 11 ppm As), gray (maximum, 50 ppm As) and black shale (maximum: 240 ppm As) from several members of the Passaic Formation, indicate that black shale has the highest arsenic concentrations. Electron microprobe analysis of the black shale identified pyrite (FeS<sub>2</sub>) as the major source of arsenic (see image). In two separate black bed members from the lower part of the Passaic Formation the maximum arsenic concentrations

measured in pyrite were 40,000 and 3000 ppm. A domestic well near the black bed with 40,000 ppm As contained 48 ppb As. A municipal well intersecting but cased off from the bed with 3000 ppm As had a concentration of 44 ppb As.

A conceptual model for arsenic mobilization and transport in the Newark Basin involves the oxidation of pyrite in the recharge area, which releases the arsenic, followed by transport along the ground-water flow path. The reduced dissolved oxygen content and an increasingly alkaline environment along the flow path facilitates the solubility of arsenic.

**GEOC 21 [675235]: Arsenic mobilization under reducing conditions beneath a landfill in Maine**

**Alison R. Keimowitz**, Saugata Datta, Martin Stute, H. James Simpson, Steven N Chillrud, Monique Tsang, and James Ross, Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, NY 10964, ark@ldeo.columbia.edu

**Abstract**

Elevated levels of dissolved arsenic (~300 ppb) have been detected beneath and in plumes extending away from a closed landfill in Maine. Field monitoring and laboratory experiments indicate that the source of the dissolved arsenic is primarily the natural sediments, which contain about 6 ppm arsenic. This arsenic becomes mobilized by strongly reducing conditions (average oxidation-reduction potential is -95 mV) which result from landfill leachate. Natural reducing conditions in nearby wetlands also mobilize arsenic from the sediment. Extensive remediation efforts at this site have included installation of a clay cap; groundwater extraction, oxidation, and reinjection; and subsurface oxidation by injection of magnesium peroxide. A number of factors prevent these interventions from being feasible methods of remediating arsenic at the site at reasonable costs.

**GEOC 22 [668469]: Arsenic in groundwater in southeastern Wisconsin: Sources of arsenic and mechanisms of arsenic mobilization**

**Tara L. Root**<sup>1</sup>, Jean M. Bahr<sup>1</sup>, and Madeline Gotkowitz<sup>2</sup>. (1) Department of Geology and Geophysics, University of Wisconsin - Madison, 1215 W. Dayton St., Madison, WI 53706, Fax: 608-262-0693, tara@geology.wisc.edu, (2) Wisconsin Geological and Natural History Survey

**Abstract**

Moderately high arsenic concentrations occur in groundwater in glacial and upper bedrock aquifers throughout southeastern Wisconsin. There is no evidence of anthropogenic sources of arsenic in the region. The objective of this study is to determine the source(s), and geochemical controls on the mobility of the naturally occurring arsenic in this region. Approximately 10% of the wells in the study area have arsenic concentrations above the new U.S. Environmental Protection Agency drinking water standard of 10 ppb. Maximum arsenic concentrations are on the order of 80 ppb. Preliminary results indicate that the arsenic in the groundwater is dominantly As (III). Geochemical analysis of core collected during sonic drilling shows arsenic concentrations ranging from less than detection to 5 ppm in most samples. Higher concentrations of arsenic occur in an organic horizon in the glacial aquifer (21 ppm) and in residuum (15 ppm) at the base of the glacial aquifer. Ongoing work includes mineralogical analysis and selective extractions to determine the solid phase associations of arsenic in these core samples. We are also routinely sampling arsenic-impacted wells for water chemistry and conducting aquifer tests to characterize the hydrogeology of the area. Our preliminary results and hypotheses regarding the cause(s) of the arsenic contamination will be presented in this paper.

**GEOC 23 [678872]: The molecular biology and biochemistry of bacterial respiratory arsenate reduction**

**Chad W. Saltikov**, Davin Malasarn, and Dianne K. Newman, Division of Geological and Planetary Sciences, California Institute of Technology, Mailstop 100-23, Pasadena, CA 91125, Fax: 626-683-0621, saltikov@gps.caltech.edu

**Abstract**

Microbial metabolic activity is increasingly thought to play a significant role in controlling the speciation and mobilization of arsenic (As) in the environment. Various metabolic processes can affect the geochemical cycle of As, but one we are particularly interested in is respiratory arsenate reduction (RAsR). RasR results in the formation of the toxic metalloid arsenite (As(III)) from the reduction of particulate or soluble arsenate (As(V)). Under anaerobic conditions, As(V)-reduction is coupled to the oxidation of organic carbon and bacterial growth. Although numerous As(V)-respiring bacteria have been isolated from a variety of environments, little is known about the mechanism for As(V) respiration. We are investigating the biochemistry and molecular biology of RAsR in the metal reducing bacterium *Shewanella* sp. strain ANA-3. We have identified a two-gene operon, *arrAB*, which encodes a new class of anaerobic reductase specific for arsenate. I will discuss our emerging model of how bacteria respire As(V), as well as the practical application of detecting the activity of respiratory arsenate reducers in environmental samples.

**GEOC 24 [663355]: Anaerobic geochemistry and microbiology of arsenic in Holocene alluvial aquifers: Origin of natural contamination and remediation implications**

**James A. Saunders**<sup>1</sup>, Shahnewaz Mohammad<sup>2</sup>, Ming-Kuo Lee<sup>2</sup>, and Nic E. Korte<sup>3</sup>. (1) Department of Geology and Geography, Auburn University, 210 Petrie Hall, Auburn, AL 36849, Fax: 334-844-4486, saundja@auburn.edu, (2) Department of geology and Geography, Auburn University, (3) consultant

**Abstract**

Natural arsenic contamination of groundwater in young (post-Ice Age) alluvial aquifers is a worldwide human health problem, particularly in developing nations that must use these waters. Our research shows that several geologic, geochemical, and microbiologic processes operate in conjunction to cause this problem: 1) development of shallow groundwater in "flat" river floodplains with low hydraulic gradients and sluggish flow; 2) deposition of reactive arsenic-bearing hydrous ferric oxyhydroxides (HFO) and solid organic matter in alluvial deposits (original As source was river water flowing over HFO in bottom sediments); and 3) development of anaerobic conditions where iron-reducing bacteria (FeRB) mediate reductive dissolution of HFO coupled to organic matter oxidation. At one of our field sites, we have cultured FeRB from moderately reducing, As- and Fe-rich groundwaters, but could not from more oxidizing, low Fe and As groundwaters. Further, at another field site, we have stimulated the release of high levels of dissolved As (>1000 ppb!!) in a few weeks from HFO's by FeRB. This was accomplished by injection of dissolved organic carbon into originally oxidized groundwater in a shallow alluvial aquifer. Remediation of As-contaminated groundwater may occur by stimulating sulfate-reducing bacteria (SRB) metabolism. SRB can remove As by coprecipitation in iron sulfide if dissolved Fe concentrations are elevated, but As may form soluble and stable As-thio complexes at low iron concentrations and elevated dissolved hydrogen sulfide. Thus, sulfide minerals appear to be a SINK for As in anaerobic alluvial aquifers, and not the SOURCE as many have proposed.

**GEOC 25 [665230]: Microbial mobilization of arsenic from mine tailings under aerobic conditions**

**Joyanto Routh**, and Ambujom Saraswathy, Department of Geology and Geochemistry, Stockholm University, 10691 Stockholm, Sweden, Fax: 46 8 674 7855, joyanto.routh@geo.su.se

**Abstract**

We report data on arsenic (As) mobilization involving dissimilatory As reduction (DAsR) under aerobic conditions. DAsR results in reduction of As(V) to the more mobile and toxic As(III) species, and has important environmental implications. We obtained four isolates from contaminated mine tailings from Adak in Västerbotten district, northern Sweden. We inoculated the

sediments in minimal medium for enrichment cultures, and pure strains were obtained by successive isolation. Arsenic speciation was analyzed spectrophotometrically, and bacterial growth verified by measuring optical density, protein content, and dry weight. The API and 16S RNA methods were used to identify the bacteria as (*Arthrobacter*, *Chromobacterium*, *Intrasporangiaceae*, and *Terrabacter tumescens*). These bacteria were capable of growing in 5 mM As concentration, and reducing >70% As(V) within 12 days. They also preferred using As(V) over other terminal electron acceptors (SO<sub>4</sub>, PO<sub>4</sub> and NO<sub>3</sub>). The sterile controls did not show growth or As(V) reduction.

**GEOC 26 [671456]: Arsenic release coupled with biodegradation of organic compounds in contaminated groundwater plumes**

**Jamie L. deLemos**, Carl Renshaw, Benjamin C. Bostick, Stefan Sturup, and Xiahong Feng, Department of Earth Sciences, Dartmouth College, 6105 Fairchild, Hanover, NH 03755

**Abstract**

Arsenic contamination is a persistent problem at many mixed waste sites. Natural and anthropogenic sources of As, as well as the mechanism controlling As mobility were investigated at a contaminated landfill near Portsmouth, NH. Dissolved As and benzene concentrations were analyzed before and after cap emplacement, and X-ray adsorption spectroscopy and selective sequential extractions were utilized to investigate the association of As within the solid phase. Experimental results demonstrate that As(V) is associated with ferrihydrite within an overburden clay-rich aquitard (As~ 20 ppm, hydraulic conductivity  $K=7 \times 10^{-7}$  cm/s). Batch sorption studies indicate that benzene strongly partitions into the clay layer ( $K_d=220$  L/Kg). Dissolved benzene concentrations have decreased since capping the landfill, most likely due to natural attenuation. These data are consistent with microbial decomposition of benzene and other organic compounds promoting Fe(III) dissimilatory reduction, breaking down ferrihydrite, and releasing Fe(II) and As(V) into solution.

**GEOC 27 [676075]: Natural attenuation as a strategy for managing arsenic-contaminated groundwater**

**Janet G. Hering**, Environmental Science and Engineering, California Institute of Technology, 1200 E. California Blvd, MS 138-78, Pasadena, CA 91125,  
Fax: 626-395-2940, [jhering@its.caltech.edu](mailto:jhering@its.caltech.edu)

**Abstract**

For arsenic, natural attenuation (i.e., "naturally occurring processes in the environment that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants") depends on contaminant immobilization in the subsurface through sorption and precipitation processes, whose effectiveness may be strongly influenced by redox transformations. Microbial processes can, either directly or indirectly, influence the mobility and toxicity of arsenic. Natural attenuation, as a remediation strategy, is predicated on the identification of a point of compliance at some distance from the source of contamination, over which natural processes can act to mitigate the hazard posed to human health. For such mitigation to occur, gradients within the subsurface system must favor arsenic immobilization. Various scenarios will be considered; cases in which arsenic is introduced through human activities will be compared with those in which it is naturally-occurring in the subsurface environment but mobilized by human-induced alterations in subsurface conditions.

**GEOC 28 [676234]: Natural attenuation of arsenic under fluctuating redox conditions in contaminated estuary sediments**

**Robert Root**<sup>1</sup>, Peggy A. O'Day<sup>1</sup>, Nelson A. Rivera Jr.<sup>1</sup>, and Dimitri Vlassopoulos<sup>2</sup>. (1) Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, Fax: 480-965-8102, [robroot@asu.edu](mailto:robroot@asu.edu), (2) S.S. Papadopulos & Associates, Inc

Abstract

Natural attenuation of an arsenic plume in shallow groundwater flanking San Francisco Bay, California is demonstrated by down-gradient arsenic concentrations in soil and groundwater dropping from  $6.68 \times 10^{-3} \text{ mol kg}^{-1}$  and  $1.3 \times 10^{-4} \text{ M}$  to  $1.1 \times 10^{-7} \text{ mol kg}^{-1}$  and  $<5.0 \times 10^{-8} \text{ M}$ , respectively, as the plume reaches estuary sediments. In situ examination of arsenic and iron in shallow sediments (0-3.6 m) with synchrotron x-ray absorption spectroscopy (XAS) demonstrated variable speciation with depth, indicative of cm-scale subsurface redox changes. Speciation of dissolved arsenic was determined by ion exchange liquid chromatography for comparison with sediment speciation determined by XAS. In shallow (0.5-1.5 m), reduced sediments, arsenic is precipitated as amorphous to poorly-crystalline arsenic sulfides (realgar and orpiment local structures). In intermediate to deep sediments (1.5–3.6 m) where fluctuating redox environments are associated with boundaries between reduced sediments and oxygenated groundwater, As(V) is attenuated by sorption to iron (II,III) oxides and iron oxyhydroxides. We propose that release of As(III) to groundwater is maximized during transitions between sulfur-reduced and iron-oxidized conditions associated with variable groundwater levels.

**GEOC 29 [677916]: A general biogeochemical model for arsenic cycling in shallow aquifers**

**Peggy A. O'Day**, Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, Fax: 480-965-8102, oday@asu.edu, and Dimitri Vlassopoulos, S.S. Papadopoulos & Associates, Inc

**Abstract**

The chemical speciation of arsenic in sediments and porewaters of groundwater aquifers is the critical factor that determines whether dissolved arsenic accumulates to potentially toxic levels. Under oxidized conditions, As(V) is removed from solution primarily by adsorption to iron oxyhydroxides and perhaps to phyllosilicates. Under sulfate-reduced conditions, reduced arsenic is precipitated as the arsenic sulfide minerals realgar (AsS) or orpiment (As<sub>2</sub>S<sub>3</sub>), perhaps as nanoparticles. Reduced arsenic does not substitute into pyrite. In systems in which the rate of microbial sulfate reduction is limited and the ratio of dissolved iron to sulfide is relatively high, removal of sulfide by FeS/pyrite precipitation leads to a maximum in dissolved As(III) concentrations. In the transition from sub-oxic to oxidized conditions, arsenic uptake and release is linked to the precipitation and dissolution of Fe(II,III) oxides. Release of As(III) to solution is favored in subsurface transitions between sub-oxic and sulfate-reduced zones where cycling between oxidized and reduced arsenic and iron may also be coupled to microbial nitrogen cycling.

**GEOC 30 [675156]: Speciation and distribution of arsenic in the Mahomet Aquifer, Illinois**

**Thomas R. Holm**<sup>1</sup>, Walton R. Kelly<sup>1</sup>, Steven D. Wilson<sup>1</sup>, George S. Roadcap<sup>1</sup>, Johnathan L. Talbott<sup>2</sup>, and John W. Scott<sup>2</sup>. (1) Groundwater Section, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820, Fax: 217-244-3054, (2) Illinois Waste Management & Research Center

**Abstract**

Groundwater samples were collected from approximately 100 wells in the Mahomet Aquifer in Tazewell and Champaign Counties. A reliable, robust method for arsenic (As) speciation in groundwater was developed based on HPLC with ICP-MS detection. The spatial distribution of As was complex; wells with over 50 mg/L were often located less than one mile from wells with <1 mg/L arsenic. The percentages of wells with over 10 mg/L As were roughly equal in the shallow, intermediate, and deep parts of the aquifer. In most samples over 90% of the total dissolved As was As(III) with the balance being As(V). None of the samples had detectable (>1 mg/L) methylated species. Less than 10% of the total As was retained by a 0.45 mm filter. The As speciation was consistent with the measured pH and oxidation-reduction potential values. High arsenic concentrations were associated with low sulfate concentrations and with high concentrations of bicarbonate, ammonium, fluoride, and organic carbon.

**GEOC 31 [676198]: Redistribution of arsenic in soils by natural hydrogeologic processes**

**Kevin A. Doherty**, Knoll Environmental, Inc, 69 Wexford Street, Needham, MA 02494, Fax: 781-449-1623, kdoherty@knollenvironmental.com, and Rudolph Hon, Department of Geology and Geophysics, Boston College

**Abstract**

Analysis of elevated arsenic (30 to 800 ppm) within soils of a broad W-E traverse in Central Massachusetts reveals a pattern of higher concentrations of naturally occurring arsenic at lower elevations, and lower arsenic concentrations at higher elevations. Arsenic levels at each end of the traverse return to the background levels (< 20 ppm). Arsenic at the hillside sites vs. sites located in the valleys are on average 50% lower, indicating arsenic migration along the direction of groundwater flow. We suggest that groundwater recharged at higher elevations dissolves small amounts of arsenic which is then transported to the flat lying aquifers while the dissolved arsenic is allowed to precipitate prior to its discharge to the surface drainage system. Slightly reduced water due to a decaying organic litter can mobilize minor arsenic which is then re-precipitated when the groundwater enters a zone of atmospheric influence near its discharge point.

**GEOC 32 [675766]: Vertical migration and speciation of smelter-ash arsenic in island soils of Puget Sound, Washington**

Brett T. Beaulieu, and **Kaye S. Savage**, Geology Department, Vanderbilt University, Nashville, TN 37235, brett.t.beaulieu@vanderbilt.edu, k.savage@vanderbilt.edu

**Abstract**

Arsenic released from a copper smelter, and deposited on forested soils of glacial origin on Puget Sound islands, has migrated vertically in the soil column. As concentrations up to »800 ppm are present at 10-15 cm depth. We used X-ray absorption spectroscopy to investigate how arsenic, released from the smelter as arsenic trioxide, has interacted with soil constituents, and to explore how arsenic speciation may promote or limit arsenic mobility and bioavailability in this region.

As(III) released from the smelter has been uniformly oxidized to As(V) in near-surface soils; EXAFS data suggests surface complexes on fine soil particulates. Arsenate in a sandy, organic-rich sample is associated with iron, with a small contribution from aluminum. In a sample with a larger clay fraction, aluminum is the main second shell backscattering element. Two potential mobilization pathways are considered: particle-mediated transport, and desorption followed by dissolved transport and resorption during intermittent wetting events.

**GEOC 33 [676664]: Arsenic geochemical behavior in semiarid soils contaminated by mine processing wastes**

**Francisco Romero**, Margarita Gutiérrez-Ruíz, Pilar Fernández-Lomelín, and Mario Villalobos, Laboratorio de Análisis Físicos y Químicos del Ambiente (LAFQA), Instituto de Geografía, UNAM, CU México 04510, Mexico, Fax: 011-52-55-5622-4352, fmrch@hotmail.com

**Abstract**

Arsenic behavior in soils contaminated by mining wastes were studied in 3 different semiarid sites of North Mexico: a) soils of pH 8-9 contaminated by Na-Ca arsenate residues of pH 10-11; b) soils originally acidified to pH 2-3 by oxidation of tailings rich in pyrite, arsenopyrite and Pb and Zn sulfides, and neutralized to final circumneutral pH values; and c) soils of pH ~7 contaminated by As<sub>2</sub>O<sub>3</sub>- and Pb sulfate- containing powders. Concentrations of arsenic were determined in selective chemical extractants, including water-soluble and total fractions. Its distribution between As(III) and As(V) was determined in some extracts. Soil fines were also studied by electron microscopy and X-ray diffraction. Water soluble As was found in lower concentrations in soils than in original wastes and decreased with deposition time. Results suggest that mechanisms of immobilization of arsenic are due to previously detected sorption processes on Fe oxides, but also to formation of insoluble arsenates of Pb and Zn. The latter are supported by thermodynamic calculations which suggest that at total contents of trace metals and major species found in these soils, highly insoluble arsenates of heavy metals are formed. X-ray diffraction pattern

analyses detected the following secondary minerals: mimetite [Pb<sub>5</sub>Cl((As,P)O<sub>4</sub>)<sub>3</sub>], lironite [Cu<sub>2</sub>Al(As,P)O<sub>4</sub>(OH)<sub>4</sub>·4H<sub>2</sub>O] and kegelite [Pb<sub>12</sub>Zn<sub>2</sub>Al<sub>4</sub>Si<sub>11</sub>S<sub>4</sub>O<sub>54</sub>]. Electron microscopy also shows evidence of As-Pb associations. Risk assessment methods for populations exposed to these soil environments were applied and yielded predictions of low bioavailability. These findings and further spectroscopic studies may provide a scientific basis for recommending and prioritizing future remediation strategies in these types of contaminated environments.

**GEOC 34 [674944]: Arsenic uptake processes in reducing environments: Implications for active remediation and natural attenuation**

**Richard T. Wilkin**, Office of Research and Development, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, 919 Kerr Research Drive, Ada, OK 74820, Fax: 580-436-8703, wilkin.rick@epa.gov

**Abstract**

Reductive dissolution of iron oxyhydr(oxides) and release of adsorbed or coprecipitated arsenic is often implicated as a key process that controls the mobility and bioavailability of arsenic in anoxic environments. Yet a complete assessment of arsenic transport and fate requires an understanding of uptake processes in iron-reducing and sulfate-reducing redox regimes, conditions often encountered in wetland systems that receive discharge of contaminated groundwater and in iron-based reactive media used for groundwater remediation. Under these redox conditions, arsenic is typically present in solution as an uncharged oxyanion or as a mixture of charged thioarsenic complexes with S/As ratios that range from 1:1 to 4:1. Depending on the aqueous speciation of arsenic, which is largely a function of pH and dissolved sulfide concentration, chemical uptake pathways include sorption to and/or coprecipitation with iron sulfides (mackinawite and pyrite), mixed iron-valence precipitates (green rust), and/or organic matter.

**GEOC 35 [674472]: Assessment of safe water options for villages in Bangladesh**

**Phillip T Crisp**<sup>1</sup>, Ahmedul H Chowdhury<sup>1</sup>, Andrew Lau<sup>2</sup>, and Quazi Quamruzzaman<sup>3</sup>. (1) School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Anzac Pde, Kensington, Sydney 2052, Australia, Fax: 610-2-9385-5966, p.crisp@unsw.edu.au, (2) GHD Group, (3) Dhaka Community Hospital

**Abstract**

The most promising options for safe water supplies in arsenic-affected villages are: 1. dugwells (with surface layer collection), 2. very-shallow tubewells (to dugwell depth), 3. pond-sand filters, 4. combined air oxidation-precipitation-iron metal adsorption systems (for arsenic-affected tubewells), and 5. rainwater collection systems (optimized for size and elimination of first-flush). All options can be constructed by villagers from local materials. To provide convenience and acceptance, sources 1-4 should be combined with a pump (hand or electric), an elevated tank and a reticulation system (in-ground plastic pipes, concrete aprons and taps). Option 1 is cheapest and simplest (or Option 2, if proven adequate), since costs can be shared. Option 3 is satisfactory, if microbiologically adequate (relatively clean pond or river). Option 4 is useful if groundwater is saline. Option 5 is expensive, since only one family is supplied. The systems are under construction for comparative testing in five villages.

**GEOC 36 [675848]: Characterization of arsenic containing water treatment residuals**

**Hun-Young Wee**, and Timothy A. Kramer, Department of Civil Engineering, Texas A&M University, 3136 TAMU, college station, TX 77843, weehy@neo.tamu.edu

**Abstract**

Further treatment of water processing residuals with elevated arsenic levels is required before disposal into a landfill in order to prevent arsenic release in natural environments. In this study, characterization of water treatment residuals and arsenic desorption/leachability were conducted. In particular, the Toxicity Characteristic Leaching Procedure (TCLP), competitive

desorption with phosphate, sulfate, and chloride, and effect of pH were evaluated. Arsenic leaching was generally underestimated through TCLP. Competitive desorption of arsenic with phosphate was considerable but desorption with sulfate and chloride was insignificant. Effect of pH on arsenic leaching was studied at 4, 6, 8, and 10. Arsenic leaching was observed at low and high pH (4 and 10). Especially, at high pH (pH 10), arsenic leaching was greatest because surface charge of adsorbents (ferric hydroxide, aluminum hydroxide) is changed negatively so this increase repulsion between adsorbents and arsenic anions. The results obtained suggest that the worst conditions for arsenic leaching/release in residuals are phosphate competition at high pH.

