



Molecular Studies of Soil Organic Matter

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ACS DIVISION OF GEOCHEMISTRY

SPRING 2003 NEWSLETTER

224th NATIONAL ACS MEETING
MARCH 23-27, 2003
New Orleans, Louisiana

The ACS Division of Geochemistry is very pleased to announce that **Dr. John M. Hayes** has been awarded the **2003 Geochemistry Division Medal**.

Dr. Hayes will be recognized during the **GEOCHEMISTRY MEDAL AWARD SYMPOSIUM** at the New Orleans National Meeting.
A banquet in his honor is scheduled for Tuesday evening (March 27th).

New Orleans National Meeting Program and Abstracts

DIVISION OF GEOCHEMISTRY

Final Program, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003
W. M. Landing and S. Carroll, Program Chairs

SUNDAY MORNING

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Soil Microbial Processes

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

E. Lichtfouse, W. Wells, and B. Glaser, Organizers, Presiding

J. A. Rice, Organizer

8:30 — Introductory Remarks.

8:45 —1. Appearance, characteristics, and microbial processing of humic substances in municipal wastes. Z. K. Filip

9:15 —2. Preservation of biopolymers in fossil bones. E. Geigl, U. Baumer, J. Koller

9:35 —3. Effect of organic fertilizers on genetic and functional diversity of soil microorganisms. R. Calbrix, K. Laval, S. Barray

9:55 — Intermission.

10:15 —4. Differentiating between old and new microbially derived soil organic matter by means of compound-specific stable isotope ($\delta^{13}\text{C}$) analysis. B. Glaser, S. Frey, N. Millar, J. Six, G. Guggenberger, W. Zech

10:35 —5. Impact of soil organisms on the fate of carbon in soils. P. M. Chamberlain, H. Black, J. Chaplow, N. McNamara, A. Stott

10:55 —6. Biological availability of hydrophobic organic contaminants and quality of organic carbon. H. L. Fredrickson, J. S. Furey, J. W. Talley, M. Richmond

11:15 —7. Microbial processing of humic acids from soils with various contents of metals. Z. K. Filip, P. Bielek

SUNDAY AFTERNOON

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Fossil Carbon in Soils

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

J. A. Rice, B. Glaser, and W. Wells, Organizers, Presiding

E. Lichtfouse, Organizer

1:30 — Introductory Remarks.

1:40 —18. Does the C isotope signature of polycyclic aromatic hydrocarbons indicate biological sources? W. Wilcke, M. Krauss, W. Amelung

2:00 —19. Molecular characterization of soil organic matter from an ancient coking plant site and correlation with potential sources. P. Faure, L. Mansuy-Huault, X. Su

2:20 —20. Cometabolism of natural and anthropogenic aromatics in estuarine sediments. C. L. Osburn, T. Donowick, M. T. Montgomery

2:40 —21. Preferential degradation of PAHs over natural organic matter by bacteria in intertidal sediments. M. T. Montgomery, T. J. Boyd, C. L. Osburn, J. G. Mueller, D. C. Smith

3:00 — Intermission.

3:20 —22. Analyses of polyacrylamide-based flocculants in agricultural soil samples. J. Schwarzbauer, A. Kronimus, H. Neumann-Hensel

3:40 —23. Low-temperature air oxidation of n-alkanes in the presence of Na smectite. P. Faure, L. Schlepp, M. Elie, V. Burkle-Vitzthum, R. Michels

4:00 —24. Black carbon in soils: Implications for fertility and pollutant sequestration. W. C. Hockaday, P. G. Hatcher

4:20 —25. Sorption and bioavailability of organic contaminants on black carbon. R. Kookana, N. Singh, S. Grocke, E. Krull, J. O. Skjemstad

MONDAY MORNING

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Dynamics of Soil Organic Matter

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

J. A. Rice and E. Lichtfouse, Organizers, Presiding

B. Glaser and W. Wells, Organizers

8:30 — Introductory Remarks.

8:40 —36. Compound-specific stable isotope approaches to the investigation of carbon cycling in soils. R. P. Evershed, Z. Crossman, C. Evans, I. D. Bull, P. M. Chamberlin, H. Black, P. Ineson

9:10 —37. Nature and dynamics of H₂O₂-resistant organic matter: In search of the stable C compartment of soils. C. Chenu, A. F. Plante, L. Grasset, M. Balabane, A. Mariotti, D. Righi

9:30 —38. Using molecular markers to elucidate sources, production, and fate of dissolved organic matter in forest soils. K. Kaiser

9:50 —39. Impact of source organic carbon composition on soil organic matter cycling. R. L. Fimmen, D. D. Richter Jr., D. Vasudevan

10:10 — Intermission.

10:30 —40. Soils millennium carbon pool. G. Gleixner, C. Kramer

10:50 —41. Contrasting effect of N content and soil texture on organic matter composition in forest soils as studied by ¹³C and ¹⁵N NMR spectroscopy. M. Dignac, H. Knicker, I. Kögel-Knabner

11:10 —42. Kinetics and efficiency of Soxhlet extractions for the removal of compounds causing water repellency in soils. C. T. Llewellyn, S. H. Doerr, P. Douglas, K. A. Mainwaring, C. P. Morley

11:30 —43. Molecular characterization of organic matter in B and C horizons of an acid forest soil. C. Rumpel, K. Eusterhues, I. Kögel-Knabner, F. Gonzalez-Vila, W. Michaelis, L. Schwark

MONDAY AFTERNOON

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Novel Tools for Soil Analysis

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

E. Lichtfouse and W. Wells, Organizers, Presiding

B. Glaser and J. A. Rice, Organizers

1:30 — Introductory Remarks.

1:40 —51. Compound-specific nitrogen isotope measurements of soil amino acids. R. Bol

2:00 —52. Aliphatics in Andic soils: Insights into free compounds and molecular building blocks of biopolyesters and chemically resistant biopolymers. D. F. W. Naafs, P. F. van Bergen, K. G. J. Nierop, J. W. de Leeuw

2:20 —53. MALDI-TOF MS as a new means of characterizing condensed tannins in soil. C. J. Engelke, H. Knicker, I. Kögel-Knabner

2:40 —54. GC-GC: A new window on the world of complex mixtures. E. B. Ledford Jr., C. A. Billesbach, J. Termaat 3:00 — Intermission.

3:20 —55. NMR: A tool to study the interactions between organic pollutants and soil components. A. Delort, B. Combourieu, P. Besse, M. Sancelme, C. Forano

3:40 —56. ¹⁵N-CPMAS nuclear magnetic resonance spectroscopy and biological stability of soil organic nitrogen in whole soil and particle-size fractions. R. J. DiCosty, D. P. Weliky, S. J. Anderson, E. A. Paul

4:00 —57. Determination of soil nitrogen availability and humic acid composition as influenced by forest residue management using solid-state NMR and stable isotopes. N. J. Mathers, Z. Xu, S. E. Boyd

4:20 —58. Characterization of soil organic matter in tropical rice soils by advanced solid-state NMR. K. Schmidt-Rohr, J. Mao, D. C. Olk

TUESDAY MORNING

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Dynamics of Soil Organic Matter

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

W. Wells and J. A. Rice, Organizers, Presiding

E. Lichtfouse and B. Glaser, Organizers

8:30 — Introductory Remarks.

8:40 —98. Compound-specific isotope tracing of organic compounds from dung in temperate grassland soil. J. A. J. Dungait, R. P. Evershed, R. Bol

9:00 —99. Effects of added organic matter quality on soil properties: Dynamics of carbon and structural stability along the decomposition. S. Abiven, S. Menasseri, P. Leterme

9:20 —100. Molecular analysis of the biodegradation effects on the organic content of four sewage sludges of various origins. E. Jardé, L. Mansuy-Huault, P. Faure

9:40 —101. Formation and structure of humic substances in composted municipal solid wastes. T. A. Holtzlander, P. G. Hatcher, Y. Chen

10:00 — Intermission.

10:20 —102. Carbon sequestration and carbon cycling processes in agricultural ecosystems. K. J. Dria, D. H. Stinner, B. R. Stinner, P. G. Hatcher

10:40 —103. Variation in lipid abundance and composition among different particle-size fractions of a forest and a cropped soil. K. Quenea, S. Derenne, C. Rumpel, C. Largeau, A. Mariotti

11:00 —104. Water repellency of sandy soils: The role of hydrophobic organic compounds. C. P. Morley, S. H. Doerr, P. Douglas, C. T. Llewellyn, K. A. Mainwaring

11:20 —105. Dynamics of N exchange between corn (*Zea mays* L.) roots and soil microbes. J. E. Molina, C. E. Clapp, R. R. Allmaras, M. F. Layese, J. M. Baker

TUESDAY AFTERNOON

Section A

Convention Center -- Room 386

Geochemistry Division Medal Award Symposium Honoring John M. Hayes: Molecular and Isotopic Indicators of Natural Processes

R. H. Byrne, Organizer

1:30 — Introductory Remarks.

1:45 —118. Provenance and/or process recorded in extraterrestrial organic solids. G. D. Cody, C. M. O. Alexander, F. Tera

2:15 —119. Ancient microbial signatures and the ecology of the Archean world. K. H. Freeman, J. Eigenbrode, C. Snape, R. E. Summons, G. D. Love

2:45 —120. Dynamics of soil organic molecules. E. Lichtfouse

3:15 — Intermission.

3:35 —121. Forensic applications of multiple stable isotope analyses. J. R. Ehleringer

4:05 — Discussion.

4:35 —122. Nature's scribes. J. M. Hayes

WEDNESDAY MORNING

Section A

Convention Center -- Room 386

Molecular Studies of Soil Organic Matter

Novel Tools for Soil Analysis

Cosponsored with European Association of Chemistry and the Environment, and Division of Environmental Chemistry

E. Lichtfouse and J. A. Rice, Organizers, Presiding

B. Glaser and W. Wells, Organizers

8:30 — Introductory Remarks.

8:40 —123. Informative graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter: The van Krevelen diagram. S. Kim, R. W. Kramer, H. M. Cho, P. G. Hatcher

9:00 —124. Probing structure-activity relationships in soil organic matter by combining time-dependent ¹³C NMR spectroscopy with inverse high-performance liquid chromatography. M. Schilling, D. Osborne, W. T. Cooper

9:20 —125. Stochastic synthesis model for the evolution of natural organic matter. S. E. Cabaniss, G. R. Madey, P. A. Maurice, L. Leff, Y. P. Huang, X. R. Xiang, E. M. Chanowich, O. Olapade

9:40 — Intermission.

10:00 —126. Spectroscopic and macroscopic studies of the interactions between Suwannee River fulvic acid and mineral particle surfaces. T. H. Yoon, S. B. Johnson, G. E. Brown Jr.

10:20 —127. Electrochemical properties of natural organic matter. J. T. Nurmi, P. G. Tratnyek

10:40 —128. X-Ray microscopy and C 1s NEXAFS studies of 3d metal interactions with humic acid. M. Nachtegaal, C. J. Jacobsen, D. L. Sparks

11:00 —129. A study of organo-copper complexes in soils by thin layer chromatography. C. Parat, E. Lichtfouse

11:20 — Concluding Remarks.

Abstracts

GEOC 1: Appearance, characteristics, and microbial processing of humic substances in municipal wastes. Zdenek K. Filip, Langen Building, Federal Environmental Agency, Paul Ehrlich Strasse 29, 63225 Langen, Germany, Fax: +49-6103-704-147, zdenek.filip@uba.de

Humic substances (HS) are usually the refractory part of natural organic matter, and in municipal wastes they can retain inorganic and organic micropollutants. We were able to isolate HS from freshly collected wastes. In model landfills the amounts and analytical characteristics of HS varied during the disposal period. In general their quantity and qualitative patterns resembled those of humic acids from a podzol soil. With time of waste disposal, the concentration of proteinaceous and lipidic components was diminished, while that of aromatic structures was increased. Under laboratory conditions, when added as a supplementary nutrient source, up to 64 % of HS was utilized and this percentage was enhanced to about 88 % when HS were used as the sole source of carbon. If serving as a sole source of nitrogen for soil microbial assemblages, HS was usually completely utilized. Spectroscopic analysis (UV, VIS, FTIR) indicated losses in aliphatic structural units, and a relative enhancement in aromatic structures. For their high susceptibility to microbial degradation, HS will not play an important role in a long-term stabilization of landfilled municipal wastes.

GEOC 2: Preservation of biopolymers in fossil bones

Eva-Maria Geigl¹, Ursula Baumer², and Johann Koller². (1) Departement de Biologie des Genomes, Institut Jacques Monod, Tour 43, 2, Place Jussieu, Paris 75005, France, Fax: +33-144275716, geigl@ijm.jussieu.fr, (2) Doerner-Institut

We have found DNA, in solution a fragile macromolecule, to escape complete degradation and fossilization over several hundreds of thousands of years when bound as condensates in appropriate "molecular niches" and stabilized by minerals and insoluble organic matter. In this insoluble form it is not amenable to PCR analysis. To develop analysis methods for this diagenetically altered, complexed DNA and to understand the molecular mechanisms leading to preservation of DNA and other biopolymers in a geological context, we have begun to chemically characterize biopolymers in modern, subfossil and fossil bones and in their surrounding sediments. Furthermore, we are trying to correlate the results of the molecular analyses with the taphonomic factors prevailing on the sites of preservation. We will discuss the results and implications of our analyses of both, DNA and lipids, and some of the diagenetic agents that we suspect to be responsible for their preservation.

GEOC 3: Effect of organic fertilizers on genetic and functional diversity of soil microorganisms

Raphael Calbrix¹, Karine Laval¹, and Sylvie Barray². (1) BioSol, ESITPA, 13 rue du Nord, Rouen 76000, France, Fax: 33 2 35 07 48 97, rcalbrix@hotmail.com, (2) LMDF, University of Rouen

Organic matters are currently recycling by farming practices. Those organic matters come from farming activities and also from urban waste such as green waste, and sewage sludge. The aim of this study is to observe the influence of organic improvement on soil microbial communities. In order to analyse the impact of four types of improvement (sewage sludge, poultry manure, compost and mineral) on microbial communities, molecular and traditional tools are used: biomass is estimated by microbial carbon fumigation-extraction method, by total extracted soil DNA quantification and by enumeration of cultivable micro-organisms, (ii) microbial community diversity is characterized with molecular fingerprints and metabolic profiles (Biolog). Actually, our results seem to show a transient increase of total biomass according to total extracted DNA and cultivable micro-organisms methods which appear more sensitive than carbon extraction-fumigation method that reveals no variation. Statistical analysis of metabolic profiles and genetic diversity are still under process.

GEOC 4: Differentiating between old and new microbially derived soil organic matter by means of compound-specific stable isotope (d13C) analysis

Bruno Glaser¹, Serita Frey², Neville Millar³, Johan Six⁴, Georg Guggenberger¹, and Wolfgang Zech¹. (1) Institute of Soil Science and Soil Geography, University of Bayreuth, Universitätsstr. 30, D-95440 Bayreuth, Germany, Fax: +49-921-552246, bruno.glaser@uni-bayreuth.de, (2) Department of Natural Resources, University of New Hampshire, (3) Institute of Plant Science, ETH, (4) Department of Agronomy and Range, Davis University

There is strong scientific evidence that microbial residues such as amino sugars may be stabilized in soil. However, up to now, no investigation has been carried out to quantify both the amount and timing of such stabilization. This is primarily due to methodological constraints, because when biomarkers such as amino sugars are conventionally analyzed by means of gas chromatography and flame ionization detection, it is not possible to differentiate between stabilized (old) and recently produced (new) amino sugars. Therefore, the aim of the present study was to test whether compound specific isotope analysis (d13C) of amino sugars extracted from soil could be used to differentiate between old and new microbial residues. For this aim a new method for the d13C analysis of amino sugars was developed and parameters concerning accuracy and precision are presented. Additionally, preliminary results of new amino sugar formation in soil after labeling with 13C enriched glucose and depleted CO₂ from a FACE experiment are presented. While only very low amounts of new glucosamine and muramic acid have been formed during a 32 days laboratory incubation, a seven years field incubation with elevated CO₂ showed a significant enrichment new glucosamine and muramic acid in the soil organic matter. Thus, our results corroborate current assumptions that microbial residues are stabilized in soil to a significant extent.

GEOC 5: Impact of soil organisms on the fate of carbon in soils

Paul M Chamberlain, Helaina Black, Jacky Chaplow, Niall McNamara, and Andy Stott, Merlewood Research Station, Centre for Ecology and Hydrology, Windermere Road, Grange-over-Sands LA11 6JU, United Kingdom, Fax: 44-15395-34705, pmch@ceh.ac.uk

Processing of plant materials by soil microbes and fauna underlies soil organic matter (SOM) formation and the long-term fate of carbon in soils. The chemical basis of processes regulated by soil organisms needs to be elucidated if SOM formation is to be understood correctly. We utilised the distinct stable carbon isotopic (d13C) differences between SOM produced under C₄ vegetation (d13C -13.6‰) and that of a C₃ plant, *Alnus glutinosa* (alder, d13C -28.9‰), with and without a soil Collembolan species, to investigate the different routes and rates of carbon transfer into soil via the biological community. Bulk and compound-specific d13C techniques were utilised to determine the d13C values of bulk SOM, soil lipids, respired CO₂, Collembola and microbial PLFAs. Results indicate that Collembola play a significant role in the movement of carbon from the litter layer into soil, and in the transformation of litter into SOM.

