

ACS DIVISION OF GEOCHEMISTRY

Fall 2002 NEWSLETTER

224th NATIONAL ACS MEETING
August 18-22, 2002
Boston, MA

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Message from the Chairperson

Greetings from the Division Executive Committee! We had a very successful meeting in Orlando in April, with over 150 papers presented in the Geochemistry Division alone and co-sponsorship of several other symposia in other divisions. Symposia on topics ranging from isotopes to microbes to synchrotrons to nanoscience made for a fun and stimulating week. One of the highlights was a Division poster session and social hour associated with a three-day symposium on Minerals and Nanoparticles. Thanks to all of the symposium organizers, speakers, and attendees for a making Orlando such a success.

The ACS Fall National Meeting takes place in Boston, August 18-22. The Geochemistry Division is sponsoring several symposia on biogeochemistry, metal complexation, and equilibrium modeling – full abstracts in this issue. Contact Bill Landing (landing@ocean.fsu.edu) if you have any questions about Geochemistry events in Boston.

In 2003, the Spring ACS National Meeting will be held in New Orleans, March 23-27. The Spring meeting is shaping up to be an exciting one with eight symposia on the slate in the Geochemistry so far, and several co-sponsored symposia (see below). A highlight of the meeting will be the award of our second Geochemistry Medal to an individual who has made outstanding contributions to geochemistry, and a Division Medal Award Symposium with invited speakers. The OASys electronic abstract system will open in mid-September for all symposia with contributed papers, and abstract deadline (on-line) will be late November. Don't miss out!

It's not too early to be thinking about the 2003 Fall National Meeting, which will be held in New York City, September 7-11. If you have an idea for a symposium or would like to be involved in program planning, contact Program Chair Susan Carroll (carroll6@llnl.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). This money can be used to pay expenses for invited speakers or to support symposium-related activities. We are happy to assist all symposium organizers in submitting an application.

If you are getting this newsletter, then you are already a Geochemistry Division member. But don't forget that **WE NEED MORE MEMBERS!** Our 2for-1 membership campaign is going for 2002, so encourage your friends, colleagues, and students to join and support the Division. The Geochemistry Division exists only by the will, involvement, and enthusiasm of its members, and we are looking for 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.

Peggy O'Day
Division Chair, 2002

Business Meeting

The Divisions general business meeting in Boston is scheduled for Tuesday evening. Details will be available at the Division table at the meeting. Members are strongly encouraged to attend and help the Executive Committee formulate plans for our division for 2003 and beyond.

Councilor's Report

It's not just about the money

Typically, governance (specifically the ACS Council) is not the most exciting aspect of ACS activities, but things have been heating up of late and I think that it is timely to let you all know what is going on.

The ACS Council is currently considering changes to the Society's Constitution and Bylaws as they relate to financial support to Local Sections and Divisions. This process has been going on for a few years now¹ and I have been one of those most involved in pushing the case for increased financial support for Divisions. Currently the ACS provides about four times more support to Local Sections than it provides to Divisions, and that seems disproportionate to those of us working to provide services to Division members. However, the specific changes that now being considered, in my opinion are not in the best long term interests of the Divisions or the Society and I have voiced my strong opposition to the current proposal. I, in collaboration with officers from other Divisions, have prepared an alternative proposal that is now being discussed among the officers of all of the Divisions and which will likely be formally proposed after the Boston meeting.

Additional details of this debate and the petitions to amend the Society's documents can be found at: http://membership.acs.org/g/geoc/Councilor/proposed_ammendments.html. In the interests of saving space, I won't bore you with the details here. If you are interested then please visit the web site or contact me personally. I'd be thrilled to see members of the Division taking direct interest in these issues!

I think that there is now a general consensus (not unanimity) among members of the Council that financial support to divisions is both inequitable and inadequate and that it needs to be increased. I also believe that increased support is likely to happen at some point over the next year or two. That will be a very good thing since it should alleviate some of the financial stresses on our Division and allow us to pursue some new initiatives to enhance the Geochemistry Division and the services that we provide to you, the members.

What is not clear is the form the changes that lead to increased support will take and what "strings" will be attached. My views are as follows:

- Financial support to Divisions should be increased.
- Increased support to Divisions should not come at the expense of Local Section support.
- Increased support to Divisions should not be implemented in a way that erodes membership incentives for Divisions or in a way that forces inter divisional competition for fixed funds.
- Support to Divisions and Local Sections should not be structured in such a way that it codifies, or could be interpreted as codifying, either group as superior or inferior to the other.
- The dues of members of the Society who are NOT members of Divisions should generally not be used to support Divisions. (A valid case can be made that healthy Divisions contribute to the overall health of the Society. It can, therefore, be argued that all members benefit to some extent from Division activities and should contribute to Divisional support, but this should be minimal in the case of members who have not elected to belong to Divisions. In my opinion it is not appropriate to force those members to support groups to which they have not chosen to belong.)

I am working hard to try to ensure that these principles are incorporated into the revisions to the Society's bylaws. I will try to keep all GEOC members informed of the progress of these efforts through the Division's web page and through these newsletters.

Ken Anderson
Councilor
kbanderson@anl.gov

¹Accomplishing change at the ACS is a bit like mating elephants - Everything is done at a high level, there is a great deal of roaring and bellowing, and it takes a couple of years before it produces any results!

Member-Get-A-Member Campaign

This year the Division is sponsoring a 2 for 1 membership drive called our Member-Get-A-Member Campaign. Simply put, any existing member can sponsor a new member and the Division will honor both memberships for the price of one. You can split the dues any way you want. If you have already renewed your membership, there is nothing more to pay. Simply fill out the form available on the Division's web site <http://membership.acs.org/g/geoc/> under Member-get-a-Member Campaign, and mail or fax it to the address on the form. It's that simple. A copy of the form also appears at the end of this newsletter.

If you have not already renewed your Division membership, we would like encourage you to do so soon. You can renew by phone by calling 800-333-9511 (International members and Ohio residents 614-447-3776), or on line at http://store.acs.org/cgi-bin/technical_divisions_application.pl . The cost of membership is very nominal: \$10 for ACS members, \$12 for Non ACS members. Discounts are available for students and emeritus members. By default, membership also includes a subscription to *Geochemical Transactions* (+\$40), but members who do not wish to receive the journal can "opt-out" and continue their membership at the \$10/\$12 rate.

Newsletter Editor Needed

After doing the newsletter for about 5 years now, and also working to develop the Geochemistry Division Website, I have decided to hang up my hat and move on to other things. As a result, the Division is actively seeking a replacement Newsletter Editor to start with the Spring 2003 Newsletter. I will remain available to help with the transition and to assist the new editor with whatever support they need. Please contact either myself or any Division Officer if you are willing to or know someone who might like the position. It is really very little work now that we are doing electronic newsletters and is a great way to get involved with the Division. Thanks to all who have helped me with this job for the past 4 years.