**GEOC 37 [663757]: Subsurface arsenic speciation analysis**

**Ning Xu**<sup>1</sup>, Chunming Su<sup>2</sup>, Jihua Hong<sup>1</sup>, and Richard Wilkin<sup>2</sup>. (1) ManTech Environmental Corp, 919 Kerr Research Dr, Ada, OK 74821, Fax: 580-436-8501, xu.ning@epa.gov, (2) USEAP

**Abstract**

While possible legislative changes in the drinking water limit for arsenic make its detection at low levels more important than ever, it is the chemical forms of arsenic that make the difference in their toxicity. In the natural environment, arsenic exists in two stable inorganic chemical oxidation states: arsenite and arsenate. Arsenite is more mobile in subsurface than arsenate, and its toxicity is 25 to 50 times more than that for arsenate. Arsenic can also exist in stable organic forms in certain environments, but the toxicity of organo-arsenic compounds are far less than those of the inorganic forms. Consequently, it is necessary to develop an analytical method that can separate the different arsenic species and can detect them individually for their toxicity assessment. A method has been developed to separate and analyze four arsenic species of concern in ground water monitoring: arsenite, arsenate, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The four arsenic species are first separated by an ion chromatograph (IC), then reacted to form arsenic hydride through a hydride generation (HG) apparatus, and finally detected by an atomic fluorescence spectrometer (AFS). The system is very sensitive and is able to quantify each arsenic species at the 4 to 6 microgram per liter level. It has been used successfully to monitor the ground water arsenic speciation variations in a heavily contaminated site. It has also been used extensively for the evaluation of subsurface permeable reactive barriers (PRBs) for in-situ treatment of arsenic in ground water, especially for understanding the role of "green rust", a by-product from the PRB wall, in arsenic species removal through an adsorption/co-precipitation process.

**GEOC 38 [676039]: Mechanisms of organic arsenic adsorption on nanocrystalline titanium dioxide**

**Chuanyong Jing**, Salem Baidas, and Xiaoguang Meng, Center for Environmental Systems, Stevens Institute of Technology, 1 Castle Point on Hudson, Hoboken, NJ 07030, Fax: 201-216-8303, cjing@stevens-tech.edu

**Abstract**

Batch adsorption tests, electrophoretic mobility measurements, Fourier transform infrared (FTIR) spectroscopy, and surface complexation modeling were employed to investigate the mechanisms of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) adsorption on the nanocrystalline titanium dioxide (TiO<sub>2</sub>). The shift of the pHPZC to the lower pH range and decreased adsorption percentage with the increasing pH indicated that both MMA and DMA were as anionic species. Phosphate has the same adverse effect on the adsorption of organic arsenic as on inorganic arsenic. The removal of organic arsenic was greatly enhanced in the presence of UV light. Up to 95% MMA and DMA was removed at pH=5 with UV light, and the removal efficiency was increased with decreasing pH. Dissolved oxygen had no effect on the removal of organic arsenic, while hydrogen peroxide had adverse effects. Efficient treatment processes may be developed for removing organic arsenic from water with the nanocrystalline TiO<sub>2</sub>.

**GEOC 39 [676201]: In situ arsenic removal by zerovalent iron: An accelerated pilot test simulating long-term permeable reactive barrier performance**

**Dimitrios Vlassopoulos<sup>1</sup>**, Charles B. Andrews<sup>1</sup>, Michael Rafferty<sup>1</sup>, Peggy A. O'Day<sup>2</sup>, and Nelson A. Rivera Jr.<sup>2</sup>. (1) S.S. Papadopulos and Associates, 7944 Wisconsin Ave, Bethesda, MD 20814, Fax: 301-718-8909, [dvllassopoulos@sspa.com](mailto:dvllassopoulos@sspa.com), (2) Department of Geological Sciences, Arizona State University

**Abstract**

Arsenic removal by zerovalent iron (ZVI) is a potentially cost-effective method for remediation of contaminated groundwater, but experience until recently has been limited to laboratory and ex-situ implementation. A pilot-scale (1.8 m<sup>3</sup>) gravity-flow reactive barrier was installed and operated at a former pesticide manufacturing site to investigate media longevity, site-specific (hydrochemical) effects on performance, and operation/maintenance issues associated with in-situ implementation. Performance was monitored over a one year period and included both chemical and hydraulic parameters. Initially, during the first 200 pore volumes, influent As concentrations averaging 3 mg/L were reduced by more than 2 orders of magnitude. Effluent As levels then gradually increased over time, with As removal stabilizing at 90-95% from 1,000 to more than 4,000 pore volumes. An irreversible decrease in permeability was also observed over this time, presumably due to accumulation of oxide, carbonate, and possibly silicate corrosion products. Ultimately this resulted in arsenic breakthrough due to development of preferential pathways through the media.

**GEOC 40 [674946]: Transport of As(III) and As(V) in experimental subsurface systems** Mark O. Barnett<sup>1</sup>, **Tanja Radu<sup>1</sup>**, Jae K. Yang<sup>2</sup>, and Jeremiah C. Hilliard<sup>3</sup>. (1) Department of Civil Engineering, Auburn University, 238 Harbert Engineering Center, Auburn, AL 36849, Fax: 334-844-6290, [barnettm@eng.auburn.edu](mailto:barnettm@eng.auburn.edu), [radutan@mail.auburn.edu](mailto:radutan@mail.auburn.edu), (2) LG Institute of Environmental Science and Health, (3) CH2M Hill

**Abstract**

Sources of arsenic in natural groundwater may be both geogenic (i.e., natural) and anthropogenic. In order to understand the migration of arsenic in the subsurface, it is necessary to understand the mechanisms of arsenic adsorption and desorption processes and their effect on transport. Although the adsorption of arsenic to solid phases has been relatively well studied in batch systems, arsenic adsorption dynamics are much different in column studies with flowing water. The goal of this study was to investigate the adsorption and transport of arsenite [As(III)] and arsenate [As(V)] in experimental subsurface systems containing iron-coated sand. Column studies examined the effect of pH, flow rate, and phosphate on arsenite/arsenate mobility. The pH effect was examined by comparison of experiments performed at both pH 4.5 and 9. The increase in pH led to a significant increase in arsenite adsorption but decreased arsenate adsorption. In addition, both arsenite and arsenate exhibited rate-dependent transport in the columns. The competing effect of phosphate was examined by introducing phosphate solution to the column with adsorbed arsenite/arsenate and vice versa. The results indicated that phosphate decreased arsenite's/arsenate's ability to adsorb on iron coated sand with a resulting increase in mobility. In general, but not under all circumstances, arsenite adsorbed less and was more mobile than arsenate. These results have significant implications to the subsurface behavior of arsenic in both natural and contaminated environments.

**GEOC 41 [675611]: Uptake of arsenic by *Pteris cretica*: in situ XANES study of living plants**

**Marianna A. Kissell**, Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100, Fax: (631) 632-8240, [mkissell@ic.sunysb.edu](mailto:mkissell@ic.sunysb.edu), Mark Fuhrmann, Environmental Sciences Dept, Brookhaven National Laboratory, and Richard J. Reeder, Department of Geosciences, SUNY at Stony Brook

**Abstract**

Using x-ray absorption spectroscopy we investigated the uptake, oxidation state and distribution of arsenic in a known As-hyperaccumulating fern species, *Pteris cretica*. During short-term uptake, bare roots were exposed to a 500 ppm Na-arsenate solution and XAS spectra of roots and adjacent solution were taken. For longer uptake, ferns in soil were exposed to a 1000

ppm Na-arsenate solution distributed across the soil surface. Both experiments allowed for in situ study of living plants with synchrotron radiation. The bare root experiment showed arsenic concentration in the leaves reached approximately 2400  $\mu\text{g/g}$  within 48 hours, primarily as As(V). The soil experiment showed a significant amount of As(V) was reduced to As(III) over 8 days. To improve our understanding of arsenic behavior in plants used as environmental remediators, future work will attempt to identify electron donors promoting As reduction, identify cells used to store As, and characterize As-complexation in the leaves.

**GEOC 42 [673720]: Arsenic uptake, hyperaccumulation, and detoxification in Chinese Brake fern: an mechanistic approach**

**Yong Cai**<sup>1</sup>, Weihua Zhang<sup>2</sup>, Jinhui Su<sup>2</sup>, Min Feng<sup>2</sup>, Lena Q. Ma<sup>3</sup>, and Kelsey Downum<sup>4</sup>. (1) Dept. of Chemistry and Southeast Environmental Res. Center, Florida International University, University Park, Miami, FL 33199, Fax: 305-348-3772, cai@fiu.edu, (2) Department of Chemistry, Florida International University, (3) Soil and Water Sciences Department, University of Florida, (4) Department of Biological Sciences, Florida International University

**Abstract**

Chinese Brake fern (*Pteris vittata*), a recently discovered arsenic hyperaccumulator, can be potentially used in phytoremediation of arsenic in arsenic-contaminated sites. The effective use of this plant for phytoremediation requires an understanding of the plant processes that control uptake and detoxification of arsenic from soil. There is little information available regarding the mechanism of arsenic uptake, tolerance, and accumulation in plants that hyperaccumulate this inorganic element. In this paper, we will report the recent progress in our group. The objectives of these studies were to 1) investigate the response of thiols in Chinese Brake fern upon exposure to arsenic in order to determine whether thiols are involved in arsenic accumulation in Chinese Brake; 2) characterize the thiols that respond to arsenic exposure in this plant; 3) investigate the uptake kinetics of arsenic and phosphate; and 4) evaluate arsenic uptake and thiol formation in the plant under exposure to different arsenic species.

**GEOC 43 [675431]: Phytofiltration of arsenic from drinking water**

**Mark P. Elless**, Charissa Y. Poynton, and Michael J. Blaylock, Edenspace Systems Corporation, 15100 Enterprise Court, Suite 100, Chantilly, VA 20151, Fax: 703-961-8939, elless@edenspace.com

**Abstract**

The recent discovery of a natural arsenic-hyperaccumulating plant has led to its performance evaluation for removing arsenic from drinking water in a process termed phytofiltration. The brake fern's (*Pteris vittata*) arsenic-accumulating capabilities have been harnessed to remediate such contaminated soils, following its discovery that showed the ability to accumulate and tolerate high concentrations (up to 22,000 mg/kg by dry weight) of arsenic in its foliage. *Pteris* ferns are now being evaluated under an NIH grant as an alternative technology to remove arsenic from drinking water. A prototype phytofiltration system has been constructed for performance evaluation towards optimization of this technology. The effect of source water quality (pH, dissolved ions, As oxidation state), *Pteris* species, as well as growth and operating conditions on the efficiency of the hydroponic removal of trace levels of arsenic are being investigated. The cost effectiveness of this technology compared to conventional technologies will also be presented.

**GEOC 44 [674469]: Photoactive removal of As(III) from water using novel active material**

**Marc A. Anderson**<sup>1</sup>, Eunkyoo Lee<sup>1</sup>, Timothy J. Lee<sup>1</sup>, Isabel Tejedor<sup>1</sup>, and Tom Holm<sup>2</sup>. (1) Environmental Chemistry and Technology Program, University of Wisconsin- Madison, 660 North Park ST, Madison, WI 53706, Fax: 608-262-0454, nanopor@wisc.edu, (2) Groundwater Section, Illinois State Water Survey

## Abstract

The oxidation status of arsenic in source waters significantly affects the adsorption capacity of adsorbents. Many arsenic removal processes have been found to be ineffective for arsenite, As(III), which is uncharged at the pH of drinking water. Removal of As(III) is generally accomplished by oxidizing it to arsenate, As(V), which can be removed by adsorption or ion-exchange mechanisms. During the authors' testing, a TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed oxide was developed which has been shown to effectively remove As(III) without requiring a separate oxidation process. A heterogeneous photocatalytic adsorbent (Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) was synthesized by sol-gel techniques. This composite acts as a photocatalyst that can oxidize As(III) to As(V), with the latter species being adsorbed by the adsorbent. The materials (Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) were mixed as a stable suspension (sol) that was used to coat glass beads. After the coated beads were fired, the resulting thin films served as both a photocatalyst and an adsorbent.

## **GEOC 45 [676068]: Chemistry of a simple and effective groundwater arsenic filter Based on iron composites: A large scale Bangladesh experiment**

**Abul Hussam**<sup>1</sup>, Abul K. M. Munir<sup>2</sup>, M. Alauddin<sup>3</sup>, Zafreen A. Hossain<sup>3</sup>, Amir H. Khan<sup>4</sup>, and Charles C. Chusuei<sup>5</sup>. (1) Chemistry Department, George Mason University, MSN3E2, Fairfax, VA 22030, Fax: 703-993-1055, ahussam@gmu.edu, (2) Department of Environment, Sono Diagnostic Center, (3) Department of Chemistry and Chemical Technology, Islamic University, (4) Department of Chemistry, University of Dhaka, (5) Chemistry Department, University of Missouri

## Abstract

In Bangladesh, thousands of people are suffering from arsenical keratosis and many people have died of cancer after prolonged drinking of groundwater containing arsenic. To purify this water, we have developed a simple three-pitcher (locally known as '3-Kolshi'), a two bucket, and a continuous flow well-head water filtration system based on treated cast iron composite as the active material. The 3-Kolshi system was tested by passing more than 10,000 L of groundwater containing 80-1900 microgram/L of arsenic. The filtered water contained  $12 \pm 10$  microgram/L As (total), no detectable As (III), and significantly reduced major, minor and trace metals. The bucket filter was tested with 100,000 L of groundwater with similar results. The filtration process was monitored by measuring As (total), As(III), 23 other metals, 9 anions, pH, dissolved oxygen, redox potential, conductivity, temperature and flow rate. A complete conversion of Fe(0) to nonmagnetic hydrous ferric oxide (HFO) as the most active component for arsenic removal is indicative of an oxidizing environment sustained by continuous diffusion of air in Kolshi and optimally designed bucket system. Experimental data and theoretical calculations show no breakthrough of arsenic. A continuous decrease of As(total) concentration below 10 microgram/L indicates a progressive increase in filter efficiency. Blank filters showed weak retention and breakthrough at 100 L. These observations are explained by reactions under oxic condition at composite iron-water interface and interactions of inorganic arsenic species with insitu formed hydrous ferric oxide (HFO). X-ray photoelectron spectroscopy (XPS) of surface composition for composite iron, spent iron layer, and naturally occurring HFO showed differences in binding energy characteristics of Fe, O, C, and Si.

## **GEOC 46 [671341]: Comparison of pilot and rapid small scale column tests (RSSCTs) for arsenic removal by porous iron oxides (GFH and E-33)**

**Paul Westerhoff**, and Mohammad Badruzzaman, Department of Civil and Environmental Engineering, Arizona State University, Engineering Center Room ECG 252, Box 5306, Tempe, AZ 85287-5306, Fax: 480-965-0557, p.westerhoff@asu.edu

## Abstract

Nano-structured iron oxides/hydroxides are increasingly being evaluated and selected for arsenic removal in drinking water systems. Granular ferric hydroxide (GFH, US Filter) and E-33 (Severn Trent) are commercially available iron based adsorbents. GFH was characterized as a highly porous (micropore volume 0.0394 cc/g, mesopore volume 0.0995 cc/g) with a BET surface area of  $235 \pm 8$  m<sup>2</sup>/g. E-33 has a similar surface area and pore size distribution. Intraparticle mass transfer mechanisms of iron-arsenate inner sphere complexes onto porous sorbents are similar to that of physically adsorbed organics

onto granular activated carbon (GAC). Rapid small-scale column tests (RSSCTs) developed over last two decades for simulating removal of organic compounds by GAC were extended in this study for arsenate adsorption onto GFH and E-33. Proportional diffusivity based modified scaling equations were employed to design RSSCTs and the results were obtained for arsenate breakthrough as a function of bed-volumes treated with GFH and E-33 medias using model waters and six groundwaters from Arizona. All RSSCTs depict that E-33 shows better adsorbability of arsenate than GFH, and are consistent with results from pilot testing. Dry mass based adsorption densities from the column tests at a comparable point for arsenic breakthrough were 1.73 to 1.90mgAs/mg for GFH and 1.94 to 3.04 mgAs/mg for E-33 depending water quality (pH, silica, initial arsenic). Performance differences between GFH and E-33 were attributed to the adsorption of competing ions (silica, vanadium, and phosphate) and/or the formation of precipitates (silicates, calcium carbonate) that may block off the internal pores. Using SEM with EDX used (not virgin) GFH media contained 5 times more silicon and 9 times more calcium on the surface than used E-33. The results establish RSSCT as a potential bench-top packed bed experimental method to simulate the adsorbent utilization profile of a several months long pilot plant in several days with an acceptable level of accuracy.

### **GEOC 47 [675950]: Pilot scale study of polymer enhanced ultrafiltration process for the removal of arsenic from ground water**

**Hermes D. Gallo**, School of Chemical Engineering and Materials Science, University of Oklahoma, 100 E. Boyd room T-334, Norman, OK 73019, Fax: 405-325-4217, danielgallo@ou.edu, Edgar J. Acosta, Department of Chemical Engineering, University of Oklahoma, John F. Scamehorn, Institute for Applied Surfactant Research and School of Chemical Engineering and Materials Science, The University of Oklahoma, and David A. Sabatini, Department of Civil Engineering and Environmental Science, University of Oklahoma

#### **Abstract**

In this work we describe a pilot scale study of the use of the polymer enhanced ultrafiltration (PEUF) technology for removing arsenic ions (in the form of negative arseniate). Specifically, the arseniate ions complex with a cationic polymer, followed by removal of the arsenic-polymer complex by an ultrafiltration membrane, leaving the water pass through the membrane with a low arsenic concentrations. Adding a chloride salt of a multivalent cation can regenerate the polymer for further use. This study shows that it is possible to remove up to 99% of arsenic with final arsenic concentrations below the new 10 ppb standard level and with water waste of less than 5%. Further cost analysis shows that the capital cost is dominated by the cost of the ultrafiltration units and that is very competitive with all other alternative technologies. The operational costs are dominated by the costs of polymer regeneration, which is in turn a function of the concentration of competitive ions such as sulfate. We provide further discussion on the conditions that make this technology more attractive than other alternatives. We will also discuss some other technical issues, such as effect of pH, effect of polymer dosage, flow configuration, pressure drop, gel formation, etc.

### **GEOC 48 [634642]: Removal of arsenic anions from water using polyelectrolyte-enhanced ultrafiltration**

**John F Scamehorn**<sup>1</sup>, Preeyaporn Pookrod<sup>2</sup>, and Kenneth J. Haller<sup>2</sup>. (1) Institute for Applied Surfactant Research, University of Oklahoma, 100 E Boyd, Norman, OK 73019, Fax: 405-325-5813, scamehor@ou.edu, (2) School of Chemistry, Suranaree University of Technology

#### **Abstract**

Polyelectrolyte-enhanced ultrafiltration (PEUF), using cationic poly(diallyldimethyl ammonium chloride) polyelectrolyte was used to remove arsenic(V) from dilute aqueous solutions. In PEUF, a water-soluble polyelectrolyte of opposite charge to that of the target ion binds the charged arsenate complex. The solution is then treated by ultrafiltration with membrane pore sizes small enough to block the polymer. Only the residual unbound arsenate concentration is present in the permeate solution passing through the membrane. Arsenic rejections as high as 99.95% are obtained and increase with increasing polymer concentration and decreasing ionic strength (added salt concentration). Arsenic rejection increases with increasing pH (pH of 6.5 to 8.5) as the divalent/monovalent arsenic complex ratio in solution increases, improving arsenate binding to the polymer.

Gel point concentration (polymer concentration at which flux becomes zero) was found to be 655 to 665 mM, (approximately 5.98 to 6.07 wt%).

#### **GEOC 49 [675371]: Removal of arsenic(V) from drinking water by clay membranes**

Jun Fang, and **Baolin Deng**, Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, Fax: 573-882-4784, jf3y9@missouri.edu, dengb@missouri.edu

##### **Abstract**

While many treatment technologies are available for arsenic removal from drinking water including coagulation/ filtration, lime softening, activated alumina adsorption, ion exchange, and membrane processes, most of these approaches are expensive and only suitable for large water systems. In this study, membranes made of low-cost clay minerals were explored for arsenate removal. Bentonite, kaolinite, and illite were selected for membrane preparation. Feed water containing arsenic was pumped through the compacted clay membranes and the effluent was collected at the lower pressure side for arsenic analysis. The ability of clay membranes to retain arsenic was investigated at various pH levels, initial arsenic concentrations, and background ion concentrations. The influence of applied pressure on the permeate flux and arsenic removal efficiency was also examined. The results indicated that a greater than 90% rejection of arsenic could be achieved from water spiked with 50-100mg/l of arsenate using the clay membranes.

#### **GEOC 50 [673151]: Utility of Zeolites in arsenic removal from water**

**Siddhesh S. Shevade**, US-EPA, 919 Kerr Research Drive, Ada, OK 74820, Fax: 580-436-8703, shevade.siddhesh@epa.gov, and Robert Ford, National Risk Management Research Laboratory, US-EPA

##### **Abstract**

Zeolites are well known for their ion exchange and adsorption properties. So far the cation exchanger properties of zeolites have been extensively studied and utilized. The anion exchanger properties of zeolites are less studied. Zeolite Faujasite Y has been used to remove arsenic from water in continuous flow reactions below WHO's and EPA's maximum contamination limits. The zeolites showed a very good arsenic removal capacity with contact time less than 2 min. The arsenic removal capacity of the zeolites over a wide pH range may be useful in determining the next generation water treatment processes. The effect of various cationic, anionic and organic water pollutants has been studied on arsenic removal capacity of zeolites. In situ FTIR characterization has been carried out to find out the arsenic removal mechanisms.

#### **GEOC 51 [654956]: A new highly selective resin for the removal of arsenate in groundwater**

Spiro D Alexandratos, and **Laurent Dambies**, Department of chemistry, Hunter College, 695 Park avenue, New York, NY 10021, alexsd@hunter.cuny.edu, ldambies@hunter.cuny.edu

##### **Abstract**

Much research has been focused over the past few years to the synthesis of resins for arsenic removal. This includes the preparation of ion exchange, chelating or metal loaded resins (Fe,Zr,Cu, La...). To meet the new EPA guideline for arsenic in drinking water of 10 ppb, these resins have to be selective and with a high sorption capacity at low concentration. We have prepared a new synthetic resin containing a polyol derivative and studied its affinity for As(V). Arsenate isotherm studies done at neutral pH between 0 and 4 ppm fit a Langmuir isotherm with an affinity coefficient of 280 L.mmol<sup>-1</sup> and a saturation capacity of 0.8 mmol.g<sup>-1</sup>. In most of the batch studies, the resin was able to remove As(V) below 10 ppb. Arsenate sorption is pH-dependent with a maximum uptake between pH 5 and 7. Although sorption is negligible for pH >10, removal of As(V) at pH 1.5 is still important. Neither sulfate nor phosphate interfere with arsenate sorption. Arsenate is believed to be removed via an ion exchange-complexation mechanism. Different tests carried out in batch with commercially available products such as

Amberlite IRA-900, Alcoa CPN activated alumina and Apyron products demonstrate the superiority of the new resin. A treatment combining a pre-oxidation treatment to oxidize As(III) to As(V) and sorption on the polyol resin is a promising technology for arsenic removal in groundwater.