GEOC 6: Biological availability of hydrophobic organic contaminants and quality of organic carbon

Herbert L Fredrickson, Environmental Laboratory, U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Rd, Vicksburg, MS 39180-6199, Fax: 601-634-4002, fredrih@wes.army.mil, John S. Furey, Environmental Laboratory, DynCorp, Jeffrey W. Talley, Department of Civil Engineering & Geological, University of Notre Dame, and Margaret Richmond, Environmental Laboratory, ASI Corp

Approximately 400 million cubic yards of sediments are dredged from U.S. ports, harbors, and waterways each year to maintain the nation's navigation system. Approximately 10-20% of this material is impacted with organic contaminants. Much of this dredged material is placed in diked Confined Disposal Facilities. The U.S. Army Corps of Engineers (COE) would like to recycle this material for beneficial uses, but is required by The Clean Water Act to assess the potential for contaminants to accumulate in biota. Simple models based on fugacity (e.g., Koc) have been developed and widely used to predict the partitioning of hydrophobic organic contaminants (HOC) between organic matter and organism lipid. Recent publications have shown that the quality of organic carbon can greatly affect the bioavailability of HOC. Sequestration of HOC in organic carbon will reduce toxicity, but will also reduce the apparent efficacy of bioremediation as judged by total solvent extractable HOC.

Sediments from 8 current COE dredging projects were collected and characterized with respect to HOC types and levels, particle size distributions, total organic carbon, cation exchange capacity, total C, H, N, O and S, readily-desorbable HOC fraction using solid phase extraction materials, HOC thermal desorption energy, soot content, microbial biomass and community composition using phospholipid fatty acid analysis, potential rates of HOC biodegradation, and bioaccumulation into the oligochaete *Lumbricus variegatus*. Empirically measured HOC body burdens were correlated to Koc-derived predictions, and HOC and organic matter characteristics.

The results show the proportion of the solvent extractable HOC that was available for microbial degradation and accumulation into *Lumbricus variegatus* varied from sediment to sediment. Koc-derived predictions of HOC partitioning into biomass did not consistently correlate to bioavailability. Both the quantity and quality (e.g. soot) of organic carbon are important determinants for predicting bioavailability. Information on the readily-desorbable HOC fraction should improve the accuracy with which predictions of rates HOC bioaccumulation and biodegradation can be made.

GEOC 7: Microbial processing of humic acids from soils with various contents of metals

Zdenek K. Filip, Langen Building, Federal Environmental Agency, Paul Ehrlich Strasse 29, 63225 Langen, Germany, Fax: +49-6103-704-147, zdenek.filip@uba.de, and Pavol Bielek, Soil Science and Conservation Research Institute

We attempted to elucidate whether humic acids (HA) with a large proportion of mineral components, and extracted from a pseudogley soil with various contents of metals could be easily processed, i.e. utilized by microorganisms indigenous to the same soil, and whether microbial activities cause any structural changes in HA. Depending on nutrient conditions in the individual cultures and origin of HA, between 44% and 67% was utilized. The lowest utilization rate was obtained for HA from soil heavily contaminated with Mg. In the presence of HA, the microbial growth was enhanced up to 261%. Different species of bacteria and fungi utilizing HA could be identified. The HA preparations re-isolated from microbial cultures exhibited distinct changes in elemental and structural characteristics. Diminished contents of ash in HA, and specific alteration in FTIR spectra indicated a splitting of organic and mineral components to occur in HA exposed to microbial processing.

GEOC 8: Clusters and iron (II) monosulfide

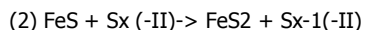
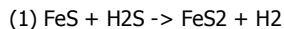
David Rickard¹, Mariette Wolthers², Sijerk J. Van der Gaast³, Ian Butler¹, George Luther III⁴, Andrew Griffiths¹, and Anthony Oldroyd¹. (1) Department of Earth Sciences, Cardiff University, Cardiff CF103YE, United Kingdom, Fax: +44 2920874991, rickard@cardiff.ac.uk, (2) Department of Geochemistry, Utrecht University, (3) Royal Netherlands Institute for Sea Research (KNIOZ), (4) College of Marine Studies, University of Delaware

Iron(II) monosulfide, FeS_{am}, is nanocrystalline and displays a disordered tetragonal mackinawite structure. It consists of two end-member phases with different long-range ordering and primary particle sizes of 2.2 x 1.7 nm (a=b=0.40 nm, c=0.67 ± 0.01 nm) and 7.4 x 2.9 nm (a=b=0.37 nm, c=0.53 ± 0.02 nm). The proportion of the 2nm phase decreases with ageing. The formation of two FeS phases is consistent with competing pathways involved in FeS_{am} formation from aqueous solution. The 2nm phase consists of ca 75 FeS units and may be equivalent to precipitated aqueous FeS clusters which have tetrahedral geometry as determined by voltammetry. The reactivity of FeS_{am} is dependent on the proportion of the two end-member phases. These in turn are dependent on the conditions of formation, especially pH, and the age of the precipitate. These observations partly explain the differences in FeS_{am} reactivity and solubility in experimentation and in the environment.

GEOC 9: Geochemical implications of the polysulfide vs sulfide pyrite formation reactions based on real time measurements of soluble reactants

George W. Luther III¹, Martial Taillefert², Tim F. Rozan¹, and David Rickard³. (1) College of Marine Studies, University of Delaware, Lewes, DE 19958, Fax: 302-645-4007, luther@udel.edu, (2) School of Earth & Atmospheric Sciences, Georgia Institute of Technology, (3) Department of Earth Sciences, Cardiff University

Over the last seven years, we have used solid-state voltammetric Au/Hg microelectrodes to make measurements in marine and freshwater environments. The electrode can distinguish current signals at discrete potentials for free sulfide (H₂S/HS⁻), polysulfide ions (S_x²⁻) and soluble iron sulfide (FeS_{aq}) in sediments and waters including hydrothermal vent waters. Rate laws have been determined for two pyrite reactions given below and FeS_{aq} appears to be the most reactive iron monosulfide phase:



The detection of polysulfide species occurs only at oxic/anoxic interfaces in sediments and waters whereas both free sulfide and FeS_{aq} coexist in many environments below these interfaces. These data suggest that (i) reaction 1 is a dominant geochemical reaction at pH < 7.5 and (ii) the polysulfide reaction occurs primarily at oxic/anoxic interfaces unless polysulfides can be generated for fast reaction at mineral surfaces (e.g., FeOOH and MnO₂). The reaction of free sulfide with S₈ does not appear to be a significant reaction in sediments and water. Above the orifice at hydrothermal vents, polysulfides are not detected indicating that reaction 1 dominates with the production of dihydrogen.

GEOC 10: The nucleation and growth of hexagonal pyrrhotite in hydrothermal solutions

Liane G. Benning, School of Earth Sciences, University of Leeds, Leeds LS2 9JT, United Kingdom, Fax: 44-113-3435259, liane@earth.leeds.ac.uk, and Christopher Cahill, Department of Chemistry, George Washington University

The growth kinetics of iron sulphides in high temperature hydrothermal fluids is not well understood despite their vital importance in most ore forming environments. In low temperature reducing solutions, a mixture of ferrous iron and reduced hydrosulphide spontaneously precipitates a poorly ordered Fe-S colloids, which readily transforms to mackinawite. However, at hydrothermal temperatures mackinawite becomes unstable and converts into other well crystallized Fe-S phases (greigite, pyrite, pyrrhotite) via temperature and redox dependent processes. In this study, the chemical and physical conditions controlling the transformation of mackinawite to hexagonal pyrrhotite at temperatures below 300°C were evaluated experimentally using in situ synchrotron-based energy dispersive X-ray diffraction (ED-XRD). Time dependent changes in Bragg peak areas were used to derive nucleation and growth kinetics, transformation mechanisms and activation energies for this reaction. These data provide a quantitative measure for the formation and stability of metal-sulphides directly from/in reduced, aqueous hydrosulphide solutions under hydrothermal conditions and thus further our understanding of processes governing ore formation.

GEOC 11: Nucleation and growth of pyrite on pyrite seeds

Ian Butler¹, David Rickard¹, Stephen Grimes², and Anthony Oldroyd¹. (1) Department of Earth Sciences, Cardiff University, Cardiff CF103YE, United Kingdom, Fax: +44 2920874991, butlerib@cardiff.ac.uk, (2) Department of Geology, Royal Holloway and Bedford New College University of London

In an anoxic chemostatic reaction system, the rapid nucleation of pyrite from aqueous suspensions of FeS_{am} with excess H₂S(aq) at environmentally realistic concentrations and ambient temperatures is facilitated by the presence of a pre-existing pyrite surface. Where a pyrite surface is not present, metastable FeS_{am} suspensions may persist for months without pyrite formation. The first formed pyrite precipitate is an epitactically controlled overgrowth of pyrite microcrystals 0.1-2mm in size. Epitactic control of microcryst orientation is maintained throughout several generations of pyrite overgrowths. Two further pyrite textures develop on the neoformed overgrowth. Radiating globular pyrite develops where flow in the reaction system is advective, and framboidal pyrite develops where transport is rate limiting. The results suggest that hydrodynamic controls contribute to pyrite texture development in experimental systems. Our results illustrate that pyrite texture is influenced by subtle changes in physico-chemical environment, with consequences for applications of pyrite textures as paleoenvironmental indicators

GEOC 12: Sulfur isotope partitioning during pyrite formation

Ian Butler¹, Michael E. Böttcher², Rickard David¹, and Anthony Oldroyd¹. (1) Department of Earth Sciences, Cardiff University, Cardiff CF103YE, United Kingdom, Fax: + 44 2920874991, butlerib@cardiff.ac.uk, (2) Max Planck Institute for Marine Microbiology

Sulfur isotope partitioning during pyrite formation from FeS_{am} and excess H₂S(aq) (pH6) or S₄2-(aq) (pH10) was investigated at temperatures of 80-100°C using reactants of known isotopic composition, under conditions of strict anoxia. For runs in which H₂S is the primary electron acceptor, the isotopic composition of the product pyrite sulfur reflects stoichiometric addition of H₂S to FeS_{am}. For experiments where zerovalent sulfur is present in S₄2-(aq), the sulfur isotopic composition of the product pyrite indicates isotopic exchange. Both results are consistent with reaction mechanisms proposed on the basis of kinetic data. The results contradict some previously published reports and suggest that the isotopic composition of sedimentary pyrite reflects a mixture of the isotopic composition of the FeS_{am} at the time of reaction and that of the sulfide source.

GEOC 13: Botanical constraints on pyrite formation

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Pyrite is precipitated within the cells of plants and algae at ambient temperatures by pre-treatment with an Fe(II) solution followed by reaction with aqueous S(-II). The botanical system precludes the involvement of any oxidizing agent other than H₂S and or penetration of the cells by particulates, such as FeS_{am}. The results suggests that the reaction involves the oxidation of an aqueous FeS cluster by H₂S or even a direct reaction with aqueous Fe(II). The rate of pyrite formation is determined by the rate of H₂S diffusion into the cells. The supersaturation limit for pyrite formation in these cells approaches 10¹⁴, which is similar to the value found for pyrite nucleation on pyrite seeds. Biological surfaces, such as plant and algal cells, appear to have a similar surface activity to pyrite seeds. However, an independent common rate determining process, such as transport through the diffusion boundary layer, cannot be excluded.

GEOC 14: Capture of Mo in pyrite-forming environments: Seemingly paradoxical effect of polysulfides

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Coprecipitation with FeS₂ is an important sink for marine Mo. EXAFS suggests that cuboidal Fe-Mo-S clusters form, probably preceded by reduction of MoO₄²⁻, the form of Mo in seawater. Sulfide, alone, is a poor reductant for Mo, producing MoVI thioanions instead. When polysulfides as well as H₂S are present, Mo is diverted to MoIV or MoV₂ (poly)sulfido anions. Experiments suggest that polysulfide-induced reduction will occur in nature over a broad range of dissolved S₈ activity. No S₈ threshold or critical redox potential for Mo reduction exists. The seemingly paradoxical process in which an oxidizing agent (polysulfide) induces reduction, is known to occur not only in the chemistry of MoVI, but also in the chemistry of other thioanion forming trace elements, e.g. VV, WVI and ReVII. Solutions supersaturated by 10⁹ with respect to molybdenite, MoS₂, produced no precipitate in 40 days, supporting the established view that MoS₂ precipitation is unimportant in sedimentary environments.

GEOC 15: A laboratory-scale flow reactor design to study metal sulfide interactions with carbon species under hydrothermal conditions

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An important aspect of chemo-autotrophic organic synthesis in hydrothermal systems is the presumed reactivity of transition metal sulfide surfaces. Here, we present a flow-through quartz reactor design which allows for the reconstruction of real-life hydrothermal environments in which surface mediated reactions on so-called 'black smokers' can be studied under laboratory controlled conditions. The system was designed to deliver up to nine different feeds in programmable concentrations under varying pressures and temperatures. To prevent gas exchange induced chemical equilibrium shifts and to mimic flow properties and residence times of oceanic hydrothermal systems, the reactor is designed as a non-headspace flow-through setup. Effluent is analyzed either on-line or by fraction collection. We present results on the kinetics of metal sulfide surface transition based on effluent analysis and mineralogy of the in-situ precipitated solid membranes. In addition, we show preliminary results on the interaction of these membranes with low molecular weight carbon species such as CO₂, n-octanol, and carbon sulfides.

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GEOC 16: Comparing EXAFS with sequential extractions for probing metal speciation in contaminated sediments

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Characterizing the chemical speciation of metal contamination is key for understanding their fate in the environment. Often, operationally defined sequential extraction methods are used to assess speciation. In contrast, X-ray absorption spectroscopy (XAS) directly probes metals within complex environmental matrices. Here we compare XAS and the Tessier sequential extraction method for determining the speciation of Zn in contaminated sediments. XAS was also used to probe the chemical composition of the residual fractions of the sequential extraction procedure. The analysis of contaminated lake sediments was compared to results using artificial samples amended with various zinc phases. XAS confirms that sequential extraction of the artificially amended samples more or less adheres to the scheme outlined by Tessier. However, sequential extraction of the lake sediments fails to detect a sulfide phase that is distinctly revealed by XAS. This suggests that various forms of sulfide respond differently to the sequential extraction procedure.

GEOC 17: The influence of humic acid on the mobilization of heavy metals from a mixed metal sulfide ore concentrate

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Humic acid (HA) had a range of effects on the mobilisation of Cu, Zn, Cd and Pb from a sulfide ore concentrate (OC) at pH 6, which was influenced by light conditions. Copper mobilisation was accelerated under darkness, due to ligand promoted dissolution resulting from surface complexation. Carbon depth profiles of reacted OC, determined using secondary ion mass spectrometry, showed that HA interacted with its surface. Copper mobilisation was further enhanced under illumination, which was attributed to highly reactive singlet oxygen (1O_2) generated by adsorbed and/or aqueous HA. Photosensitised oxidation of iodide to triiodide by HA indicated the presence of 1O_2 . Photo-irradiation also enhanced the release of Zn and Cd compared to dissolution under darkness due to the semiconducting properties of ZnS and CdS and not the presence of HA, which inhibited their dissolution. Lead mobilisation was not affected by HA. However, aqueous complexation with HA kept Pb in solution.

GEOC 18: Does the C isotope signature of polycyclic aromatic hydrocarbons indicate biological sources?

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In temperate environments of the northern hemisphere incomplete combustion of fossil fuels is the main source of polycyclic aromatic hydrocarbons (PAHs). The high abundance of naphthalene and partly also perylene in tropical soils lead us to the assumption that there are up to now unknown, possibly biological sources of these compounds. We used the C isotope signature of individual PAHs in temperate and tropical soils and in tropical wood and termite nests to distinguish different PAH sources. The mean $\delta^{13}C$ values of perylene decreased in the order, temperate soils (-27.0‰) > termite nests (-31.4‰) > tropical soil (-32.4‰) while those of naphthalene (-24.6‰ to -26.2‰) were similar among these samples and tropical wood. Our results support the assumption that perylene in the tropical environment is recently biologically produced as indicated by the depletion in ^{13}C . The C isotope composition of naphthalene, however, cannot be used to distinguish different sources.

GEOC 19: Molecular characterization of soil organic matter from an ancient coking plant site and correlation with potential sources

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In this study, the soil organic matter from an ancient coking plant was investigated. In complement, organic particles isolated from these soils (coke, coal and asphalt) susceptible to be potential sources of organic pollutants were characterized. Even if the extract yield and the hydrocarbon proportion in each soils analyzed show a high variability, PAHs distributions (included in the EPA priority pollutant list) are similar. Moreover, these PAHs distributions are not easily reliable to the different isolated particles investigated. On the contrary, the distribution of the saturated hydrocarbons provides useful information so as to correlate soils signatures and isolated particles fingerprints. The n-alkanes distribution allows determining three major contributions in soils: (i) asphalt, (ii) coke and (iii) higher plant input. Moreover the distribution of specific biomarkers (pentacyclic triterpanes) enables to point out the specific contribution of coal.

GEOC 20: Cometabolism of natural and anthropogenic aromatics in estuarine sediments

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We hypothesized that environments receiving large inputs of natural (lignin) and contaminant (PAH, TNT) aromatic carbon compounds can support natural attenuation by indigenous microbial communities. In two environments (Charleston Harbor, SC and San Diego Bay, CA) we have observed fast turnover (< 100 days) of sentinel PAHs where sediment lignin concentration is high though ambient PAH concentration is low. In San Diego Bay, a highly bioturbated core exhibited fast turnover rates of phenanthrene and fluoranthene, which correlated down core with lignin concentration, though ambient concentration of these PAHs were low (<0.10 microgram per gram sediment). Lignin geochemistry was used to correlate pulp mill effluent, highly concentrated in lignin, with high turnover of PAHs in Charleston Harbor, SC and to identify sources of organic matter to estuarine sediments. To our knowledge, this is the first application of organic geochemistry to environmental forensic studies of estuarine sediments.