John Schaumloffel
schaumjc@oneonta.edu
607-436-3432

ACS Legislative Action Center

Interested in how what is going on in Washington will affect the chemical sciences, ACS, funding from various agencies, etc.? [Check out the ACS Legislative Action Center by clicking here!](#)

Geochemistry Division Elections for 2003

This year we have the following positions open for election with terms starting on Jan. 1 2003:

- Program Chair Elect – election to this leads to Division Chair in the third year
- Secretary (3 year term)
- Division Councilor (3 year term)

Anyone interested in running for election or in nominating a member should contact George Luther, chair of the nominating committee, at the address below. If you nominate someone, provide their e-mail or phone number so that the committee can contact the nominee!

George W. Luther, III
302-645-4208
FAX: 302-645-4007
luther@udel.edu

Call for Volunteers

The Geochemistry Division Needs Your Help! There are many ways in which members can contribute further to the Geochemistry Division and thereby help the geochemistry community develop and grow. The following are a few suggestions for volunteer activities within the Division. If you are interested in any of these, or if you have an idea for something which is not listed, please contact Andy Bishop (Membership Chair) at anbishop@shell.com.

Contribute an Idea for Programming

Is there a topic you would like to see covered by the geochemistry division at a National Meeting? If so, let us know. You do not have to commit yourself to actually organizing the symposium. We can always find someone to do that. But if you have a great symposium topic, pass it on!

Organize a Symposium

You've got the idea, and you want to run the meeting. No problem. As soon as you think of something, drop us a line, and we can get the ball rolling. Organizing a symposium is a lot easier now with all of the Internet programming tools at your disposal. We can help you find speakers, attract additional funding for overseas speakers' travel costs and tips for scheduling the program.

Run a Short Course at a National Meeting

This is not something we have traditionally done, but many other divisions do run short courses on relevant topics at National Meetings. If there is a topic you would like to teach, and you think some of your fellow colleagues would be interested, let us know.

Help Man the Division Table at a National Meeting

If you are going to a National Meeting, and you have a little time to spare, you can really help the Exec out by volunteering to sit at the Division Table for a couple of hours. It's a great way to meet more of your colleagues, and participate directly in the division.

Geochemistry Division Trivia

Who said "Geochemists do it – on the land, in the sea, in the air, or anywhere!"?

(Answer on the division web site in the "Division History" section)

Upcoming Symposia

225th ACS National Meeting in New Orleans, LA March 23-27, 2003

- [Geochemistry Division Medal Symposium](#) Participation by Invitation of the Awardee
- Organic Geochemistry in Contemporaneous Environments, Ancient Sediments and Laboratory Simulations.
In Honor of Professor Earl W. Baker [Call for Papers](#)
- Ancient Biomolecules: New Perspectives in Archaeology and Palaeobiology [Call for Papers](#)
- Organic Solids in Petroleum Production [Call for Papers](#)
- Molecular Studies of Soil Organic Matter [Call for Papers](#)
- Tracers of Organic Matter Cycling in River Systems Call for Papers
- The Impact of Nanoparticle Growth and Transformation Processes on Contaminant Geochemical Cycling [Call for Papers](#)
- Metal Sulfide Formation And Reactivity: A Multi-Disciplinary Approach To The Role Of Metal Sulfide Minerals In Past And Present Environments [Call for Papers](#)

Geochemistry Division Officers

<p style="text-align: center;"><u>Chairperson</u> Peggy O'Day Geology Department Arizona State University Tempe, AZ. 85287-1404 (480) 965-4581 Fax: (480) 965-8102 oday@asu.edu http://geology.asu.edu/geochem/index.html</p>	<p style="text-align: center;"><u>Treasurer</u> 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 brandes@utmsi.utexas.edu http://msi40.utmsi.utexas.edu/staff/brandes/</p>
<p style="text-align: center;"><u>Past Chair/Awards Chair</u> Dr George Cody Carnegie Institute Geophysical Laboratory 5251 Broad Branch Rd NW Washington D.C. 20015 (202) 686-2410 x2479 Fax: (202) 686-2419 cody@gl.ciw.edu</p>	<p style="text-align: center;"><u>Membership Chair</u> Andy Bishop Shell International E&P Inc Bellaire Technical Center 3737 Bellaire Blvd Houston TX 77025-1206 (713) 245-7273 FAX: (713) 245-7599 anbishop@shell.com</p>
<p style="text-align: center;"><u>Chair Elect/Program Chair</u> William M. Landing Florida State University Department of Oceanography 325 Oceanography-Statistics Bldg. Tallahassee, Florida 32306-4320 USA (850) 644-6037 FAX: (850) 644-2581 wlanding@mailier.fsu.edu http://ocean.fsu.edu</p>	<p style="text-align: center;"><u>Councilor</u> Ken B. Anderson Argonne National Lab 9700 South Cass Ave. Argonne, IL 60439-4831 (630) 252-1928 FAX: (630) 252-9288 kbanderson@anl.gov http://www.anl.gov</p>
<p style="text-align: center;"><u>Secretary</u> Virender K. Sharma Florida Institute of Technology Chemistry Department 150 University Blvd Melbourne, FL 32901 (321) 674-7310 Fax: (321) 674-8951 vsharma@fit.edu</p>	<p style="text-align: center;"><u>Alternate Councilor</u> George W. Luther III College Marine Studies University of Delaware Lewes, DE 19958-1298 (302) 645-4208 (302) 645-4007 luther@udel.edu http://www.ocean.udel.edu/faculty/luther/luther.html</p>
<p style="text-align: center;"><u>Program Chair Elect</u> Dr. Susan Carroll Lawrence Livermore National Laboratory (925) 423-5694 FAX: (925) 423-1997 carroll6@llnl.gov</p>	
<p style="text-align: center;"><u>Newsletter/Website Editor</u> John C. Schaumloffel State University of New York College at Oneonta Department of Chemistry Oneonta, NY 13820 (607) 436-3432 FAX: (607) 436-2654 schaumjc@oneonta.edu http://www.oneonta.edu/faculty/schaumjc</p>	

Division of Geochemistry American Chemical Society



What's **HOT?**

Geochemistry Division programming stems primarily from the members of the Division. Tell us what subjects/areas you feel deserve to be considered for future symposia. **We welcome all suggestions.**

Suggested Symposia Topic:

Are you willing to consider helping to organize such a symposia? Organizing Geochemistry Division symposia is not onerous. The Division's Program Chair takes care of most of the work, including all of the logistics. The primary roles of symposia organizers are:

- To define the scope of the symposia and invite key speakers to participate
- To promote the symposia and to help serve as a focal point for information relating to the symposia
- To assist the program chair to organize submitted abstracts into sessions for the presentations.

The Division contributes up to \$600 per symposium to support the organization of the symposium and we also support organizers who apply for external support, such as PRF funds, by undertaking much of the effort involved.

Most organizers find the effort involved both easily manageable and satisfying.