**GEOC 52 [675530]: Metals Remediation Compound (MRC™): A new slow release product for in situ metals remediation**

**Anna Willett**, and Stephen S. Koenigsberg, Regenesis, 1011 Calle Sombra, San Clemente, CA 92673, [anna@regenesis.com](mailto:anna@regenesis.com)

**Abstract**

Metals Remediation Compound (MRCTM) is a slow-release metals remediation product that removes dissolved arsenic from groundwater via *in situ* immobilization (precipitation and sorption to soil particles). MRC consists of an organosulfur compound that complexes with dissolved arsenic and sorbs, as a complex, to solid media. A potential endpoint for the immobilized arsenic is an arsenic sulfide solid. MRC was tested for removal of dissolved arsenic, chromium, and copper mixtures in a horizontal soil column. In 27 days, arsenic was reduced from 26 mg/L to 0.5 mg/liter, chromium was reduced from 15 mg/L to 0.7 mg/liter, and copper was reduced from 4 mg/L to < 0.1 mg/liter. Flow was then begun to assess the stability of the immobilized metals. Three pore volumes of water exposed to oxygen were flushed through the column for 30 days and concentrations of dissolved metals in the effluent did not increase.

**GEOC 53 [674905]: Evaluation of the effectiveness of quicklime-based stabilization/solidification (S/S) in arsenic (As) contaminated soils**

**Deok Hyun Moon**, and Dimitris Dermatas, Civil, Environmental and Ocean Engineering, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, [dmoon@stevens-tech.edu](mailto:dmoon@stevens-tech.edu)

**Abstract**

The effectiveness of quicklime-based stabilization/solidification (S/S) to immobilize arsenic (As) in soil environments was evaluated by performing semi-dynamic leaching tests. Both artificial and field soil samples, contaminated with As, were tested. Based on these tests, the long term As leaching mechanisms were determined. The controlling As immobilization mechanisms were elucidated using X-Ray diffraction (XRD) mineralogical analyses and batch geochemical testing. S/S effectiveness was evaluated by measuring As cumulative fraction release, effective diffusion coefficients ( $D_e$ ) and leachability indices (LX) for the tested soils. Upon treatment, all soils were found to be acceptable for "controlled utilization". Study findings indicated that the controlling mechanisms for As leaching and immobilization were diffusion and precipitation, respectively. In order to further investigate As immobilization mechanisms, an in-depth mineralogical study was designed and undertaken. Arsenic immobilization was confirmed to be precipitation controlled. The following major Ca-As precipitates were identified by XRD analyses: Ca-As-O,  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$ .

**GEOC 54 [666029]: Consequences of disorder in biological reactions for chemical transport in unsaturated porous and fractured geologic media**

**Randall A. LaViolette**, and Daphne L. Stoner, Chemical & Biological Sciences, Idaho National Engineering & Environmental Laboratory, P. O. Box 1625, Idaho Falls, ID 83415-2208, Fax: (208) 526-8541, [yaq@inel.gov](mailto:yaq@inel.gov)

**Abstract**

Under a wide variety of circumstances, geologic media may support consortia of microbiological organisms, e.g., biofilms. Some of these consortia are capable of removing or transforming contaminant in a flow, which suggests that these organisms might be employed in a "natural" or a stimulated *in situ* treatment of contaminants in the subsurface. The essential features of the complicated (and possibly complex) interactions between consortia, contaminant, flow, and geologic media are clarified with mesoscale models that are locally simple but capable of producing emergent behavior. This work will focus on the role

that spatial and chemical disorder plays in the fate of contaminants in subsurface flows, and in particular the consequent anomalies predicted for contaminant transport and concentration.

**GEOC 55 [674191]: Microbial biofilms: geochemically reactive environmental interfaces**

**Lesley A. Warren**, and Elizabeth A. Haack, School of Geography and Geology, McMaster University, 1280 Main St. West, Hamilton, ON L8S 4K1, Canada,  
Fax: 905-546-0463, warrenl@mcmaster.ca

**Abstract**

Microbial biofilms are essentially biologically driven, geochemically reactive interfaces between solid surfaces and aqueous solution. Field investigation of acid rock drainage (ARD) associated biofilms characterizing: (1) microgeochemical gradients (pH and O<sub>2</sub>), (2) metal fractionation, and (3) microbial communities; over both seasonal and diel timescales, indicates biofilms are highly metal reactive. Results show that biofilms accumulate metals seasonally within two microbially controlled solid fractions: amorphous hydrous manganese oxide (HMO) biominerals and the organic biofilm matrix. The biofilm geochemical microenvironment, driven largely by microbial activity, dynamically impacts biofilm metal behaviour over diel timescales. On-going research aims to characterize the linkages amongst observed biofilm geochemical gradients, microbial activity, and metal dynamics in these highly reactive interfacial structures. We are using X-ray Absorption Spectroscopy (XAS) to identify and characterize HMO biominerals and molecular biological approaches to characterize microbial strains. Our model, thus far, of biofilm biogeochemical architecture will be presented.

**GEOC 56 [676511]: Bacterial-silica interactions: Affinity or Fate?**

**Liane G. Benning**<sup>1</sup>, V. Phoenix<sup>2</sup>, N. Yee<sup>1</sup>, and O. Hammer<sup>3</sup>. (1) School of Earth Sciences, University of Leeds, Leeds LS2 9JT, United Kingdom, Fax: 44-113-3435259, liane@earth.leeds.ac.uk, (2) Department of Geology, University of Toronto, (3) Physics of Geological Processes, University of Oslo

**Abstract**

The formation of silica sinters in modern or ancient hot springs follows a multi-step process governed by an increase in bacterial EPS with concomitant but inorganically driven silica poly-condensation followed by microbially aided aggregation of silica nanospheres. Silica polymerization and thus silica nucleation in the presence of cyanobacteria is not enhanced but in a first stage cyanobacteria react by increasing the amount of EPS in their sheath. This process enhances the accumulation of inorganically nucleated silica nanoparticles into larger silica aggregates, which upon further addition of silica will lead to cyanobacterial fossilization. Experimental and theoretical evidence indicates that the polymerization of silica monomers leads to the formation of branching clusters that eventually collapse to form a spherical particle. Although, the parameters controlling this collapse are unclear, some evidence indicates that it may be the dehydroxylation of silanol or silane clusters which leads to the formation of the first nanospheres.

**GEOC 57 [676138]: Rapid oxidation of pyrite surfaces by Thiobacillus ferrooxidans and T. thiooxidans**

**Benjamin C. Bostick**<sup>1</sup>, Kristin Lester<sup>2</sup>, Colin Doyle<sup>3</sup>, Tom Kendelewicz<sup>4</sup>, Gordon E. Brown Jr.<sup>4</sup>, Scott Fendorf<sup>4</sup>, and Alfred M. Spormann<sup>5</sup>. (1) Department of Earth Sciences, Dartmouth College, 6105 Fairchild, Hanover, NH 03755, (2) Department of Civil and Environmental Engineering, Stanford University, (3) Department of Geological and Environmental Sciences, Stanford University, (4) Department of Geological & Environmental Sciences, Stanford University, (5) Department of Civil & Environmental Engineering, Stanford University

## **Abstract**

Pyrite oxidation is the critical step in the formation of acid mine drainage, which acidifies the environment, and releases associated toxic metals. Microbes accelerate pyrite oxidation, and, as such, understanding of their role in the production of acid mine drainage. Here, we probe pyrite oxidation by *Thiobacillus ferrooxidans* and thiooxidans using surface-sensitive photoelectron spectroscopy and compare them with chemically oxidized surfaces. Microbial oxidation resulted in the formation of distinct oxidized surface species distributed non-uniformly over the pyrite surface. In contrast, chemical oxidation proceeds through a similar mechanism but without the build-up of passivating oxidation products. Both mechanisms occurred at isolated regions of the surface that were not correlated with step edges or other topographical features. These results demonstrate that microbial oxidation occurs through a similar mechanism to chemical oxidation, but that kinetics influence the products that form.

## **GEOC 58 [677693]: Accelerated calcite dissolution caused by alginic acid**

**Tod D. Perry**, Owen W Duckworth, C. J. McNamara, Scot T Martin, and R. Mitchell, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, Fax: 617-496-1471, [tperry@deas.harvard.edu](mailto:tperry@deas.harvard.edu)

## **Abstract**

Bacteria living on mineral surfaces promote dissolution through production of metabolic by-products including organic acids and exopolysaccharides (EPS). Carbonate minerals, especially calcite, are abundant and an important carbon sink. Microbially mediated dissolution of these minerals, which is an essential part of mineral cycling, is poorly understood. EPS has been observed to cause both dissolution and passivation of minerals but the effects have not been quantified for calcite and the mechanisms are not well understood. The effect of alginic acid, a model environmental polymer, on calcite dissolution was assessed using an atomic force microscopy/flow-through reactor. Alginic acid was found to increase calcite dissolution rate over a wide range of pH values. Microbially produced polymers may dramatically affect calcite dissolution. Quantifying these interactions may help the understanding of the role of microorganisms in global mineral cycling.

## **GEOC 59 [675178]: Interactions of polysaccharides and polypeptides with silica and Fe-oxide surfaces**

**J. D. Kubicki**<sup>1</sup>, R. Kramer Campen<sup>2</sup>, and Kideok Kwon<sup>1</sup>. (1) Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, Fax: 814-863-8724, [kubicki@geosc.psu.edu](mailto:kubicki@geosc.psu.edu), (2) Department of Geosciences, Pennsylvania State University

## **Abstract**

We have shown that the polysaccharide dextran (a model for LPS) has little attraction to silica and higher affinity to Fe-oxides. These observations have been explained by ab initio calculations on the H-bonding interactions between the monomer units of dextran and surface functional groups of silica, hematite, and goethite. Furthermore, the affinity of the polysaccharide for Fe-oxides has been observed to depend on the concentration of surface functional groups on a crystal face. Surfaces with higher densities of relatively less acidic Fe-OH terminal groups tend to have higher affinities for this neutral polysaccharide. We also calculated the interaction energy between lysine and silica in a same way as dextran monomer calculation. The minimum energy calculations showed that lysine forms much stronger H-bonding (-116 kJ/mol) than dextran monomer (-42 kJ/mol). These preliminary calculations are in qualitative agreement with the colloid-probe AFM results.

## **GEOC 60 [674407]: Modeling Reactive Ionic Diffusion within Bacterial Electrical Double-Layer**

**Chongxuan Liu**<sup>1</sup>, Andrew R. Felmy<sup>2</sup>, and John M. Zachara<sup>1</sup>. (1) Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, 3335 Q Avenue, Mail Stop K8-96, Richland, WA 99352, Fax: 509-376-3650, [chongxuan.liu@pnl.gov](mailto:chongxuan.liu@pnl.gov), (2) Environmental Dynamics and Simulation, Pacific Northwest National Laboratory

## Abstract

A reactive ionic diffusion model of multi-components is developed for simulation of reactive diffusion within bacterial electrical double layer. Formal model formulation is presented and a numerical solution procedure is demonstrated for spherical geometry. The developed model is applied to evaluate the rates of ionic mass transfer between bacteria and bulk solution using the electrochemical properties of a *Shewanella* species as an example. The rate simulation indicated that there are two opposite-charged electrical currents within the bacterial double layer during ionic diffusion driven by chemical and electrostatic potentials. The magnitude of the two currents is a function of space and time, ionic compositions, and bacterial charge density. The two currents are neutralized near the membrane surface, yielding a net zero current in the diffusion system. The rate simulation also showed that diffusion is an efficient mass transfer mechanism between bacteria and bulk solution. The time scale is 0.001 – 0.1 s for a non-reactive tracer to reach equilibrium within the bacterial electrical double layer in response to its changes in bulk solution. Such fast diffusive rate results in localized non-equilibrium chemical conditions within the double layer for reactive species, even they are related by aqueous speciation reactions that are typically treated as equilibrium ones in bulk phase reactive transport modeling. Overall, these results demonstrated that the geochemical conditions within bacterial electrical double-layer could be significantly different from bulk solutions during active bacterial metabolism and/or respiration processes, which drive ionic mass transfers between bacteria and bulk solution.

## **GEOC 61 [675506]: Metal adsorption to kaolinite in the presence of siderophores**

**Sarah Hepinstall**, Department of Civil Engineering & Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, shepinst@nd.edu, and **Patricia A. Maurice**, Department of Civil Engineering and Geological Sciences, University of Notre Dame

## Abstract

Siderophores are metal-complexing ligands with a high affinity for Fe(III), produced by microorganisms in Fe-deficient environments. Siderophores also form strong complexes with other metals such as Cd and Pb. Thus, their presence in soils can potentially influence heavy metal mobility. This study examined the effects of siderophores on Pb adsorption to kaolinite using batch adsorption experiments as a function of pH and [Pbaq] in 0.1 M NaClO<sub>4</sub> at 22C, in the dark. The trihydroxamate siderophore, desferrioxamine B (DFO-B) slightly enhanced Pb adsorption to kaolinite at pH 6 and less. At pH > 6, Pb adsorption was greatly inhibited, most likely because at the higher pH values, DFO-B in solution outcompeted surface adsorption sites for Pb. The monohydroxamate ligand acetohydroxamic acid (aHA) also enhanced Pb adsorption slightly at pH < 6, but decreased Pb adsorption at higher pH. Further investigations using Cd; DFO-E and DFO-D; and modeling of the experimental systems are ongoing.

## **GEOC 62 [675016]: Reduction of Co<sup>III</sup>EDTA Coupled with Microbially Mediated Goethite Reduction**

**Akemi Ito**<sup>1</sup>, **Frank Huang**<sup>1</sup>, and **Baolin Deng**<sup>2</sup>. (1) Department of Environmental Engineering, New Mexico Tech, Socorro, NM 87801, akemi@nmt.edu, (2) Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, Fax: 573-882-4784, dengb@missouri.edu

## Abstract

Five chemical and microbiological pathways for reduction of ethylenediaminetetraacetatocobalt(III) (Co<sup>III</sup>EDTA) were individually examined in an anoxic batch system. Iron reducing bacteria *Shewanella alga* strain BrY, which can also reduce Co<sup>III</sup>EDTA directly, was used as a model bacterium. Goethite, one of the most abundant ferric oxides in the environment, was added as an electron acceptor. Various cobalt and iron species were monitored as a function of time. The microbial Co<sup>III</sup>EDTA reduction rate and dissolved Fe<sup>3+</sup> reduction rate were 10 times and 15 times faster than that for microbial goethite reduction, respectively. Bioadsorption experiments showed that Co<sup>III</sup>EDTA disappearance and Co<sup>II</sup>EDTA production followed zero order reaction kinetics. A conceptual model for Co<sup>III</sup>EDTA reduction was developed using reaction rates for individual pathways, and model simulation agreed with the experimental results in the complex Co<sup>III</sup>EDTA-goethite-microorganism system.

**GEOC 63 [676142]: Transformation of RDX by biologically produced ferrous iron species**

**Kelvin B. Gregory**<sup>1</sup>, Aaron G.B. Williams<sup>2</sup>, Gene F. Parkin<sup>2</sup>, and Michelle M. Scherer<sup>2</sup>. (1) Department of Microbiology, University of Massachusetts, 203 Morrill IV North, Amherst, MA 01003, kgregory@microbio.umass.edu, (2) Department of Civil and Environmental Engineering, University of Iowa

**Abstract**

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a toxic munitions compound that often contaminates soil and groundwater at military installations. We have measured RDX removal by reduced mineral phases formed from the respiration of *Geobacter metallireducens* on ferrihydrite. Mössbauer spectra of the mineral phases produced by *G. metallireducens* reveal a complex mixture of ferric and ferrous iron phases that appears to evolve the longer it is incubated. The biologically-reduced solids reacted to transform RDX in a highly pH-dependent reaction. In addition, RDX was rapidly transformed in the presence of ferrous iron (Fe<sup>II</sup>) and chemically synthesized magnetite (Fe<sup>II</sup>Fe<sup>III</sup><sub>2</sub>O<sub>4</sub>). The adsorption of Fe<sup>II</sup> on magnetite was highly pH-dependent as was the subsequent transformation of RDX. These results suggest that attenuation of RDX contamination may be expected in natural or engineered environments where ferrous iron is abundant or microbial iron reduction is taking place.

**GEOC 64 [675809]: Spatial comparison of sedimentary fatty acid profiles in the coastal mid-Atlantic (USA) Potomac River basin**

**Gregory D. Foster**, and Cassi L. Walls, Department of Chemistry, George Mason University, 4400 University Drive, Fairfax, VA 22030, Fax: 703-993-1055, gfoster@gmu.edu

**Abstract**

Sedimentary fatty acids can be differentiated among vascular plant, algal, and bacterial sources at the watershed scale, which can be correlated to ecological changes and contamination of the aquatic environment in rapidly urbanizing landscapes. A comparison of fatty acids in sediments along a 320 km longitudinal transect of the Potomac River (middle-Atlantic United States) was conducted to identify the primary sources of geolipids. In all sediments, C16 and C18 fatty acids predominated in nearly equal proportions, indicating algal inputs to geolipid pools were important throughout the entire river in early summer. Freshwater sediments, in contrast, contained much greater proportions of C22-C28 even numbered fatty acids, indicative of terrestrial plant inputs, while marine sediments showed an enrichment of C14 fatty acids, being primarily associated with diatomaceous algae. Distinct compositional differences among sedimentary fatty acids occurred at the freshwater/marine transitional zone of the Potomac River. The fatty acid profiles revealed a continuum of geolipid sources along the downstream transect ranging from the upland Appalachian Province to the Coastal Plain of the Potomac River basin.

**GEOC 65 [678840]: Multinuclear NMR investigation of speciation in lead aluminoborosilicate glasses**

**April M. Sawvel**, Energy and Environment, Lawrence Livermore National Laboratory, 7000 East Avenue, L-221, Livermore, CA 94550, Robert Maxwell,

Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, and William L. Bourcier, Earth and Environmental Sciences Directorate,

Lawrence Livermore National Laboratory

**Abstract**

Structural speciation in a series of glasses in the systems PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, PbO-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and PbO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> were studied using solid-state nuclear magnetic resonance (NMR) methods. Specifically, <sup>29</sup>Si, <sup>27</sup>Al, <sup>11</sup>B, and <sup>207</sup>Pb NMR methods were applied to develop structural insights into the roles of Pb, B, and Al in the silicate network. The general composition range studied was (PbO)<sub>x</sub> [(B<sub>2</sub>O<sub>3</sub>)<sub>1-z</sub> (Al<sub>2</sub>O<sub>3</sub>)<sub>z</sub>]<sub>1-x</sub> (SiO<sub>2</sub>)<sub>1-x</sub> where x = 0.35, 0.5, and 0.65 and z = 0.0 and 0.5. Glasses in these families are often used as Mixed Oxide Dielectrics (MODs) for electrical device applications. Though the PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system has been studied by NMR methods [1], no work has been reported on the ternary system PbO-Al<sub>2</sub>O<sub>3</sub>-

SiO<sub>2</sub> or on the quaternary system PbO-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. <sup>207</sup>Pb experiments were carried out using spin echo mapping, while the <sup>29</sup>Si, <sup>11</sup>B, and <sup>27</sup>Al experiments were carried out using magic angle spinning (MAS). Speciation in lead borosilicate glasses followed trends established previously: more covalent lead was observed with increased lead content [1,2]. Aluminum was observed to form an aluminosilicate rich framework within the lead borosilicate matrix. Lead speciation was seen to change from ionic lead bonding at low lead content to more covalent lead speciation at high lead content. This is presumed to be the result of a shift towards a two-phase structure consisting of an aluminosilicate framework and lead borate rich regions.

**GEOC 66 [675521]: NMR detection of chemical weapons manufacturing byproducts in environmental media**

**Sarah C. Chinn**<sup>1</sup>, M. Lee Davisson<sup>1</sup>, J.G. Reynolds<sup>2</sup>, Carolyn J. Koester<sup>1</sup>, Adam H. Love<sup>3</sup>, Robert Maxwell<sup>1</sup>, and Andrew L. Vance<sup>1</sup>. (1) Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, L-231, Livermore, CA 94550, chinn7@llnl.gov, (2) PO Box 808, L-092, Lawrence Livermore National Laboratory, (3) Environmental Science Division, Lawrence Livermore National Laboratory

**Abstract**

The environmental fate and transport of organophosphorus nerve agents is of utmost importance and is well known at high concentrations. However, while low-level chemical weapon (CW) signature detection methods exist, little information is known about the adsorptive character or chemical persistence of these signatures. These questions are important both for the detection of illicit CW manufacturing as well as human health risks associated with terrorist attacks. We are using solid state <sup>31</sup>P NMR and GC/MS experiments to examine the fate and transport properties of low concentrations of several model CW compounds. The results for sensitivity tests and environmentally relevant scenarios will be discussed.

**GEOC 67 [672736]: NMR Investigation of Metal Complexation with Natural Organic Matter**

**Xiang Xu**, Department of Geology, University of Illinois at Urbana-Champaign, 245 NHB, 1301 W Green St, Urbana, IL 61801, Fax: 217-244-4996, xiangxu1@uiuc.edu, and R. J. Kirkpatrick, Department of Geology, University of Illinois at Urbana-Champaign

**Abstract**

<sup>133</sup>Cs and <sup>35</sup>Cl NMR T<sub>1</sub> relaxation studies of the Cs<sup>+</sup> and Cl<sup>-</sup> complexation by Suwannee River natural organic matter (NOM) provide significant, new insight into the interaction of these species with NOM. Experiments were done with neat CsCl solutions and mixed solutions that contain CsCl and NOM at unbuffered pHs of about 3.3, 7 and 12. <sup>133</sup>Cs 1/T<sub>1</sub> relaxation rates of CsCl-NOM solution mixtures increase dramatically with decreasing [Cs<sup>+</sup>]/NOM, whereas they remain essentially constant for neat CsCl solutions. These data suggest that essentially all of the Cs interacts with the NOM at low concentrations and that the interacting fraction decreases with increasing [Cs<sup>+</sup>]. A 2-site exchange model provides quantitative information about the concentration dependence of the fraction of bound Cs and the bound-Cs/NOM ratio. In contrast, the <sup>133</sup>Cs NMR spectra of the neat solutions and mixtures contain only a single peak whose chemical shift depends on [Cs<sup>+</sup>] but not on the presence or absence of NOM. Thus, there are no observable Cs-NOM complexes that have lifetimes longer than ca. 10<sup>-3</sup> sec, and the Cs that is associated with the NOM is probably principally in the Gouy (diffuse) layer surrounding the NOM molecules. The <sup>35</sup>Cl NMR chemical shift and T<sub>1</sub> relaxation rates show that there is no significant complexation between Cl<sup>-</sup> and NOM.

**GEOC 68 [674130]: Possible Al-F bonding environments in F-bearing Na-aluminosilicate glasses from calculation of 19F NMR shifts**

**John A. Tossell**, and Yun Liu, Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, tossell@chem.umd.edu

## **Abstract**

Using both Hartree-Fock and hybrid Hartree-Fock - density-functional methods at the 6-311+G(2df,p) basis set level  $^{19}\text{F}$  NMR chemical shifts are calculated for possible Al-F species in Na-aluminosilicate glasses. The accuracy of the method is carefully checked by calculating  $^{19}\text{F}$  NMR shifts for several well-characterized crystalline materials. Almost all possible Al-F bonding environments in Na-aluminosilicate glasses, including terminal F, corner-shared F species (i.e. both Al-F-Al and Al-F-Si) and edge-shared F species (i.e. Al-(FF)-Al) for 4-, 5- and 6-coordinated Al species have been investigated. A clear trend is found between the chemical composition of the environment and the F NMR shift. With more and more bridging oxygen (BO) in the vicinity, the F becomes less shielded no matter whether it is terminal or shared. Both  $\text{Na}^+$ -free and  $\text{Na}^+$ -bearing cluster models are used to investigate these trends. Terminal F are found to be highly shielded with chemical shifts from  $-172$  ppm to  $-216$  ppm. Corner-shared F are found have a broad chemical shift distribution from  $-104$  ppm to  $-197$  ppm. Edge-shared F species have chemical shifts from  $-143$  to  $-172$  ppm. Many corner and edge-shared F environments could possibly contribute to the  $-147$  ppm broad peak reported in  $^{19}\text{F}$  NMR spectra of F-containing aluminosilicate glasses.