GEOC 21: Preferential degradation of PAHs over natural organic matter by bacteria in intertidal sediments

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The health risk of polycyclic aromatic hydrocarbons (PAHs) to estuarine environments can be reduced if PAHs are preferentially metabolized by bacteria over natural organic matter (NOM). We used ¹⁴C-radiotracers to determine bacterial mineralization rates and turnover times of the most common PAHs (naphthalene, phenanthrene and fluoranthene) relative to total NOM metabolism (³H-Leucine incorporation rate). We sampled 12-15 intertidal sediment stations at a creosote-impacted salt marsh every three to four months from March 1998 until November 2001. In late fall, increases in naphthalene mineralization rates often preceded increases in total PAHs. Then bacterial production would decrease as PAH concentrations reached their annual maximum and as ambient temperature decreased with winter. Fluoranthene mineralization rates would then increase prior to reduction in total PAH concentrations in the sediments. Seasonal shifts in PAH mineralization may be the result of competition with natural organic matter as a bacterial substrate.

GEOC 22: Analyses of polyacrylamide-based flocculants in agricultural soil samples

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Agricultural soils are strongly affected by xenobiotic substances as a result of intense anthropogenic treatment. Next to a wide variety of low molecular weight compounds including pesticides and fertilizers macromolecular compounds of anthropogenic origin also enter this soils. The presented investigation focussed on a selected group of polymers, the polyacrylamide based flocculants commonly used in waste water treatment plants for precipitating heavy metals and other contaminants. Consequently, these compounds appear with high concentrations in sewage sludge. The irrigation of sewage sludge on agricultural soils as fertilization leads to the spreading of the associated flocculants into the pedosphere. In addition, these substances seem to have ecotoxic effects on plants. Analytical methods for detecting flocculants in soil samples are not published so far. Thus pathways in the environment or accurate correlation with toxic effects cannot be made. This study developed initial steps in detecting anthropogenic polyacrylamide based polymers in soil samples.

GEOC 23: Low-temperature air oxidation of n-alkanes in the presence of Na smectite

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This study concerns the catalytic effects of clay on organic matter and especially n-alkanes during oxidation carried out at low temperature. The influences of clay minerals were investigated to understand their role better during natural oxidation of organic matter. n-Alkanes oxidation experiments in presence of Na-smectite were carried out at 100°C during 512 hours and reveal an important production of oxygen-bearing molecules to the detriment of initial n-alkanes. Thus, Na-smectite allows to initiate the auto-oxidation of n-alkanes due to its chemical (charged sheets) and/or physical (high specific area) properties. The evolution of oxygen-bearing molecules distribution enables to distinguish two competitive chemical pathways. On one hand, alcohols and ketones are produced with an aliphatic chain length similar to the starting n-alkanes. On the other hand, aliphatic chain cleavages occur and principally produce 1-alcohols, 2-ketones, carboxylic acids and 3-substituted γ -lactones. These oxygen-bearing compounds are more and more preponderant and evidence the fact that cleavage mechanisms become progressively dominant.

GEOC 24: Black carbon in soils: Implications for fertility and pollutant sequestration

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As the need for remediation of polluted soils intensifies, assessment of factors controlling pollutant bioavailability is motivated by its relevance to the selection of site-specific strategy. While significant progress in the study of clay and mineral components of soils has been made, the sorption potential of relatively abundant combustion byproducts, in anthropogenic soils, demands investigation. An exploratory study of surface and bulk characteristics of charcoals recovered from forest fires occurring between 1901 and 1998 reveals the diagenetic alteration of this potentially important sorbent. Scanning electron microscopy, accompanied by x-ray spectra provide evidence that the nature of the surface ranges from fractal to amorphous, and with aging the surface of char particles acquire the elemental composition of the soil horizon in which they reside (mineral versus organic). Solid-state CPMAS ¹³C NMR spectra reveal the prevalence of a humic constituent in chars recovered from organic soil horizons. Furthermore, SEM suggests that a significant portion of these organics may be living microbial biomass.

GEOC 25: Sorption and bioavailability of organic contaminants on black carbon

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Sorption largely governs the mobility and bioavailability of non-ionic organic contaminants in soils. On the basis of partitioning theory, sorption of organic compounds is expressed per unit mass of organic carbon (K_{oc}) with little consideration of the nature of soil organic matter (SOM). SOM is highly heterogeneous and its chemistry varies with soil type as a function of vegetation, hydrology, geomorphology and land use. Many soils contain black carbon, especially in regions where fires (forest, grass) are a common occurrence. In order to understand the sorption characteristics of black carbon, we studied the sorption behaviour of selected hydrophobic organic compounds on a range of charred materials. Charred materials were collected from the field after fires. The chemistry of carbon was characterised by solid state ¹³C NMR. The sorption affinity varied markedly among different types of charred materials collected from the field. While some materials had relatively low affinity to the two organic compounds, the others sorbed 100% of the applied amount. It was concluded from the study that the heterogeneity in sorption affinity of natural charred material is related to the parent material (grass, wood) from which it is formed. The high sorption affinity of black carbon can strongly influence the bioavailability for organic compounds in soils and sediments.

GEOC 26: Calculation of the visible-UV spectra of As and Sb sulfides and polysulfides

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Several different spectral methods are available for the identification of polysulfide and metal sulfide species in solution, but they all suffer from limitations. Recently we have shown that visible-UV spectra in aqueous solution can be accurately calculated for arsenic(III) bisulfides, such as As(SH)₃, As(SH)₂S⁻ and their oligomers. The calculated lowest energy transitions for these species are diagnostic of their protonation and oligomerization state. We here extend these studies to As and Sb III and V bisulfides and to polysulfides Sn-2, n=2-5, and the bisulfide anion, SH⁻. The difficulty of these calculations is greater than that for the As(III) bisulfides since the As and Sb(V) species are more acidic and therefore highly charged anions become important. In general, small and/or highly charged anions are more difficult to describe than larger, monovalent anions. We have used both Hartree-Fock based (CI Singles and Time-Dependent HF) and density functional based techniques (TD B3LYP) and have used both explicit water molecules and a polarizable continuum (within the COSMO formalism) to describe the effects of hydration. We correctly reproduce the general trends, with absorption energies increasing from polysulfides to As, Sb bisulfides to SH⁻. As and Sb (III) species, both monomers and dimers, also absorb at characteristically lower energies than do analog As and Sb (V) species. The polysulfides, on the other hand, show no simple systematic changes in UV spectra with chain length, n, or with protonation state.

GEOC 27: Adsorption on sulfide surfaces and origin of life problem

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It has been postulated that on sulphide minerals, pre-biotic chemistry evolved surface metabolites able to synthesize new materials and structures, and able to spread onto vacant surfaces. The goal of our program is to identify plausible reaction partners and pathways for anabolic synthesis on iron pyrite as a model. We use molecular dynamics calculations to model the adsorption of polyatomic species on surfaces derived from the (001) surface. We report results for the adsorption of water, bicarbonate, formate, carbonate and phosphate on (001) terrace, step,

corner and kink sites. Structural complexity of the unit cell yields a groove on (001) that affects adsorption motifs, and unusual step and kink sites. We will discuss how this might impact catalysis. This work is set in perspective with theoretical and experimental work of the de Leeuw, Schoonen and Hochella groups.

GEOC 28: Bonding and stability of lipid coatings on pyrite

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The binding of lipids, which have two hydrophobic tails linked to a hydrophilic head group (primarily phosphocholine groups), to polycrystalline pyrite in gaseous and aqueous environments has been investigated as a oxidation-inhibiting coating on the metal sulfide. Experimental data shows that the adsorption of the lipid on the pyrite suppresses the oxidation of the metal sulfide by as much as 80% at a pH of 2. Attenuated total reflectance (ATR) Fourier-transform infra-red spectroscopy (FTIR) experiments have shed light on the binding of the lipid to the pyrite surface, as well as whether the lipid forms an adsorbed bilayer structure.

GEOC 29: Fate of RNA in the presence of pyrite: Relevance to the origin of life

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Whether life arose from a surface, oceanic or subsurface environment, the prebiotic organic compounds co-existed with a suite of minerals. The objective of this study is to understand the fate of RNA in the presence of pyrite at the bulk and molecular scales using batch experiments and FT-IR. Preliminary experiments were performed using crushed and acid-cleaned pyrite stirred in an anoxic RNA solution. A rapid decrease in solution RNA concentration was observed. Recovered pyrite was re-suspended in fresh de-oxygenated de-ionized water with no RNA detection suggesting either irreversible adsorption or RNA destruction. An FT-IR-Drift analysis was performed. Comparing an RNA spectrum with the recovered pyrite revealed a major loss of RNA peaks from the pyrite grains suggesting no surface-bound RNA. We speculate that a loss of structurally intact RNA could have resulted from pyrite-induced hydrogen peroxide formation and subsequent reactivity. 35 microMolar H₂O₂ was measured mid-experiment.

GEOC 30: Influence of light on the oxidation of pyrite: Developing a mechanistic model

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In earlier work, we reported that illumination of pyrite slurries increases their oxidation rate. Moreover, we showed that the addition of phosphate inhibits the oxidation in the dark, but that illumination negates this inhibition. Our current working model features the notion that illumination affects different steps of the process. On the basis of the band structure of pyrite, we propose that the production of a photoelectron/hole pair produces a Fe(III) site on the surface. Formation of Fe(III) sites may explain several observations, including the fact that the PO₄-inhibition is negated. However, we have also found that the activation energy for the formation of sulfate in the oxidation process is affected by illumination. This suggests that light also affects surface reactions that lead to the formation of sulfate. Developing a mechanistic model for the oxidation of pyrite is of importance in developing techniques to abate the effects of acid mine drainage.

GEOC 31: A vibrational spectroscopic study of pyrite oxidation

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The ability to perform flow-through experiments while analyzing in situ using attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy has allowed for the investigation of pyrite oxidation with either ferric iron or molecular oxygen as oxidant. Specifically, the proposed step-wise oxidation of the pyrite disulfide group has been examined. The experimentally observed presence of multiple sulfur species at the pyrite surface directly confirms the step-wise oxidation and the equivalence in oxidation products between experiments using different oxidants verifies the independence of the sulfur oxidation mechanism. In conjunction with above experiments, a novel photochemical ATR cell was employed to study the effect of light on pyrite oxidation. Photochemical experiments verify an increase in the rate of pyrite oxidation with illumination, although, light experiments show an increased complexity when oxygen is the oxidant. The results, however, do suggest that the mechanism of sulfur oxidation is affected by illumination.

GEOC 32: Intermediate sulfur species in pyrite oxidation pathways

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Pyrite, FeS₂, oxidation proceeds via a number of intermediates along several distinct pathways. The dominance of different pathways under different environmental conditions may reflect different rates of pyrite oxidation and affect intermediates available for microbial metabolism. At low pH, we have defined rate laws and proposed pathways for elemental sulfur and tetrathionate oxidation by ferric iron and oxygen. Coupling this data with previous thiosulfate oxidation kinetics data facilitates a more complete description of pathways involving surface-bound thiosulfate or polysulfides. H₂O₂ and hydroxyl radicals (generated in these experiments with Fenton's reagent) have been shown to be important in the oxidation of some sulfur intermediates generated by pyrite oxidation under different conditions. These reactions are discussed within the framework of the molecular orbital considerations for pyrite oxidation originally proposed by Luther (1987).

GEOC 33: Versatile metabolic capabilities and changing growth rates are important to development of bioleaching biofilms of *Ferroplasma* spp

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"*Ferroplasma acidarmanus*" was isolated from an acid mine drainage site in Iron Mountain, California. In extreme conditions there (solution pH 0.5 and metals at 10's g/l) it constitutes 85±7% of microbial biofilm populations. Growth capabilities of *Ferroplasma* spp. in chemostat conditions were investigated. *Ferroplasma* spp oxidise iron in the presence (chemolithoheterotrophic) or absence (chemolithoautotrophy) of organic substrate. Also, growth occurs on organic substrate either aerobically, or during anaerobic ferric iron reduction. Growth rates are fastest while oxidising iron (chemolithoheterotrophy, 0.48/day), and slowest for autotrophy (0.09/day). Periodic flooding of the Iron Mt. mine results in almost complete washout of microbial biofilms. Following flooding events, rapid biofilm recovery (densely packed cells) is evident on the pyrite ore. Flexibility of growth schemes would be important for establishment and predominance of *Ferroplasma* spp., within the biofilms, between washout periods. Such detail improves understanding of the presence and role of acidophilic microorganisms in bioleaching environments.

GEOC 34: Trace metal respeciation during partial oxidation of anoxic wetland sediments

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The immobilization of trace metals into sulfide phases may significantly reduce the availability of these elements in wetland systems. However, physical and chemical changes in the system can result in exposure of the anoxic sediments to oxidizing conditions, potentially re-releasing these metals into soluble forms. Sediments containing significant concentrations of zinc and iron sulfide phases were exposed to oxygen-saturated water in a Teflon reactor over a period of 3-4 weeks. Metal concentrations in the reactor effluent were monitored throughout the experiments, while changes in Zn and Fe speciation in the sediment phases were determined by X-ray Absorption Spectroscopy of the reacted samples. In the oxidized portions of the reactor, 50-70% of the ZnS initially present was removed during the oxidation reactions. Dissolution of the sulfide phases did not, however, result in substantial release of soluble Zn, apparently due to the formation of a secondary mixed ZnCO₃-Zn(OH)₂ precipitate phase.

GEOC 35: Tracing the sources of sulfate and sulfide at hydrocarbon seep sites

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Thiotrophic organisms near gas hydrates at cold seep sites require sufficient fluxes of sulfur and methane, and may alter the observed chemistry of these areas. The origin and fates of sulfur can be traced through stable isotopic analysis of sulfates and sulfides in porewaters. Cores from the Blake Ridge and Louisiana slope were collected to characterize sulfur cycling within porewaters of sediments near gas hydrates. Seawater sulfate (+20‰), consumed by coupled microbial processes of sulfate reduction and methane oxidation, is the source of the interstitial water sulfur isotopic signature. At the Blake Ridge, a progressive downcore isotopic enrichment ranging from +20‰ in the upper sediments to +26‰ at depth reflects this process. Likewise, downcore depletions in $\delta^{34}\text{S}$ result from the large fractionation associated with dissimilatory sulfate reduction. These results lend support to the observation that the sulfide required and consumed by chemosynthetic organisms is produced by sulfate reduction of seawater.

GEOC 36: Compound-specific stable isotope approaches to the investigation of carbon cycling in soils

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Carbon cycling in soils is driven largely through the activities of microbial and micro-invertebrate communities. However, the opaque and complex nature of the soil ecosystem coupled with the small size of the organisms involved in carbon cycling generally makes their presence and specific roles difficult to detect and/or differentiate. Compound-specific stable isotope techniques, based on gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), offer a powerful new means of studying the soil ecosystem using either natural abundance or stable isotopically enriched substrates as tracers. This paper will provide an overview of the instrumental analytical techniques and approaches that we are using to provide new insights into the activities of soil dwelling organisms with specific emphasis on their diverse roles in carbon cycling. Examples drawn from our recent and current work will be used to illustrate the possibilities that exist for the application of the GC-C-IRMS technique in this area.

GEOC 37: Nature and dynamics of H₂O₂-resistant organic matter: In search of the stable C compartment of soils

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Quantifying the stable pool of soil carbon is essential for predicting changes in C stocks with land use. H₂O₂ oxidation has been proposed to isolate black carbon and interfoliar stable C. In clay sized fractions isolated from silty soil with different land uses, we quantified H₂O₂ resistant C, analyzed its dynamics considering the history of the soils and using ¹³C natural abundance and investigated its chemical nature by pyrolysis. H₂O₂ was found to account for about 15% of clay associated C in the studied soils regardless of their history. Clay associated H₂O₂ resistant C does not seem to equate with a stable pool of C in soils.

GEOC 38: Using molecular markers to elucidate sources, production, and fate of dissolved organic matter in forest soils

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Changes in marker compounds such as lignin-derived CuO oxidation products, hydrolysable neutral and acidic carbohydrates, and hydrolysable amino sugars during the course of the year give direct information on the contribution of different sources (plant material vs. bacterial and fungal biomass) to dissolved organic matter and on processes that govern the production of dissolved organic matter in forest floor layers and

mineral topsoils. Moreover, the analyses of marker compounds allow to trace the fate of dissolved organic matter during its passage through the deeper mineral soil and the export into surface waters. Selective changes in certain compounds hint to mechanisms that control the retention of dissolved organic matter in soil.

GEOC 39: Impact of source organic carbon composition on soil organic matter cycling

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We hypothesize that the composition of source dissolved organic carbon (DOC) influences DOC-soil mineral interactions, leads to alterations in mineralogy and influences carbon-storage potential. Chemical composition of DOC from different source material, litter layer and mineral soils from pine and oak forests and a hayfield was characterized by ATR-FTIR, ^{13}C -NMR, fluorescence spectroscopy and analysis of carbohydrates. Soil mineralogy was characterized by BET-surface area, total C/N, and Fe/Al-oxide content. Pine litter-DOC contains fulvic acids of smaller molecular size (vs. oak/hayfield litter-DOC). Additionally, pine mineral soil-DOC shows an enrichment of carboxylate functionalities (1697cm^{-1}) compared to oak and hayfields. These differences in source DOC characteristics possibly explain the low soil-C, surface-area, and Fe-oxide content of the pine mineral soil (0.67%, 1.05m²/g, 1.88mg-Fe/g) as compared with oak (2.65%, 6.62m²/g, 10.67mg-Fe/g) and hayfield (2.04%, 7.53 m²/g, 17.64mg-Fe/g). DOC from pines appears to have contributed to soil acidification, leached soil-oxides, and decreased overall soil-carbon storage potential.