Name _____

Address _____

Phone No. _____ (Number at which you can be reach during business hours)

EMAIL ADDRESS _____

PLEASE PRINT CLEARLY

(Please attach your business card if available)

Mail or Fax to: **William M. Landing**
Department of Oceanography
Florida State University
Tallahassee, FL 32306-4320
Fax (850) 644-2581

Technical Program and Abstracts for the Boston, MA ACS Meeting

SUNDAY MORNING

Biogeochemistry of Organic Contaminants in Aquatic Ecosystems: Honoring Dr. James G. Quinn
Cosponsored with Division of Environmental Chemistry

SUNDAY AFTERNOON

Biogeochemistry of Organic Contaminants in Aquatic Ecosystems: Honoring Dr. James G. Quinn
Cosponsored with Division of Environmental Chemistry

MONDAY MORNING

Biogeochemistry of Organic Contaminants in Aquatic Ecosystems: Honoring Dr. James G. Quinn
Cosponsored with Division of Environmental Chemistry

MONDAY AFTERNOON

Section A

Convention Center -- Room 205

Biogeochemistry of Marine Organic Matter in the Contemporary Environment and Ancient Sediments.

In Honor of Professor James G. Quinn. *Cosponsored with Division of Environmental Chemistry*

J. W. Farrington, C. M. Reddy, and T. L. Wade, *Organizers*

1:30 —1. Carbon isotopic composition of biomarkers in oceanic sediments as proxies for continental vegetation. G. Eglinton

1:50 —2. Carbon isotope ratios of nucleic acids from environmental samples. A. L. Sessions, J. M. Hayes, A. M. Pearson, E. DeLong

2:10 —3. δD of fatty acids in sediment trap materials and in sediments. S. P. Sylva, A. L. Sessions, J. M. Hayes, S. Wakeham

2:30 —4. Temporal and spatial offsets in molecular proxy records induced by sediment redistribution. T. I. Eglinton, N. Ohkouchi, G. Mollenhauer, R. R. Schneider, L. D. Keigwin, J. M. Hayes

2:50 —5. Compositional assessment of photochemical modifications of riverine dissolved organic matter using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. E. B. Kujawinski, E. Kaiser, M. A. Freitas

3:10 — Intermission.

3:30 —6. Environmental geochemical approaches to defining the fate, effects, and sources of hydrocarbons in the Exxon Valdez spill zone: Prince William Sound. P. D. Boehm, D. S. Page, G. S. Douglas, W. A. Burns, A. E. Bence, P. J. Mankiewicz

3:50 —7. Composition, distribution, and sources of polycyclic aromatic hydrocarbons in sediments of the Western Harbour of Alexandria, Egypt. A. E. Mostafa, A. O. Barakat, Q. Yaorong, T. L. Wade

4:10 —8. The Pettaquamscutt River, RI Revisited: New trends in the PAH sediment profile. A. L. C. Lima, C. M. Reddy, T. I. Eglinton

4:30 —9. Identification of a nonmethylene interrupted docosadienoic fatty acid in *Lucinoma Aequizonata* (*Bivalia*). J. W. Farrington, J. Sulanowski

TUESDAY MORNING

Section A

Convention Center -- Room 205

Metal Complexation in Natural Waters

Spectroscopic Studies of Metal Complexation

Cosponsored with Division of Environmental Chemistry

B. M. Voelker, *Organizer*

8:30 — Introductory Remarks.

8:45 —10. Changes in the natural fluorescence of fulvic acid caused by the binding of Al(III): Can fluorescence quenching and fluorescence enhancement occur simultaneously? D. K. Ryan, M. D. Hays

9:15 —11. Study of fulvic-aluminum(III) ion complexes by ^{27}Al solution NMR. N. Lee, D. K. Ryan

9:45 —12. UV-Raman spectroscopy and ab initio calculations of carboxylic acids-Al solutions. J. D. Kubicki, C. C. Trout

10:15 — Intermission.

10:40 —13. Experimental and theoretical investigation of siderophores and their Fe^{3+} complexes in aqueous solutions. D. C. Edwards, S. B. Nielsen, A. Jarzecki, S. C. B. Myneni, T. Spiro

11:10 —14. X-ray absorption spectroscopic investigation of nickel(II) complexation by naturally occurring organic compounds. T. J. Strathmann, F. M. M. Morel, S. C. B. Myneni

TUESDAY AFTERNOON

Section A

Convention Center -- Room 205

Metal Complexation in Natural Waters

Field studies

Cosponsored with Division of Environmental Chemistry

B. M. Voelker, *Organizer*

1:30 — Introductory Remarks.

1:45 —15. Dissolved iron complexation and speciation in the Gulf of Mexico. W. M. Landing, R. T. Powell, A. Wilson-Finelli

2:15 —16. Iron-colloids in the North and South Atlantic and North Pacific. E. A. Boyle, J. Wu, B. Bergquist

2:45 — Intermission.

3:10 —17. Evidence for strongly complexed Hg(II) in natural waters. H. Hsu, D. L. Sedlak

3:40 —18. In situ Cu speciation measurements in Boston Harbor using DGT. G. R. Fones, J. W. Moffett

4:10 —19. Withdrawn.

WEDNESDAY MORNING

Chemical Science Using Synchrotron Radiation

What is Synchrotron Radiation and What are its Major Applications?

Cosponsored with Division of Analytical Chemistry

WEDNESDAY AFTERNOON

Section A

Convention Center -- Room 205

Chemical Equilibrium Measurement and Modeling

E. T. Urbansky, *Organizer*

1:30 —20. Application of surface complexation/precipitation modeling to contaminant leaching from weathered steel slag. D. S. Apul, M. Weimer, K. H. Gardner, T. T. Eighmy, A. Fallman, R. Comans

1:50 —21. Calculation of solubility equilibrium constant of $\text{HCl}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$ at 40°C. Y. Li

2:10 —22. Chemical mechanism of Cl_2^- formation and decay by laser-flash photolysis in aqueous solution containing chloride ions and hydrogen peroxide. X. Yu

2:30 —23. Heavy metal desorption from natural sediment. Y. Gao, A. T. Kan, M. B. Tomson

2:50 —24. Modeling the 90th percentile lead level in metropolitan Boston. W. Sung

3:10 — Intermission.

3:30 —25. Predicting the behavior of hazardous metals in sulfidic waters: Importance of sulfur(0) activity. G. R. Helz

3:50 —26. Prediction of the component solubility of the system of $\text{LiCl-HCl-MgCl}_2\text{-H}_2\text{O}$ at 20°C. Y. li

4:10 —27. Reactivity of water in fused silica. R. M. Van Ginhoven, H. Jonsson, B. Park, L. R. Corrales

4:30 —28. Surface-catalyzed transformations of aqueous endosulfan. J. L. Ferry, S. S. Walse

4:50 —29. Water in the local structure of Nd^{3+} coprecipitated with calcite. S. H. Withers, A. Schulte, G. Braunstein, R. E. Peale, W. P. Hess, K. M. Beck, R. J. Reeder

Chemical Science Using Synchrotron Radiation

Synchrotron Techniques and their Applications

Cosponsored with Division of Analytical Chemistry

Carbon isotopic composition of biomarkers in oceanic sediments as proxies for continental vegetation.