## **GEOC 69 [667405]: Solid state aluminum-27 NMR studies of the aluminum distribution in aluminosilicates**

**Becky A. Gee**, Department of Chemistry and Biochemistry, Long Island University, 1 University Plaza, Brooklyn, NY 11201, Fax: 718-488-1465, bgee@liu.edu

## **Abstract**

There is significant fundamental interest in the spatial distribution of aluminum atoms in aluminosilicate materials. The spatial ordering of aluminum atoms in a number of aluminosilicate compounds is probed by solid state aluminum-27 NMR spectroscopy. Among the methods used is dipolar dephasing of the aluminum-27 magnetization following a Hahn spin echo pulse sequence. In this work, aluminum-27 spin echo decay experimental data will be compared to calculated data based on aluminum atomic distribution models. The possibility of applying this solid state NMR approach and others to probe the aluminum ordering in aluminosilicate materials will be discussed.

## **GEOC 70 [675042]: Adsorption of heavy metals on iron oxide coated silica**

**Ying Xu**<sup>1</sup>, Lisa Axe<sup>1</sup>, Sungmin Maeng<sup>1</sup>, Paras Trivedi<sup>2</sup>, Thipnakin Boonfueng<sup>1</sup>, Trevor A. Tyson<sup>3</sup>, and Kaumudi Pandya<sup>4</sup>. (1) Department of Civil and Environmental Engineering, New Jersey Institute of Technology, 323 Dr. Martin Luther King Blvd., Newark, NJ 07102, Fax: 973-596-5790, yx3@njit.edu, (2) Department of Civil and Environmental Engineering, University of Alaska at Fairbanks, (3) Department of Physics, New Jersey Institute of Technology, (4) National Synchrotron Light Source, Brookhaven National Laboratory

## **Abstract**

Iron oxides have a great capacity for metal ions, exist widely in soils and sediments as discrete particles or surface coatings, and have a significant impact on metal distribution. In an effort to improve models when competing ions are present, this study focuses on the preparation and characterization of model systems of oxide-coated silica for evaluating sorption mechanisms. Hydrated iron oxide (goethite and amorphous ferric oxide-HFO) has been coated on silica sand and characterized with X-ray diffraction, X-ray fluorescence, particle size analysis, scanning electron microscopy, energy dispersive X-ray analysis, surface charge distribution, and extraction analysis. The iron oxide coatings were found non-uniformly distributed on silica where an average of 0.059% and 0.047% (mass) of Fe was observed for goethite-precipitation-coated-silica and goethite-adsorption-coated-silica, respectively. Similarly, 0.041% (mass) of Fe was observed on HFO-precipitation-coated silica. The iron-oxide coatings increased surface area, microporosity, and adsorption characteristics of silica.

**GEOC 71 [676195]: Complexation and transport of contaminant uranium associated with corroding steel and stainless steel surfaces**

**Gary P. Halada**<sup>1</sup>, Charlotte Eng<sup>1</sup>, A. J. Francis<sup>2</sup>, and Cleveland J. Dodge<sup>2</sup>. (1) Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794-2275, Fax: 516-632-8052, ghalada@ms.cc.sunysb.edu, (2) Environmental Sciences Department, Brookhaven National Laboratory

**Abstract**

Corroding surfaces of mild and stainless steels are composed of oxides and oxyhydroxides of their constituent elements. Passive films formed on stainless steels are enriched in species of secondary metals which yield corrosion-inhibiting electronic properties. Uranium may associate with these layers through exposure to hexavalent species common to former nuclear processing facilities, often forming mixed complexes which affect sequestration and corrosion properties. Also, contaminant uranium present in soil will be found liganded with complex organic components. Understanding how this affects electron transfer reactions that govern the ability of corrosion products to incorporate uranium is essential in development of a realistic model for contaminant complexation and environmental transport. Complimentary vibrational and electron spectroscopies, in situ electrochemistry and synchrotron techniques, and molecular modeling are used to characterize the association of uranium with corrosion products and passive layers and the impact of organic ligands on electron transfer, uranium association with surfaces and mechanisms of decontamination.

**GEOC 72 [675254]: EXAFS investigation of Ni sorption to hydrologically conditioned amorphous Mn oxyhydroxides**

**Elizabeth A. Haack**<sup>1</sup>, Thomas P. Trainor<sup>2</sup>, D. Scott Smith<sup>3</sup>, Corrie Kennedy<sup>1</sup>, and Lesley A. Warren<sup>1</sup>. (1) School of Geography and Geology, McMaster University, 1280 Main St. West, Hamilton, ON L8S 4K1, Canada, Fax: 905-546-0463, haackea@mcmaster.ca, (2) University of Chicago, Consortium for Advanced Radiation Sources, (3) Department of Chemistry, Wilfrid Laurier University

**Abstract**

Hydrous manganese oxides (HMO), play an important controlling role in the sequestration and transport of trace metals in natural environments. Sorption of metals to a number of natural and synthetic Mn oxides and oxyhydroxides has been examined in the literature. However, the effects of variable hydrologic conditions reflecting natural environments for HMO surface chemistry and reactivity, has not been explicitly examined. Ni sorption to synthetic HMO conditioned under three variable hydrologic regimes (freshly precipitated, cycles of wet and dry conditions, and dried) was characterized by batch experiments and spectroscopic analysis by XAS. EXAFS results indicated that pH was the most important control on the mechanism of Ni sorption to the HMO. Integrated with these results will be a discussion of the surface chemistry of the HMO under variable hydrologic conditions, and the ability of conventional surface-complexation models to accurately reflect the molecular-level mechanisms of Ni sorption to HMO.

**GEOC 73 [675100]: Formation and characterization of a ternary Fe(III)-U(VI)-citric acid complex with implications for uranium mobility**

**Cleveland J. Dodge**, and A. J. Francis, Environmental Sciences Department, Brookhaven National Laboratory, 30 Bell Avenue, Building 490A, Upton, NY 11973-5000, Fax: 631-344-7303, dodge1@bnl.gov

**Abstract**

In the presence of ferric and uranium ions citric acid forms a ternary complex. Potentiometric titration and UV-vis spectrophotometry established the existence of the complex, and gel filtration chromatography showed the stoichiometric ratio of the components. Extended X-ray absorption fine structure (EXAFS) analysis and time-of-flight mass spectrometry (TOF-SIMS) revealed that the structure is comprised of two tridentate mononuclear U-citrate units coordinated in bidentate fashion to a dinuclear Fe(m-O)(m-citrato) core. Although the ternary complex is recalcitrant to biodegradation, photodegradation

proceeds by way of a photo-Fenton reaction with precipitation of U from solution as an oxyhydroxide. In comparison, the binary U-citrate complex undergoes uranium reduction followed by a hydroperoxy radical oxidation of the uranium to the mineral schoepite. The formation of ternary complexes of uranium with naturally-occurring organic compounds and metal ions such as iron can affect the stability and mobility of uranium in the environment.

#### **GEOC 74 [675006]: Surface properties of manganese oxide coated montmorillonite**

**Thipnakarin Boonfueng**, and Lisa Axe, Department of Civil and Environmental Engineering, New Jersey Institute of Technology, 323 Dr. Martin Luther King Blvd., Newark, NJ 07102, Fax: 973-596-5790, txb7685@njit.edu

##### **Abstract**

Amorphous (hydrous manganese oxide (HMO)) and crystalline manganese oxides (birnessite and pyrolusite) were coated on montmorillonite. The HMO coating was amorphous, while birnessite and pyrolusite coatings were poorly crystalline due to the presence of montmorillonite, which appears to have inhibited crystallization. SEM images suggest a uniform coating of HMO at a load of 50% g Mn/g mont or greater. However, EDX revealed the presence of Mn, Si, and Al suggesting non-uniform coverage. The particle size distribution (PSD) of HMO coated montmorillonite increased with loading where the mean diameter shifted from 4 to 12 nm, which is consistent with the HMO PSD and suggests a limiting capacity for the Mn oxide. The larger PSD may introduce microporosity as compared to the montmorillonite surface. The coating surface charge behaves similar to HMO where the pHzpc was  $2.7 \pm 0.5$ , while HMO pHzpc was  $2.35 \pm 0.5$ , and montmorillonite pHzpc was  $4.5 \pm 0.5$ .

#### **GEOC 75 [675411]: Assessing the PAH sorption characteristics of glassy polymers as model NOM systems in contaminant binding studies**

**Frank V. Schindler**<sup>1</sup>, Frank J. Novotny<sup>2</sup>, and James A. Rice<sup>1</sup>. (1) Department of Chemistry and Biochemistry, South Dakota State University, Shepard Hall, Box 2202, Brookings, SD 57007, Fax: 605-688-6364, frank\_schindler@sdstate.edu, (2) School of Science, Mathematics, and Technology, Adams State College

##### **Abstract**

Contaminant-natural organic matter (NOM) interaction models have been proposed that predict that NOM contains a rigid, glassy polymer-like, sorption domain that binds contaminants strongly. The objective of this study is to determine the nature of the PAH sorptive interactions of authentic glassy polymers. Sorption isotherms were developed by sorbing <sup>14</sup>C-labeled PAHs from aqueous solution to glassy polymers possessing a range of glass transition temperatures (i.e., 15° to 175°C). The exponent N in the Freundlich equation,  $S=K_F C^N$ , was used to quantify the degree of nonlinearity. Greater distributions of high energy sorption sites, which are characteristic of nonuniform sorbents, yield lower N values. The N values of all isotherms are near one, indicating that linear sorption is occurring in these systems. Since these systems are homogeneous relative to NOM systems, sorption linearity is not surprising. No relationship exists between degree of linearity and glassy character of model polymer. These results will be compared and contrasted to the characteristics of PAH-NOM interactions.

#### **GEOC 76 [675340]: Uranium complexation with polyphosphates**

**Gustavo J. Vazquez**, Cleveland J. Dodge, and A. J. Francis, Environmental Sciences Department, Brookhaven National Laboratory, 30 Bell Avenue, Building 490A, Upton, NY 11973-5000, Fax: 631 344-7303, gus@bnl.gov

##### **Abstract**

Inorganic polyphosphates (polyP) are simple linear polymers produced by a wide variety of microorganisms and are distributed throughout the bacterial cell. One of their many biological functions is to act as a chelator of metals. In this study we investigated the interaction of equimolar short chain polyP (1400-1900 Da) with uranium. Potentiometric titration indicated the U-polyP complexation occurred at a slower rate compared to U-phosphate. Elemental analysis (U, P) of the solution at pH 3.2 (unadjusted), 4.5, and 6.0 showed the gradual precipitation of the U-polyP complex. The precipitate contained varying P:U

ratios as a function of pH, indicating the presence of different uranium phosphate phases. EXAFS analysis of the U-polyP complex showed a mixed-phase uranium hydroxophosphato species, in contrast to uranium phosphate resulting from the interaction of uranium with monophosphate. These results suggest that the mechanism of complexation between uranium and polyP is different than with uranium and monophosphate.

**GEOC 77 [676194]: Biogeochemical processes controlling multi-element transport in vadose zone sediments**

**Corrie Kennedy**<sup>1</sup>, Lesley A. Warren<sup>1</sup>, and Craig Cooper<sup>2</sup>. (1) School of Geography and Geology, McMaster University, 1280 Main St. West, Hamilton, ON L8S 4K1, Canada, Fax: 905-546-0463, kennedcm@mcmaster.ca, (2) Idaho National Engineering and Environmental Laboratory

**Abstract**

Understanding the potential impact of microbial processes on vadose zone associated mobility and geochemical behaviour of metals is fundamental to the development of strategies to prevent their migration to groundwater supplies. Behaviour of a suite of metals (U(VI), As, Cr, Co, and Zn) at varying concentrations, was examined in laboratory batch microcosms using INEEL (Idaho National Engineering and Environmental Laboratory) contaminated vadose zone soils under both sterile (abiotic) and variably carbon amended, biotic (stimulation of resident microbial consortia) conditions at circumneutral pH. Results will be presented evaluating microbial linkages to metal geochemistry, from a combined suite of analyses including geochemical fractionation of metals associated with soil components (sequential extraction), microbial characterization and surface analyses.

**GEOC 78 [675797]: Arsenic in groundwater at landfill sites in northern central Massachusetts**

**Matthew J Mayo**<sup>1</sup>, Rudolph Hon<sup>1</sup>, William C. Brandon<sup>2</sup>, and Robert Ford<sup>3</sup>. (1) Department of Geology and Geophysics, Boston College, 140 Commonwealth Avenue, Chestnut Hill, MA 02467, mayomb@bc.edu, (2) Region 1, United States Environmental Protection Agency, (3) National Risk Management Research Laboratory, US-EPA

**Abstract**

Elevated arsenic levels in groundwater near landfill sites in Northern Central Massachusetts pose a potential threat to the human health and the environment. Concentrations in excess of 3000 microgram/l were detected at several sites in groundwater in the direct downgradient path from landfills suggesting a link between the landfill leachate and the source of arsenic. Variation diagrams of conservative tracers (Na, Cl, total carbon) along the upgradient-to-downgradient sections point to a proportional mixing between the landfill leachate and the upgradient groundwater. Arsenic fails to correlate with any of the mixing indicators but instead it correlates with the decreasing measured redox potential (ORP) and Fe and Mn. Origin of arsenic is explained by a reductive dissolution of HFO (hydrated ferric oxides) caused by a reducing environment due to a microbial conversion of DOC into DIC. Mitigation of arsenic could be achieved by maintaining an adequate supply of dissolved oxygen.

**GEOC 79 [679336]: Measured Sticking Efficiencies of *Enterococcus faecalis* Using Atomic Force Microscopy**

**Tracy L. Cail**, Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, tcail@vt.edu, and Michael F. Hochella Jr., Department of Geological Sciences, Virginia Tech

**Abstract**

Sticking efficiency is the probability of attachment of a particle to a collector and is a function of the forces of attraction and repulsion between these surfaces at the nanoscale. In this study, the sticking efficiencies of live *Enterococcus faecalis* cells in different aqueous solutions were measured using atomic force microscopy (AFM). Individual bacterial cells were attached to the ends of silicon nitride cantilevers and brought into contact with a silica glass collector surface in aqueous solution. Contact-mode AFM was used to measure the interaction forces with piconewton resolution as the surfaces were moved together and subsequently separated at a controlled rate. Intersurface potential energies were determined by integrating force data with

respect to cell-collector separation distance and sticking efficiencies were calculated from potential energy using Spielman and Friedlander's (1974) method. Results were compared with results of a previous study that measured the sticking efficiency of carboxylated polystyrene microspheres to a glass collector surface.

**GEOC 80 [661305]: Production and release of carbonyl sulfide from the rice paddies in the south area of the Yangtze River**

Jinhua Zhang, Weichuan Qiao, and **Zhen Yang**, Department of Environmental Science and Engineering, Nanjing University of Science and Technology, Xiaolingwei 200#, Nanjing 210094, China, Fax: 0086-025-4316753, yangz@mail.njust.edu.cn, yangz@mail.njust.edu.cn

**Abstract**

Carbonyl sulfide (COS) from the rice paddies in the south area of the Yangtze River was measured with a closed chamber method in the field. In addition, some other sulfur gases were also detected. It was found that COS comprises the dominant part of sulfur emission in this area. The significant fluctuation of COS was not observed with the different manure. Comparing the measured data shows that blank paddy soil was the main source of COS gas, rice plant was its dominant sink. Linear regression analyses of COS emission rate with respect to the soil Eh, pH, and air temperature were also performed, the obtained correlation coefficient were 0.90, 0.87, and 0.81 respectively. The annual COS emission rate from the areas ranged from 32.1 to 76.4mg S m<sup>-2</sup> year<sup>-1</sup>.

**GEOC 81 [675205]: Arsenic speciation in reducing waters with specific attention to the roles of zero-valent sulfur and Pb(II)**

**Carla S. Neuberger**, and George R. Helz, Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, ccoynel@wam.umd.edu

**Abstract**

Arsenic is commonly more mobile in reducing (including sulfidic) groundwaters than in oxidizing ones. In the presence of S<sup>-II</sup>, arsenite is converted to thioarsenites, which potentially are reactive with S(0) and with hazardous metals. Further enhancement of both As and metal mobility could be a consequence. To explore this, the solubility of As<sub>2</sub>S<sub>3</sub> (orpiment) has been measured in the absence and presence of solid S(0) and PbS (galena). Experiments were carried out in glass ampoules. After equilibration for several weeks, ampoules were opened, syringe filtered and analyzed for total sulfide, total As, total Pb and pH by a battery of methods. Zero valent sulfur provides oxidizing capacity, due to the formation of polysulfide ions. There is the possibility that oxidation of some As(III) to As(V) occurs but the effect is small. Consistent with theoretical calculations by Tossell, formation of Pb-thioarsenites contributed negligibly to solubilities. Ag(I) is currently under investigation.

**GEOC 82 [675877]: Volcanic ashes as source of As in Pampean sediments, Argentina**

**Gabriela Roman-Ross**, Environmental Geochemistry Group, LGIT, OSUG, University Joseph Fourier, B.P. 53, 38041 Grenoble, France, Fax: +33 76828101, Gabriela.Roman-Ross@obs.ujf-grenoble.fr, and Laurent Charlet, Environmental Geochemistry Group, LGIT, OSUG, Université Joseph Fourier

**Abstract**

Two mechanisms have been invoked in the literature to explain the release of As in the aquifers of Central Region of Argentina: 1) leaching of volcanic materials and 2) desorption of adsorbed As on iron oxides. With the aim to study the role of volcanic materials in As distribution in loess we have studied forty tephra layers obtained from a lacustrine core in Northern Patagonia. Genesis and evolution of Argentinean loess have been related to the last glacial events in Patagonia and it includes a widespread presence of volcanic glass shards. Arsenic concentrations associated to reactive iron in the solid phases were

determined using sequential extraction techniques. As/Fe ratios obtained from volcanic ashes and loess agree with theoretical values related to maximum As concentrations adsorbed on amorphous iron. These results are consistent with the fact that As is closely associated to Fe oxides in both volcanic materials and loess sediments.

**GEOC 83 [673876]: Differential pulse cathodic stripping voltammetric speciation analysis of trace level inorganic arsenic compounds in natural water samples**

**Yi He**<sup>1</sup>, **Yan Zheng**<sup>2</sup>, Mala Ramnaraine<sup>3</sup>, and **David C. Locke**<sup>1</sup>. (1) Department of Chemistry, Graduate Center and Queens College of The City University of New York, 65-30 Kissena Blvd, Flushing, NY NY 11367, Fax: 718-997-5531, (2) School of Earth and Environmental Science, Graduate Center and Queens College of The City University of New York; Lamont-Doherty Earth Observatory of Columbia University, 65-30 Kissena Blvd, Flushing, NY 11367, Fax: 718-9973299, (3) Bronx High School of Science

**Abstract**

Inorganic arsenic in water at mg/l level can be speciated to As (III) and As (V) by differential pulse cathodic stripping voltammetry (DPCSV). Only As(III) is deposited on Hg electrode in the presence of Cu, Se in a HCl medium. Thus determination of total As is performed by reducing As(V) to As(III) by sodium meta-bisulfite/sodium thiosulfate and ascorbic acid in H<sub>2</sub>SO<sub>4</sub> medium. As(V) is quantified by difference. The detection limit (S/N >3) was 0.5 mg/l with a linear range from 4.5 to 180 mg/l, but the RSD (N=6) was 2.4% for As(III) and 8.0% for As(V). Analysis of NIST 1640 natural water standard yielded total [As] 26.5 ± 3.4 mg/l (n=3) compared to the certified value of 26 mg/l. Results obtained on several natural water samples also compared well with those obtained by ICP-MS and GFAAS. Ions (phosphate, iron, manganese) common in groundwater with arsenic were found to have negligible interference.

**GEOC 84 [674016]: A rapid colorimetric method for measuring arsenic concentrations in groundwater**

**Ratan K. Dhar**<sup>1</sup>, Yan Zheng<sup>2</sup>, J. Robenstone<sup>3</sup>, and Alexander van Geen<sup>3</sup>. (1) School of Earth and Environmental Sciences, Queens College and Graduate School & University Center, City University of New York. New York, USA, 65-30 Kissena Boulevard, Flushing, New York, NY 11367-1597, Fax: 718-997-3299, rdhar@ldeo.columbia.edu, (2) School of Earth and Environmental Sciences, City University of New York and Columbia University, New York, USA, (3) Lamont-Doherty Earth Observatory, Columbia University

**Abstract**

Arsenic contaminated groundwater consumed by millions of people in the developing world has become a major health concern, particularly in Bangladesh. We report here an optimization of the colorimetric method of Johnson and Pilson (1972) that lowers the detection limit for As to <10 ug/L in groundwater containing high phosphate. The optimization includes an increase in the concentration of three reagents: the oxidizing reagent used for sample pre-treatment and both the ascorbic acid and antimonyl tartrate present in the color reagents. These modifications lower the reaction time from 2-3 hours to 10 minutes. Analysis of a NIST natural water standard by the optimized method yields As concentration of 22 ± 5 µg/L (n=3), compared to a certified value of 26.7 ug/L. Mean recovery for different groundwater samples was 101 ± 2.6% (n=43). Colorimetric analysis of a set of 43 groundwater samples from Bangladesh also agrees well with laboratory analysis by atomic absorption.

**GEOC 85 [674138]: Preservation and stabilization of arsenic species during chemical extraction from soils**

**Myron Georgiadis**, Department of Chemistry, Florida International University, Miami, FL 33199, Fax: 305-348-3772, mgeorg03@fiu.edu, Yong Cai, Dept. of Chemistry and Southeast Environmental Res. Center, Florida International University, and Helena Solo-Gabriele, Dept. of Civil, Arch., & Environ. Engineering, University of Miami

## **Abstract**

Concern for arsenic in the environment and its potential for harm require methods for accurate quantitation. Since the toxicity of arsenic can vary greatly among its different chemical species, it is important to preserve them during analysis in order to properly assess potential health hazards. Soils and sediments provide a unique challenge for the extraction and preservation of such arsenic species. Reabsorption or possible species interconversion may occur during the extraction process, which can lead to false interpretation since sediment/soil standard reference materials for arsenic speciation are not currently available for verification. This study focuses on method development for the preservation and stabilization of arsenic species during chemical extraction of arsenic from soils. A number of chemical extractants have been used to test their potential for extraction and stabilization of arsenic species during the extraction process. Chelating agents are also used in an effort to prevent soil reabsorption and reduce specific arsenic availability for conversion.