GEOC 40: Soils millennium carbon pool

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We determined molecular turnover rates of soil organic matter using natural labelling techniques. Both, pyrolytic and compound specific ^{13}C values of soil organic matter, determined unexpected turnover times. The compound specific results using biomarkers from microbial cell walls identified for the first time members of soils millenium carbon pool.

GEOC 41: Contrasting effect of N content and soil texture on organic matter composition in forest soils as studied by ^{13}C and ^{15}N NMR spectroscopy

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The accumulation of OM in forest soils depends on the amount and quality of the litter and on the contrasting importance of the decomposition and stabilization processes. The soil N content influences litter biodegradation, and the clay and sand contents influence stabilization processes. N content and soil texture of Oh and A horizons of Norway spruce sites were determined in this study, and tentatively related to the composition of SOM, as followed by ^{13}C and ^{15}N solid-state NMR spectroscopy. Only some of the sites with low C/N ratios experience very efficient degradation. On the other hand, high content of sand does not always lead to the protection of polysaccharides, indicating the importance of the litter quality. The PSRE technique, used to describe the quality of OM in Oh horizons showed that the differences in the humification degree of OM could possibly be due to differences in the litter input quality.

GEOC 42: Kinetics and efficiency of Soxhlet extractions for the removal of compounds causing water repellency in soils

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The determination and analysis of compounds responsible for water repellency in soils usually involves removing soil organic material by some extraction process. It should be noted, however, that whether or not there is a good correlation between what is extracted and what is initially present in the soil depends on the efficiency, and selectivity (if any), of the extraction process. In this paper we present results from a detailed

evaluation of the kinetics and efficiency for Soxhlet extraction, using non-polar and polar solvents, with non-wettable and wettable sandy dune soils. Extraction efficiency was assessed by: the mass of the extract; water repellency assessments pre- and post-extraction; DRIFT analysis of absorbance from aliphatic C-H units before and after extraction; the ability of extracts to induce water repellency after reapplication to acid washed sand (AWS); GC-MS analysis of the extracts; and the evaluation of the removal of standard compounds from AWS.

GEOC 43: Molecular characterization of organic matter in B and C horizons of an acid forest soil

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Organic matter in B and C horizons of mineral soils is extremely important in terms of carbon sequestration of soils because it may contain stabilized carbon compounds. The aim of this study was to examine the composition of the organic matter found in deeper soil horizons and to compare it with the surface soil horizon. The conceptual approach included the analyses of bulk soil and particle size fractions by elemental analyses and isotopic characterization. The chemical structure of the organic matter was examined by ¹³C CPMAS NMR spectroscopy and pyrolysis GC/MS. Additionally single plant litter compounds were analyzed. Isotopic analyses pointed to an increasing degree of organic matter stabilization with depth. The chemical composition of the organic matter of the B horizons suggest that root-derived compounds are stabilized preferentially. In the C horizons, microbial compounds seem to dominate.

GEOC 44: Porphyrin geochemistry: A chemist's view of the contribution from Strasbourg

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The study of geoporphyrins began with Alfred Treibs historical findings. Since the 1930's the understanding of their origin, structure, distribution, or diagenesis, was improved by the work of several research groups and the constant improvement of analytical, spectroscopical, and synthetic methods. Significant landmarks of geoporphyrin studies after A. Treibs initial results are the mass spectroscopic studies by Earl Baker, the isolation and structure determination of numerous geoporphyrins by several groups in particular in England, France, and Australia. In the recent years the details of chlorophyll diagenesis, starting from the pigments present in the most recent sediments have improved our understanding of the various steps leading from chlorophylls to geoporphyrins. This presentation will provide an overview of the contribution of the Strasbourg chemists to this field during the years 1984-1995. The presentation will concentrate on the specific aspects of this contribution : isolation of pure geoporphyrins, structure determination, partial and total synthesis of reference compounds, model reactions. It will also stress the synergy between analytical and synthetic chemistry that is crucial in a complex research field like porphyrin geochemistry.

GEOC 45: Total synthesis of DPEP, abelsonite, and related sedimentary porphyrins

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The presence of metalloporphyrins in oil shales, petroleum and other organic-rich sedimentary materials was first reported by Treibs in the 1930's, but it was not until the 1960's that Baker demonstrated the wealth of complex pseudohomologous series that were present in these materials. Many of these molecular fossils are structurally related to deoxophylloerythroetioporphyrin (DPEP), a porphyrin with a fused five-membered exocyclic ring. Due to its significance as the parent structure for a whole host of naturally occurring petroporphyrins, a number of total and partial syntheses of DPEP have been reported. However, none of these approaches have been entirely satisfactory. In this paper, we report a new synthesis of DPEP via a "Western" ring closure of a b-bilene intermediate. This approach gives excellent yields of DPEP and has been utilized in the synthesis of 8 related geoporphyrins. Of particular note, the first synthesis of the porphyrin mineral Abelsonite is reported. This nickel(II) pentamethylporphyrin is found in crystalline form in association with oil shales, and its structure demonstrated by mass spectrometry and nOe difference proton NMR spectroscopy in 1984. The new synthetic route allows the synthesis of virtually any known porphyrin molecular fossil.

GEOC 46: Senescence/death, predation, and early diagenetic alterations of chlorophyll-a

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Much of our research over the past decade has involved unraveling the myriad of anastomotic pathways by which chlorophyll-a degrades. It is these initial steps which appear to "fate" the further diagenetic processing of chlorophyll residues. That is, certain steps lead to the retention of the chlorophyll-derived phorbins while others lead to opening of the isocyclic ring and/or the entire macrocycle. This divergence either then leads to (1) the DPEP series porphyrins or (2) to either certain ETIO-porphyrins or total pigment destruction. We view this divergence as the pyropheorbide and purpurin routes, respectively. These principles will be discussed using data collected on senescent/dead unialgal cultures, sediment traps, and surficial sediments from lakes, estuaries and the deep sea.

GEOC 47: Chlorophyll oxidation products in natural waters

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Numerous studies of sedimentary tetrapyrrole distributions indicate that processes leading to transformation of chlorophylls can occur very early during diagenesis and include reactions within the water column. Recent reports also suggest such an early origin for selected chlorophyll oxidation products. Chlorophyll oxidation products are of particular interest as likely precursors of selected aetioporphyins found in ancient sediments and oils. Typically, chlorophyll oxidation products represent only a minor portion of sedimentary pigment distributions, necessitating the use of highly sensitive and specific methods for their analysis. Photosynthetic pigments distributions from lacustrine and marine water columns, analysed using high-performance liquid chromatography tandem-mass spectrometry, reveal the presence of a range of oxidation products. The presence of the oxidation products in the water column confirms that oxidation occurs during the earliest stages of diagenesis. Changes in the distributions as a function of time and depth demonstrate a relationship with the development and turnover of phytoplankton.

GEOC 48: Effects of pigment-protein complexes on chlorophyll-a degradation in natural oxic and anoxic seawaters

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A series of microcosm experiments was conducted to examine how chlorophyll-a bound in various algal pigment-protein complexes degrades in oxic and anoxic seawaters. The system consisted of natural oxic and anoxic seawaters collected from the stratified layers in Cariaco basin and laboratory-cultured algae (*Emiliania huxleyi*). The pigment-protein complexes were released from the algae cells using detergent and sonication treatments and then separated by polyacrylamide gel electrophoresis. Chlorophyll-a and its derivatives in each protein complex (including psaA, psaB, and LHC-I in photosystem I, and CP43, CP47 and LHC-II in photosystem II) were measured with HPLC after extraction. Three-month incubation results showed that the size and structure of pigment-protein complexes had different effects on oxic and anoxic degradation of chlorophyll-a bound in these complexes. Chlorophyll-a in all complexes degraded at similar rates in anoxic seawater. By contrast, chlorophyll-a bound in photosystem II degraded faster (~2X) than that in photosystem I in oxic seawater. Oxidative degradation of chlorophyll-a in all complexes was generally faster than anoxic degradation. More derivatives of chlorophyll-a occurred in small size protein complexes (e.g., LHC-I and LHC-II) than in other large size protein complexes and more accumulated in anoxic than in oxic seawater.

GEOC 49: Sedimentary distributions of pigments from obligate anaerobic photoautotrophs: Structural distributions and significance

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Bacteriochlorophylls c, d and e, the light harvesting pigments of anaerobic photoautotrophs, occur as suites of homologues according to two main structural variations: the extent of alkylation on the tetrapyrrole macrocycle and the nature of the esterifying alcohol. These differences have minimal effect on in vitro UV/vis spectra, necessitating use of more rigorous analytical methods. Liquid chromatography-tandem mass spectrometry using an ion trap provides the necessary level of structural information from successive stages of fragmentation.

The pigment distributions in sediment cores from two lakes in the Larsemann Hills, east Antarctica, reveal significant differences among derivatives of bacteriochlorophylls c and d. Sediments from Kirisjes Pond, deposited during a marine incursion, are characterised by highly

alkylated macrocycles. Conversely, in Pup Lagoon, where sediment accumulation was initiated during a marine basinal phase, the distributions are characterised by a wider range of esterifying alcohol and a lower degree of alkylation in the tetrapyrrole macrocycle.

GEOC 50: Laboratory simulations of early cross-linking reactions of kerogen

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In a study of heat assisted irreversible moisture removal from 3 mature coals modification of the chemistry of the coal surface was influenced by the order and the intensity of the heating program in the presence of moist air. The hydrophilic properties and surface area were features controlling irreversible moisture removal to a thermally stabilised product coal. Three sub-bituminous coals were used. Studies of fixed bed treatments in a flow of moist air enhanced chemical reactions over 700 and 1160°C for short periods. The water functioned as a reactant. Tracking the Equilibrium Moisture Content (EMC) over a time profile showed a minimal value of the EMC for Blair Athol coal persisted between 4 to 10 hrs. A temperature pulse increase of 5 to 200°C was used during this EMC minimum. Changes induced were monitored by DRIFT, BET surface areas and SSC13-NMR spectroscopy proved the involvement of aliphatic carbons. Vitrinite maceral carbon was more resistant than Inertinite carbons. Petrography showed that bitumens released are pushed back into the coal particles during the higher temperature pulse. In the SSC13-NMR ethers and esters were observed. These reactions are the cross-linking reactions of coal chemists but hitherto without direct chemical proof. (1) ORICA Technical Center, Gate 3, Ballarat Rd., Deer Park. Vic. 3032. Australia.

GEOC 51: Compound-specific nitrogen isotope measurements of soil amino acids

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Amino acids are the most important organic nitrogen (N) fraction in soils. Compound specific stable isotope (^{15}N) measurements do provide new insights into the soil N dynamics. Our methods and results of such measurements on soil amino acids in grassland systems will be presented within the wider overview of compound specific nitrogen (^{15}N) isotope measurements.

GEOC 52: Aliphatics in Andic soils: Insights into free compounds and molecular building blocks of biopolyesters and chemically resistant biopolymers

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Three main sources of plant-derived aliphatics have been distinguished in soils: (a) free (extractable) lipids, (b) the biopolyesters cutin and suberin and (c) chemically resistant non-hydrolyzable biopolymers (e.g. cutan and suberan). The molecular building blocks of these three aliphatic fractions have been studied in great detail using: (1) solvent extraction followed by gas-chromatography (GC) and GC-mass spectrometry (MS) to study free aliphatics, (2) base hydrolysis followed by GC-MS to analyze ester-linked aliphatics and (3) ruthenium tetroxide oxidation followed by GC-MS to obtain detailed information about the molecular building blocks of the chemically resistant (aliphatic) fraction. This latter fraction was shown to be highly aliphatic by pyrolysis and was isolated through sequential chemical degradation techniques including acid hydrolysis and HF/HCl, which were applied to the base hydrolysis residue. Current analyses include ^{13}C NMR.

GEOC 53: MALDI-TOF MS as a new means of characterizing condensed tannins in soil

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Condensed tannins are plant polymeric polyphenols of high ecological importance, but their fate in soil is mostly unknown. Their ability to form complexes with proteins, thought to have a profound effect on the N-cycle in soil, is dependent on polymer length and polymer length distribution. Matrix-Assisted Laser Desorption/Ionisation Time-of-Flight (MALDI-TOF) mass spectrometry can be used to investigate tannin polymers without fragmentation and over a high mass range. Although successfully applied to fresh foliage unexpected difficulties in extracting and measuring tannins from soil were encountered. Data will be presented analysing the nature of this interference and tannin interactions with selected fractions of soil organic matter.

GEOC 54: GC-GC: A new window on the world of complex mixtures

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Comprehensive Two-Dimensional Gas Chromatography, or GCxGC, has revolutionized the practice of gas chromatography. With GCxGC, it is routine to separate thousands of chemical species in a single run. GCxGC also sorts compounds naturally by chemical class, and increases sensitivity by typically a factor of five. These advantages are gained at no cost in analysis time, as compared to conventional GC practice. GCxGC has found extensive application in petroleum analysis. This paper discusses the basics of GCxGC instrumentation and software, and explores application of GCxGC to semivolatile organic content of soil matrices, particularly hydrocarbons in soil.

GEOC 55: NMR: A tool to study the interactions between organic pollutants and soil components

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Fate of pollutants in the environment is greatly dependent on adsorption-desorption mechanisms that take place at the interface between organic and inorganic soil colloids. These processes control transport and mobility of pesticides and thus their bioavailability for plant or microbial uptake and degradation. Nuclear magnetic resonance (NMR) is a powerful method to assess interactions of xenobiotics (pesticides, PAH, hazardous compounds...) with soil components including soil organic matter and inorganic structures (mainly clay fraction). First, a short overview of the different liquid and solid state NMR approaches which have been developed in this area will be presented. Second, two examples illustrating the interactions of pesticides with a hydrated synthetic hydrotalcite used as a soil model by using liquid state HR (high-resolution)-MAS NMR will be detailed. This new technique allows to reach the real fingerprint of an environmental material, which is usually highly hydrated with mobile pollutant at its surface.

GEOC 56: 15N-CPMAS nuclear magnetic resonance spectroscopy and biological stability of soil organic nitrogen in whole soil and particle-size fractions

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Solid-state ¹⁵N cross-polarization magic-angle spinning nuclear magnetic resonance spectroscopy (CPMAS-NMR) is a powerful tool for the noninvasive determination of the chemical structure of soil organic nitrogen (SON). Our objectives were to (1) test whether CPMAS-NMR is quantitative for both heterocyclic and noncyclic SON, (2) quantify SON functional groups by CPMAS-NMR during the decomposition of clover in soil (before and after fractionation of the incubated, clover-amended soil into particle-size fractions), and (3) determine the relationship between N mineralization and N chemical structure during clover decomposition in soil. Integration of the spectrum of a test sample containing both heterocyclic and noncyclic N established that CPMAS-NMR was quantitative for SON in the absence of severe peak overlap. Throughout a 14-month incubation of a sandy loam soil amended with ¹⁵N-clover, the composition of clover-derived N was always 85-90% amide, 5-10% guanidinium N of arginine, and 5% amino. Peak overlap was not severe and no significant amounts of heterocyclic N were detected. These results were found in the whole (unfractionated) soil and in the particle-size fractions that were obtained after fractionation of the incubated whole soil. Correlation of ¹⁵N-NMR signal intensity with soil ¹⁵N concentrations as determined by mass spectrometry strongly suggested that all ¹⁵N was detected by NMR. Adjustment of the N mineralization rate constants from the incubation study for field temperatures suggested that the proteinaceous N has medium-term stability in the field (mean residence time=7 yrs). We conclude that any humification of the clover-N during the 14-month incubation involved incorporation of protein-N into humus without change of functional group. Discrepancies in N composition between this and other studies may be due to the shortness of the incubation in this study or the assumption in other studies that all proteinaceous soil N is hydrolyzable during wet chemical extraction.

GEOC 57: Determination of soil nitrogen availability and humic acid composition as influenced by forest residue management using solid-state NMR and stable isotopes

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Solid-state C-13 NMR with CPMAS was applied to humic acids (HAs) extracted from 0-10 cm soils collected from areas under windrows of harvest residues (UW) 3 years after establishment, and those areas between the windrows (BW), in a second-rotation hoop pine plantation. The NMR spectra of the HAs showed that the C composition of the UW HAs was different from that of the BW HAs. Potentially mineralizable N (PMN) of the UW soils was greater than that of the BW soils. PMN was also positively correlated with HA-aromatic C ($p < 0.05$). There was a 1.43-2.17% of the N-15 apparently immobilised in the HA from application of ammonium sulphate (AS) solution (100 mg N/kg and 99% N-15 excess) and mixing with the soils for ca. 10 min before anaerobic incubation. This compared with 2.19-2.40% immobilised after the 7-day anaerobic incubation with N-15 labelled AS. In addition, the apparent N-15 immobilisation was positively correlated with HA-aromatic C ($r = 0.83$). HA-Fe was positively correlated with HA-alkyl C ($r = 0.93$), indicating that HA-Fe may be preferentially bonded to branched-chain polymethylene structures.