Geoffrey Eglinton, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Rd, Woods Hole, MA 02543, geoff@geglinton.freeserve.co.uk

Aerosols containing both mineral and organic matter are transported by wind systems over thousands of kilometers, resulting in the gradual formation of sedimentary deposits on polar ice sheets, land areas, and deep-sea sediments. Specific organic compounds (biomarkers) within deep-sea sediments are helpful in identifying the changing nature and distribution of the aerosol source (mainly vegetation) over geologic time. In particular, long-chain, even carbon number n-alkanols (C22-C32) and their isotopic compositions (^{13}C and ^{14}C) can be used to interpret the space and time-averaged leaf wax contributions from C3 and C4 vegetation. Pollen grains also provide an independent proxy for vegetative source areas. As a means to investigate the phytogeographical distribution on the African continent, a series of Eastern Atlantic sediment cores have been analyzed for n-alkanols, pollen, and other biomarkers. These results will be discussed in the context of how climate and other environmental processes affect the C3 versus C4 phytogeography.

Carbon isotope ratios of nucleic acids from environmental samples.

Alex L. Sessions¹, John M. Hayes¹, Ann M. Pearson², and Ed DeLong³. (1) Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Mail Stop 4, Woods Hole, MA 02543, Fax: 508-457-2164, ASessions@whoi.edu, (2) Earth and Planetary Sciences, Harvard University, (3) Monterey Bay Aquarium Research Institute

We are developing an interface to connect high-performance liquid chromatography with isotope-ratio-monitoring mass spectrometry. The interface consists of a Ni wire travelling at 2 – 4 cm/s on which the HPLC effluent is coated, dried, and combusted to yield CO_2 for isotopic analysis. This system can measure $^{13}\text{C}/^{12}\text{C}$ ratios of involatile organic compounds containing < 10 nmol C with a precision and accuracy better than 0.2 permil. As a first application, we are examining the carbon-isotopic compositions of nucleic acids extracted from environmental samples as a way to connect molecular phylogeny (16S rRNA phylotypes) with metabolic function. DNA extracted from concentrates of anaerobic methane-oxidizing microbes from Eel River Basin, CA has a ^{13}C value of –55 permil, consistent with methane being the major carbon source for these organisms. Further developments should allow us to separate RNA molecules with specific sequences, and thus target individual species for isotopic analysis.

δD of fatty acids in sediment trap materials and in sediments.

Sean P. Sylva¹, Alex L. Sessions¹, John M. Hayes¹, and Stu Wakeham². (1) Department of Geology and Geophysics, Woods Hole Oceanographic Institution, 266 Woods Hole Rd, MS#4, Woods Hole, MA 02543, Fax: 508-457-2164, ssylva@whoi.edu, (2) Skidaway Institute of Oceanography

In order to investigate whether the δD of organic compounds (mainly fatty acids) can be a useful tracer of upper water column processes, we are examining compounds extracted from sediment trap materials and sediments. In particular, samples from the Ross Sea, Black Sea, and Arabian Sea have been targeted based on their distinct geographic locations. Initial δD values for n-C14 to n-C30 fatty acids range from -320 to -110 ‰ (vs. VSMOW) and are similar to values observed by Sauer et. al. (2001) for sterols isolated from a variety of aquatic sediments. Future efforts will be directed at comparing the δD values of each fatty acid within a particular sample as well as from different sites.

Temporal and spatial offsets in molecular proxy records induced by sediment redistribution.

Timothy I. Eglinton¹, Nao Ohkouchi², Gesine Mollenhauer³, Ralf R. Schneider³, Lloyd D. Keigwin⁴, and John M. Hayes⁴. (1) Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Rd, Fye Laboratory, MS#4, Woods Hole, MA 02543, Fax: 508-457-2164, teglinton@whoi.edu, (2) Institute for Frontier Research on Earth Evolution (IFREE), (3) Fachbereich Geowissenschaften, University of Bremen, (4) Department of Geology and Geophysics, Woods Hole Oceanographic Institution

Rapidly deposited marine sediment sequences, such as those on continental margins and pelagic drift deposits, are important archives of short-term climate variability. Deciphering and providing chronologies for these records often involves measurement of properties and radiocarbon ages of foramineral microfossils. Molecular organic signals are often measured in parallel to capture a range of paleoclimate information. A key premise underpinning such multiproxy records is that the indicators derived from a given sediment horizon are of equal age. We have observed variable and substantial (up to 7000 yr) radiocarbon age differences between planktonic foraminifera and haptophyte-derived alkenones isolated from identical depth intervals in Bermuda Rise and Namibian Margin sediments. We attribute these temporal offsets to lateral advection of alkenones on fine-grained particles. On the Bermuda Rise, this process appears to influence alkenone-based sea-surface temperature proxy values. We suggest that sediment redistribution processes require consideration in the interpretation of molecular stratigraphic records.

Compositional assessment of photochemical modifications of riverine dissolved organic matter using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry.

Elizabeth B. Kujawinski, Department of Environmental Science, Barnard College, 3009 Broadway, New York, NY 10027, Fax: 212-854-5760, ekujawinski@barnard.edu, Edith Kaiser, EAWAG, and Michael A. Freitas, Department of Chemistry, The Ohio State University

The molecular characterization of dissolved organic matter (DOM) is elusive because the material is macromolecular and contains numerous polar hydrophilic functional groups. The combination of electrospray ionization (ESI) with ultrahigh-resolution mass spectrometry such as Fourier transform mass spectrometry (FT-ICR MS) generates mass spectra with thousands of unique peaks per sample. We have used this technique to compare the composition of riverine DOM as a function of collection method (ultrafiltration versus C18 resin adsorption) and of photochemical alteration. ESI FT-ICR negative ion mode mass spectra were obtained for each sample (ultrafiltered DOM and C18-adsorbed DOM) before and after photochemical irradiation. Changes in molecular composition were assessed using a comparative program which identified mass differences corresponding to particular functional group changes. Few changes in molecular composition were observed for the irradiated C18 DOM sample. However, significant changes in molecular composition were observed for the irradiated ultrafiltered DOM sample.

Environmental geochemical approaches to defining the fate, effects, and sources of hydrocarbons in the Exxon Valdez spill zone: Prince William Sound.