### **GEOC 86 [674325]: Determination of arsenic sorption characteristics in sediment porewater using an iron oxyhydroxide-doped gel probe**

**Kate M. Campbell**, Department of Environmental Science and Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, [katec@caltech.edu](mailto:katec@caltech.edu), Janet G. Hering, Environmental Science and Engineering, California Institute of Technology, and Suvasis Dixit, Environmental Science and Technology, California Institute of Technology

## **Abstract**

A gel probe sampler has been constructed to study arsenic geochemistry in sediment porewater. The gel consists of a polyacrylamide polymer matrix doped with amorphous iron oxyhydroxide. It is cut into slabs and placed in a "ladder" formation in a Plexiglas probe, which is then inserted into sediments and allowed to equilibrate with sediment porewater. The arsenic and iron are quantitatively recovered by acid digestion and measurement with ICP-MS and colorimetric methods. The probe performance has been validated in the laboratory and will be deployed at a field site at Haiwee reservoir (Olancho, CA), which is part of the Los Angeles aqueduct system. Insertion of the probe into reservoir sediments and simultaneous measurements of porewater and sediment composition will allow us to compare the extent of sorption of arsenic onto the fresh iron oxyhydroxides in the gel to the arsenic loading in the ambient sediments. Such comparison will provide insight into the biogeochemical controls on arsenic remobilization in this system.

### **GEOC 87 [672725]: Preservation of sulfidic waters containing dissolved As(III)**

**Joanne A. Smieja**, Department of Chemistry, Gonzaga University, E. 502 Boone Ave., Spokane, WA 99258, Fax: 509-323-5804, [smieja@gonzaga.edu](mailto:smieja@gonzaga.edu), and Richard Wilkin, USEAP

## **Abstract**

Field samples for arsenic analyses are commonly preserved by acidification with hydrochloric or nitric acid. In some suboxic samples, appreciable concentrations of hydrogen sulfide are observed due to the microbial respiration of sulfate-reducing bacteria. If both As(III) and sulfide are present in natural waters, several reactions are possible. In this study, solutions containing variable concentrations of sulfide (0 to 25 ppm) and arsenite (0.35 to 10 ppm) were subjected to several different preservation treatments. If a near-neutral water sample contained 1 ppm arsenite and as little as 0.4 ppm sulfide, loss of dissolved arsenic was observed upon acidification. These results have implications concerning the practice of acidifying water samples for the purpose of preserving total arsenic values. An alternative three-step preservation method involving base addition, oxidation, and acidification was investigated as an appropriate technique for preserving sulfide-bearing aqueous samples for total arsenic.

### **GEOC 88 [676190]: Treatment of arsenic and organoarsenic compounds by ultrasound irradiation**

**Kevin O'Shea**, Sahar Motamedi, Yong Cai, and Tielian Xu, Department of Chemistry, Florida International University, Miami, FL 33199, Fax: 305-348-3773, osheak@fiu.edu

### **Abstract**

The presence of arsenic in drinking water is a serious problem and has attracted worldwide attention. Many of the current treatment options require oxidation of As (III) to As (V) using chemical oxidants followed by adsorption or precipitation. The employment of ultrasonic irradiation could eliminate the need for chemical oxidants in the treatment of arsenic species. As(III) and As(V), mono-methyl arsonic acid (MMA), and di-methyl arsonic acid (DMA) were treated with ultrasonic irradiation and monitored by HPLC-Fluorescence detection. Pulsed and continuous modes of ultrasonic irradiation were applied to the arsenic species and the mass balances, kinetic parameters, role of different saturation gases and the solution pH evaluated. The kinetic parameters determined in these studies may be useful for the development of models to predict the fate, redox conversion, and remediation of these species in aquatic environments.

### **GEOC 89 [674951]: Speciation of arsenic sorbed on ferrihydrite determined by voltammetry in sodium phosphate and hydrochloric acid extracts**

**Zheng Mo**, School of Earth and Environmental Sciences, Queens College and Graduate School and University Center, City University of New York, 65-30 Kissena Blvd., Flushing, NY 11367, Fax: 718-997-3299, and Yan Zheng, School of Earth and Environmental Sciences, Queens College and Graduate School and University Center, City University of New York

### **Abstract**

Sequential extraction has been widely adopted to illuminate different arsenic carrying phases in particulate samples. Often total arsenic is quantified in the extracts but not the speciation, e.g., arsenate and arsenite. Here we apply cathodic stripping voltammetry capable of detecting 0.5 ug/l arsenate and arsenite to speciate arsenic sorbed on synthetic ferrihydrite that is sequentially extracted by 1 M  $\text{KH}_2\text{PO}_4$  (pH 5) and 1M HCl under anaerobic conditions. Adsorption of arsenate and arsenite to synthetic ferrihydrite at As/Fe ratio of 0.2-2 mg/g reached equilibrium within 24 hrs and addition of L-ascorbic acid prevented oxidation of arsenite during loading. Greater than 80% of sorbed As was extracted by 1 M  $\text{KH}_2\text{PO}_4$  and 1 M HCl. Preliminary results show a recovery of arsenite ranging from 15% to 50% in 1M  $\text{KH}_2\text{PO}_4$  extract. We intend to enhance the recovery of arsenite under better controlled anaerobic conditions and through the addition of L-ascorbic acid.

### **GEOC 90 [676114]: Arsenic transport and transformation associated with MSMA application on a golf course green**

**Jill Schrlau**<sup>1</sup>, Min Feng<sup>1</sup>, Yong Cai<sup>2</sup>, George H. Snyder<sup>3</sup>, Ming Chen<sup>3</sup>, and John L. Cisar<sup>4</sup>. (1) Department of Chemistry, Florida International University, University Park, Miami, FL 33199, Fax: 3053483772, Gau123@aol.com, (2) Dept. of Chemistry and Southeast Environmental Res. Center, Florida International University, (3) FEREC, University of Florida, (4) FLREC, University of Florida

### **Abstract**

The impact of extensively used arsenic-containing herbicides on ground water beneath golf courses has become a topic of interest. Although currently used organoarsenicals are less toxic, their application into the environment can produce the more toxic inorganic arsenicals. The influences of soil composition on arsenic retention and species conversion have been investigated at the Fort Lauderdale Research and Education Center, University of Florida, IFAS. Percolate water was collected after monosodium methanearsonate (MSMA) application for speciation and total arsenic analyses. It showed that either addition of peat or sand coatings could enhance arsenic retention in soil. Meanwhile, species transformations occurred in soil, resulting in co-occurrence of four arsenic species, MMA, DMA, AsIII, AsV in percolate water. The results indicated that soil composition can significantly affect both arsenic retention in soil and arsenic species in percolate water, providing important information on how to manage and reduce the risks posed by MSMA application.

**GEOC 91 [674188]: Binding of arsenic to dissolved colloidal materials derived from golf course soils**

**Zhangrong Chen**, Department of Chemistry, Florida International University, University, Miami, FL 33199, Fax: 305-348-3772, zhrchen@hotmail.com, and Yong Cai, Dept. of Chemistry and Southeast Environmental Res. Center, Florida International University

**Abstract**

The distinction between 'free' metals and colloidal complexed metals in aqueous solution is important for research involving the mobility or bioavailability of metals in the environment. In this study, the equilibrium dialysis method (molecular weight cutoff=500 and 3500 Da) was applied to determine 'free' and 'bound' As, Fe and Al in seven golf-course soil extracts. A significant fraction of the arsenic is bound to dissolved colloids materials (molecular weight cutoff between 500 and 3500 Da). Most of Al, Fe exists as colloids with molecular sizes larger than 3500 Da. The extent of arsenic binding depends on the kind of colloid substances derived from selected soils. Soil properties, and hence the characteristics of the resulting colloidal carriers determine the rate of arsenic transport and potential contamination to the groundwater.

**GEOC 92 [675876]: Spectroscopic studies of As(V) uptake by calcite**

**Vasso G. Alexandratos**, Eef.J. Elzinga, Richard J. Reeder, and Martin Schoonen, Department of Geosciences, State University of New York at Stony Brook, ESS Building, Stony Brook, NY 11794-2100, Fax: 631-632-8240, valexand@ic.sunysb.edu

**Abstract**

Spatially resolved spectroscopic observations reveal that surface properties play an important role in controlling arsenate interaction with calcite. Operation of the spiral growth mechanism on the calcite (10 $\bar{1}$ 4) surface results in the formation of two characteristic non-equivalent pairs of vicinal faces denoted as "+" and "-" respectively, which differ in the structure of growth steps. Synchrotron  $\mu$ -XRF reveals that "-" vicinal faces are distinctively enriched in As(V) compared to the "+" vicinals. This interaction causes formation of macrosteps on the "-" vicinal faces of the calcite surface. Macrosteps increase in density as the concentration of arsenate increases. EXAFS analysis confirmed that As is present in the calcite structure as tetrahedral AsO<sub>4</sub><sup>3-</sup> complex possibly substituting in CO<sub>3</sub><sup>2-</sup> sites and causing distortion to the local environment. Results imply that bulk partition coefficients for As(V) depend on the availability of different calcite surface sites.

**GEOC 93 [674605]: Characterization of a bimetal oxide adsorbent and its adsorption mechanism for Arsenic(V)**

**Yu Zhang**, Research center for eco-environmental sciences, Chinese Academy of Sciences, Shuangqing road 18, Haidian, Beijing 100085, China, Fax: +86-10-62923543, zhangyu@mail.rcees.ac.cn, Min Yang, Research center for eco-environmental sciences, Chinese Academy Sciences, Hong He, Research center for eco-environmental sciences, CAS, and Xia Huang, Environmental science and engineering, Tsinghua University

**Abstract**

A bimetal oxides adsorbent prepared by doping Ce(IV) ions into an Fe(II)/Fe(III) mixed solution (the mother solution of Fe<sub>3</sub>O<sub>4</sub>) shows significantly higher arsenic adsorption capacity than their correspondent two oxides. XRD measurement results demonstrated that Fe<sub>3</sub>O<sub>4</sub> crystal phase disappeared gradually with the increasing addition of Ce(IV) ions, resulting in the co-existence of Ce and Fe with different valences and formation of solid solution. A preparation temperature over 450°C triggered the phenomena of dehydration, phase changes, and valence changes of the adsorbent, and transformation of the structure from solid solution minicrystals to crystals of respective oxides (Fe<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>). A characteristic M-OH group by FTIR, which was different from conventional M-OH groups of metal oxides, was found in the bimetal oxides system, and the substitution of M-OH groups at Fe-Ce system surface by As(V) ions was found to play an important role in adsorption mechanisms of CFA. Keywords: Arsenic Removal, Adsorption, Iron oxide, Cerium

**GEOC 94 [676071]: Removal of arsenic from water by granular titanium dioxide**

**Sunbaek Bang**<sup>1</sup>, Maria E Pena<sup>1</sup>, Manish Patel<sup>2</sup>, and Xiaoguang Meng<sup>1</sup>. (1) Center for Environmental Systems, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, Fax: 201-216-8303, sbang@stevens-tech.edu, (2) New Jersey Department of Environmental Protection

**Abstract**

A novel granular titanium dioxide adsorbent was developed for removal of arsenic from water. Laboratory and field experiments were conducted to investigate effectiveness of the adsorbent for arsenic removal from challenge water and groundwater, respectively. The challenge water containing 50 mg/L As(V), 0.04 mg/L PO<sub>4</sub><sup>3-</sup>, 20 mg/L SiO<sub>2</sub>, 250 mg/L NaHCO<sub>3</sub>, and other common cations and anions was prepared daily with distilled water in accordance with NSF International Standards 53 (ANSI/NSF 53-2001). Laboratory column tests demonstrated that the treatment capacity of granular titanium dioxide was more than 2.5 times greater than that of GFH. Field filtration tests were conducted at a wellhead in New Jersey with a filter containing 3-L of the granular titanium adsorbent. Total arsenic concentration in the well water was approximately 47 µg/L and was in As(V) form. Approximately 42,000 bed volumes of water were filtered at an empty bed contact time (EBCT) of 3 min before the effluent arsenic concentration increased to 10 µg/L.

**GEOC 95 [675762]: Adsorption technologies for small-scale treatment of arsenic**

**Fabiola Brusciotti**<sup>1</sup>, Pradeep Yadav<sup>2</sup>, Paul Duby<sup>1</sup>, James (Chip) Kilduff<sup>3</sup>, and Nada M. Assaf-Anid<sup>2</sup>. (1) Earth and Environmental Engineering Department, Columbia University, 500 W 120 th Street, 918 Mudd, New York, NY 10027, Fax: 212-8547081, fb118@columbia.edu, (2) Chemical Engineering Department, Manhattan College, (3) Civil and Environmental Engineering, Rensselaer Polytechnic Institute

**Abstract**

Arsenic removal by adsorption was studied in small-scale flow-through and batch systems using natural and commercial adsorbents and mixtures thereof -mainly: activated alumina, activated carbon, zeolite, and ferric hydroxide. Removal from laboratory-prepared water spiked with 150 to 550 ppb arsenic was assessed in the presence of competing ions such as sulfate. Flow-through experiments did not require adsorbent pre-conditioning and took place in 100-ml beds packed with 20 mesh adsorbent granules at a flow of 5.4 L/hr. Batch experiments utilized 0.02 cm granules of zeolite mixed with powdered FeCl<sub>3</sub> at zeolite/As and FeCl<sub>3</sub>/As ratios in the range 2,000-40,000 and 8-100, respectively. Percent removals were as high as 99% and the final arsenic concentration of the treated water reached less than 5 ppb.

**GEOC 96 [675760]: Chemical factors affecting arsenic removal at water treatment plants**

**Thomas R. Holm**<sup>1</sup>, Steven D. Wilson<sup>1</sup>, Johnathan L. Talbott<sup>2</sup>, and Walton R. Kelly<sup>1</sup>. (1) Groundwater Section, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820, Fax: 217-244-3054, tomholm@sws.uiuc.edu, (2) Illinois Waste Management & Research Center

**Abstract**

Arsenic removal at water treatment plants was characterized. Arsenic is partially removed from potable water by conventional iron-removal processes, probably by adsorption of arsenate (As(V)) to hydrous ferric oxide (HFO). Competition experiments involving As(V) and substances commonly found in natural water, including phosphate, bicarbonate, silica, and organic matter, have shown that under some conditions these substances decrease the extent of As(V) adsorption to HFO. Therefore, these substances may affect arsenic removal from potable water. In this study, samples of untreated groundwater and treated water were collected from several water treatment plants in Illinois. A simple linear model based on water analyses agrees closely ( $r^2 > 0.99$ ) with the Phase I arsenic removal data. A chemical equilibrium model based on the adsorption model of Dzombak and Morel qualitatively agrees with the arsenic removal data. The effects of common anions on arsenic removal by manganese greensand are consistent with their effects on As(V) adsorption to HFO.

### **GEOC 97 [674761]: Colloidal transport of As from smelter sites in Cornwall, UK**

**Sam Shaw**, Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, United Kingdom, Fax: +44 (0)1865 272 072, sams@earth.ox.ac.uk, and Ben Hull-Bailey, Department of Earth Sciences, University of Oxford

#### **Abstract**

The release of arsenic from historic arsenic smelter sites in Cornwall, UK has caused significant pollution to local water sources. Colloidal transport associated with nanometer-scale ( $>5\text{-}500\text{nm}$ ) particles is one of the major pathways for arsenic release from these sites. Soils and sediments from these areas contain up to 60,000 ppm arsenic, present mainly as pharmacolite ( $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ ) and  $\text{Fe}_2\text{As}^{3+}\text{As}^{5+}_3\text{O}_{12}$ , a high temperature ( $>750^\circ\text{C}$ ) phase formed during the smelting process. Colloid release from the smelter sediments was studied using laboratory-based column experiments by flowing two solutions of varying ionic strength through the columns in the presence of malonic acid. The colloidal material generated was characterized by ATEM, XRD, Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, and chemical sequential extraction techniques. Results indicate that the arsenic is transported both in solution and associated with amorphous colloidal particles formed via a break-up and release mechanism.

### **GEOC 98 [676116]: Influence of phosphate on arsenic accumulation in *Pteris vittata***

**Weihua Zhang**, Department of Chemistry, Florida International University, University Park, Miami, FL 33199, Fax: 305-348 3772, wzhang01@fiu.edu, Yong Cai, Dept. of Chemistry and Southeast Environmental Res. Center, Florida International University, Lene Q. Ma, Soil and Water Sciences Department, University of Florida, and Kelsey Downum, Department of Biological Sciences, Florida International University

#### **Abstract**

*Pteris vittata*, an arsenic (As) hyperaccumulator, is a potential plant to be used in phytoremediation of As-contaminated sites. Understanding the regulation factors for As accumulation in this plant is critical for its application in phytoremediation. In this study, As accumulation in 0.5 mM phosphate solution and the influence of phosphate on As accumulation in 0.5 mM arsenate cultured solution were investigated using hydroponic systems. Results indicated that As accumulation rates in leaflets and rachises can be described using a hyperbola model [As accumulation rate in leaflets =  $(115.2 \cdot \text{As concentrations in solutions}) / (0.37 + \text{As concentrations in solutions})$ ,  $R^2=0.995$ ,  $P=0.0029$ ; and As accumulation rate in rachises =  $(75.5 \cdot \text{As concentration in solution}) / (2.41 + \text{As concentration in solution})$ ,  $R^2=0.998$ ,  $P<0.0001$ ]. Phosphate obviously inhibited As accumulation in leaflets, whereas the inhibition was not obvious in rachises and roots. The influence of phosphate on As accumulation rate in leaflets in 0.5 mM As solution can be described by a hyperbolic decay model [As accumulation rate =  $(133.6 \cdot 0.43) / (0.43 + \text{P concentration in solution})$ ,  $R^2=0.927$ ,  $P=0.0056$ ]. These models are useful to predict As accumulation and to evaluate the influence of phosphate on As accumulation in the application of this As hyperaccumulator.

### **GEOC 99 [675510]: Mechanisms of arsenic removal by zero valent iron reactive barriers**

**Nelson A. Rivera Jr.**<sup>1</sup>, Peggy A. O'Day<sup>1</sup>, Dimitri Vlassopoulos<sup>2</sup>, and Robert Root<sup>1</sup>. (1) Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, Fax: 480-965-8102, Nelson.Rivera@asu.edu, (2) S.S. Papadopoulos & Associates, Inc

#### **Abstract**

Zero valent iron has been employed in reactive barriers to remove arsenic from highly contaminated sites. A field column test ran for 19 days using groundwater from a contaminated site in New Jersey. Analysis by XAS showed that starting material was dominated by iron (II, III) oxide rather than by iron metal. The reacted material was separated and studied by XAS and chemical characterizations. XAS showed that the local structure of arsenic is bidentate bonding of As (V) tetrahedra to Fe (III) octahedra. These results indicate the formation of arsenic-iron oxyhydroxides, suggesting co-precipitation rather than

adsorption as the major arsenic removal mechanism. Laboratory column studies using in situ measurements are investigating flow rates and solution composition that optimize arsenic uptake by this co-precipitation mechanism.

#### **GEOC 100 [676205]: Remediation of an arsenic contaminated site**

**Michael Rafferty**, Charles B. Andrews, Dimitrios Vlassopoulos, and Kinsley M. Binard, S.S. Papadopulos and Associates, 217 Church Street, San Francisco, CA 94114, Fax: 415-701-0305

#### **Abstract**

The 1990 Bay Road site is located in the city of East Palo Alto, California. The approximately 23-acre site includes a property used to formulate agricultural chemicals for over 60 years. Other properties include commercial, residential, undeveloped, and mixed-use properties, a school, a non-tidal wetland, and a tidal wetland. Arsenic is the primary compound of concern in the soil and groundwater at the site and was determined to be a reliable indicator of other compounds. Remediation began in 1981 with an investigation of the extent of arsenic in soil and groundwater. Since then various remedies were investigated. Many were implemented including soil excavation and off-site disposal, soil fixation, property deed restrictions, capping, slurry wall installation, and phytoremediation. Additional studies into natural attenuation and fixation of arsenic were conducted. The remedies have been effective. Site conditions are now deemed protective of human health and the environment.

#### **GEOC 101 [675639]: Arsenic removal by zero-valent iron: Field tests in rural Bangladesh and at the Vineland Chemical, NJ, Superfund Site**

**Zhongqi Cheng**<sup>1</sup>, Nikolaos P. Nikolaidis<sup>2</sup>, Alexander Van Geen<sup>1</sup>, Richard C. Bailey<sup>3</sup>, and Matthew Westgate<sup>4</sup>. (1) Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, NY 10964, czhongqi@ldeo.columbia.edu, (2) Department of Environmental Engineering, Technical University of Crete Polytechniopolis, (3) Severson Environmental Services, (4) US Environmental Protection Agency, Region II

Abstract  
Cartridges containing mixed zero-valent iron filings and sand were pilot-tested in two very different settings. In Bangladesh, a two-week long experiment was conducted to treat groundwater pumped from two wells containing 308 and 533 ug/L As. An aeration vessel followed by a particle removal filter was added downstream of the Fe-filing column to reduce Fe levels. Effluent As level remained below 10 ug/L (the WHO drinking water limit) after about 600 pore volumes and the two units treated 1830 L and 1140 L groundwater successfully. A longer-duration testing is underway at the Vineland Chemical site, which is highly contaminated with both organic and inorganic forms of As. The treat plant inlet waste stream contains varying levels and forms of As (up to 2000 ug/L). On-site speciation analysis was performed to determine the removal efficiency for different As species. Preliminary results indicate complete removal of As(V), significant reduction of As(III) and probably some organic As as well.

#### **GEOC 102 [675878]: Microcosm studies examining the release of arsenic from Bangladesh aquifer sediments**

**Brian J Mailloux**<sup>1</sup>, Alexander Van Geen<sup>2</sup>, Zhongqi Cheng<sup>2</sup>, and Saugata Datta<sup>2</sup>. (1) Columbia Earth Institute, Columbia university, New York, NY 10115, bjm2103@columbia.edu, (2) Lamont-Doherty Earth Observatory of Columbia University

#### **Abstract**

Microcosm studies were conducted in order to determine the mechanisms that control the release of arsenic from the shallow aquifer sediments of Bangladesh. Microcosms were incubated with fresh sediments collected using a "needle sampler" that collects microbially pristine sediment in conjunction with the local "hand flapper" well drilling technique. Sediments were selected from portions of the aquifer in order to provide starting conditions with a range of extractable Fe(II)/Fe(III) ratios and aqueous arsenic concentrations. Groundwater and amendments were added to the microcosms to promote either continued reduction and/or mineral precipitation. Results indicate that microbial activity is required for the release of arsenic and that the geologic history of the aquifer sediments is an important factor in determining the amount of arsenic released. The comparison

of results from different zones of the aquifer and with different treatments will improve our understanding of the mechanisms that control the release of arsenic.

### **GEOC 103 [679151]: Molecular characterization of novel arsenic oxidizing or reducing isolates**

**E. Danielle Rhine**, E. Garcia-Dominguez, and Lily Y. Young, Biotechnology Center for Agriculture and the Environment, Rutgers, The State University of New Jersey, 59 Dudley Road, Cook College, New Brunswick, NJ 08901, Fax: 732-932-0312, rhine@aesop.rutgers.edu

#### **Abstract**

Due to the relative abundance in the environment, arsenic toxicity has become an important issue of current public and environmental health. Some heterotrophic and autotrophic microorganisms have been isolated that are able to derive energy from the oxidation of arsenite ( $\text{As}^{3+}$ ) to arsenate ( $\text{As}^{5+}$ ). Bacterial isolates have been reported with the ability to use  $\text{As}^{5+}$  as a terminal electron acceptor, resulting in the dissimilatory reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$ . Microbial transformation appears to be an important component in the geochemical cycling of arsenic in the environment. In order to expand the diversity of environmental isolates able to either oxidize or reduce arsenic, several enrichment cultures were established using sediment or soil obtained from a range of environmental sites. Several novel autotrophic arsenite-oxidizing cultures were isolated from either Onondoga Lake sediment (freshwater, NY), an industrial arsenic contaminated soil (NJ), or a sediment from an oil refinery waste-collecting lagoon (Venezuela). Novel dissimilatory arsenate reducing microorganisms were isolated from either Arthur Kill sediment (estuary NY/NJ harbor), an industrial arsenic contaminated soil (NJ), an oil refinery waste-collecting lagoon sediment (Venezuela), or a soil from a contaminated gas station (Venezuela). DNA was extracted from the isolates and RFLP revealed that several different microorganisms were isolated from these contaminated soils and sediments. DNA was also sequenced for phylogenetic characterization. Enrichment and isolation of microorganisms with the ability to oxidize arsenite or reduce arsenate can aid in understanding the biogeochemical cycling of arsenic within the environment, as well as the development of potential bioremediation approaches.