GEOC 58: Characterization of soil organic matter in tropical rice soils by advanced solid-state NMR

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The structures of soil organic matter from a continually submerged, triple-cropped lowland rice soil and that from an aerobic dryland rice soil were investigated and compared using advanced solid-state nuclear magnetic resonance (NMR) techniques. Quantitative ¹³C NMR shows that the humic acid (HA) from the submerged triple-cropped rice soil with large amounts of rice-straw input is rich in lignin derivatives (ca. 45% of carbon) but almost free of charcoal. Significant amounts (>35%) of nitrogen bonded to aromatic rings were detected by ¹⁴N-¹³C NMR. The ¹³C and ¹⁵N chemical shift and relatively high NCO:NCH ratio indicate NCO bonded to aromatic rings. In contrast, the corresponding HA fraction extracted from the dryland soil with lower lignin input shows predominantly NCO and NCH signals of easily degradable peptides, as well as some heterocyclic N. Nitrogen species bonded to aromatics are considered as not readily plant-available and their accumulation coincides with a substantial long-term grain-yield decline.

GEOC 59: Characterization of the chemical structure of Coorongite by ¹³C NMR, pyrolysis GC-MS, and tetramethylammonium hydroxide thermochemolysis

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Coorongite is a black rubbery deposit found in shoreline sands of lacustrine deposits of the Coorong district of South Australia and is derived from wind-driven accumulations of the algae *Botryococcus braunii*. Using ¹³C NMR spectroscopy (employing the ramp cross polarization and Bloch decay methods), pyrolysis GC-MS, and TMAH thermochemolysis GC-MS, we have shown that the macromolecular structure of the Coorongite consists of long paraffinic carbon chains that are crosslinked by ether and ester bonds. Compared to the *B. braunii* algaenan, the macromolecular structure of the Coorongite is more crosslinked, which implies the occurrence of more extensive oxidative alteration during the formation of the Coorongite. It is suggested that, during early diagenesis, soluble low molecular weight lipids in *B. braunii* are oxidatively polymerized, thus forming the macromolecular structure of the *B. braunii* algaenan. The continuous oxidative degradation of the *B. braunii* algaenan eventually leads to the formation of the Coorongite.

GEOC 60: Application of integrated GC-matrix isolation FTIR-MS for the analysis of organic geochemical samples

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Gas chromatography-mass spectrometry (GC-MS) has been a workhorse technique in organic geochemistry for several decades. It has been successfully applied to the investigation of numerous problems in petroleum geochemistry, environmental geochemistry, forensic geochemistry and others. However, GC-MS alone can be inadequate for structural identification in a number of important circumstances. For example, it is often difficult to differentiate closely related isomeric compounds by GC-MS unless both MS and chromatographic behavior are already known. GC-MS can also fail to provide sufficient data for unambiguous identification of completely unknown compounds. In principle, integration of GC-MS with spectroscopic analysis can help to overcome these limitations.

In this presentation we will describe the application of integrated GC-matrix isolation FTIR-MS for the analysis of organic geochemical samples. We will describe this newly available technique and demonstrate its efficacy as a powerful analytical tool with results of preliminary analyses of a variety of different types of compounds including saturated, aromatic and functionalized terpenoids.

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

GEOC 61: C25 highly branched isoprenoid: An age-related biomarker in oil

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The highly branched isoprenoids (HBIs) show an unusual branching structure and a confirmed link with diatoms. These compounds have mostly been reported in recent or immature sediments, or in immature bitumen/oil, and most often as various alkenes or sulfur-containing derivatives. We used published mass spectra of the C20, C25 and C30 HBIs to search for their occurrence by gas chromatography-mass spectrometry (GC-MS), using relative retention time and mass fragmentation. Our investigations show that the C25 HBI commonly occurs in petroleum, but the C20 and C30 HBIs were not commonly detected. We analyzed a suite of over 100 oil samples for their C25 HBI concentrations by using the m/z 238 fragment ion and an internal quantification standard. All samples containing C25 HBI above a concentration limit of 100 ppm in the saturate fraction are Late Cretaceous and younger suggesting the application of C25 HBI concentration as an age-related biomarker for the oil source.

GEOC 62: Structural details for an aliphatic polyaldehyde extract and algaenan from *Botryococcus braunii* race A

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Through solution state NMR spectroscopy and Q-TOF Mass Spectrometry studies of the soluble polyaldehyde extract from *Botryococcus braunii* race A, combined with HR-MAS NMR spectroscopy and solid-state ¹³C NMR spectroscopy of the intact algaenan isolated from the same race of algae, it is has been possible to advance the structural understanding of these geochemically important biopolymers. We find that the polyaldehyde extract in this study not to be polymeric in nature but to consist simply of a mixture of unsaturated polyaldehydes with an average chain length of ~32 carbons. We find the algaenan results from the reticulation of the polyaldehyde chains via ether linkers and are able to propose an average structure for the algaenan. In essence the algaenan consists of ether and ester cross-linked polymethylenic structures containing an average chain length of about 40 carbons and mid-chain olefinic carbons. Cross linking probably occurs via oxidative polymerization of these olefinic structures.

GEOC 63: Development of field analytical capability for on-site detection of light hydrocarbon gases in near-surface soils and sediments as a tool for fault detection

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Gas chromatography has used for years by laboratories to analyze light hydrocarbon gases (C1 to C4) in soil and sediment samples. Anaerobic metabolism of organic materials in sub surface soils produces a wide variety of by-products, some of which are the small C1 to C5 hydrocarbon compounds with very high vapor pressures. If petroleum is present in deep subsurface strata, the soil gas composition in near surface samples uniquely includes ppb levels of the C2 to C4 alkanes and alkenes as well as methane and hydrogen. We have developed a field portable gas chromatograph that can detect these C2 to C4 compounds in near surface soil gas samples at ppb detection limits appropriate for this application. Furthermore, the samples can be analyzed immediately after collection so that soil gas data can be used to select additional sampling sites. This capability allows not only the detection of petroleum from near surface soil gases, but the location of the surface expression of geologic faults in areas such as swamps and marshes. Soil gas profiling has the potential to be used for a number of important applications from petroleum prospecting through environmental assessments to geologic fault detection. The nature and quantity of other volatile soil gas compounds can be used to indicate the natural attenuation processes occurring subsurface using various carbon sources (such as chlorocarbon degradation producing vinyl chloride and ethane metabolites, or ethylene and propylene from petroleum hydrocarbon sources). Further, when this type of chemical information is integrated with appropriate geologic data, important conclusions can be drawn about localized environments, and these conclusions can then be used for a variety of applications including geologic risk assessments.

GEOC 64: Enthalpies of solution, proton exchange, and metal exchange of porphyrins and metalloporphyrins: Discussion of conformational and electronic considerations

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Porphyrins and metalloporphyrins have shown great diversity in their conformation in solution. Enthalpies of solution, proton exchange and divalent metal exchange of several porphyrins in 1,1,2,2-tetrachloroethane were determined and are discussed. The enthalpies of solution varied from ~0 kcal/mole for 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin to + 10.6 for 2,3,7,8,12,13,17,18-octaethylporphyrin. The enthalpies of protonation to form the dication in solution using trifluoroacetic acid varied from -27 kcal/mole to -71 kcal/mole. The enthalpies of metallation in solution varied but to a much lesser extent. The enthalpies of proton exchange and metal exchange of these porphyrins in solution were also determined. Conformational and electronic influences on these results are discussed.

GEOC 65: Nonplanar deformations cause the red shifts in the UV-visible bands of ruffled tetraalkylporphyrins

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Experimental data show that nonplanar porphyrins have red-shifted optical spectra. The red shifts have been attributed to the large nonplanar deformations that invariably accompany steric crowding of bulky peripheral substituents, the generally accepted interpretation. However, recent studies of constrained porphine and tetraalkylporphyrin structures produced only small red shifts in the calculated transitions in spite of substantial ruffling. On this basis, it was suggested that the red shifts were actually the result of in-plane nuclear reorganization. We have examined a series of ruffled tetraalkylporphyrins containing Ni or Zn using INDO/S calculations to obtain optical transitions for molecular mechanics structures. The calculated transitions agree well with experiment for energy-optimized tetraalkylporphyrin structures, but structures ruffled by artificial constraints produce only a small fraction of the observed red shift, consistent with DFT studies. Nevertheless, we show that the large red shifts arise from ruffling-symmetry nonplanar deformations not present in the artificially constrained structures.

GEOC 66: Mass spectrometric analyses of porphyrins and geoporphyrrins

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The complexity of geoporphyrrin mixtures precludes routine isolation and characterization of the individual porphyrinic components; therefore it has been necessary to turn to non-traditional approaches to their analyses. In particular, mass spectrometry has proved an invaluable tool in the analyses of such mixtures. An overview of the developments of mass spectrometric and tandem mass spectrometric methods for the analyses of geoporphyrrin mixtures will be presented. The discussion will be extended to include a study of unusual fragmentation processes for distorted synthetic porphyrin systems. In addition, a simple mass spectrometric technique for the determination of the ionization energies of porphyrins will be described.

GEOC 67: Geoporphyrrin fingerprinting standards

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The advent of detailed high performance liquid chromatography (HPLC) has allowed the isolation and, with mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectrometry, the characterization of a great many individual geoporphyrrin structures. However, accompanying this quantum leap was a trend towards overlooking the entire geoporphyrrin array. That is, a standard for the "fingerprinting" of geoporphyrrin arrays, actually already available and used, needs to be re-introduced to these studies. This paper will cover the maturation of geoporphyrrins and how the low voltage electron impact MS, or any equivalent molecular ion producing methodology, can and does allow for a common fingerprint from which the DPEP(aka CAP)-to-ETIO and alkylation indices are easily obtained. Thus, the individual contribution of each geoporphyrrin can then be assessed realistically.

GEOC 68: Reservoirs in watersheds: On the use of biogeochemical characteristics to determine origins and diagenesis of sedimentary organic matter

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Sediments can provide a historical record of cumulative changes to a reservoir and its drainage area. However, to read this record properly one must understand the biosynthetic origins of the sedimentary organic matter (OM), the changes OM undergoes upon transport through the watershed and after deposition, and the relationships between anthropogenic changes in watersheds and reservoirs and the organic materials being deposited in sediments. One of the most useful aspects of this limnological approach is its potential ability to produce quantitative information on elemental and energy cycling and fluxes, as well as qualitative information on biomass, community composition and physiological status.

Undisturbed sediment cores were collected at twelve sites in West Point Lake, a large hydropower reservoir located on the Chattahoochee River 110 km downstream from Atlanta, GA. The Chattahoochee River drains an 8,754-km² watershed comprised of urban and residential land (30%), and forest and agricultural land (70%). The cores were cut into 3 cm sections. Bulk elemental analyses of each section included TOC, total and isotopic C, H, N, O and S. Fatty acids in the total lipid (geolipid) and polar lipid (phospholipid membrane biomass) fractions were methylated and analyzed by capillary GC-MS. Principal component analysis was used to compare fatty acid profiles with respect to depth and reservoir location. Compound specific isotopic ratio mass spectrometry was used to determine carbon isotopic ratios in selected fatty acids.

The results show the biogeochemical characteristics varied depending on location in the reservoir. Depth, hydraulic distance from the main channel and travel time from the dam were the most important factors in understanding variations in the microbial community. Several fatty acids were identified as important markers for discriminating between locations and allochthonous carbon. The isotopic ratios gave information on processes occurring in the reservoir.

GEOC 69: Organic and inorganic markers of short time-scale shifts in environmental conditions in a South Texas reservoir subsequent to its impoundment

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Our study of Lake Corpus Christi, which serves as the major source of fresh water for a population of more than 300,000 residents in South Texas, has shown temporal fluctuations of arsenic in both the dissolved and particulate phases of the reservoir. Sediment concentrations suggest a strong influence of previous historical inputs, whereas dissolved values point to present fluctuations in hydrodynamic regime of the reservoir as a major control in lake-wide concentrations of arsenic. Elemental, isotopic, and organic biomarker signatures in sediments suggest that high releases of nutrients from soils following their impoundment (probably as a rapid flush), have fertilized phytoplankton blooms and led to eutrophic conditions in the Lake. Depletion of this nutrient source and the "capping" of the flooded soils by fresh sediments, then led to a subsequent crash in the algal communities and reverted the Lake to a mixed input system (allochthonous as well as autochthonous)

GEOC 70: Photodegradation of particulate organic matter in Mississippi River suspended particulates: Preliminary evidence

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Exposure of Mississippi River suspended particulate matter (SPM) to a solar simulator for several days resulted in significant to major losses of organic carbon from the particulate phase. Most carbon appeared in the dissolved phase, indicating that the process was not one of wholesale oxidation. The reaction appeared to be first order with respect to irradiation time. Preliminary seasonal data suggest that carbon-rich SPM during autumn is less susceptible to this degradation than SPM during spring, which has lower carbon concentrations but accounts for much more carbon flux. Deposited particulate matter from the river bed showed similar susceptibility to this reaction. If verified for field conditions, this reaction may play a role in the large decreases in organic carbon concentrations observed between riverine SPM and continental shelf sediment concentrations in systems such as the Mississippi.

GEOC 71: Sources of organic carbon on the Louisiana shelf: The use of chemical biomarkers to trace organic matter in Mississippi River plume sediments

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In this study we analyzed surface sediment from the Gulf of Mexico for a suite of biomarkers (phytoplankton pigments, stable carbon isotopes, and lignin phenols by TMAH thermochemolysis). The study was conducted during April and October, 2000, representing periods of high and low Mississippi River discharge, and encompassing an area within and around the dispersive path of the Mississippi River. Organic carbon (%OC) in surface sediment ranged from 0.28 to 1.4 during high discharge and from 0.59 to 1.8 during low discharge. $\delta^{13}\text{C}$ values ranged from -20.6 to -22.9 ‰, and from -14.9 to -21.8 during each discharge period. Chlorophyll a in sediment during high discharge ranged from 0.3 to 1.2, and from 0.1 to 8.9 $\mu\text{g/g}$ during low discharge. Lambda values (analogous to the lambda-8 parameter from CuO lignin analyses) ranged from 0.01 to 0.31 ng/100mgOC during high discharge, and from 0.05 to 0.30 during the low discharge period.

GEOC 72: Temporal and spatial abundance of amino acids in the Mississippi River plume: Effects of microbial and sorption/desorption processes

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Water samples were collected on the Louisiana Shelf (March 2002 and October 2002) from 12 stations within a sampling grid in the Mississippi River Plume. River and "blue water" stations were sampled outside the grid as end-members. Individual DFAA (mol%), POC, PON, DOC, DON, and bacterial abundance/productivity were measured across a salinity and suspended particle gradient. DFAA concentrations ranged from 9.22 to 94.26 μM . Higher concentrations of DFAA occurred in the plume/marine water mixing zones. Basic amino acids (AA) were the most abundant across the entire sampling grid, with the highest concentration in the river end-member (~20 mol%). The highest neutral AA concentrations were in the marine end-member (~15 mol%). Bacterial abundance/productivity were de-coupled from DFAA maxima. Abundance/productivity were highest (1.13×10^9 cells/L, 8.59×10^{-7} gC/L/h) northwest of the river mouth in an area that is a confluence of riverine and estuarine inputs (Mississippi River and Barataria Bay).

GEOC 73: Simultaneous automated DIC and DOC analysis on low ppm carbon water samples for ^{13}C isotope measurements in natural systems

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A method for the automated ^{13}C analysis of dissolved inorganic and organic carbon species has been developed to operate on a Finnigan MAT DeltaPlus Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS). The system uses an OI Analytical Model 1010 TOC Analyser with a 53 samples autosampler coupled to the IRMS with a Finnigan MAT ConFlo III interface. A special Scrubber-Conditioning adapter conditions the output of the TOC Analyser for direct coupling to the ConFlo III. For natural and anthropogenic carbon species, the ^{13}C stable isotope has proven to be an excellent environmental tracer. Analytical performance tests were carried out on various organic compounds from easily oxidisable (sugar) to difficult (humic acids). A set of natural samples were also analysed to confirm the flexibility of the system. Analytical precision (2 sigma) is typically <0.20‰ with sample reproducibility from 0.10 to 0.25‰ depending on reactivity of material. We believe this to be the first successful use of a TOC Analyser for both dissolved inorganic and, specifically, dissolved organic species for ^{13}C stable isotope analysis in an automated continuous flow IRMS system. Routine analysis is achieved fairly quickly, is relatively simple with little or no sample manipulation and will allow new and exiting studies for stable isotope research in both natural abundance and organic tracer studies not easily achieved before.

GEOC 74: Assessment of aromaticity indices in soil humic acids based in spectroscopic, pyrolytic, and wet chemical degradation data

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In this study the structural characteristics of humic acids (HAs) from 16 Mediterranean soils have been approached by analytical pyrolysis, oxidative degradation with sodium perborate and spectroscopic techniques (FT-IR, UV-V, ^{13}C -NMR). Up to 250 analytical descriptors were tabulated for each HA, and the total matrix was processed by bi- and multivariate data analyses. Very significant ($P < 0.01$) linear regression coefficients were obtained between the optical density of the HA (e.g., at 465 nm, referred to as E4) and the ^{13}C -NMR signal area in the 110-140 ppm or 140-160 ppm spectral regions. Negative correlations were also obtained between E4 and atomic H/C ratio, and positive correlation

with the percentage of N and of aromatic compounds, mainly of high degree of oxidation. There were also very significant negative correlations with the percentage of aliphatic degradation products as well as with the yields of lignin-derived methoxyphenols. This latter fact indicated that the extent of the lignin domain in HAs is not necessarily an index for aromaticity, but to all appearances is indicating diagenetic alteration or selective preservation of plant-inherited macromolecules in comparatively immature HAs.