Paul D. Boehm¹, D.S. Page², G.S. Douglas¹, W.A. Burns³, A.E. Bence⁴, and P.J. Mankiewicz⁴. (1) Oil and Gas Sector, Battelle, 255 Bear Hill Road, Waltham, MA 022451, Fax: 781-895-1506, boehmp@battelle.org, (2) Bowdoin College, (3) Burns Consulting, Inc, (4) ExxonMobil Upstream Research Company

Defining the fate and effects of oil spills in the marine environment requires hydrocarbon chemistry data of sufficient quality to allow source identification through fingerprinting methods and an unbiased sampling design that allows the identification of non-spill hydrocarbon sources. Hydrocarbon chemistry is used to identify and quantify the sources of polycyclic aromatic hydrocarbons (PAH), including the Exxon Valdez oil spill, oil seeps, eroding petroleum source rocks, coal formations, forest fire fallout, recent biogenic inputs and current and past human activities, in subtidal sediments of Prince William Sound, Alaska. A random sampling and worst-case, non-random, site study provides chemistry data that allow the fate of the spilled oil to be determined through the calculation of environmental half-life values for the PAH. Those half-lives range from 2.0 - 7.4 months for upper intertidal areas. The potential for ecological effects of the spilled oil is assessed through concurrent sediment toxicity measurements using a standard bioassay as part of the study design. A toxicity threshold for total PAH of 2,600 ng/g was found by dose-response analysis. This threshold agrees well with the onset of ecological stress as defined by reductions in infaunal community structure parameters.

Composition, distribution, and sources of polycyclic aromatic hydrocarbons in sediments of the Western Harbour of Alexandria, Egypt.

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The composition, distribution and the source of polycyclic aromatic hydrocarbons (PAHs) in surficial sediments of the Western Harbour of Alexandria were investigated. To document the spatial PAH input, surficial sediment samples from 23 locations throughout the harbour were analysed. The total PAH load determined in the surficial sediment samples ranged from 7.9 to 131149 ng g⁻¹ dry wt. Generally, most of the samples having total concentrations of PAHs greater than 5000 ng g⁻¹ dry weight. The highest concentration of total PAHs was recorded in sediments of the inner harbour. Ratio values of specific compounds such as phenanthrene to anthracene, fluoranthrene to pyrene, methyl-phenanthrene to phenanthrene, methyl-dibenzothiophenes to dibenzothiophenes, alkylated to non-alkylated and high molecular weight to low molecular weight PAH, were calculated to evaluate the possible source of PAH contamination in the harbour sediments. However, chrysene and perylene were used as indicator of terrigenous input. Two main sources of PAH in the study area have been found: pyrolytic and petrogenic. Interferences of rather petrogenic and pyrolytic PAH contaminations were noticed for most samples. The dominant sources of PAH appear to be the combustion processes through run-off, industrial and sewage discharges, and atmospheric input. The concentrations of PAHs were generally above levels expected to cause adverse biological effects.

The Pettaquamscutt River, RI Revisited: New trends in the PAH sediment profile.

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In the 1970s and 1980s, sedimentary records of polycyclic aromatic hydrocarbons (PAH) in the Northern Hemisphere revealed several distinct trends in the concentrations of these compounds. A typical PAH profile showed an increase in concentration beginning around 1880, to a maximum in the 1950s and 1960s, and a slow decrease during the 1970s and 1980s. However, two very recent investigations in the United States have observed either increased inputs beginning in the 1990s or relatively constant inputs since the 1980s. Neither of these studies indicate a continual decrease in recent PAH inputs, suggesting that the declining trend that began in the 1970s has, at best, stabilized. In this study, we have revisited the site of one of the first PAHs studies, the Pettaquamscutt River (RI) and constructed a high-resolution record (< 1 cm resolution over 70 cm) that spans the pre-industrial era to the end of the 20th century. This record is being used to examine past changes in PAH input and composition and to further evaluate the relationship between urbanization and PAH emission

Identification of a nonmethylene interrupted docosadienoic fatty acid in *Lucinoma Aequizonata* (Bivalia).

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Fatty acids found in the bivalve *Lucinoma aequizonata* (bivalia) sampled from the benthos at a depth of 530 meters of water at the edge of the oxygen minimum zone off Peru at 15 deg S. included high concentrations of the non-methylene interrupted docosadienoic acid nC22:2(n7,15). The position of the dienoic bonds was elucidated by fused silica column gas chromatography-mass spectrometry of the dimethyl disulphide adducts. Highest concentrations of the nC22:2(n7,15) acid are associated with the endosymbiotic bacteria bearing gills of this bivalve which suggests that the acid may play a role in the symbiotic relationship.

Changes in the natural fluorescence of fulvic acid caused by the binding of Al(III): Can fluorescence quenching and fluorescence enhancement occur simultaneously?

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The binding of Al(III) by natural organic compounds such as fulvic acid (FA) is an important reaction in the environment in soils and acidic waters. Several researchers have employed the natural fluorescence of the organic matter to study complexation, and in particular the quenching of fluorescence has been used extensively. Reports for Al(III) have demonstrated fluorescence quenching and fluorescence enhancement under a variety of conditions and with different organic materials. Our studies have shown that it is quite likely that the natural fluorescence of the free humic ligand is quenched or reduced while the corresponding Al(III)-fulvic acid complex formed shows an enhanced fluorescence at slightly different wavelengths as the Al(III) concentration is increased at pH 4.0. Quantitative modeling of this behavior gives predicted curves that fit the experimental data and provide reasonable estimates of binding constants and ligand concentrations, but only if a two-site binding model is used. Conditional stability constants (logK) for site one and two are 6.5 and 5.1 respectively. The ligand concentration for site one is 13 μM with site two having a concentration of 6 μM .

Study of fulvic-aluminum(III) ion complexes by ^{27}Al solution NMR. Norman Lee, and David K. Ryan, Department of Chemistry, University of Massachusetts Lowell, Olney Hall, 265 Riverside Street, Lowell, MA 01854, norman_lee@student.uml.edu

Aluminum is an important metal to study under environmentally relevant conditions, because of its prevalence in soil, enhanced mobilization under acidic conditions and its ability to bind with humic materials. We have employed solution aluminum-27 nuclear magnetic resonance spectroscopy to study the hydrolysis and complexation of Al(III) by fulvic acid(FA). Our previous studies of Al-FA complexation with fluorescence showed an interesting competition between Al hydrolysis and FA complexation. Three regions of distinct Al(III) behavior exist versus pH in an Al(III)-FA system. Below, pH 3 very little binding occurs and Al(III) is predominantly in a free, ionic form. Above pH 4, Al-FA complexes are dominant until hydrolysis take over at higher pH values. Aluminum(III) ion starts to undergo strong hydrolysis at pH 5 where $\text{Al}(\text{OH})_{3(s)}$ precipitates out readily and re-dissolves to form $\text{Al}(\text{OH})_{4(aq)}$ at basic pH values. ^{27}Al NMR has demonstrated humic-Al(III) complexes at pH < 5 using both laboratory & environmental samples. This study focuses on investigating the Al-FA complexes at pH 5 to 3, FA concentration from 2 g/L to 0.05 g/L and Al(III) concentration from 10 mM to 0.1 mM. Aluminum spectra are obtained using a multinuclear probe on a Bruker 250 MHz high resolution NMR spectroscopy instrument. Computer simulation metal speciation models VMINTEQ and WinHumicV are also employed to explore the aqueous aluminum speciation at different pH conditions and concentrations.

UV-Raman spectroscopy and ab initio calculations of carboxylic acids-Al solutions.