### **GEOC 104 [674553]: Two-year operation of an air/iron treatment system for the removal of arsenic from simulated Bangladeshi tubewell water**

**Ahmedul H Chowdhury**, and Phillip T Crisp, School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Anzac Pde, Kensington, Sydney 2052, Australia, Fax: 610-2-93855966, ahmedulh@hotmai.com

#### **Abstract**

A model system for As(III) removal from simulated Bangladeshi tubewell water (in mg/L: As(III) 0.2, Fe(II) 5,  $\text{Ca}^{2+}$  40,  $\text{Na}^{+}$  50,  $\text{SO}_4^{2-}$  9, Cl<sup>-</sup> 70,  $\text{HCO}_3^{-}$  133,  $\text{PO}_4^{3-}$  6,  $\text{SiO}_4^{2-}$  20) was operated indoors for a period of 2 years at the rate of 8 L per day. The system comprised: 1. water storage tank with tap regulator, 2. tank with internal baffles which forced water repeatedly down through crushed brick and up to the surface, 3. tank containing scrap iron metal, 4. water lock to maintain water level, and 5. storage tank. In tank 2, particles of  $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  (I) were retained in the crushed brick, while As was partially precipitated with I and partially oxidised by air to As(V). Arsenic removal in tank 2 varied from 95% to 50-30% (in the presence of  $\text{PO}_4^{3-}$  &  $\text{SiO}_4^{2-}$ ). Output water was <0.002 mg/L for 18 mo, rising to 0.004 mg/L after 24 mo.

### **GEOC 105 [676772]: Arsenic distribution in underground aquifer water in Bangladesh and potential source of arsenic-freewater**

**Bhajan K. Biswas**<sup>1</sup>, Gautam K. Basu<sup>2</sup>, Dipankar Chakraborti<sup>2</sup>, and Richard H. Loeppert<sup>1</sup>. (1) Soil & Crop Sciences Department, Texas A&M University, College Station, TX 77843-2474, Fax: 979-845-0456, bbiswas@ag.tamu.edu, (2) School of Environmental Studies, Jadavpur University

## Abstract

The objective of this study was to identify the areas of As contamination in a study of groundwater samples in Bangladesh, including the deltaic region and the flood plain of the Padma-Brahmaputra-Meghna Rivers. A sector-wise study of underground aquifer water was conducted by analysis of water from 34,000 tube wells. Arsenic concentration of water was evaluated as a function of geographic location, geomorphology, and depth. Arsenic contamination in groundwater varied widely among the various areas. The younger aquifer, which contains finer sediments lying at shallow depth, had a higher concentration of As in its groundwater. A trend of higher As concentrations was observed in aquifers located along the major river flood plain areas. Sporadic occurrences of very high ( $>1000 \mu\text{g L}^{-1}$ ) As in ground water were identified. The major delta region contained As rich aquifer water. The regions of the Barind tract formed by the Pleistocene red clay, Tableland, east-northeast hill tract, and the southern parts of the hill tract had low ( $<3 \mu\text{g L}^{-1}$ ) As concentrations in the aquifer water. In West Bengal, India, along the Bhagirathi River where Quaternary to recent sediment from the delta, As rich aquifer water was found. Results from 34,000 tube-wells covering 64 districts of Bangladesh show that 62% of Bangladesh's population and area are at risk of As poisoning.

## GEOC 106 [675221]: Atomic-scale x-ray analysis of ion adsorption at the rutile-water interface

Zhan Zhang<sup>1</sup>, Paul Fenter<sup>1</sup>, Likwan Cheng<sup>1</sup>, Neil C. Sturchio<sup>2</sup>, and Michael J. Bedzyk<sup>3</sup>. (1) Environmental Research Division, Argonne National Laboratory, ER-203, C-137, 9700 Cass Ave., Argonne, IL 60439, Fax: 630-252-5498, zhanzhang@northwestern.edu, (2) Department of Earth and Environmental Sciences, University of Illinois at Chicago, (3) Materials Science and Engineering Department, Northwestern University

## Abstract

A fully atomistic understanding of ion adsorption at the rutile (110)-water interface is obtained by using high-resolution X-ray techniques. Bragg X-ray standing wave (XSW) measurements probe the  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Y}^{3+}$  ion distributions. A model-independent Fourier synthesis approach, which images ion distribution from XSW data, reveals that  $\text{Sr}^{2+}$  and  $\text{Y}^{3+}$  adsorb in the tetradentate site between the surface terminal oxygen (TO) and bridging oxygen (BO) sites.  $\text{Zn}^{2+}$  adsorbs mostly as a monodentate species to the BO sites, with some  $\text{Zn}^{2+}$  bridging the TO sites. Precise ion sites (both laterally and vertically) were obtained with XSW triangulation. High resolution crystal truncation rod (CTR) measurements of the rutile water interface show that water molecules form a surface hydration layer with well-defined vertical and lateral positions. CTR measurements also indicate that  $\text{Rb}^{+}$  ions adsorb (at  $\text{pH}=12$  with  $[\text{Rb}^{+}]=1\text{M}$ ) in the tetradentate site. These measurements are discussed in the context of other recent studies.

## GEOC 107 [675194]: Periodic density functional theory calculations of Sr(II) and Zn(II) adsorption onto the (110) face of rutile

J. D. Kubicki, Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, Fax: 814-863-8724, kubicki@geosc.psu.edu, and A. V. Bandura, St. Petersburg State University

## Abstract

Periodic DFT energy minimizations were performed with Sr(II) and Zn(II) adsorbed onto the (110) face of rutile using the program CASTEP (Accelrys, Inc.). A 3-layer thick slab of rutile (alpha-titanium dioxide) was relaxed with the central layer of atoms constrained to mimic the bulk experimental crystal coordinates. Both the Sr(II) and Zn(II) were surrounded by a solvation sphere of water molecules on the side opposite the rutile crystal face in order to approximate the water-mineral interface. Sr(II) was found to be stable in a quadridentate configuration bonded to two terminal Ti-OH oxygen atoms and two bridging (Ti-O-Ti) oxygen atoms. This configuration is essentially the same as that derived by Fenter and coworkers using X-ray standing wave (XSW) spectroscopy. Zn(II) was predicted to be stable in two configurations suggested by XSW spectroscopy: a monodentate complex to a bridging oxygen atom and a bidentate configuration bonded to two terminal Ti-OH oxygen atoms.

**GEOC 108 [675890]: Long-Period X-ray Standing Wave (XSW) studies of Pb(II) ion distributions at organic thin film–mineral interfaces**

**Tae Hyun Yoon**, Department of Geological & Environmental Sciences, STANFORD UNIVERSITY, Stanford, CA 94305-2115, Fax: 650-725-2199, taeyoon@stanford.edu, Thomas P. Trainor, University of Chicago, Consortium for Advanced Radiation Sources, Peter Eng, GSECARS, Consortium for Advanced Radiation Sources, University of Chicago, John R. Bargar, Stanford Synchrotron Radiation Laboratory, and Gordon E. Brown Jr., Department of Geological and Environmental Sciences, Stanford Synchrotron Radiation Laboratory

**Abstract**

The distribution of Pb(II) ions at organic thin film (e.g., PolyAcrylic Acid (PAA))– single crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) and (1-102) interfaces was studied using synchrotron-based XSW techniques. The PAA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interface is a simple analog of naturally occurring organic thin films on mineral surfaces, which are thought to play important roles in the sequestration of trace heavy metals in natural soils and aquatic systems. In this work, very thin (30 – 120nm), flat (rms roughness < 2nm) PAA films containing Pb(II) ions (<50mM) were prepared on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surfaces, and their Pb(II) La fluorescence yield (FY) XSW and reflectivity profiles were collected at APS (ID-13) and SSRL (11-2) beamlines. Highly resolved XSW FY profiles provide unique information on Pb(II) partitioning between the PAA film and corundum surface. Compared to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(1-102) surface was more reactive to Pb(II) adsorption, and more adsorbed Pb(II) ions were observed on the (1-102) surface as pH increased.

**GEOC 109 [675966]: Fourier reconstruction of adsorbate crystallographic distributions using X-ray standing waves**

**Likwan Cheng**<sup>1</sup>, Michael J. Bedzyk<sup>2</sup>, Neil C. Sturchio<sup>3</sup>, and Paul Fenter<sup>1</sup>. (1) Argonne National Laboratory, Argonne, IL 60439, lcheng@anl.gov, (2) Northwestern University and Argonne National Laboratory, (3) University of Illinois at Chicago and Argonne National Laboratory

**Abstract**

The quantitative distribution profile of a surface adsorbate relative to a given set of substrate lattice planes can be reconstructed with a multiple-order Fourier-expansion series whose components are characterized by phases and amplitudes experimentally determined through multiple-order X-ray standing wave measurements. We reconstruct the density profiles of Cu (II) incorporated at the calcite 1014 surface (by adsorption from an aqueous solution) in the 1014 and the 0006 directions, using a Fourier series composed of the 1014 and 2028, and of the 0006 and 00012 components, respectively. Both reconstructed Cu density profiles show a peak that is shifted and has a reduced height in comparison to the bulk Ca (II) peak. These features indicate adsorbate relaxation and partial disordering; the latter is likely in part due to the heterogeneous orientations of its oxygen octahedra, whose distortion is revealed by in-plane EXAFS results. These findings show that substitutional incorporation of Cu (II) at the calcite surface occurs in the presence of Jahn-Teller distortion.

**GEOC 110 [641333]: Structure of Chromate Bound to Quartz-Water Interfaces from Second Harmonic Generation Studies**

**Franz M. Geiger**, Amanda L. Mifflin, and Kathrine A. Gerth, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IN 60208, Fax: 847-491-7713, geigerf@chem.northwestern.edu

**Abstract**

Hexavalent chromium contamination in ground water is widespread and has received much attention in the past decades. Much research has focused on the interaction of chromium with geosorbents, and much is known about the structure of chromate adsorbed at geosorbents. However, studies focusing on chromium binding to geosorbent surfaces under environmentally representative chromium concentration conditions are difficult to undertake, and here we present a novel application of the nonlinear optical laser spectroscopy surface second harmonic generation (SHG) to elucidate the structure of chromate adsorbed

to quartz/water interfaces. The experiments are carried out on-line, at room temperature and at chromate concentrations ranging from  $1 \times 10^{-6}$  to  $2 \times 10^{-4}$  M. The surface-bound chromate is spectroscopically identified via a two-photon resonance of one of its ligand-to-metal charge transfer bands with the fundamental probe light; the recorded SHG signal has negligible signal contributions from either bulk phase. A polarization analysis of the SHG signal shows a nonlinear optical response directed predominantly along the surface normal, consistent with the electric dipole of the surface-bound chromate being directed along the surface normal. Adsorption isotherms measured at pH values ranging from 4 to 11 indicate that chromate forms two to three hydrogen bonds when bound to the quartz-water interface; its free energy of adsorption is 38(1) kJ/mol. The pH dependence of the free energies of adsorption is discussed in the context of quartz-water interfacial structure and hydrogen bonding. Finally, a significant blue shift of the nonlinear electronic surface spectrum obtained from the surface-bound chromate compared to the bulk UV-VIS spectrum suggests a distortion of the ligand field energy levels, which could be due to either the formation of hydrogen bonds to the quartz/water interface, a geometric change in the ligand field structure, or both.

### **GEOC 111 [668596]: A spectroscopic investigation of ferrous iron adsorbed on oxides**

**Aaron G.B. Williams**, Department of Civil and Environmental Engineering, The University of Iowa, 4105 Seamans Center, Iowa City, IA 52245, Fax: 319-335-5660, [awilliam@engineering.uiowa.edu](mailto:awilliam@engineering.uiowa.edu), and Michelle M. Scherer, Civil and Environmental Engineering, University of Iowa

#### **Abstract**

To better understand the physical and chemical changes that occur at the oxide-water interface when ferrous iron (FeII) sorbs to the surface, we have spectroscopically isolated the sorbed FeII signal by adding aqueous FeII as  $^{57}\text{FeII}$  (only  $^{57}\text{Fe}$  is Mössbauer active). To minimize the contribution of the underlying Fe oxide to the Mössbauer signal, the oxide is synthesized from  $^{56}\text{Fe}$ . Preliminary data reveals distinct differences for the fate of FeII sorbed on iron oxide surfaces opposed to non-iron oxide surfaces. Mössbauer spectra of FeII bound to non-iron oxides ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) exhibit clearly identifiable FeII species, whereas FeII bound to iron oxides exhibit more complex spectra demonstrating both a continuation of the underlying oxide structure ( $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-FeOOH}$ ) and the formation of nanoparticle aggregates ( $\gamma\text{-FeOOH}$ ). Both Mössbauer spectra and contaminant reduction rates will be measured for a range of geochemical conditions in an attempt to link surface speciation with reactivity. A better understanding of how Fe surface speciation is related to reactivity is essential to understand contaminant reduction and trace element cycling in subsurface environments rich in FeII.

### **GEOC 112 [672279]: Using variable angle ATR FT-IR spectroscopy to probe the mineral-water interface**

**Michael J. Borda**, and Martin A Schoonen, Department of Geosciences, Center for Environmental Molecular Science, The State University of New York at Stony Brook, E.S.S. Building, Stony Brook, NY 11794-2100, Fax: 631-632-8240, [mborda@ic.sunysb.edu](mailto:mborda@ic.sunysb.edu)

#### **Abstract**

The vast majority of reactions on earth take place at surfaces and at interfaces. One of the fundamentally interesting regions, from an environmental science standpoint, is the mineral-water interface. The use of attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy offers the opportunity to investigate the mineral-water interface and specifically examine adsorbed species in real-time and in situ. In a typical ATR experiment, a mineral, in the form of sub-micron particles, is deposited on an internal reflection element (IRE) and exposed to a solution. The angle of incidence of the incoming IR beam controls the number of bounces of the IR beam within the IRE and the depth of penetration of the evanescent wave into the mineral-water interface. Spectra collected with short penetration depths are dominated by contributions from the surface region, while spectra collected with larger penetration depths have a larger contribution of the solution phase. In addition to changing the angle of incidence, the choice of IRE can also play a significant role in the effective penetration depth of the ATR experiment. ZnSe crystals offer greater than five times more penetration depth at the same geometry as a Ge IRE. By tailoring both the IRE and the experimental geometry we have explored the effect these variables have on a well-studied

adsorbate/adsorbent system. Using the model goethite/sulfate system we show a series of spectra emphasizing the usefulness of multiple angle ATR FT-IR spectroscopy to environmentally relevant materials.

**GEOC 113 [675488]: Computer modelling of cation segregation to oxide and mineral surfaces in the presence of water**

**Steve C. Parker**, David C. Cooke, Sebastien Kerisit, and Arnaud S. Marmier, Department of Chemistry, Bath University, Claverton Down, Bath BA2 7AY, United Kingdom, Fax: -44-1225 826231, s.c.parker@bath.ac.uk

**Abstract**

The aim of this presentation will be to describe our recent progress in modelling the structure of oxide and mineral surfaces in contact with water and in particular to review our attempts at studying the competitive adsorption of different cations. We are currently using a range of techniques that include the use of DFT electronic structure methods to evaluate the structure and stability of the surfaces. Recent advances now allow us to use these reliable energies to construct phase diagrams of the surface composition as a function of oxygen and water chemical potentials. The disadvantage of these approaches is that simulation of surfaces in contact with many layers of water is computationally expensive. Thus we are also applying molecular dynamics simulations where the interatomic forces are represented by a potential model. However, increasingly, electronic structure calculations are employed to assess and aid in the development of reliable parameters for the potential model. Once the model is tested, molecular dynamics techniques can be applied to calculate the mineral surfaces and the effect of immersion in solution. In addition to giving structural information of surface species, we are also extending our work to use thermodynamic integration methods to evaluate the free energy profile of water and cations as a function of distance to the mineral surface. Thereby evaluating the free energies of adsorption and surface migration. The results of our surface studies for a number of minerals will be given, including, calcite, alumina and iron III oxide, and in each case the structure and energetics of the adsorbed cations will be described.

**GEOC 114 [676115]: X-ray absorption spectroscopy (XAS) study of mercury(II) adsorption in mercaptan-functionalized mesostructured silicas with a wormhole framework structure**

**Chia-chen Chen**<sup>1</sup>, Kim F. Hayes<sup>2</sup>, Emily McKimmy<sup>3</sup>, and Thomas J Pinnavaia<sup>3</sup>. (1) Department of Civil Engineering, University of Texas, Austin, TX 78712, chiacc@mail.utexas.edu, (2) Department of Civil and Environmental Engineering, University of Michigan, (3) Department of Chemistry, Michigan State University

**Abstract**

Mesoporous silicates with high surface area and readily accessible pore structure have been developed and functionalized with 3-mercaptopropyltrimethoxysilane to provide effective uptake of mercury from water. In preparing these materials, mercaptan functional groups have been directly incorporated into a wormhole mesostructure, assembled through hydrogen bonding between a neutral amine surfactant and an uncharged silica precursor, resulting in a high mole fraction (up to 0.5) of mercaptan functionalized sites (denoted MP-HMS). We have examined the mercury uptake effectiveness of MP-HMS functionalized with molar ratios of S/Si of 0.10 and 0.50 over the Hg/S molar ratio range of 0.05–1.4. To provide a molecular level understand of the highly effective trapping of Hg by these and related mercaptan-functionalized materials (loading capacity up to 1.5 mmol Hg/g or 310 mg/g), the near-coordination environment of sorbed Hg has been investigated using XAS. Based on the XAS analysis, the mechanistic basis for the high Hg uptake by MP-HMS is discussed.

**GEOC 115 [676069]: Spectroscopic characterization of U(VI) sorption at the calcite-water interface**

**Evert J. Elzinga**<sup>1</sup>, C. Drew Tait<sup>2</sup>, Richard J. Reeder<sup>1</sup>, Kirk D. Rector<sup>3</sup>, Robert J. Donohoe<sup>3</sup>, and David E. Morris<sup>3</sup>. (1) Department of Geosciences, SUNY at Stony Brook, Stony Brook, NY 11794-2100, eelzinga@notes.cc.sunysb.edu, (2) Chemistry Division, Los Alamos National Laboratory, (3) Biosciences Division, Los Alamos National Laboratory

## **Abstract**

The uptake of U(VI) by the calcite surface from pre-equilibrated calcite-saturated solutions was characterized using batch experiments and EXAFS and luminescence spectroscopies. Results indicate the formation of triscarbonate-like adsorption complexes at U(VI) solution concentrations  $<500 \mu\text{M}$ , with a change in interaction with calcite surface sites as the surface coverage increases, and the formation of U(VI) hydroxide precipitates at higher solution concentrations, consistent with isotherm data and speciation calculations. Consequently, multiple uranyl species are likely to exist at the calcite surface during interaction of U(VI)-containing waters in the near-surface environment.

## **GEOC 116 [660966]: Computer simulation studies of aqueous uranyl interactions with clay mineral surfaces**

**Jeffery A. Greathouse**, Chemistry, St. Lawrence University, Canton, NY 13617, Fax: 315-229-7421, [jgreathouse@stlawu.edu](mailto:jgreathouse@stlawu.edu), and Roberto T. Pabalan, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute

## **Abstract**

Monte Carlo and molecular dynamics simulations have been performed to investigate the nature of surface complexes formed between aqueous uranyl cations and the basal plane of montmorillonite clay. We focused on the two-layer hydrate with a  $d(001)$  spacing of  $14.7 \text{ \AA}$ , which complements X-ray absorption spectroscopic experiments on similar systems. The location of negative charge sites within the clay lattice controls the type of surface complex formed. Uranyl cations remain fully hydrated near octahedral charge sites in an outer-sphere surface complex. The pentaquo complexes are tilted slightly from the clay surface normal and move between ditrigonal cavities. Modeling clays with tetrahedral charge sites is more difficult because the negative charge is now much closer to the aqueous layer. In this case our preliminary results indicate that the uranyl cation can form stable inner-sphere surface complexes in which one or two first-shell water oxygen atoms are replaced by surface oxygen atoms.

## **GEOC 117 [673945]: Molecular dynamics modeling of confined water**

Jianwei Wang, Andrey G. Kalinichev, and **R. James Kirkpatrick**, Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green St., Urbana, IL 61801, Fax: 217-244-4996, [jwang7@uiuc.edu](mailto:jwang7@uiuc.edu), [kirkpat@uiuc.edu](mailto:kirkpat@uiuc.edu)

## **Abstract**

Molecular-level knowledge of the structure and dynamics of confined water is important for better understanding of many natural phenomena, including mineral-water interactions, clay swelling, ion adsorption and exchange in aqueous geochemical systems, etc. Molecular dynamics (MD) simulations can provide invaluable new insight in many ways complementing conventional spectroscopic and electrochemical experimental information. We performed a series of MD simulations for 3 to  $30 \text{ \AA}$  thick water layers held in nano-confinement between parallel  $19 \text{ \AA}$  thick electrostatically neutral brucite,  $\text{Mg}(\text{OH})_2$ , substrate layers. The results provide greatly increased, structurally detailed understanding of the surface related effects on the spatial variation in the water structure, local density, hydrogen bond organization, and low-frequency vibrational dynamics of  $\text{H}_2\text{O}$  molecules at the surface. Water structure is significantly influenced by the brucite surface, with both H-bond donations to surface oxygens and H-bond acceptance from surface hydrogens in the first layer of  $\text{H}_2\text{O}$  molecules playing a key role.

## **GEOC 118 [674072]: Molecular models of interlayer adsorption of water and halocarbons by clay minerals**

**Louise J. Criscenti**, and Randall T. Cygan, Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185-0750, [ljcrisc@sandia.gov](mailto:ljcrisc@sandia.gov)

## **Abstract**

The fate of chemical contaminants in the environment is influenced by the ability of clay minerals to sorb and attenuate their dispersal. Our ability to understand sorption processes is partly provided by spectroscopic data. However, due to the complexity of clay-like minerals and analytical difficulties in examining mineral surfaces in solution, theoretical approaches provide another means to understand these complex processes. A general energy forcefield suitable for the simulation of clay minerals has been developed that describes the structure and behavior of water, hydroxyl, surface species, and both inorganic and organic intercalates. The swelling behavior of Na-montmorillonite with different trichloroethene-water compositions has been compared. Initial simulations indicate that there are two stable configurations of Na-montmorillonite with intercalated trichloroethene that are analogous to those calculated for clay swelling with water. Molecular dynamics simulations with both water and trichloroethene in the interlayer suggest that water molecules are preferred near the clay surface.