GEOC 75: Fate of microbial biomass in soil

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Soil microorganisms contribute to the formation of refractory organic matter by their metabolism and to a certain extent also by their biomass. We investigated the contribution of microbial biomass to humus formation during incubation of soil with genetically (lux gene) and isotopically (¹³C) labeled *Escherichia coli* cells. We traced the survival of the entire cells and the fate of nucleic acids, amino acids, amino sugars and fatty acids. After 15 weeks, about 60% of the added ¹³C was lost as CO₂. At the same time, no luminescence was detectable after enrichment of the *E. coli* cells, but the lux gene was still detected by PCR. Thus, the genetic information and a significant part of the carbon originating from biomass were retained in the soil. Data on the distribution of the label on different biomolecules will be presented and discussed with regard to the contribution of microbial biomass to the formation of refractory soil organic matter.

GEOC 76: Determination of dissolved organic nitrogen speciation in soil extractions

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The ninhydrin-colorimetric method is commonly used for determining dissolved organic nitrogen (DON) speciation in soil extracts. However the general reactivity of ninhydrin towards ammonia, primary amines, secondary amines, amino acids (AA) and amides results in overestimation of AA concentrations. In contrast, the fluorescent reagent o-phthalaldehyde (OPA) displays high specificity to primary amines. We present an improved method for determining DON speciation in soil extracts based on tandem use of ninhydrin-colorimetric and OPA-fluorescent techniques. We find that OPA has high specificity to non-peptide-AA's and accurately predicts total AA concentration to within ±5% in complex heterogeneous DON solutions. OPA is significantly less sensitive to secondary amines and peptide-amines. Additionally, OPA, which requires 5μM-reactive-N in the extract as compared to 3mM-reactive-N required for ninhydrin-colorimetric assay, shows greater analytic sensitivity. Measurement of NH₃ along with ninhydrin-colorimetric and OPA-fluorescent techniques allows quantitative determination of ammonia-N, peptide-N and AA-N within soil extracts for improved DON speciation.

GEOC 77: Changing of humus condition of gray-earth depending on type, subtype, kind, and variety of ground

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In the present work we have investigated: influence of mineral fertilizers manure, composts, prepared from household wastages, kinds of various culture, humus content. Besides the changing humus condition of earth depending on type, subtype, kind and variety of ground. The results of research show, that the mineral fertilizers in moderate doses increases the humus content. Injection of high doses of nitric fertilizers strongly influences the humus content. Thus mineralization of humus prevails above humification. On the other hand increased doses of nitric fertilizer reduces the coefficient of humification of alfalfa weight determined using C-14. It is explained by reduction of the ratio of C:N from the injection of nitric fertilizers, especially in high doses, both increasing the content of nitrate and strengthening the process of denitrification. In injection of manure and composts of organic waste in doses of 20-40tons/hectare, the humus content is increased from year to year. Study of the humus content at various agricultural cultures shows, that at cultivation of alfalfa, garden cultures of the humus contents will be increased, cultivation of wheat, or such row-crop cultures as cotton plant, tobacco, corn essentially are reduced the humus content. Besides the humus content, agricultural yield depends on mechanical structure, type, subtype of ground. The research has shown that hydro-morph ground contains humus more than in auto-morph.

GEOC 78: Thermal studies of H₂O₂-resistant soil organic matter

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H₂O₂ oxidation was proposed as a method to isolate a soil fraction pertaining to the stable C pool. We investigated the nature of clay associated H₂O₂ resistant organic matter using thermal analysis (DTG and DSC) and pyrolysis.

GEOC 79: Effect of grassland restoration on organic matter and microbial communities

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The aim of this study was to appreciate the composition of organic matter and microbial communities of a series of ageing grassland soils and to confront the emerging molecular microbial ecology methods to classical approaches of soil studies. After systematic quantification of total Carbon and particular organic matter, an analysis of microbial communities was performed. Total microbial DNA has been assayed to estimate the microbial biomass and compared with the classical determination of the Carbon associated with biomass. Those data were enriched by enumeration of cultivable micro-organisms and by measurement of microbial Carbon mineralisation due to microbial activity. The diversity of micro-organisms was estimated by electrophoretic analysis of bacterial or fungal rDNA internal transcribed spacer (RISA) and confronted to BIOLOG catabolic profiles. Apart from a confirmation of the pertinence to use molecular tools in soil studies, we highlighted that as early as two years after grassland restoration, most of the bio-indicators assessed clearly increase along the ageing gradient.

GEOC 80: Biodegradation potential of chlorinated hydrocarbons and nitro-aromatic compounds in constructed wetlands: A bench-scale study in nitrate-reducing conditions

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NACs are introduced into the environment due to their extensive agricultural and industrial usages. Nitro groups in the aromatic ring are often implicated as the cause of the toxicity of such compounds. Use of pesticides, propellants, herbicides, dyes, plastics, fumigants, pharmaceuticals, landfill dumping of industrial wastes, military use of explosives like trinitrotoluene or TNT, RDX, HMX, etc. cause the nitroaromatic compounds to enter soil, water and food chain by several routes. 2-, 3-, and 4-Nitrotoluenes are monitored in landfill gas. Of these, 4-Nitrotoluene is a highly toxic, irritant and it is readily absorbed into the skin. The widespread contamination of soil and groundwater by CH and NACs necessitates that contaminated soil and groundwater systems should be studied and remediated for the benefit of the living world and maintenance of the ecosystem.

GEOC 81: Elemental cycling rates in bioturbated Skidaway salt marsh

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Saltmarsh sediment is a complex geochemical system with a number of highly coupled processes occurring simultaneously. Complete characterization of this system requires a comprehensive approach in which all critical processes are considered concurrently in an interrelated manner. Recent studies in saltmarsh systems of the US Atlantic Coast documented the significant recycling of iron and complex spatial overlapping of the terminal electron acceptor sequences (Kostka et al. 2002). The iron recycling has been attributed to the reoxidation of reduced iron due to bioturbation and bioirrigation by infauna, and phytoirrigation by vegetation. This study utilizes the comprehensive reaction-transport modeling approach with a complete biogeochemical data set to quantitatively describe the couplings between organic matter diagenesis and the reduction and cycling of various terminal electron acceptors.

GEOC 82: GoM hydrocarbon seal identification using mud gas isotope logging

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Reservoir seals are not as well understood as either source or reservoir rocks, and evaluating and predicting reservoir seals remains problematic. Within this context, mud gas isotope logging is a promising technique for both complementing existing seal analysis methodology and empirically verifying the presence of any seal, regardless of origin. Isotopic measurements made on mud gas samples surrounding a sealing interval can be used to determine the effectiveness of a seal as well as establish likely migration pathways and reservoir compartmentalization. By measuring changes in background isotopic signal of intact seals vs. seals that leak, calibration between physical property measurements of the seals and their ability to seal can be determined. To illustrate this technique, case histories using mud gas isotope data are provided for: 1) wells with leaky seals and low gas saturation in the underlying reservoir, and 2) wells with intact seals and high reservoir gas saturations.

GEOC 83: High-resolution study of bacteriochlorophylls in sediments of an Antarctic lake

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Kirisjes Pond is a small lake in the Larsemann Hills, east Antarctica. It remained ice-free throughout the last glaciation, providing a continuous sedimentary record dating back 40,000 years. A previous study of the sedimentary pigment distributions showed the presence of bacteriochlorophyll c and d derivatives in two samples from around 6500 years b.p. Palaeontological data indicate a marine incursion to have occurred at this time. The bacteriochlorophylls indicate the development of a stratified water column with an anoxic photic zone dominated by phototrophic bacteria. Bacteriochlorophylls exist as homologous series' with variations in the extent of alkylation of the macrocycle that are related to the conditions under which the bacteria grow. Detailed characterisation of the sedimentary bacteriochlorophyll homologues by liquid chromatography-tandem mass spectrometry reveals highly complex distributions. Analysis of the marine section of the core at high stratigraphic resolution provides information about changes in environmental conditions at the time of sedimentation.

GEOC 84: Pigment biomarkers from sediments of an Antarctic lake spanning a subglacial period

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Throughout the last glacial maximum, Progress Lake in the Larsemann Hills, east Antarctica maintained a subglacial lake environment in which the sediments were protected from erosion. Accordingly, the sediments represent a continuous palaeoenvironmental record dating from the late Pleistocene to the present. Analysis of the sedimentary pigments by high performance liquid chromatography-tandem mass spectrometry has enabled the identification of components including those present in low abundance. Chlorophyll a- and b-derived components are indicative of oxygenic photoautotrophs whereas those derived from bacteriochlorophyll a provide evidence of photoautotrophic prokaryotes and imply dysoxic or anoxic conditions. Changes in the exact nature and distributions of the transformation products reflect both shifts in the photoautotrophic community of the lake and changes in the lake environment. Interestingly, the total pigment abundance profile shows marked variations and attests to a period of highly suppressed biological activity extending several thousand years after the time of the glacier's retreat.

GEOC 85: Shipboard extraction of interstitial waters for stable sulfur isotope analysis

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Analyses of interstitial waters from cold seeps on the Louisiana Slope in the Gulf of Mexico and the Blake Ridge, coastal South Carolina, have furthered the understanding of the sulfur cycle in marine sediments. Reported here are improvements in methodology for collection of porewaters for sulfur isotopic analysis. Traditional extraction techniques include squeezing, pressing, or centrifugation. Of utmost importance is exclusion of oxygen during isolation of sulfides from sediment cores. Oxidation of sulfides to sulfate represents a sampling artifact, and confounds interpretation of sediment porewater sulfate and sulfide concentrations and isotopic data. Although porewater extraction within a glovebag presents the optimal anaerobic conditions, the technique is cumbersome and labor intensive given the layout and facilities of the research vessel. We present here modifications to the Reeburgh extraction procedure, which precludes the necessity of extraction within a glovebag. These modifications represent a reliable and great simplification of shipboard porewater extraction.

GEOC 86: Design and implementation of an integrated sampling platform for geochemical investigations of Maine lakes

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Using NSF funds, the Colby Chemistry and Geology departments have constructed a floating laboratory and coring facility for geochemical research and teaching. Built upon a 24-foot pontoon boat, the lab is equipped for real-time pH, O₂, t, pE, Fe(II), H₂O₂, NO₃⁻, NO₂⁻, PO₄³⁻, and depth measurements. An articulated crane allows deployment of a towed fish with an in situ sensor array and intake manifold for a continuous pumping system. The crane also allows deployment of vibracoring equipment and recovery of 10 m length sediment cores. Detailed hydrographic profiles will be presented to demonstrate the high-resolution water column measurement capabilities of the system. Corresponding sediment profiles extend these water-column measurements over decadal time scales. The boat also provides an excellent platform for field-based student laboratories. The excitement and logistics of involving students in this project will be described.

GEOC 87: Seasonal changes in the abundance and composition of dissolved and particulate organic carbon in the lower Mississippi and Pearl rivers

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Monthly samples from the lower Mississippi (MR) and Pearl (PR) rivers were examined for the abundance and composition of dissolved and particulate organic carbon (DOC and POC), from August 2001-July 2002. Carbon functionality of ultrafiltered dissolved organic carbon (UDOC) was determined using solid-state ¹³C-NMR. DOC and UDOC in the MR and PR ranged from 3.2-6.2 and 0.65-1.71 mg L⁻¹ and 3.0-11.9 and 0.84-4.96 mg L⁻¹, respectively. UDOC was negatively correlated with water discharge (R=-0.73) in the MR, while it was positively correlated in the PR (R=0.78). UDOC in both rivers was dominated by aliphatic and carbohydrate carbon (59.5 %). Pigment concentrations in both rivers were higher in summer, when suspended particle concentrations were low; concentrations in the MR were almost always higher than the PR. The smaller watershed of the PR makes carbon dynamics in this system more susceptible to local weather patterns than the MR.

GEOC 88: Solubility and deposition of Saharan and Asian dust to the open ocean

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The transport and deposition of continental dust is a critical source of iron to sustain phytoplankton primary productivity in the open ocean. Over geologic time, variations in the dust supply are correlated with large excursions in atmospheric carbon dioxide levels and global temperature. This research is aimed at measuring the solubility of Fe and Al in aerosol dust in order to constrain global biogeochemical models of ocean productivity and atmospheric CO₂ levels. Samples of aerosol dust and rainfall were collected on three oceanographic research cruises in the Gulf of Mexico (to collect Saharan dust) and one cruise in the northwestern Pacific (to collect Asian dust). The aerosol samples were analyzed by energy dispersive X-ray fluorescence for total Fe and Al. Replicate filters were extracted with either pH 8 seawater or ultrapure water to quantify the soluble fraction of both Fe and Al. Rain samples were analyzed either unfiltered or filtered to quantify the solubility of Fe and Al in wet deposition. In general, we find aerosol Fe solubilities on the order of 5-10%; significantly higher than many global models have assumed. The solubility of Fe and Al in rainfall collected in the open Gulf of Mexico ranged from 20-70%, also much higher than is usually assumed.

GEOC 89: Reductive immobilization of uranium(VI) at the oxide-water interface

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The capacity for dissimilatory metal-reducing bacteria (DMRB) to reduce U(VI) associated with Fe(III) oxide surfaces was examined with *Geobacter sulfurreducens* and a variety of synthetic and natural Fe(III) oxides. Our results demonstrate that DMRB can reduce U(VI) associated with Fe(III) oxide surfaces, whereas surface-bound biogenic Fe(II) did not catalyze extensive abiotic U(VI) reduction. The rate and extent of U(VI) reduction was influenced by the nature of the Fe(III) oxide substrate. U(VI) reduction was slower and less extensive in Fe(III) oxide-

bearing coastal plain subsurface sediments relative to synthetic oxides. Catalytic quantities of the electron-shuttling agent AQDS led to more rapid and extensive U(VI) reduction in these materials, which suggests that sorption of U(VI) to enzymatically inaccessible surface sites can account for the observed inhibition of U(VI) reduction. Our results indicate that enzymatic reduction of sorbed U(VI) is likely to be a primary mechanism for reductive immobilization of U(VI) in anaerobic sediments.

GEOC 90: Reactivity of surface Fe(II) bound to iron oxides

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Fe(II) associated with iron mineral surfaces is known to facilitate reduction of a wide range of environmental contaminants. The mechanism of Fe(II)-mineral catalysis, however, is unclear. The focus of this study is to determine how the availability of Fe(II) in conjunction with iron mineral surfaces affects rates of contaminant reduction. To probe what factors control the reactivity of iron minerals, we are studying the reduction of nitrite by Fe(II) adsorbed to lepidocrocite in batch reactors.

Data thus far shows that nitrite is removed in the presence of both Fe(II) and lepidocrocite, but is negligible with either alone. The primary product is nitrous oxide. The concentration of dissolved and adsorbed Fe(II) seems to play an important role in the rate of nitrite reduction, and preliminary data suggests that Fe(II) regeneration of the mineral surface may be a significant rate-determining factor.

GEOC 91: Effects of pH on boric acid bonding mechanisms onto hydrous ferric oxide

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Boron is an important micronutrient at trace levels, but high B levels in soils and waters are often responsible for toxicity effects. It is therefore important to understand reactions that may affect B availability in soils. In this study, Attenuated Total Reflectance Fourier transform Infrared (ATR-FTIR) spectroscopy was employed to investigate mechanisms of boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$) adsorption on hydrous ferric oxide (HFO). It was found that boric acid adsorbs via both physical adsorption (outer-sphere) and ligand exchange (inner-sphere) reactions, and that boric acid is the preferred form of boron at the HFO surface under all conditions studied. Both trigonal and tetrahedral boron are seen at the HFO surface, and a mechanism where boric acid reacts to form either trigonal or tetrahedral surface complexes was proposed. The presence of outer-sphere boric acid complexes has important implications for boron transport and availability. Since physically-bound boric acid can be readily leached, it can be expected to move with water flow in soils. Outer-sphere boron would also be expected to be more available for plant uptake than more strongly bound boron complexes because it should more readily return to the soil solution when concentrations in the bulk decrease.

GEOC 92: Characterization and reactivity of nanoparticulate goethite

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Of the many nanoscale mineral phases present in the environment, iron (oxy)hydroxides (ferrihydrite, goethite) are among the most common and most reactive in terms of metal contaminant uptake. However, in natural aqueous systems nanoparticles aggregate to form a wide distribution of particle sizes ranging from several nanometers to microns. To study the effects of particle size on metal uptake, a series of goethite batches was synthesized with discrete particle size ranges varying from micron length to the nanoscale and characterized by BET surface area analysis, laser light scattering, TEM, and XRD. The differently-sized goethites were then used in batch uptake experiments with Cd(II), Cu(II), Hg(II), and Zn(II), metal contaminants frequently associated with acid mine drainage systems. Selected sorption products were analyzed with EXAFS spectroscopy to investigate potential changes in the mode of metal uptake and the degree of total uptake as a function of particle size, particularly in the nanoscale region.

GEOC 93: Catalytic reduction of nitrite and nitrate by formate vs H₂: Flow-through column investigation

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Catalytic reduction of nitrate has been reported in recent years only with bimetallic Pd catalysts (example, Pd-Cu) for its potential application in the treatment of drinking water impacted with nitrate above the regulated level. In this investigation, nitrate reduction is reported with monometallic Pd catalyst in a bench-scale flow through column reactor. Further, a comparison of kinetics of nitrate/nitrite reduction with gaseous H₂ vs. formate as reductant is presented. The parameters affecting the reaction kinetics include: influent pH, nitrate and formate concentrations, and buffering by dissolved CO₂. The kinetics of nitrate and nitrite reduction at the experimental conditions investigated can be modeled using Michaelis-Menton kinetics. The application of formate as a reductant instead of H₂ minimizes catalyst deactivation and manifests a higher activity for nitrate removal due to an in situ buffering effect. Formate appears to be a superior reductant in terms of reduced catalyst deactivation, increased nitrate removal and improved operational safety for field applications.