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Carboxylic acids have been used as analogs of DOM. We have developed a method for studying carboxylic acids in water using UV resonance Raman spectroscopy that can produce measurable vibrational spectra at lower concentrations than visible Raman or normal IR methods. Assignments in vibrational spectra can be aided by ab initio calculations. To determine which theoretical method would be best suited for modeling carboxylic acids in solution, we examined explicit and continuum solvation calculations. The continuum solvation method provided results as accurate as the explicit solvation method but was more efficient computationally. UVRR spectra were then obtained for Al-carboxylic acid solutions and the observed frequencies compared to explicit solvation calculations on different Al-acid complexes. The excellent agreement obtained between the observed frequencies and model complexes allow us to distinguish among various possible bonding geometries that can be used to constrain models of larger Al-fulvic acid complexes.

Experimental and theoretical investigation of siderophores and their Fe^{3+} complexes in aqueous solutions.

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Siderophores are organic macromolecules excreted by bacteria to selectively complex Fe^{3+} in iron-limiting situations. Hydroxamate siderophores are ubiquitous in the environment, but their molecular properties are poorly understood. In order to better characterize hydroxamate siderophores, the structure of acetohydroxamic acid (aHa) has been determined by spectroscopic and theoretical methods. Aqueous aHa was analyzed using infrared and Raman spectroscopy as a function of pH and various Fe^{3+} concentrations. These experimental studies were complemented by theoretical vibrational spectra calculations (Gaussian 98). Our theoretical studies are in good agreement with the experimental data and we propose new assignments for the N-O stretching frequency. This is an important structural feature in both aHa and hydroxamate siderophores because of its presence in the inner-coordination sphere of Fe^{3+} . This molecular information is necessary for determining the structure and reactivity of siderophores in aqueous solutions and on mineral surfaces.

X-ray absorption spectroscopic investigation of nickel(II) complexation by naturally occurring organic compounds.

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Natural waters contain a wide range of naturally-occurring organic compounds (NOOCs), including both low molecular weight organic ligands and polymeric humic substances. The transport, reactivity, bioavailability, and toxicity of metal ions is significantly affected by complexation reactions with NOOCs. We used X-ray absorption spectroscopy (XAS) to characterize the speciation of Nickel(II) in aqueous solutions containing different NOOCs. A series of simple organic ligands are selected to obtain a systematic variation in the identity, number, and spatial arrangement of metal-binding functional groups, and to serve as models for the complexation of Ni(II) by more complex humic substances. Spectroscopy-derived structures of Ni(II)-organic ligand complexes are compared with structures predicted from molecular modeling and thermodynamic equilibrium calculations. Nickel(II) complexation by humic substances is examined as a function of humic source and fraction, [Ni(II)]:[Humic] ratio, solution pH, and the presence of other metal ions.

Dissolved iron complexation and speciation in the Gulf of Mexico.

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In an attempt to more fully understand the chemical processes that control Fe concentrations in surface waters, the Surface Water Iron Speciation Study (SWISS) began in 2000. We are attempting to characterize as many aspects of the Fe cycle as possible in an area that has predictable periods of high and low atmospheric dust deposition. Collaborators are measuring aspects such as aerosol solubility, particulate Fe, total dissolved Fe, reduced Fe, colloidal Fe, hydrogen peroxide, light attenuation and dissolved thorium deficiencies in the upper water column. We hope to fully characterize the processes that lead from Fe solubilization to stabilization in the water column and eventually to uptake by phytoplankton. To date, two cruises have occurred during low dust (spring 2001) and high dust (late summer 2001) periods. This talk will focus on the role of organic Fe-complexing ligands in controlling the chemistry of Fe during these two contrasting periods. Using ultra-clean sampling and analytical procedures, seawater samples were filtered through 0.2 μm filters, then size fractionated using a Filtron cross-flow ultrafiltration system (CFF) with a polysulfone 1,000 Dalton cutoff membrane. Colloidal Fe concentrations were highest along the northeastern Gulf coast and off the Mississippi River plume (3-5 nM) as a result of terrestrial aquatic humic ligand input. Compared to the April 2001 period, the particulate (1-1.5 nM) and colloidal Fe concentrations (0.7-1.3 nM) were both significantly higher in the surface waters of the open Gulf during the August 2001 cruise when elevated dust levels are encountered. Fe-complexation was measured using competitive ligand exchange cathodic stripping voltammetry (CSV). On the April 2001 cruise, we detected 5 nM of strong Fe-complexing ligands in the >1kDa size fraction in the northeastern Gulf of Mexico, likely resulting from terrestrial aquatic humic substances. In the open Gulf, we detected 5-6 nM of strong Fe-complexing ligands in the <1kDa fraction, most likely due to in-situ microbial production. Additional CSV analyses from the August 2001 cruise (during the high dust season) will soon be completed, along with colloidal DOC measurements.

Iron-colloids in the North and South Atlantic and North Pacific. Edward A. Boyle, Department of Earth, Atmospheric, and Planetary Sciences, MIT, E34-258 Mass. Institute of Technology, 77 Mass. Ave., Cambridge, MA 02139, Fax: 617-253-8630, eaboyle@mit.edu, Jingfeng Wu, University of Alaska Fairbanks, and Bridget Bergquist, Department of Earth, Atm., and Planetary Sciences, MIT

Recent evidence indicates that iron occurs in seawater in part as truly soluble (<0.02 μm) and colloidal (0.02-0.4 μm) forms. Other evidence shows that iron is complexed by organic ligands, and recent evidence also indicates that these organic ligands exist both in soluble and colloidal form. But there is very little data informing us on the spatial variability of iron colloids and soluble iron ligands throughout the ocean. In order to fill this gap, we have collected surface water and profile samples from throughout the Atlantic Ocean (47degN to 25degS) and North Pacific (northwestwards of Hawaii) on four research cruises between 1999-2002. These samples have been processed at sea to separate iron into total, <0.4 μm , <0.02 μm , and excess <0.02 μm ligand classes. 1 ml subsamples of these separates are stored and later analyzed by Fe-54/Fe-56 isotope dilution mass spectrometry using a MicroMass IsoProbe multiple collector plasma mass spectrometer, which uses a hexapole collision cell (Ar, H₂ gases) to eliminate the ArO⁺ interference on Fe-56 and the ArN⁺ interference on Fe-54. As an example of the results, a station collected in January 2001 at 8 degN, 45 degW shows <0.4 μm Fe concentration of 0.5 nmol/kg at the surface sharply increasing to a maximum of 1.1 nmol/kg at 200 m, gradually decreasing to 0.8 nmol/kg at the bottom (4200 m). Soluble (< 0.02 μm) increases from 0.2 nmol/kg at the surface to a maximum of 0.6 nmol/kg at 1500m decreasing to 0.4 nmol/kg in the North Atlantic Deep water (3200 m).