## **GEOC 119 [663693]: Effect of lipids on sorption/desorption hysteresis of hydrophobic organic compounds in natural organic matter**

**Guangwei Ding**, Department of Chemistry & Biochemistry, South Dakota State University, SH 121, Box 2202, Brookings, SD 57007, Fax: 605-688-6364, dingguangwei@hotmail.com, and James A Rice, Chemistry & Biochemistry, South Dakota State University

## **Abstract**

The chemical composition of natural organic matter plays a major role in regulating its capacity to retain hydrophobic organic compounds. Naphthalene and phenanthrene were used to study the correlations between sorption/desorption isotherm nonlinearity and compositional data from soil and peat organic matter (with or without lipids) obtained from quantitative  $^{13}\text{C}$  solid-state NMR spectroscopy. The sorption experiments were conducted using a batch equilibration method. Desorption experiments were carried out immediately following the sorption experiments by 3 successive decant-refill cycles. Hysteresis was observed in all samples. Nonlinear sorption behavior was increased by removal of lipids from the organic matrix. Desorption increased from low to high naphthalene and phenanthrene solution concentrations and then decreased at the highest concentration point for natural organic matter with or without lipids. The hysteresis index, obtained from the ratio of the  $N$  values (Freundlich exponent) for desorption and sorption, was lower in the lipid-extracted organic fractions than those of same samples without lipid extraction. The relationship between the extent of hysteresis and the characteristics of  $^{13}\text{C}$  solid-state NMR spectra indicated that altering natural organic matter composition through lipid extraction greatly affects the desorption phenomenon.

## **GEOC 120 [642274]: Creating mixed planar Fe/Al oxide surfaces for metal-ion sorption studies**

**Christine F. Conrad**, School of Marine Science, College of William and Mary, Virginia Institute of Marine Science, P.O. Box 1346, Gloucester Point, VA 23062, cfconrad@vims.edu, Catherine J. Chisholm-Brause, Applied Science, College of William & Mary, and Michael J. Kelley, Applied Science, College of William and Mary

## **Abstract**

Metal-ion sorption in natural systems is controlled largely by interactions with Fe and Al hydroxides. Insufficient understanding of the structure and composition of reactive surface sites has made it difficult to understand metal sorption reactions at the molecular scale on these complex natural surfaces. Previously, we have demonstrated the effectiveness of a novel experimental approach for understanding metal sorption behavior using planar  $\gamma\text{-Al}_2\text{O}_3$ . The current work builds upon this technique by creating mixed Fe/Al planar oxide surfaces for use in metal-ion sorption studies. Varying Fe/Al ratios have been obtained by sequentially coating planar  $\gamma\text{-Al}_2\text{O}_3$  with ferric iron. The surface properties and reactivity of the resulting materials were characterized by several spectroscopic and microscopic techniques. Subsequent use of these well-defined mixed oxides in metal sorption studies can provide a better understanding of how the reactivity and morphology of complex surfaces affect the behavior of metal-ion uptake relative to pure phase materials.

### **GEOC 121 [669260]: Effect of oxygen on siderite and rhodochrosite dissolution**

**Owen W. Duckworth**, and Scot T Martin, Division of Engineering and Applied Sciences, Harvard University, Engineering Sciences Laboratory, 40 Oxford St, Cambridge, MA 02138, Fax: 617-496-1471, duckwort@fas.harvard.edu

#### **Abstract**

Siderite ( $\text{FeCO}_3$ ) and rhodochrosite ( $\text{MnCO}_3$ ) affect the cycling of metals in aqueous environments.  $\text{FeCO}_3$  and  $\text{MnCO}_3$  dissolution is investigated under oxic and anoxic conditions. Under anoxic conditions, dissolution rates for both minerals are consistent with parallel proton and hydrolysis dissolution pathways. For siderite under oxic conditions the dissolution rate is below the detection limit for  $6.0 < \text{pH} < 10.3$ , and  $\text{Fe}(\text{OH})_3$  hillock formation preferential to steps is observed in concurrent AFM micrographs. At  $\text{pH} > 10.3$ , the oxic dissolution rate is greater than under the corresponding anoxic conditions, possibly due to electron transfer reaction between  $[\text{Fe}^{3+}(\text{OH})_4]^{-}(\text{aq})$  and  $>\text{Fe}^{\text{II}}\text{OH}$ . For rhodochrosite at  $5.8 < \text{pH} < 7.7$  under oxic conditions, the macroscopic dissolution rate equals the anoxic dissolution rate though micrographs show the formation of a  $\text{Mn}_2\text{O}_3$  tabular precipitate. For  $\text{pH} > 7.7$  under oxic conditions, the dissolution rate decreases, and an  $\text{MnOOH}$  hillock film grows across the surface. These (hydr)oxide films affect the properties of mineral surfaces.

### **GEOC 122 [674388]: Chromium Speciation in Soils: A Selective Extraction and Coprecipitation Study**

**Bin Hua**<sup>1</sup>, Baolin Deng<sup>1</sup>, James E. Amonette<sup>2</sup>, Edward C. Thornton<sup>3</sup>, and John yang<sup>4</sup>. (1) Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, huab@missouri.edu, (2) EMSL, Pacific Northwest National Laboratory, (3) Field Hydrology and Chemistry Group, Pacific Northwest National Laboratory, (4) Faculty of Environmental Sciences, Lincoln University

#### **Abstract**

Hexavalent and total chromium in the soil samples from the Hanford site, Washington, were measured by four established selective extraction procedures and by XANES analysis. Higher amounts of Cr(VI) were detected by XANES than by extraction in some soil samples, suggesting that there was a fraction of non-extractable Cr(VI) present in the soils. To investigate whether the non-extractable Cr(VI) existed in the structure of minerals such as calcite, a number of calcite precipitates were prepared in the presence of various concentrations of Cr(VI). Hydrochloric acid was used to dissolve calcite for analysis of coprecipitated Cr(VI). The results showed that the coprecipitated Cr(VI) was present and could not be extracted by any of the selective extraction procedures. X-ray diffraction (XRD) analysis revealed that coprecipitation of Cr(VI) in carbonate had an influence on the crystal structure of  $\text{CaCO}_3$ .

### **GEOC 123 [671104]: Mechanisms of Cobalt Adsorption and Co-Precipitation with Manganese Oxide using Microscopic Techniques**

**Young-Shin Jun**, and Scot T. Martin, Division of Engineering and Applied Sciences, Harvard University, 40 Oxford St., Cambridge, MA 02138, Fax: 617-496-1471, kokoliko@deas.harvard.edu

#### **Abstract**

Heavy metals are an important concern for human health. Their transport and speciation through aquifers into drinking water supplies are largely regulated by adsorption and co-precipitation with iron and manganese oxides. However, quantitative understanding of these processes is limited by our current knowledge of the microscopic mechanisms. In the current work, cobalt adsorption and co-precipitation with manganese oxides are studied by atomic force microscopy. A manganese oxide film is grown by dissolution of a rhodochrosite substrate in the presence of variable cobalt concentrations at  $\text{pH}=6$ . As compared to rhombohedral pits normally occurring during rhodochrosite dissolution, cobalt preferentially distorts one half of the pit forming an internal angle of  $90^\circ$ . In the absence of cobalt, manganese oxide film growth is limited to lateral directions: the film terminates when encountering vertical elements such as terrace steps or pit edges. In contrast, the film readily grows

across these vertical elements in the presence of cobalt. Furthermore, the macroscopic dissolution rate decreases by 50% in the presence of cobalt. Even so, associated microscopic surface observations show more rapid rhodochrosite pit expansion and film growth in the presence of cobalt. Our observations are consistent with cobalt acting as a promoter of dissolution followed by precipitation of a solid solution of cobalt-manganese oxide of lower solubility than the manganese oxide alone.

#### **GEOC 124 [674119]: Lipid coatings on pyrite surface – an AFM study**

**Xiang Zhang**<sup>1</sup>, Daniel R. Strongin<sup>1</sup>, and Martin A. A. Schoonen<sup>2</sup>. (1) Department of Chemistry, Temple University, 1901 N. 13th St., Philadelphia, PA 19122, (2) Department of Geosciences, SUNY-Stony Brook

#### **Abstract**

Pyrite, FeS<sub>2</sub>, oxidation in nature leads to a severe environmental problem referred to as acid mine drainage. Previous studies in our group have shown that the adsorption of two-tail phospholipids on pyrite suppress the extent of pyrite oxidation down to a pH of 0.7. Based on the comparison of the suppression effects of 3 different lipids we suggested that the nature of the hydrophobic tail was an important attribute. The actual surface structure of the lipid coatings, however, on pyrite was not directly determined in our prior studies. In the current study, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate the morphology of the pyrite surface with and without adsorbed lipid. Both polished pyrite single crystals and pyrite powder were studied. In the single crystal circumstance, AFM was used to determine the thickness of the lipid coating under various experimental conditions relevant to pyrite oxidation. The thickness of the coating ranged from a bilayer to multilayer depending on the nature of the lipid.

#### **GEOC 125 [674417]: Interrogating microbe/mineral interactions and contaminant speciation using laser-based optical and chemical imager (LOCI)**

**Jill R. Scott**, Paul L. Tremblay, and Timothy R. McJunkin, Department of Chemistry, Idaho National Engineering and Environmental Laboratory (INEEL), 2525 N. Fremont Ave., MS 2208, Idaho Falls, ID 83415, Fax: 208-526-8541, scotjr@inel.gov

#### **Abstract**

Our primary focus has been development of the laser-based optical and chemical imager (LOCI) that provides optical and chemical imaging of complex, heterogeneous sample surfaces. LOCI combines a Fourier transform mass spectrometer (FTMS), unique laser-scanning system, custom optics for surface fluorescence and Raman detection, and software for automated data acquisition and analysis. A key feature of LOCI is the unique laser-scanning device that provides high spatial reproducibility true depth-profiling studies and has been automated to provide imaging capabilities. The excellent reproducibility and wavelength independence of the laser-scanning device affords the opportunity to interrogate the same sample surface via optical spectroscopy prior to obtaining mass spectra. Interpretation of mass spectra has also been automated using a Fuzzy-logic inference engine, which also produces the surface maps. Our current imaging interests include characterizing microbe affinities for specific mineral phases in basalt and determining contaminant speciation.

#### **GEOC 126 [675483]: Agent-based simulation of biocomplexity: Effects of adsorption on natural organic mobility through soils**

Lailani Arthurs<sup>1</sup>, **Patricia A. Maurice**<sup>1</sup>, Gregory Madey<sup>2</sup>, Xiarong Xiang<sup>2</sup>, and Yingping Huang<sup>2</sup>. (1) Dept. of Civil Engineering & Geological Sciences, University of Notre Dame, 152 Fitzpatrick Hall, Notre Dame, IN 46556, larthurs@nd.edu, pmaurice@nd.edu, (2) Dept. of Computer Science and Engineering, University of Notre Dame

#### **Abstract**

Natural organic matter (NOM) is a heterogeneous mixture of organic molecules that is ubiquitous in terrestrial and aquatic ecosystems, and that plays a vital role in many biogeochemical processes. NOM interactions form a complex system with emergent properties; i.e., system properties not present in the individual components, but present in the whole. To better understand the complex NOM system, we have developed a Web-based stochastic simulation of NOM interactions. Here, we focus on NOM molecular weight effects on adsorption and NOM mobility. Previous experiments have shown that relatively small NOM components adsorb quickly to soil minerals, and are gradually replaced by intermediate- to high-molecular weight components that form more stable adsorption complexes. Thus, different probabilities can be assigned for adsorption and desorption of different molecular-weight components. The simulation uses the SWARM agent-based modeling tool from the Santa Fe Institute, and is configured, started, and viewed from Web browser pages.

**GEOC 127 [675867]: Arsenic removal by gypsum and calcite: the continuum between sorption and solid-solution phenomenon**

Gabriel J. Cuello, Diffraction Group, Institut Laue Langevin, 6, rue Jules Horowitz, B.P. 156, 38042 Grenoble, France, Fax: +33 476207648, [cuello@ill.fr](mailto:cuello@ill.fr), Gabriela Roman-Ross, Environmental Geochemistry Group, LGIT, OSUG, University Joseph Fourier, and **Laurent Charlet**, Environmental Geochemistry Group, LGIT, OSUG, Université Joseph Fourier, BP 53, F-38041 Grenoble Cedex 9, France, Fax: +33 4 76828101, [Laurent.Charlet@obs.ujf-grenoble.fr](mailto:Laurent.Charlet@obs.ujf-grenoble.fr)

**Abstract**

The reactions developed during As (III or V) uptake by calcite and gypsum from aqueous solution were characterised by solubility and X-Ray and Neutron Diffraction structural studies. As-containing solids (calcite and gypsum) were grown from room-temperature supersaturated aqueous solutions doped with As(III) and As(V), respectively. Solubility data shows a continuum between sorption and formation of solid-solutions ( $\text{Ca}(\text{SO}_4, \text{HAsO}_4)$  and  $\text{Ca}(\text{CO}_3, \text{HAsO}_3)$ ). By means of Rietveld refinement of X-Ray and Neutron diffraction spectra, we have obtained unit cell volumes of these solid-solutions to vary with arsenic contents. Our results show that incorporation of As produces an expansion of the unit cell in the case of calcite, where the ratio  $c/a$  is almost independent of As concentration. On the other hand, for gypsum not only an expansion of the unit cell is observed but also a deformation, as it is shown by the different evolution of three lattice constants.

**GEOC 128 [660868]: Kinetic data for CO<sub>2</sub> sequestration in geological deposits**

**Ronald W. Breault**, and Mohammad Malik, Technology, Wheeling Jesuit University, 316 Washington Ave, NTTC G45, Wheeling, WV 26003, Fax: 304-243-8703, [rbreault@wju.edu](mailto:rbreault@wju.edu)

**Abstract**

Over the past several years, beginning primarily with United Nations Conference on Environment and Development held in Rio de Janeiro, Brazil and followed by the Kyoto Protocol to the United Nations Framework Convention on Climate Change held in Kyoto, Japan, an interest in control of CO<sub>2</sub> emissions has arisen. Two of the problems associated with the control of CO<sub>2</sub> emissions are, where does one put it and what is the permanency of the depository. Putting the CO<sub>2</sub> into geologic formations both identifies a place to put the CO<sub>2</sub> and provides a permanency unequalled by other depositories. This paper presents kinetic data on CO<sub>2</sub> adsorption in calcium oxide, magnesium oxide and magnesium silicate powders. The work on calcium oxide and magnesium oxide were conducted to provide a baseline for comparison of the naturally occurring magnesium silicate. Experiments were conducted in a constant volume batch reactor at several temperatures. Kinetic rate data is presented for the reactions along with values for the activation energy and frequency factor. The data for the magnesium silicate gave surprisingly fast rates as compared to the baseline calcium oxide rates. Reactions with magnesium silicate are approximately one order of magnitude faster.

**GEOC 129 [664568]: Experimental CO<sub>2</sub>–saturated brine-rock interactions at elevated temperature and pressure: Implications for CO<sub>2</sub> sequestration in deep-saline aquifers**

**Robert J Rosenbauer**, Coastal & Marine Geology, U.S. Geological Survey, 345 Middlefield Rd., Mail Stop 999, Menlo Park, CA 94025, Fax: 650 329-5441, brosenbauer@usgs.gov, and Tamer Koksalan, Geological and Environmental Sciences, Stanford University

**Abstract**

Carbon dioxide (CO<sub>2</sub>) storage is increasingly being viewed as a tool for managing anthropogenic CO<sub>2</sub> emissions to the atmosphere. Disposal of excess CO<sub>2</sub> into deep aquifers is one of several proposed repositories, but the details of the geochemical reactions between supercritical CO<sub>2</sub> and potential host fluids and formation rocks are largely unknown. We carried out a systematic experimental study to evaluate the potential for CO<sub>2</sub> storage/sequestration in deep-saline aquifers by solubility, ionic, and mineral trapping mechanisms, providing fundamental data for thermodynamic modeling. Results of experiments reacting CO<sub>2</sub>–saturated brine with limestone and arkosic sandstone show complex temperature and pressure dependent compositional changes. The solubility of liquid CO<sub>2</sub> and formation porosity are enhanced in the presence of limestone rocks relative to the brine alone due to calcite dissolution. Ongoing experiments are focused on the effects of multiphase H<sub>2</sub>O- CO<sub>2</sub> fluids on mineral equilibria and the potential for CO<sub>2</sub> sequestration by mineral trapping.

**GEOC 130 [674580]: Density change of underground water due to CO<sub>2</sub> dissolution**

Yongchen Song<sup>1</sup>, **Baixin Chen**<sup>1</sup>, Masahiro Nishio<sup>1</sup>, Makoto Akai<sup>2</sup>, and Takashi Oshumi<sup>3</sup>. (1) Thermal Engineering Research Group, National Institute of Advanced Industrial Science and Technology, Japan, 1-2-1 Namiki, Tsukuba 305-8564, Japan, Fax: ++81-29-851-7523, y.song@aist.go.jp, b.chen@aist.go.jp, (2) Distributed Energy System Research Group, National Institute of Advanced Industrial Science and Technology, Japan, (3) CO<sub>2</sub> sequestration Project, Research Institute of Innovative Technology for the Earth, Japan

**Abstract**

Geo-sequestration had been gradually considered to be one of the practical options to mitigate CO<sub>2</sub> concentration from the atmosphere. To estimate and understand the geophysical and geochemical dynamics of injected CO<sub>2</sub> and interactions with reservoir fluids and rocks, the physical properties of CO<sub>2</sub> solution, especially the density, are necessarily the basic data required. With focused on this, an experimental investigation was carried out to directly measure the density and density change of CO<sub>2</sub> underground water solution. In this paper, the details of the experiments, including the measurement principle and method, the error analysis, and the last measurement results, are reported. It is found, at pressure range from 10.0 to 20.0 MPa and temperature from 300.15 to 323.15 K, that the density ratio of CO<sub>2</sub> solution to underground water is increased nonlinearly with the increase of CO<sub>2</sub> mass fraction. The change rate in density due to change in dissolved CO<sub>2</sub> mass fraction appears to be independent on the pressure but sensitive to the temperature. This change rate decreases from 0.26 at temperature of 300.15 K to 0.18 at 323.15 while the CO<sub>2</sub> mass fraction is 0.04.

**GEOC 131 [674608]: A two-step mechanism model of Anothite dissolution in CO<sub>2</sub> solution**

**Baixin Chen**<sup>1</sup>, Yongchen Song<sup>1</sup>, Masahiro Nishio<sup>1</sup>, Makoto Akai<sup>2</sup>, and Takashi Oshumi<sup>3</sup>. (1) Thermal Engineering Research Group, National Institute of Advanced Industrial Science and Technology, Japan, 1-2-1 Namiki, Tsukuba 305-8564, Japan, Fax: ++81-29-851-7523, b.chen@aist.go.jp, (2) Distributed Energy System Research Group, National Institute of Advanced Industrial Science and Technology, Japan, (3) CO<sub>2</sub> sequestration Project, Research Institute of Innovative Technology for the Earth, Japan

**Abstract**

The porous structure of the cap rocks plays a key role on sequestration CO<sub>2</sub> in the underground reservoir. The cap rocks are expected to be able to have a property of sealing the fluid. However, experimental investigation found that some kinds of rocks with inside of minerals have an ability to react with CO<sub>2</sub> or CO<sub>2</sub> solution, by which the permeability of the rock will be

changed. One example is the reaction of Anorthite with CO<sub>2</sub> solution. With basis on the experimental data, a two-step dissolution mechanism model of this reaction is developed for describing the dynamics of surface chemistry and transport physics. The model developed is convenient to be implemented into the existed geo-hydrological numerical model for estimating the long-term CO<sub>2</sub> geo-sequestration performance. The preliminary results obtained from model analysis shown that Anorthite dissolution in CO<sub>2</sub> solution is mostly dominated by chemical reaction rather than the mass transfer when local Sherwood number is larger than 5 and temperature is lower than 325 K. For the environment of the CO<sub>2</sub> geological sequestration at depth about 1000 m, temperatures range from 313 to 338 K, the dissolution will be governed alternatively by chemical reaction or by fluid mass transfer depending on the variation in local Sherwood number.

**GEOC 132 [678835]: Reducing uncertainty of geochemical modeling for a better prediction of CO<sub>2</sub> fate after geological sequestration**

**Etienne Brosse**<sup>1</sup>, C. Magnier<sup>1</sup>, C. Noiriel<sup>2</sup>, and D. Bernard<sup>3</sup>. (1) Organic Geochemistry Department, Institut Français du Pétrole (IFP), 1-4 avenue du Bois Préau, 92506 Rueil Malmaison Cedex, Rueil-Malmaison, France, Fax: (33) 47 52 70 19, Etienne.BROSSE@ifp.fr, (2) ISTEEM, Université de Montpellier, (3) ICMCB, UPR CNRS 9048

**Abstract**

Understanding the fate of CO<sub>2</sub> disposed in aquifers or depleted hydrocarbon fields requires the use of reaction-transport models, able to predict the possible interaction between acidified waters and the minerals. The results delivered by such models depend on many parameters and hypotheses, of which some are still badly constrained. An example concerns the way to transpose kinetics of mineral reaction, acquired from laboratory experiments on mineral powders under high water-to-mineral ratio, to the real rock system. The presentation focuses on the simulation of flow-through experiments designed to improve the upscaling of kinetic rates. Consequences are drawn for application to several scenarii where dissolved CO<sub>2</sub> could interact with the minerals, either in the host rock or in the caprock. The reliability of such simulations is tentatively discussed considering the uncertainty that can be reasonably assumed on all the kinetic parameters.

**GEOC 133 [675468]: CO<sub>2</sub> fixation by rock-water interactions**

**J. L. Krumhansl**, Geochemistry Division, Sandia National Laboratories, MS 0750, Albuquerque, NM 87185, Fax: 505-844-7354, jlkrumh@sandia.gov, and Carlos Jove-Colon, Total System Performance Assessment - 06851, Sandia National Laboratory

**Abstract**

Subterranean sequestration is one potential avenue for preventing the unwanted buildup of anthropogenic CO<sub>2</sub> in the atmosphere. The key to gaining public acceptance is to demonstrate that the gas will not return to the surface at a later date. Interactions with potential repository host rocks and formation waters are one mechanism that may permanently fix of the gas. Many potential host formations consist of mixtures of quartz, feldspars, clays and carbonate minerals coexisting with Na-K-Ca-Mg-SO<sub>4</sub>-Cl-HCO<sub>3</sub> brines. Estimates of the amount of mineralized carbonate can be readily calculated using reaction path models such as REACT, albeit at lower injection pressures and ionic strengths than may be encountered in some sequestration operations. None the less, the trends exhibited by calculations employing less extreme conditions demonstrate significant variations in the amount of mineralized CO<sub>2</sub>, and that a surprisingly small fraction of the CO<sub>2</sub> would be fixed in some cases.

**GEOC 134 [678833]: Kinetic modeling of CO<sub>2</sub> sequestration reactions in a deep saline aquifer**

**Biniam Zerai**, Beverly Saylor, and Gerald Matisoff, Department of Geological Sciences, Case Western Reserve University, 10900 Euclid Ave, Cleveland, OH 44106-7216, Fax: 216-368-3691, bxz11@po.cwru.edu

**Abstract**

Kinetic modeling of mineral-brine-CO<sub>2</sub> reactions in the Rose Run Sandstone of eastern Ohio was conducted using The Geochemist's Workbench. Model conditions included rates of reactions compiled from the literature, a brine-rock ratio of 1:25, measured rock and brine compositions, and CO<sub>2</sub> fugacity of 100 atm. Reactions with three different mineral assemblages were modeled. For carbonate rock, the CO<sub>2</sub> fugacity changed little and almost all the CO<sub>2</sub> remained in a dissolved or free phase. In the sandstone and mixed carbonate and sandstone assemblages, CO<sub>2</sub> fugacity declined to 10 atm within 1500 years due to precipitation of siderite, dawsonite, and strontianite. The modeling indicates a maximum of 0.7 – 1 mole of CO<sub>2</sub> is fixed in carbonate minerals per 10 kg of rock reacted. However, the extent of mineral trapping will be sensitive to the rate of mineral-brine-CO<sub>2</sub> reactions relative to the rate of flow of CO<sub>2</sub> away from the site of injection.