GEOC 94: An exploratory geochemistry summer research program: Creating opportunities for underrepresented high school students and their teachers

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During the summer of 2002, students from Scotlandville Magnet High School in Baton Rouge, LA spent six weeks actively involved in geochemistry research at Colby College in central Maine. The students participated in both field and laboratory based research investigating the redox cycling of reactive oxygen species in the surface waters of Maine lakes. Unique to this program was the participation of the student's high school chemistry teacher. The high school teacher mentored students before the summer experience, provided logistical support during the summer, and has expanded on the experience using an advanced chemistry course that the students are currently taking as seniors. Details of the program logistics and assessment results will be presented.

GEOC 95: Multi-isotopic approach as analytical tool to assess the geographical origin of foodstuff and commercial frauds

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The application of stable isotope ratio principles to food science allows the detection of origin, treatment and adulteration of foodstuff.

EU officially adopted isotopic ratio techniques as a tool since more than 10 years. D-NMR and 18O/16O IRMS are used in wine analysis. In 2001, the measurement of 13C/12C isotopic ratios of ethanol from wine by IRMS has been accepted as an OIV Resolution prior to its adoption in EC legislation.

Also in industrial fruit juices production, the Comité Européen de Normalisation - Technical Commission 174 (CEN/TC 174) introduced 13C/12C of sugars, 18O/16O of water and hydrogen isotope ratio 2H/1H of water from fruit juices as routine control analysis.

The AOAC International (Association of Official Analytical Chemists - USA) adopted measurements of stable isotope to detect watering and sugaring of fruit juices and sugaring of honeys.

In this research we present some examples of multi-parametric isotope ratio analysis on different food matrix in the attempt to identify future possibilities and limitation of the technique.

GEOC 96: Structural and proteomic characterization of coral reef organisms

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It has only been within the last 20 years that corals and associated salt water organisms have been successfully grown in captivity for extended periods of time. Coral reef aquaria present scientists with the opportunity to study the coral reef ecosystem in a controlled environment. In recent years a public aquarium exhibit has been established on the Penn State campus. Included in this display is a 500 gallon coral reef tank. The use of this public aquarium for research purposes allows for the investigation of tropical marine systems to take place in a location

otherwise inhibited by its geographic location. Optical microscopy, scanning electron microscopy (SEM), and x-ray tomography imaging were used to image and characterize the macroscopic and microscopic features of several coral skeletons. In addition, mass spectrometry has been used to identify and characterize novel proteins from the marine algae *Bryopsis plumosa*. Of particular interest are proteins which may be involved in iron sequestration from seawater. Iron sequestration in marine organisms has been shown to play a major role in governing phenomena such as the rate of phytoplankton growth and ultimately the sequestration of atmospheric carbon dioxide via marine productivity.

GEOC 97: Porphyrins occurring in ancient deposits of Siberia

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Presented are the results on the study of the distribution of porphyrins presented in oil shales, bituminous argillites and carbonates, asphalts, asphaltites and oils occurring in Cambrian, Neo- and Mesoproterozoic deposits of the Siberian Platform. Pigments occurring in Mesoproterozoic carbonates are presented by chlorines. Neoproterozoic argillites contain VO-porphyrins. VO-porphyrins in asphalts of the same age are presented by two homologue series of DPEP and ETIO types, where the latter predominates with maximal content of C29 ETIO. Among DPEP homologues the contents of "odd" compounds C31, C33 and C35 are increased. The compositions of VO-porphyrins in oils and asphaltite recovered from Early Lower Cambrian deposits are nearly similar to that of asphalts of Neoproterozoic age. But among DPEP porphyrins compounds C32 and C35 predominate. The traces of nickel complexes were registered in oils. DPEP homologues significantly prevail among porphyrins in Lower-Middle Cambrian oil shales, where C30-C32 compounds are found in maximal concentrations.

GEOC 98: Compound-specific isotope tracing of organic compounds from dung in temperate grassland soil

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The majority of organic material in soils originates from plant litter, and its fate has been studied extensively. In grazed systems a significant amount of carbon is introduced to the soil from dung. The contribution from dung to soil carbon has been explored using natural ^{13}C abundance tracer techniques. This study traces the fate of plant-derived organic marker compounds from two types of ensiled cattle fodder (C3 *Lolium perenne* and C4 *Zea mays*) from preingestion, to dung after rumination, and then into the surface horizons of a C3 grassland soil. A combination of analytical chemical techniques, including GC, GC-MS and IRMS (including bulk and compound-specific methods) will be used to investigate the molecular nature and turnover dynamics of the carbon inputs from fodder, to dung, into surface soil horizons.

GEOC 99: Effects of added organic matter quality on soil properties: Dynamics of carbon and structural stability along the decomposition

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In many agricultural soils, the intensification of practices led to a decrease of soil structural stability and organic matter content in the same time. The soil organic matter is an important factor of aggregate stability under many pedoclimatic conditions. The object of our study was to observe dynamics of carbon and structural stability in the soil depending on the initial characteristics of the added organic matter. Experimental design consists in an incubation under controlled conditions of three different organic matter (cauliflower residues, straw and cattle manure) in a vegetable cropping system soil. Initial quality of the added organic matter was characterised by the C to N ratio and the Van Soest fractionation (Van Soest, 1972). Several parameters were followed during the decomposition : the quantity of mineralised carbon, the microbial biomass, the fungi biomass, the water and acid extractable polysaccharides concentrations, the C in physical fractions and the aggregate stability through the test of Le Bissonnais (1997). First results show that the large range of decomposition dynamics, due to the quality differences of the added organic matter, caused important modifications of the aggregate stability. When the cauliflower residues were decomposing rapidly, inducing a high but transient increase of the stability, the decomposition of the straw was slower but much more efficient to develop a middle-term stability. Those results suggest that initial quality of the added organic matter could be a good parameter to take into account, in order to rehabilitate soil quality

GEOC 100: Molecular analysis of the biodegradation effects on the organic content of four sewage sludges of various origins

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One phase of experiment was carried out on samples of sewage sludges from different origins (one paper-mill-PM1, one food processing-FP1 and two domestic sludges U1 and U10). Samples were incubated under aerobic conditions in the dark at 24°C with a nutritive solution. Total content of the flasks were extracted and analysed on days 0, 30, 60, 100 and 140.

The analysis of the evolution of the organic composition of all the samples evidenced a decrease in the relative abundance of the amount of IOF (insoluble organic fraction). It goes with an increase in the SOF (soluble organic fraction) content in samples U10 and PM1, and a decrease in samples FP1 and U1. These observations suggest a degradation of the macromolecular structure of the IOF, which leads to the genesis of extractable compounds. These latter will then either be degraded in their turn to form new metabolites, or produce CO₂. This study allowed to define molecular indexes of the level of biodegradation.

GEOC 101: Formation and structure of humic substances in composted municipal solid wastes

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Municipal solid waste compost was collected over a period of three months from Seville, Ohio. Bulk compost was analyzed using solid-state NMR and demonstrated little change over the time series with the exception of a slight reduction of signal within the alkane region. The humic acid, extracted using IHSS protocols, yielded two different types of material with distinct differences in appearance and chemical characteristics. NMR spectra of the darker, heavier material display an enrichment in alkane and carboxyl functionalities. The material lighter in color and mass is shown by NMR to possess a lower signature for alkanes while being enriched in carbohydrates. Although NMR spectra of the two materials differ, each material maintains a relatively consistent spectrum throughout the time series of samples, indicating little net change in compound functionalities during composting. Initial pyrolysis-GC/MS data supports the NMR findings, indicating the lighter material is enriched with carbohydrate derived compounds.

GEOC 102: Carbon sequestration and carbon cycling processes in agricultural ecosystems

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Agricultural soils may help decrease global warming by removing greenhouse gases from the atmosphere and sequestering them as soil organic matter. Currently, little is known about the carbon structural types, quantity or quality preserved by the various currently employed agricultural management practices.

Soil samples from several depths and various organic matter inputs were collected from agricultural soils that had management practices of no-tillage, conventional tillage, transition from conventional to organic, and long term organic. Samples were characterized using elemental analysis, solid-state ¹³C NMR, pyrolysis GC/MS and TMAH thermochemolysis GC/MS after appropriate sample preparation.

¹³C NMR spectra from all samples contain signals associated with paraffinic (0-45ppm), carbohydrate (60-90ppm), aromatic (110-160ppm) and carboxyl (160-190ppm) structures. NMR spectra of soil inputs are dominated by carbohydrate carbons, while these intensities are severely diminished in the soil. Preliminary elemental and NMR results suggest increased carbohydrate carbon quantities in soils subjected to long-term organic practices relative to conventional.

GEOC 103: Variation in lipid abundance and composition among different particle-size fractions of a forest and a cropped soil

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Molecular studies on soil lipids are relatively scarce although they represent 1 to 5% of the soil organic matter (OM) and may act as clues for its origin and preservation mechanisms. We examined the abundance and chemical composition of the lipids from three fractions (sand, silt, clay)

of a forest soil A horizon. Indeed, differences in bulk chemical composition and turnover were reported for OM in the different particle-size fractions of a given soil. Our results indicate that lipids represent 5% of the soil OM and preferential location in the clay fraction. GC-MS analysis of the lipids from the silty and clayey fractions point to strong similarities whilst lipids of the sandy fraction show striking differences. The chemical composition of these lipids reveals differential preservation according to particle-size. A similar study under progress on an adjacent soil cropped with maize for 22 years should yield the turnover of these lipids.

GEOC 104 : Water repellency of sandy soils: The role of hydrophobic organic compounds

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Both wettable and non-wettable soils contain hydrophobic organic materials such as: alkanes; fatty acids and amides; aldehydes/ketones; sterols. Compounds capable of causing water repellency when reapplied to acid washed sand can be Soxhlet extracted from both types of soil using an isopropanol and aqueous ammonia (7:3 v:v) mixture. This study aims to determine what differences in the amount and composition of these compounds distinguishes soils which are water repellent from those which are wettable. We present the results of Gas Chromatography (GC) and Gas Chromatography – Mass Spectrometry (GC-MS) of extracts from a wide range of wettable and non-wettable sandy soils, from five countries, under different types of vegetation. Preliminary results suggest two major differences: (i) if samples of similar origin are compared, water repellent samples generally, but not always, contain more organic material; (ii) they contain high relative molecular mass polar compounds, which are almost absent from wettable samples.

GEOC 105: Dynamics of N exchange between corn (*Zea mays* L.) roots and soil microbes

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Organic N released in soil by roots is mineralized by microbes to be recycled in roots. The dynamics of this N mineralization-immobilization turnover between corn roots and microbes was quantified by the model NCSWAP/NCISOIL with data from corn field plots. The kinetics of inorganic N-15 in the 0- to 15- and 15- to 30-cm soil layers and organic N-15 in the above-ground corn was documented for 10 years of continuous corn fertilized with 20 and 200 kg NH₄⁺-N ha⁻¹ enriched with 8.0 kg N-15 ha⁻¹ (40.0 and 4.0 atom% N-15, respectively). N-15 was added for 5 consecutive years, then stopped to obtain relaxation kinetics. Residues were not returned to allow full impact of roots and root exudation on the system's dynamics. The experimental and simulated kinetics are presented. Gross and net rates of the processes underlying these kinetics are discussed.

GEOC 106: In situ chemical analysis of ancient microfossils with STXM

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In this presentation we explore the application of synchrotron based soft X-ray microscopy and imaging to the analysis of organic chemistry recorded in ancient (up to 400 million year old) fossils. Chemical analysis is based the spectroscopic information available from carbon 1s absorption near edge spectroscopy. C-XANES spans the energy range from ca. 284 to 305 eV. Chemical information is linked to sub-micron anatomical structure by virtue of X-ray microfocusing capabilities (on the order of 30 nm X-ray spot size) and precision monochromators (energy resolution on the order of 0.01 eV). Exploiting the unique capability of scanning transmission X-ray microscopy (STXM); we have established that *Asteroxylon* (an ancient vascular plant that appeared very early in phylogeny of vascular plants) had chemically differentiated cell walls indicating that lignin biosynthesis occurred extremely early in the history of vascular plants. Other examples of ancient fossils will also be presented.

GEOC 107: New analytical methodology for investigating both volatile and nonvolatile constituents from archaeological ceramic vessels

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The study of the amorphous organic remains discovered on archaeological sites mainly relies on the analysis of the volatile molecular constituents from their total lipid extract by GC/MS. Although these constituents provide useful information about a set of lipidic substances, one must note that a fraction of the organic matter preserved is not volatile enough to be studied by this method. With the aim to enlarge the possibility of identifying a larger range of natural substances exploited through time, we combined different mass spectrometric methods, including HT-GC/MS for volatile constituents, ESI-MS/MS for non volatile soluble components and TMAH-Py-GC/MS in the case of materials presenting a high degree of polymerization. From an archaeological standpoint, this set of methods was shown to be a powerful tool for understanding the role of pottery for resinated wine transport, olive oil consumption, beeswax storage or adhesive making at various archaeological sites.

GEOC 108: Isolation of insect chitin for AMS radiocarbon dating and stable isotope analysis

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Chitin is a carbohydrate found mainly in insect exoskeletons, crustaceans and some species of fungus. Insects are often found in an archaeological context and obtaining accurate dates and isotope values can allow for study of ancient environments and seasonality. Because chitin in both modern and ancient insects is usually bound to or surrounded by other carbon-containing substances that may not be native to the insect, especially carbonate and protein, it is important to isolate the chitin in order to obtain accurate compound-specific AMS and isotope data. The technique of compound-specific analysis involves isolating a compound or set of compounds known to be indigenous to the artifact and then analyzing that specific substance, and it often results in more accurate radiocarbon dates and other analyses. Our methodology for isolating chitin and chitosan from insect exoskeletons for isotope studies and AMS determinations will be discussed.

GEOC 109: New approaches for understanding ancient proteins

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The key to success in recovering ancient biomolecules lies in the ability to identify samples with optimal preservation. We have applied matrix-assisted laser desorption-ionization mass spectrometry (MALDI-MS) to sequence modern and ancient osteocalcin and its diagenetic products from milligram quantities of bone. Sequences were obtained by peptide mass mapping and post-source decay analysis. Putative osteocalcin and/or its diagenetic products are indicated by their characteristic molecular weight by MALDI-MS and confirmed with immunological approaches from numerous bones between 800 yr BP and >53,000 yr BP. Exceptional preservation of osteocalcin is indicated by demonstrating that a portion of this protein remains after samples are heated to 100 degrees centigrade for 200 hours and that osteocalcin can be sequenced from >53,000 yr BP bones. We demonstrate how the MALDI-MS approach was applied and discuss the implications of this research in molecular paleontology.

GEOC 110: Primary structure of acidic shell matrix proteins from living bivalves: Primers of fossil peptides and amino acids

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We report the complete amino acid sequences of MSP-1, an acidic glycoprotein of the scallop shell matrix, and of an extremely acidic protein newly identified from pearl oyster shells. Both proteins are rich in Asp residues, representing 20% and 60% of MSP-1 and the pearl oyster protein, respectively. These highly enriched Asp sequences explain most of the amino acid compositions estimated for the soluble fraction of molluscan shell matrix of both living and fossil material, confirming that Asp-rich proteins indeed exist in the shell matrix as a major component. Both proteins show certain repeated structures, but the repeating motifs and overall structures differ considerably. These sequence variations suggest that preservation potential for each of those Asp-rich proteins might be different, and that they may be useful biological markers. MSP-1 and the pearl oyster protein are only yet known to be present in the calcitic shell layer. This fact implies that amino acid analysis of fossil material may lead to better constrained results when the calcitic and aragonitic shell layers are analyzed separately.

GEOC 111: Ancient protein sequences: A new direction for molecular paleontology

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For the first time, two genetically informative molecules have been sequenced from a fossil bone. In addition to mitochondrial DNA, this paper presents complete sequences for osteocalcin from bison bones >55,000 yr BP. Protein sequencing was achieved using matrix-assisted laser desorption ionization mass spectrometry following careful purification. Like DNA, protein sequences contain fundamental genetic information crucial to phylogenetic reconstruction, demonstrated here by a 129 mass unit difference between modern cow osteocalcin and the fossil bison osteocalcin sequence. Owing to its association with bone mineral, osteocalcin has demonstrated a marked stability in the laboratory and in immunological assays on fossils. The suggestion that proteins may be preserved in fossils longer than DNA, hints at the possibility of extending the genetic record farther back in time. Additional results from bison fossils between 47,000 and 500,000 yr BP from temperate environments demonstrate the potential for osteocalcin to survive in the geological record.