Evidence for strongly complexed Hg(II) in natural waters. Heileen Hsu, and David L. Sedlak, Department of Civil & Environmental Engineering, University of California, 631 Davis Hall, Berkeley, CA 94720, helenhsu@uclink.berkeley.edu

Although complexation is an important factor for the transport and bioavailability of Hg(II), little is known about the speciation of Hg(II) in natural waters because Hg(II) complexation is difficult to study at low concentrations encountered in the aquatic environment. In this study, a novel competitive ligand exchange (CLE) technique was used to measure the conditional stability constants and concentrations of Hg(II)-complexing ligands. In this method, two different competitive ligands, glutathione (GSH³⁻) and diethyldithiocarbamate (DED⁻), are added to samples in separate steps at varying concentration. After equilibration, the concentrations of hydrophilic HgH₂(GSH)₂²⁻ complexes and hydrophobic Hg(DED)₂⁰ complexes are measured by C18 solid phase extraction. The method was used to quantify Hg(II) speciation in samples from three locations: a municipal wastewater effluent, a eutrophic lake and a creek located downstream of an abandoned mercury mine. All three contained labile Hg(II)-complexing ligands with conditional stability constants similar to that of sulfur-containing ligands. The municipal wastewater effluent also contained a ligand that did not dissociate Hg(II) in the presence of either competing ligand. The ligands responsible for Hg(II) complexation in the aquatic environment may be dissolved ligands and colloidal material that contain reduced-sulfur functional groups.

In situ Cu speciation measurements in Boston Harbor using DGT. Gary R Fones, and James W. Moffett, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, Fax: 508-457-2164, gfones@whoi.edu

In recent years a new speciation tool known as DGT (Diffusive Gradients in Thin films) has been developed that can measure trace metal speciation in-situ. By deploying a suite of DGT probes with different diffusive layer compositions (Agarose [AGE] gel - pore size >20 nm and Restricted [RG] gel - pore size < 1 nm), the total dissolved (labile inorganic + labile organic) and inorganic dissolved metal fractions can be measured. During 2001 total dissolved Cu values ranged from 3.5 to 113 nM, this showed a close agreement (~ 90%) with total values determined by CLE-ASV after acidification and UV digestion. Restricted gel concentrations (labile inorganic) ranged from 1.3 to 88.4 nM. The total/inorganic (AGE/RG) fraction changed considerably both seasonally and spatially and ranged from 25 to 97%, showing how dynamic and heterogeneous Cu speciation is in Boston Harbor.

Application of surface complexation/precipitation modeling to contaminant leaching from weathered steel slag.

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The purpose of the study was to investigate the influence of natural weathering reactions on the leaching behavior of major and minor elements. Steel slag and pore fluid was sampled at four depths from a lysimeter after 4.5 years of aging outdoors at the Swedish Geotechnical Institute, Linköping, Sweden. Selective chemical extractions were conducted to determine concentrations of major sorbent phases, including hydrous ferric oxides, crystalline and amorphous iron oxides, and amorphous aluminum phases. The weathered steel slags were also subjected to a pH-dependent leaching procedure. Equilibrium speciation modeling has demonstrated that solubility reactions do not accurately describe the leaching of many of the trace elements investigated (Mo, Cd, Pb, Zn, and Cu). Current research has extended the equilibrium speciation modeling to include surface complexation on the various sorbent phases identified using published sorption constants. The results of solubility and surface complexation modeling using both PHREEQC and MINTEQA2 computer codes will be presented and compared with pH-dependent leaching data.

Calculation of solubility equilibrium constant of $\text{HCl}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$ at 40°C.

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The solubilities of $\text{LiCl-HCl-H}_2\text{O}$, $\text{HCl-MgCl}_2\text{-H}_2\text{O}$, $\text{LiCl-MgCl}_2\text{-H}_2\text{O}$ and $\text{LiCl-HCl-MgCl}_2\text{-H}_2\text{O}$ system at 20 °C have successfully been predicted by using the ion-interaction model of Pitzer and HW. In order to extend the model to the high ionic strength and wide temperature range of salt lake brine systems, we calculated the solubility of $\text{LiCl-HCl-MgCl}_2\text{-H}_2\text{O}$ system at 40°C. The solubility equilibrium constant of $\text{HCl}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$ at 40°C is not reported in the literature, thus we determined this constant according to these two models, and applied the results to the problem at hand.

Chemical mechanism of Cl_2^- formation and decay by laser-flash photolysis in aqueous solution containing chloride ions and hydrogen peroxide.

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Hydroxyl radicals were generated by laser flash photolysis of aqueous solutions containing H_2O_2 and NaCl at 248nm. Time-resolved uv-vis absorption spectroscopy was used to investigate the subsequent reactions of Cl_2^- radicals. A unified chemical mechanism of Cl^- and OH photochemical system was proposed. The absorption spectrum of Cl_2^- was determined. The equilibrium of $\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$ was investigated. The reverse reaction rate constant ($k_{-5} = (5.3 \pm 0.3) \cdot 10^4 \text{ s}^{-1}$) was determined directly. Based upon the critically analyzed forward reaction rate constant ($k_5 = (7.8 \pm 0.8) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the equilibrium constant ($K_5 = (1.4 \pm 0.2) \cdot 10^5 \text{ M}^{-1}$) was derived. The formation of Cl_2^- was found to depend on hydrogen peroxide concentration as well as chloride concentration. The pseudo-1st-order decay rate constant of Cl_2^- was found to depend on pH, chloride ion concentration and hydrogen peroxide concentration. A series of other rate constants was determined for reactions including the following species H_2O_2 , Cl^- , Cl_2^- , Cl and H_2O at $297 \pm 2 \text{ K}$.

Heavy metal desorption from natural sediment. Yan Gao, Amy T. Kan, and Mason B Tomson, Department of Civil & Environmental Engineering, Rice University, 6100 Main St., Houston, TX 77005, Fax: (713)348 5203, ygao@rice.edu

The reversibility of heavy metal sorption has been investigated in the past 20 years but contradictory results have been reported. The reversibility of cadmium, lead and zinc sorption by Utica, NY sediment is being investigated in this study. The results from the two different desorption approaches seem to be contradictory. The slope of desorption isotherm is greater than the sorption isotherm when using the replaced supernatant method suggesting that Cd, Pb and Zn sorption on Utica sediment is an irreversible reaction. In contrast, desorption observed by lowering the solution pH shows that both the desorption and sorption edges are similar, indicating that sorption is reversible. Nevertheless, Cd sorption on washed Utica sediment is enhanced, suggesting that colloids or dissolved organic ligands present in the supernatant may be responsible for the observed irreversibility. The sorption of Cd, Pb and Zn on Utica sediment, under the conditions of the current experimental procedure, is believed to be a fully reversible process. The effect of EDTA on Cd and Pb sorption was also studied. Both Cd and Pb sorption is reduced dramatically at pH >5.5 upon the addition of EDTA. At pH < 5.5, the addition of EDTA has no effect on Cd and Pb sorption. These results suggest a competitive complexation and will be discussed.