**GEOC 135 [672361]: Accessing the risks of geological storage of CO<sub>2</sub> in mature oil fields: What can we learn from numerical modeling of the Forties Field, North Sea?**

**J. Marcelo Ketzer**, Bernard Carpentier, Yann Le Gallo, and Pierre Le Thiez, Geologie-Geochemie, IFP - Institut Français du Pétrole, 1 et 4, avenue de Bois-Preau, 92852 Rueil-Malmaison, France, Fax: +33 01 47 527019, marcelo.ketzer@ifp.fr

**Abstract**

Geological storage of CO<sub>2</sub> in mature oil fields is an innovative solution to mitigate greenhouse effects in a planet with an increasing demand for energy. The precise assessment of the risks involved in the CO<sub>2</sub> storage is, however, necessary before such method be widely used. One of the main risks of the CO<sub>2</sub> storage is the dissolution, and eventual transport of CO<sub>2</sub>-charged waters in the aquifer, away from the reservoir. The efficiency of the storage can be tested by numerical modeling of the geological system involved. In order to produce an accurate model, we defined a multi-scale approach comprised of two stages: (1) simulation of the fluid flow in basinal and reservoir scales around the Forties Field, North Sea; and (2) simulation of the interaction between CO<sub>2</sub> and water. Results of the numerical modeling allowed us to evaluate present-day and future risks of the CO<sub>2</sub> storage in the Forties Field.

**GEOC 136 [676167]: CO<sub>2</sub> Sequestration in Faulted Sandstone Aquifers**

**Sangeetha M. Pasala**<sup>1</sup>, Craig B. Forster<sup>2</sup>, and Milind D. Deo<sup>1</sup>. (1) Department of Chemical and Fuels Engineering, University Of Utah, University Of Utah, Joseph Merrill Engineering Bldg, Salt Lake City, UT 84112, psangeetha@hotmail.com, (2) Department of Geology & Geophysics, University Of Utah

**Abstract**

Faults can act as barriers, conduits or integrated barrier-conduit systems. Uncertainty in knowing whether a subsurface fault will act as a barrier or conduit leads to uncertainty in evaluating the likelihood for economically sequestering CO<sub>2</sub> in sandstone aquifers. Outcrop-based studies of faulted, aeolian Navajo sandstone provide detailed, quantitative insight regarding the range of fault characteristics that might be encountered as injected CO<sub>2</sub> migrates through the faulted aquifer. The results of these studies are incorporated in interwell-scale numerical simulations of CO<sub>2</sub> injection and migration in order to assess the implications of incorrectly assessing the fluid flow properties of faults in sandstone aquifers. Simulator output shows how fault conduits and barriers can restrict migration of CO<sub>2</sub> through the aquifer as a consequence of bypassing (conduits) or compartmentalization (barriers). In addition, the simulation results reveal how the geoscientists' ability to quantify and discriminate between high-permeability vs low-permeability faults in sandstone aquifers can play an important role in designing CO<sub>2</sub> sequestration operations.

**GEOC 137 [679043]: Reactive transport modeling of cap rock integrity during natural and engineered CO<sub>2</sub> sequestration**

**James W. Johnson**<sup>1</sup>, John J. Nitao<sup>1</sup>, and Joseph P. Morris<sup>2</sup>. (1) Environmental Science Division, Lawrence Livermore National Laboratory, 7000 East Ave, L-221, Livermore, CA 94550, Fax: 925-422-7438, jwjohanson@llnl.gov, (2) Earth Science Division, Lawrence Livermore National Laboratory

## Abstract

Long-term cap rock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered geologic CO<sub>2</sub> storage sites. CO<sub>2</sub> influx that forms natural accumulations and CO<sub>2</sub> injection for EOR or saline-aquifer disposal both lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes. Influx-triggered mineral dissolution/precipitation reactions within typical shales continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them. Using our reactive transport simulator (NUFT), supporting geochemical databases and software (SUPCRT92), and distinct-element geomechanical model (LDEC), we have evaluated the net effect of these initially opposing contributions to cap-rock integrity for both natural and engineered CO<sub>2</sub> influx. The extent of geochemical alteration is nearly independent of filling mode. In contrast, geomechanical deformation—which invariably results in net aperture opening for compartmentalized reservoirs—is significantly more pronounced during engineered influx. These results limit the extent to which natural and engineered storage sites are analogous, and suggest that in both settings shale cap rocks may evolve into effective seals.

### **GEOC 138 [673728]: Soil gas surveys and autonomous geochemical stations for the monitoring of geologically sequestered CO<sub>2</sub>: Results from a leaking natural CO<sub>2</sub> reservoir below the San Vittorino Plain (central Italy)**

Giancarlo Ciotoli, **Salvatore Lombardi**, Stanley E. Beaubien, and Aldo Annunziatellis, Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", Piazzale Aldo Moro, 5, Roma 00185, Italy, Fax: 0039-(0)6-49914919, giancarlo.ciotoli@uniroma1.it, salvatore.lombarid@uniroma1.it

## Abstract

The intramontane San Vittorino basin hosts a mineral water spa and a large number of sinkholes which were formed by significant fluxes of acidic gases (CO<sub>2</sub>, H<sub>2</sub>S) from depth. This site is being studied within the EC-funded project NASCENT (NNE5-2000-00095), which is examining sealed and leaking CO<sub>2</sub> reservoirs as natural analogues for deep geological sequestration of CO<sub>2</sub>. This paper addresses the use of soil gas surveys to identify areas of elevated gas concentrations caused by migration from deep sources and then the subsequent installation of an autonomous geochemical station for temporal monitoring of high-risk sites. The soil gas results outlined a zone of anomalous CO<sub>2</sub>, CH<sub>4</sub> and He values in the north-central and extreme eastern part of the plain which can be correlated with known structural features and geophysical anomalies. The monitoring station, which measures dissolved CO<sub>2</sub> concentrations in a water well every 3 hours, has been in place for 5 months and is yielding interesting results.

### **GEOC 139 [674558]: Soil gas as a monitoring tool of deep geological storage of carbon dioxide: Results from the Encana EOR project in Weyburn, Saskatchewan (Canada)**

**David G. Jones**<sup>1</sup>, Michael H. Strutt<sup>1</sup>, Stanley E. Beaubien<sup>2</sup>, Salvatore Lombardi<sup>2</sup>, Nunzia Voltatoni<sup>2</sup>, Jean-Claude Baubron<sup>3</sup>, Carlo Cardellini<sup>4</sup>, Fedora Quattrocchi<sup>4</sup>, Domenico Granieri<sup>4</sup>, and Lynden Penner<sup>5</sup>. (1) Geochemistry, Mineralogy and Hydrogeology, British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG, United Kingdom, Fax: +44 (0)115 936 3520, dgj@bgs.ac.uk, (2) Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", (3) Bureau de Recherches Géologiques et Minières, (4) Istituto Nazionale di Geofisica e Vulcanologia, (5) J. D. Mollard and Associates Limited

## Abstract

Encana has injected carbon dioxide into the Weyburn oil reservoir since September 2000 as part of an Enhanced Oil Recovery (EOR) operation. CO<sub>2</sub> storage in the reservoir is being evaluated during injection. Systematic soil gas measurements (including CO<sub>2</sub>, CO<sub>2</sub> flux, O<sub>2</sub>, CH<sub>4</sub>, radon, thoron, helium, sulphur species and light hydrocarbons) form part of this evaluation. Data from July-September 2001 provided baseline values. Results from September 2002 give an insight into changes in near surface

data. In situ radon probes are monitoring diurnal and seasonal variations. Future datasets will be essential for assessing the CO<sub>2</sub> storage integrity of the reservoir rocks.

**GEOC 140 [675303]: High CO<sub>2</sub> gas fields: Natural analogs to the chemical evolution of CO<sub>2</sub> storage in depleted gas fields**

**Julio Friedmann**<sup>1</sup>, Robert C. Burruss<sup>2</sup>, Sean T. Brennan<sup>2</sup>, Adrian Hughes<sup>1</sup>, and Dag Nummedal<sup>3</sup>. (1) Department of Geology, University of Maryland, College Park, MD 20742, Fax: 301-314-9661, juliof@geol.umd.edu, (2) Energy Resources Team, USGS, (3) Inst. for Energy Research, Univ. Wyoming

**Abstract**

There are a specific set of chemical interactions that arise from injecting CO<sub>2</sub> into depleted hydrocarbon reservoirs, which are primarily related to the mixing of CO<sub>2</sub> with the existing immiscible brine and hydrocarbon fluids. To increase both the understanding of depleted hydrocarbon reservoirs as sequestration targets and capability to predict the short- and long-term fate of the injected CO<sub>2</sub>, we have begun to examine hydrocarbon fields that contain significant volumes of naturally occurring CO<sub>2</sub>. These fields (sometimes called low-BTU gas fields) contain from 4-80% natural CO<sub>2</sub> mixed with methane. Other gases can include H<sub>2</sub>S, SO<sub>2</sub>, N<sub>2</sub>, He, and longer-chain hydrocarbons (e.g. propane) in concentrations that range from 0-15%. Hydrocarbon fields with high CO<sub>2</sub> concentrations are both more wide-spread and abundant than commonly recognized and they serve as excellent natural analogs for CO<sub>2</sub> storage. Several important fields have significant variations of CO<sub>2</sub> content within the field, differing by depth, pressure, and geological formation. Other fields occur within the same formation but collected gas at differing pressure-temperature settings. By studying the modern and ancient chemistry of the fluid-rock-gas interactions in detail, an enhanced understanding of how injected anthropogenic CO<sub>2</sub> might change the reservoir chemistry through time as concentrations change may be gained. These fields can also be investigated as potential storage sites, as they have already held significant CO<sub>2</sub> volumes.

**GEOC 141 [674179]: Carbon sequestration in aquifers associated with ultramafic to mafic rocks**

**Juerg M. Matter**<sup>1</sup>, Taro Takahashi<sup>1</sup>, and David S. Goldberg<sup>2</sup>. (1) Geochemistry, Lamont-Doherty Earth Observatory of Columbia University, Geoscience 105B, 61 Route 9W, Palisades, NY 10964, Fax: 845-365-8155, jmatter@ldeo.columbia.edu, (2) Borehole Research, Lamont-Doherty Earth Observatory of Columbia University

**Abstract**

Aquifers associated with ultramafic to mafic rocks have a high potential for carbon sequestration due to the release of base cations, such as magnesium, calcium and iron to solution, which may facilitate precipitation of carbonate minerals. This study addresses the geochemical effects of CO<sub>2</sub> injection into reservoirs in ultramafic or mafic rocks in laboratory as well as field experiments. The dissolution rate of silicates, i.e. the release rate of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions is one of the important limiting factors for geological CO<sub>2</sub> sequestration. Flow-through column experiments have been performed to study the dissolution kinetics of Ca-Mg-silicates in a multi-mineral system in acidified solutions (pH 1 to 4). A newly developed injection system has been used to conduct small-scale CO<sub>2</sub> injection experiments in a fractured aquifer system in the Palisades Diabase, New York. The field experiments focused on the neutralization reaction of a CO<sub>2</sub>-saturated injection fluid in a fractured aquifer.

**GEOC 142 [676196]: Geologic Sequestration of CO<sub>2</sub> in a Depleted Oil Reservoir**

**Rajesh J. Pawar**<sup>1</sup>, Norman R. Warpinski<sup>2</sup>, Bruce Stubbs<sup>3</sup>, Reid B. Grigg<sup>4</sup>, John C. Lorenz<sup>2</sup>, Scott P. Cooper<sup>2</sup>, James L. Krumhansl<sup>2</sup>, Robert D. Benson<sup>5</sup>, and James T. Rutledge<sup>6</sup>. (1) Hydrology, Geochemistry and Geology, Los Alamos National Laboratory, MS T003, Los Alamos, NM 87545, Fax: 505-665-8737, rajesh@lanl.gov, (2) Sandia National Laboratory, (3) Pecos Petroleum Engineering, (4) Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, (5) Geophysics, Colorado School of Mines, (6) Geophysics, Los Alamos National Laboratory

## **Abstract**

Injection of CO<sub>2</sub> into depleted oil reservoirs is a carbon sequestration strategy that needs validation for numerous technical, safety, and policy reasons. This paper provides an overview of a DOE sponsored project whose objectives are to improve current understanding of the mechanisms associated with this sequestration option, to determine applicability of available monitoring technology and to predict the ultimate fate of injected CO<sub>2</sub> in reservoir. The main thrust of this project is characterization of CO<sub>2</sub> migration through a field demonstration experiment. Approximately 2000 tons of CO<sub>2</sub> was injected in a depleted oil reservoir located near Hobbs, NM between December 2002 and February 2003. Multiple geophysical techniques are being applied to characterize migration of injected CO<sub>2</sub>. Laboratory experiments and numerical flow/reaction simulations are being used to understand CO<sub>2</sub> interactions and to predict fate of injected CO<sub>2</sub>.

### **GEOC 143 [679038]: An overview of ocean carbon storage options**

**Ken Caldeira**, Atmospheric Science Division, Lawrence Livermore National Laboratory, 7000 East Ave, L-103, Livermore, CA 94550, Fax: 925-422-6388, kenc@llnl.gov

## **Abstract**

Several carbon management options have been proposed that would increase the storage of carbon in the ocean. These include direct injection of CO<sub>2</sub> into the ocean either from land-based facilities or from ships, fertilization of the ocean with micro- or macro-nutrients, neutralization of carbon acidity with carbonate minerals, the deep-sea burial of terrestrial organic matter, and continued release of CO<sub>2</sub> into the atmosphere. Ocean options differ greatly in their mode of action (e.g., power-plant point sources vs. open ocean fertilization), sequestration permanence (years to nearly permanent), environmental consequences (damaging to possibly beneficial), and costs (possibly cheap to expensive). An attempt is made to compare this diverse array of ocean storage options using uniform evaluation criteria. Viable ocean storage options must be effective, technically feasible, and economically competitive, and must address issues regarding environmental consequences and public acceptance.

### **GEOC 144 [676188]: Numerical experiments on the behavior of the sequestered CO<sub>2</sub> in the mid-depths ocean using eddy-resolving OGCM**

**Shigeaki Aoki**, Institute for Environmental management technology, National Institute of Advanced Industrial Science and Technology, onogawa 16-3, Tsukuba, Japan, Fax: 81-29-861-8357, aoki-s@aist.go.jp, and Toshimasa Doi, Environmental Information Group, CTI CO.,LTD

## **Abstract**

To investigate the environmental impact by the ocean sequestration of CO<sub>2</sub> in the mid-depths, a numerical simulation model based on the eddy-resolving ocean general circulation model is developed. The model uses the third order advective schemes to suppress the numerical diffusion often observed in the coarse resolution lower order models, and the horizontal resolution is less than a quarter degree.

In cases of idealized ocean configuration (simplified boundary conditions and geometry) to isolate the effect of the meso-scale eddies in the ocean, the behavior of the sequestered CO<sub>2</sub> remains fairly advective after initial diffusive stage, i.e., dense CO<sub>2</sub> is trapped and advected by meso-scale eddies. This implies the possibility that the higher environmental impacts remain in longer duration than those in the lower resolution models.

### **GEOC 145 [666303]: Non-invasive, in-situ quantification of soil carbon sequestration**

**George R. Hendrey**, Lucian Wielopolski, and Sudeep Mitra, Earth Systems Science Division, Brookhaven National Laboratory, Bldg. 490-D, Upton, NY 11973, Fax: 631 344 2060, hendrey@bnl.gov

### **Abstract**

Managing plant and ecosystem processes to accelerate carbon sequestration (CS) in soils may contribute to near-term amelioration of increases in atmospheric CO<sub>2</sub>. Quantification of CS in soils will be required to provide verifiable accounting of the process. We have developed a new method for quantifying CS to a depth of ca. 0.3m based on inelastic neutrons scattering (INS) and detection of resultant gamma emission from carbon. Unlike traditional soil sampling the INS approach is non-invasive and may be repeated at the identical site time and again thus avoiding the problem of spatial heterogeneity. By establishing a set of registered plots that can be visited year-after-year, a precise measure of changes in CS over time to a depth of 30cm can be obtained. The accuracy of INS compared to traditional soil coring was evaluated in double-blind studies conducted in a variety of forest and field plots.

### **GEOC 146 [676226]: Sequestration of CO<sub>2</sub> in peat and soil organic matter. Sorption and diffusion controlled hysteresis model**

**Peter I. Ravikovitch**, TRI/Princeton, 601 Prospect Ave., Princeton, NJ 08542, Fax: 609-683-7149, ravikovi@triprinceton.org, Alexander V. Neimark, Center for Modeling and Characterization of Nanoporous Materials, TRI/Princeton, and Joseph J. Pignatello, Department of Soil and Water, Connecticut Agricultural Experiment Station

### **Abstract**

Modeling sequestration performance of CO<sub>2</sub> in geological and terrestrial sinks requires fundamental understanding of sorption and diffusion mechanisms. We have found that CO<sub>2</sub> sorption in soils that are rich in organic matter (OM), e.g. peat, is often characterized by severe hysteresis. The focus of this research is to obtain a better understanding of the mechanisms responsible for hysteretic sorption. We studied sorption of carbon dioxide on peat, as well as on purified humin and humic acid fractions. Sorption can be described as a two-stage process characterized by different short-time and long-time kinetic mechanisms. The first stage (hours to several days) is controlled by diffusion through “rubbery” regions of OM and adsorption in (desorption from) accessible micropores in “glassy” regions of OM. The model of Diffusion-Controlled Hysteresis (DCH) is introduced to extract equilibrium isotherms and diffusion coefficients. The characteristic time scale for the second stage is much larger (months). Using the DCH model, we show that the long-time kinetics is correlated with the increasing sorption in micropores. We hypothesize that the second stage is caused by a slow diffusion into remote microporous domains, which become accessible via structural swelling and/or restructuring of the solid matrix. Implications for the prediction of CO<sub>2</sub> sequestration in peat and coal are discussed.

### **GEOC 147 [678836]: Chemical extraction of carbon dioxide from air to sustain fossil energy by avoiding climate change**

**Manvendra K. Dubey**<sup>1</sup>, Hans Ziock<sup>1</sup>, Jonah Colman<sup>1</sup>, Thomas Rahn<sup>1</sup>, and Klaus Lackner<sup>2</sup>. (1) Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545, Fax: 505-665-3107, Dubey@lanl.gov, (2) Columbia University

### **Abstract**

Fossil energy has benefited humankind, but also threatens our environment. Given that fossil fuels are plentiful, cost-effective, and energy rich, their use will be limited by our ability to mitigate their environmental impact. To achieve this, current approaches focus on capturing carbon dioxide from large point sources such as power plants. However, they are limited because they fail to address emissions from transportation and the myriad of dispersed sources that amount to more than half of all emissions. To solve this problem we have proposed (and are developing) direct carbon dioxide extraction from air as a means to capture emissions from all sources. It preserves our energy infrastructure, fuel distribution and transportation systems, eliminates piping costs to permanent carbon dioxide sequestration sites, and could restore atmospheric carbon dioxide to pre-industrial levels. Our approach binds carbon dioxide in the air (370 ppm) to an

adsorbent, which is then heated to recover a pure carbon dioxide stream for sequestration and the adsorbent for recycling. Adsorbents like lime that is used in the cement industry, or sodium hydroxide solutions are identified as a prototype. Carbon dioxide capture technologies on will be critical for most sequestration strategies. We report laboratory experiments on alkaline and polyamine adsorbents and atmospheric modeling results to better assess the scale and scope of air-capture of carbon dioxide as a means to sustain fossil energy. We are also exploring carbon dioxide uptake measurements by alkaline lakes using eddy-flux techniques that provide natural analogues to our collection scheme.

## Geochemistry Division Officers

<p style="text-align: center;"><b><u>Chairperson</u></b> William M. Landing Florida State University Department of Oceanography 325 Oceanography-Statistics Bldg. Tallahassee, Florida 32306-4320 (850) 644-6037 FAX: (850) 644-2581 <a href="mailto:wlanding@mailers.fsu.edu">wlanding@mailers.fsu.edu</a> <a href="http://ocean.fsu.edu">http://ocean.fsu.edu</a></p>	<p style="text-align: center;"><b><u>Treasurer</u></b> Jay Brandes University of Texas at Austin Marine Science Institute 750 Channel View Drive Port Aransas, TX 78373 (361) 749-6756 FAX: (361) 749-6777 <a href="mailto:brandes@utmsi.utexas.edu">brandes@utmsi.utexas.edu</a> <a href="http://msi40.utmsi.utexas.edu/staff/brandes/">http://msi40.utmsi.utexas.edu/staff/brandes/</a></p>
<p style="text-align: center;"><b><u>Past Chair/Awards Chair</u></b> Peggy O'Day Geology Department Arizona State University Tempe, AZ. 85287-1404 (480) 965-4581 Fax: (480) 965-8102 <a href="mailto:oday@asu.edu">oday@asu.edu</a> <a href="http://geology.asu.edu/geochem/index.html">http://geology.asu.edu/geochem/index.html</a></p>	<p style="text-align: center;"><b><u>Membership Chair</u></b> Position Available. Contact any officer for information.</p>
<p style="text-align: center;"><b><u>Chair Elect/Program Chair</u></b> Susan Carroll Lawrence Livermore National Laboratory (925) 423-5694 FAX: (925) 423-1997 <a href="mailto:carroll6@llnl.gov">carroll6@llnl.gov</a></p>	<p style="text-align: center;"><b><u>Councilor</u></b> Ken B. Anderson Argonne National Lab 9700 South Cass Ave. Argonne, IL 60439-4831 (630) 252-1928 FAX: (630) 252-9288 <a href="mailto:kbanderson@anl.gov">kbanderson@anl.gov</a> <a href="http://www.anl.gov">http://www.anl.gov</a></p>
<p style="text-align: center;"><b><u>Secretary / Website Editor</u></b> John C. Schaumloffel State University of New York College at Oneonta Department of Chemistry Oneonta, NY 13820 (607) 436-3432 FAX: (607) 436-2654 <a href="mailto:schaumjc@oneonta.edu">schaumjc@oneonta.edu</a> <a href="http://www.oneonta.edu/faculty/schaumjc">http://www.oneonta.edu/faculty/schaumjc</a></p>	<p style="text-align: center;"><b><u>Alternate Councilor</u></b> George W. Luther III College Marine Studies University of Delaware Lewes, DE 19958-1298 (302) 645-4208 (302) 645-4007 <a href="mailto:luther@udel.edu">luther@udel.edu</a> <a href="http://www.ocean.udel.edu/faculty/luther/luther.html">http://www.ocean.udel.edu/faculty/luther/luther.html</a></p>
<p style="text-align: center;"><b><u>Program Chair Elect</u></b> Jim Kubicki Penn State University Department of Geosciences 308 Deike Building University Park, PA 16801 (814) 865-3951 <a href="mailto:kubicki@geosc.psu.edu">kubicki@geosc.psu.edu</a></p>	<p style="text-align: center;"><b><u>Incoming Newsletter Editor</u></b> Dave Clifford Penn State University (814) 864-3523 <a href="mailto:djclifford@psu.edu">mailto:djclifford@psu.edu</a></p>