Modeling the 90th percentile lead level in metropolitan Boston. Windsor Sung, Quality Assurance, MWRA, 260 Boston Road, Southborough, MA 01772, Fax: 508-820-0187, wsung@mwra.state.ma.us

MWRA supplies metropolitan Boston with un-filtered surface water. The raw water is corrosive. Sodium hydroxide was added in 1978 to address concerns over lead levels. An interim corrosion control facility came on line in 1997 to increase pH and alkalinity to 9 and 30 mg/L as calcium carbonate. The targets were established from pipe-loop studies and expert advice. The current regulation for lead is a 90th percentile action limit of 15ppb. MWRA was able to meet this limit once in 6 rounds of sampling. A model was developed for the 90th percentile lead so that other water quality concerns can be balanced (e.g. total trihalomethane). The model parameters are the hydroxide and carbonate ions, and UV-254 absorbance (as a surrogate for natural organic matter). The model worked best when the temperature input was assumed to be constant (at 20°C) rather than varying as the raw water temperature. This was substantiated by first flush sample temperature measurements. The model suggests that MWRA can meet the lead limit by a slight increase of alkalinity (10%) without increasing the pH target.

Predicting the behavior of hazardous metals in sulfidic waters: Importance of sulfur(0) activity. George R. Helz, Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, gh17@umail.umd.edu

Bisulfide is well-known as a complexing and transporting agent for soft cations. However the extent to which zero-valent sulfur modifies the behavior of HS^- is not yet widely appreciated. Sulfur(0) combines with HS^- to form polysulfides ($\text{H}_x\text{S}_n^{2-x}$), which can be better complexing agents than HS^- , itself; e.g. S(0) saturated HS^- solutions dissolve ~10-fold more HgS than HS^- solutions containing no S(0). Similar behavior has been shown for Cu(I) and Ag. At a given pH, T&P, S(0) activity and Eh in sulfidic waters are poised by $\text{H}_x\text{S}_n^{2-x}/\text{HS}^-$ ratios. Sulfur(0) activity controls mineral stability in such series as the following: $\text{FeS} \rightarrow \text{Fe}_3\text{S}_4 \rightarrow \text{FeS}_2$. Higher S(0) activity normally promotes oxidation of dissolved trace elements (e.g. Sb(III) \rightarrow Sb(V)) but is known in at least one case to promote reduction (e.g. Mo(VI) \rightarrow Mo(V) \rightarrow Mo(IV)). The latter intriguing process is important in the immobilization of Mo in pyrite. Knowledge of the S(0) activity in sulfidic natural environments is still sparse. In a number of instances, S(0) activity considerably exceeds unity, implying supersaturation with respect to rhombic sulfur.

Prediction of the component solubility of the system of LiCl-HCl-MgCl₂-H₂O at 20°C.

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The ion-interaction model of Pitzer, together with its extended HW model, has been successfully applied for predictions of mineral solubility in natural water system of high ionic strengths and in wide temperature ranges from 0 to 300°C, but its application for predicting the component solubility of salt lake brine systems which contain high concentration of LiCl has never been investigated. The reason is that the solubility of LiCl in salt lake brines is above 13.00 molality, but the parameters of LiCl which are available to calculate the solubility of salt lake salts are not valid until the molality concentration of LiCl is below 6.0. This paper presents the solubility data of LiCl-HCl-MgCl₂-H₂O system at 20°C predicted by using the Pitzer and the HW model and the parameters obtained by us. The results indicated that the ion-interaction model gives a very good prediction of the component solubility of salt lake brine systems. According to ion-interaction model, no additional parameters need to be determined for more complex systems. The study provides theoretical basis for the manufacture process which was proposed by Gao Shiyang and employed to extract LiCl and MgCl₂·6H₂O from Qinghai and Xizang salt lakes during the summer

Reactivity of water in fused silica. Renée M. Van Ginhoven, Department of Chemistry, University of Washington, Seattle, WA 98352, Fax: (509)376-0420, rrrrr@u.washington.edu, Hannes Jonsson, Department of Chemistry 351700, University of Washington, Byeongwon Park, Center for Micro-Engineered Materials, Sandia National Laboratory, and L. René Corrales, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, PO Box 999, MS K8-91, Richland, WA 99352, Fax: 509-376-0420, rene.corrales@pnl.gov

Density functional theory calculations have been carried out to examine the reaction pathways and activation barriers of molecular water in bulk silica. A correlation between the relative stability of the product state and the height of the activation barrier has been found where the degree of stability is related to the degree of the glass network relaxation. It was found that the most reactive sites are those that lead to the greatest release of strain in the local glass network. The role of strain and relaxation upon the insertion of water molecules into the glass network will be discussed.

Surface-catalyzed transformations of aqueous endosulfan. J.L. Ferry, and s.s. Walse, Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, Fax: 803-777-9521, ferry@mail.chem.sc.edu, walse@mail.chem.sc.edu

We report the relative contributions of surface-catalyzed versus base-catalyzed hydrolysis toward the stereoselective degradation of the insecticide endosulfan. Aqueous suspensions of sea sand, TiO₂, γ-Fe₂O₃, γ-FeOOH, Laponite[®], and SiO₂ all catalyzed the hydrolysis of endosulfan to endosulfan diol. Heterogeneous and homogeneous rate constants of endosulfan hydrolysis were measured and in all cases indicate that γ-endosulfan hydrolyzes faster than α-endosulfan. This observation was explained by a more stable transition state for γ-endosulfan that was confirmed with *ab initio* molecular orbital calculations (STO-6G) on the anionic intermediates of endosulfan hydrolysis. Rates of endosulfan hydrolysis over the different surfaces corresponded to their tritium-exchange site-density. Suspended creek sediment (Bread and Butter Creek SC, 4% OC) inhibited endosulfan hydrolysis, presumably due to the partitioning of endosulfan into non-polar organic carbon associated with sediment. The effects of suspended solids on the chemical transformations of established endosulfan degradation products: endosulfan diol, endosulfan sulfate, endosulfan ether, endosulfan hydroxyether, and endosulfan lactone are also reported.

Water in the local structure of Nd³⁺ coprecipitated with calcite. s. H. Withers¹,

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Solution-grown Nd³⁺:CaCO₃ is studied as a model system relevant to radionuclide waste remediation efforts. Calcite micro-crystals were coprecipitated from solution with ~0.1% Nd³⁺ ions. Individual crystal dimensions were up to 3 mm and exhibited an irregular morphology. Calcite phase purity was verified by powder x-ray diffraction. The concentration of Nd³⁺ was measured by Rutherford backscattering spectrometry. Micro x-ray fluorescence mapping of the as-grown calcite grains indicates uniform Nd distribution. X-ray absorption fine structure indicates that Nd³⁺ is substituted for Ca²⁺ with local lattice distortion and increased first shell oxygen coordination. Temperature dependent near-infrared spectroscopy of Nd³⁺ impurities in calcite reveals large inhomogeneous line widths, similar to spectra of Nd³⁺ in dilute carbonate solution. These results suggest a broad distribution of crystal-field environments for Nd³⁺ as a result of charge compensation effects and inhomogeneous lattice strain from hydration.