GEOC 112: Proteomics methodology for protein identification in ancient art and archaeological samples

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The study of proteins in cultural heritage is an analytical challenge for many reasons : samples in tiny amounts, proteins encased in a complex media and modified by ageing and other conditions. Different non-destructive techniques (staining techniques^{1,2,3} or immunofluorescence⁴, HPLC or GC^{5,6}, GC-pyrolysis-MS⁷, FT-IR spectroscopy⁸ or Raman spectroscopy⁹) to characterize/analyze proteins were developed but doesn't allow quantification/identification of proteins. Here, we present a strategy for identifying proteins in different type of art and archaeological samples by proteomics methodology. "Proteomics" lead to the identification/quantification of proteins expressed in a cell/tissue by a set of complementary techniques (electrophoresis, mass spectrometry, genomic database searching). We applied this approach first to proteinaceous painting media. The first step was to find appropriate conditions for extracting proteins from the binding media, then to verify that proteomics approach is still efficient on the extracted material. Starting with a reconstituted painting (egg white/yolk), we identified major and minors proteins. This methodology applied to art painting samples (Niccolo di Pietro Gerini's painting "The Virgin and Child" (XIVth century) and Benedetto Bonfigli's triptych "The Virgin and Child, St John the Baptist, St Sebastian"), will open new perspectives in analysis of ancient archaeological remains.

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GEOC 113: A molecular and stable isotope assessment of land use influences on organic carbon export from a mixed land use watershed, Big Pine Creek, IN

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To gain insight into the influence of land use and hydrology on organic carbon export from agricultural land, we have initiated a molecular and stable carbon isotope study of dissolved, colloidal and particulate organic matter collected monthly and during storm events from multiple locations in Big Pine Creek watershed, a mixed land use watershed located in West-Central Indiana. The watershed is predominantly a corn-soy rotation row crop system with increasing proportions of forested land at its confluence with the Wabash River. Water samples were separated into coarse particulate organic matter, colloidal organic matter, and dissolved organic matter with glass fiber filters and cross flow ultrafiltration. The organic matter from these samples is being characterized by molecular and stable isotope techniques to determine regional and botanical

source using lignin oxidation products from cupric oxide oxidation. Ongoing analysis will investigate how differences in land use and/or land management practices may influence the extent and nature of carbon export from terrestrial systems.

GEOC 114: Isotopic tracers of nitrogen cycling in rivers and streams of the Peruvian Andes

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The Eastern Cordillera of the Peruvian Andes is a major source of organic matter, particulates, and nutrients in the Amazon River. Small scale studies of nitrogen cycling in these tropical forests and streams show very low levels of inorganic nitrogen and tight internal cycling of nitrogen. A stream tracer experiment with ¹⁵N-labeled ammonium chloride indicated that there is a large demand for reduced nitrogen in these streams, with almost 100% of all added nitrogen sorbed onto particulates within four days of the initial injection. Natural abundance isotope analyses conducted on adjacent streams, one deforested and one pristine, indicate a pervasive deforestation effect; both aquatic plants and stream particulates are less enriched in the pristine stream by 1 to 2 permil over the deforested stream. Other regional studies of natural ¹⁵N abundance in rivers and riparian zones are also underway in an attempt to constrain nitrogen loadings from the Andes to the lower Amazon.

GEOC 115: Mechanisms of carbon transfer to upland Andean river systems

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Tropical river systems draining mountain systems are thought to provide a significant source of organic and inorganic materials to associated lowland rivers, estuaries and deltas. Given the high suspended particulate levels found in these rivers, most river borne carbon has been thought to be derived from soil erosion. However, the nature of carbon sources to these rivers has been little studied. A detailed isotopic investigation of carbon sources and diagenesis in the central Andes has revealed that carbon can be partitioned into two sources: relatively fresh material with ¹³C signatures similar to freshly produced organic material (e.g. leaf litter), and highly degraded soil carbon with a very enriched ¹³C signature. Carbon transport in small streams at low flow conditions is dominated by fresh material, however the larger stream systems and rivers are dominated by transport of soil carbon generated by major erosional events (i.e. landslides). The transition to lowland river systems is marked by an apparent increase in the percentage of fresh material transferred to streams and rivers.

GEOC 116: Sources and extent of alteration of aquatic humic substances from individual molecular formulas

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High-field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry combined with Electrospray Ionization (ESI FT-ICR MS) is currently the only technique capable of fully resolving individual molecules in complex humic and fulvic acid mixtures. Resolution of the components of these mixtures within a one Dalton mass window has revealed that what appeared to be single peaks at every mass unit in lower resolution mass spectra are actually collections of multiple ions separated by as little as 0.0364 Dalton. The ultra-high resolution FT-ICR mass spectra also revealed the presence of molecular families containing ions that differ from each other in degree of saturation, functional group substitution (primarily -CH₂- vs. -NH- and -CH₄- vs. -O-), and number of -CH₂- groups (see figure). This compositional information along with the high mass accuracy provided by high-field (9.4 Tesla) FT-ICR MS make possible the identification of molecular formulas of essentially all humic and fulvic acid molecules between 300 and 1100 Dalton. Surprisingly, this data suggest that aquatic humic and fulvic acid mixtures, while extremely complex, nevertheless exhibit a high degree of order with an almost polymeric character. In this presentation we will demonstrate how molecular formulas of aquatic humic mixtures can be sorted to reveal differences in source material, biogenic alteration, and extent of photolytic alteration.

GEOC 117: Sources, composition, and fate of suspended particulate organic carbon of a small mountainous river

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We investigated the sources and fate of suspended particulate organic carbon (POC) of the Santa Clara River, a small mountainous river in CA, USA, to evaluate the efficiency of fossil-carbon export to adjacent shelf muds. Natural abundances of ^{13}C and ^{14}C were determined in bulk and biochemical fractions of POC to identify end-member sources of POC to the river suspended load, as well as to assess the extent of preservation of riverine POC in coastal marine sediments. Examination of POC isotopic values during the winter of 1997-98 indicated that, on average, 50 % of the POC suspended in the Santa Clara River was shale-derived, while the remainder originated from surface soils. Further analyses of sedimentary POC collected near the Santa Barbara Basin revealed deposition and burial of riverine POC in the shelf; shale-derived carbon appears to be concentrated in solvent-extractable fraction of the bulk POC.

GEOC 118: Provenance and/or process recorded in extraterrestrial organic solids

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The organic matter in primitive chondritic meteorites retains a record of chemical processes that initiated in the cold interstellar medium and presumably continued during the early history of the Solar Nebula. The vast majority (70-90 %) of organic carbon in chondritic meteorites is insoluble greatly complicating analysis. We have applied a number of different solid state NMR experiments (^1H and ^{13}C) designed to provide a self-consistent description of this material in terms of the distributions of carbon containing functional groups. We have studied eight meteorites spanning a broad range of petrographic types and compositional groups. All of the meteorites studied so far exhibit complex chemical structure, furthermore enormous variation in the distribution of various functional groups exists between meteorites representative of different compositional groups. We explore whether there is modification of the organic matter with parent body processing as well as correlation with isotopic and bulk composition.

GEOC 119: Ancient microbial signatures and the ecology of the Archean world

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We are evaluating the molecular constituents of several diamond-drill cores of late Archean (2.8 - 2.6 Ga) shales and carbonates in the Hamersley Basin of Western Australia. The larger goals of this work include documenting molecular signatures of microbial constituents of the ecology of the ancient Earth. Previous work has established inputs from cyanobacteria, possible inputs from eukaryotic life, while extreme carbon-isotope depletion in total organic carbon suggests an active methane cycle during this time. Our work documents contributions from all three domains of life (Bacteria, Archea and Eukaryotes) as recorded by specific lipid signatures, including methane-oxidizing and sulfur-cycling bacteria. In addition, we have subjected samples to hydropyrolysis (heating under elevated H_2 pressures) in order to compare free lipids with components bound within the kerogen matrix. Sequential heating and subsequent extraction of compounds provides several lines of evidence supporting an interpretation that the free biomarker compounds are indigenous.

GEOC 120: Dynamics of soil organic molecules

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Our understanding of the behavior of organic substances in complex, natural media has been limited for a long time due to the lack of analytical methods that allow measuring the stable isotopic composition of individual organic substances. After 1980, the development of compound specific isotope analysis (CSIA) by the team of John Hayes at the University of Indiana (1) has rapidly fostered novel research investigations in Geochemistry, Biology, Archaeology, Medicine, Food Science, Sport Science, and other fields (2). Here, examples of the application of CSIA to study the dynamics of soil organic molecules will be presented. References: 1. Matthews and Hayes, Anal. Chem. 50, 1465, 1978; Hayes et al. Org. Geochem. 16, 1115, 1990. 2. Lichtfouse, Rapid Commun. Mass Spectrom. 14, 1337, 2000.

GEOC 121: Forensic applications of multiple stable isotope analyses

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Multiple stable isotope analyses of organic and inorganic compounds are providing insights into the "geo-location" of materials of forensic interest. In this presentation, we discuss how environmental parameters get recorded and how isotopic abundances can be used to derive information about the origins of illicit drugs, explosives, and microbes that are associated with terrorist threats.

GEOC 122: Nature's scribes

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The symposium's title refers to molecular and isotopic indicators of natural processes. This presentation will focus on isotope effects as the authors of diverse signals from ancient and modern ecosystems. Variations in the natural abundance of carbon-13, particularly when measured in individual organic compounds, provide information about flows of carbon and trophic structure, about rates of algal growth and concentrations of dissolved carbon dioxide, about the origins of chemical fossils, and about the sources of carbon used by heterotrophic organisms. In sum, such investigative techniques have unified biogeochemistry and organic geochemistry, making the latter into a process-oriented science.

GEOC 123: Informative graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter: The van Krevelen diagram

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Electrospray ionization mass spectrometry (ESI-MS) is becoming an important tool to study natural organic matter (NOM) at a molecular level. Ultra-high resolution ESI-MS analyses of NOM often produce very complicated spectra. Because of the complexity, visualizing the spectrum and structural interpretations are difficult. To facilitate studying the mass spectra, we propose and demonstrate an approach that involves use of a van Krevelen plot. With this approach, complicated mass spectra can be visualized in a way that allows for 1) possible reaction pathways to be relatively easily identified and presented, and 2) qualitative analyses on major classes of compounds that comprise ultra-high resolution spectra. When combined with peak intensity data in a 3D plot, an evaluation of the relative significance of related compounds can be achieved.

GEOC 124: Probing structure-activity relationships in soil organic matter by combining time-dependent ¹³C NMR spectroscopy with inverse high-performance liquid chromatography

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Solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful methods currently available to probe the structure of condensed geochemical materials such as coals, sediments, and soils. We have combined the traditional solid state techniques (high-power decoupling, cross-polarization and magic angle spinning (CP/MAS)) with proton spin relaxation editing (PSRE) to determine the composition and spin lattice relaxation characteristics of low-carbon soils. These measurements were made possible by selective chemical treatments that concentrated soil organic matter without significantly affecting its composition.

Parallel studies of the sorptive characteristics of these soils were carried out by inverse High Performance Liquid Chromatography (HPLC). The Frontal Analysis by Characteristic Point (FACP) method was used to determine entire isotherms of solute probes from single chromatograms. In this presentation we will demonstrate how composition and spin relaxation information from NMR measurements can provide a molecular explanation for the observed sorptive properties of soil organic matter.

GEOC 125: Stochastic synthesis model for the evolution of natural organic matter

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The evolution of natural organic matter (NOM) in soils, beginning with well-defined biochemical precursors, is a complex process incorporating biochemical and abiotic reactions in a spatially heterogeneous mineral matrix. The resulting NOM mixture has emergent properties which are not readily derived from a knowledge of the precursor compounds. We have developed a stochastic simulation of the evolution of NOM, incorporating solution phase and mineral surface reactions and microbial processes in a simulated soil matrix. Individual pseudo-molecules, their transport through soil pore waters, adsorption to surfaces, various reactions, chemical and physical attributes and behaviors are simulated using the SWARM agent-based modeling tool. Preliminary results with only 10 reaction types have generated average elemental composition, molecular weight, and apparent 'aromaticity' data which are consistent with experimental data.

GEOC 126: Spectroscopic and macroscopic studies of the interactions between Suwannee River fulvic acid and mineral particle surfaces

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Fulvic acid is a major component of natural organic matter (NOM) and plays an important role in natural aquatic systems due to its ability to form strong complexes with pollutants and/or positively charged mineral particle surfaces. We determined the dominant types of interactions between SRFA and mineral particle surfaces (e.g., boehmite (g-AlOOH)) using in-situ ATR FTIR spectroscopy and macroscopic uptake measurements. FTIR spectral changes of aqueous and mineral bound SRFA were observed as the solution pH and GSRFA changed, and these observations were compared with those from our previous ATR-FTIR and quantum chemical studies of low molecular weight (LMW) organic compounds (e.g oxalate, malonate, phthalate and pyromellitate) sorbed on boehmite. The ATR-FTIR results show that the dominant type of interaction between SRFA and boehmite surfaces at pH=5.1 is outer-sphere complexation of SRFA through H-bonding of carboxylate functional groups with sites on boehmite surfaces.

GEOC 127: Electrochemical properties of natural organic matter

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Electrochemical methods offer the most direct approach to systematic characterization of the redox properties of natural organic matter (NOM), fractions of NOM, and model compounds for NOM or other putative biogeochemical electron shuttles. Although previous efforts have not yielded useful results, we have identified experimental conditions that give well-defined voltammograms for some fractions of NOM. Currently, we are extending this work on three fronts: (i) making our method more robust with more advanced electrode designs and instrumental waveforms, (ii) pursuing a more complete mechanistic understanding of what factors control electrode response in this system, and (iii) applying the method to a wider range of NOM samples for comparative analysis and ultimately generalization about biogeochemical processes such as diagenesis. Our latest results on all three of these fronts will be presented, as well as some implications of these results for the role of NOM in the fate of redox-active contaminants.

GEOC 128: X-Ray microscopy and C 1s NEXAFS studies of 3d metal interactions with humic acid

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Humic acids (HA) play an important role in the retention and mobility of metals in the environment. Despite extensive and important studies, the reactivity of HA towards metals is still not well understood. We used soft x-ray spectromicroscopy at beamline X1A1 of the National Synchrotron Light Source (NSLS) to simultaneously obtain physical (using scanning transmission x-ray microscopy, STXM) and chemical (using carbon-near edge x-ray absorption (C 1s NEXAFS) spectroscopy) information on metal-humic acid complexation in solution. Image stacks of a 0.1 g/L humic acid solution, reacted with a 0.5 mM (3d) metal solution at pH 5.0 were collected. Using principal component analysis, NEXAFS spectra were extracted (0.05 eV resolution), from regions of interest in the image stacks. Our results show shifts in intensity and position of the dominating carboxylic and phenolic peaks upon metal reaction, which can be related to electron density shifts between metal and carbon in the HA functional groups.

GEOC 129: A study of organo-copper complexes in soils by thin layer chromatography

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Copper salts are widely used as fungicide for the protection of agricultural crops, e. g. tomato and grape, against various plant pathogens such as mildew (*Plasmopara viticola*). This practice leads to the accumulation of large quantities of copper in soils, reaching up to 1000 mg Cu per Kg in vineyard soils. Despite numerous studies showing that copper is strongly linked to soil organic matter, the molecular interactions between copper ions and soil organic molecules are not well understood. This gap of knowledge stems mainly from the lack of analytical approaches enabling the characterization of organo-copper complexes in natural media. Here, we present a preliminary investigation of soil organo-copper complexes by thin layer chromatography.

GEOC 130: Grotte Chauvet (Ardèche, France): A natural experiment for bone diagenesis in karstic context

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Grotte Chauvet is famous internationally since 1995, with the discovery of the oldest cave paintings in the world. The cave floor is also littered with bones, mainly from cave bear, which present very variable macroscopical stage of preservation, from apparently pristine to a mere bone powder. About 100 bone fragments have been collected in most parts of the cave for biogeochemical investigation, i.e. carbon and nitrogen content, X-ray diffraction, isotopic analysis (¹³C, ¹⁵N) of collagen as well as isotopic analysis (¹³C, ¹⁸O) of bone and exogenous carbonates. Bone stage of preservation is not randomly scattered in the cave and it seems to depend on local environmental conditions. Grotte Chauvet yields an interesting case of "natural experiment" to study bone diagenesis in karstic conditions.

GEOC 131 Twilight zone of the fossilization process

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Intact biomolecules give way to fragmented, remnant pieces of organic matter in the process of fossilization. For the bulk of vertebrate fossil record, the transition from the biosphere to the geosphere is a complicated journey. Recent evidence suggests that the rapid changes occurring in most bones and teeth immediately after death continues for a substantial, but limited time period. During this postdeath interval, environmental evidence from the surrounding ecosystem may become locked in. The organic matter from collagen-free subfossil bone is an extremely complex mixture of compounds that is heterogeneous not only in structure, but also in isotopic composition. This presentation will discuss the partial chemical characterization of these isotopically distinct fractions from subfossilized bone, and suggest which fractions may be most useful in past ecosystem reconstruction.

GEOC 132: Diagenesis in the lab: Incubation of modern bone and enamel apatite under controlled conditions

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We present the results of the first experiments designed to examine the effects of both inorganically and microbially-mediated reactions on carbon and oxygen isotope compositions of modern bone and enamel apatite during early diagenesis. Unlike previous published experimental protocols that involved heating or acid etching to promote a rapid but very aggressive alteration of the apatites, we chose to simulate natural conditions by measuring labelled isotopic exchange between apatites and water-saturated natural soils. Experimental results are discussed regarding the current opinions on diagenetic alteration of biogenic apatites, with emphasis on: (1) the efficiency of acid pre-treatments for removing contaminants such as secondary carbonate, (2) the kinetics of oxygen and carbon isotope exchange between apatite and aqueous fluids under inorganic conditions and in the presence of micro-organisms, (3) the reliability of enamel isotopic compositions as proxies of past environments.

GEOC 133: Fossil tooth enamel: A method to detect, quantify, and correct the effects of diagenesis on stable oxygen isotopes

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This study represents the first attempt to describe and to model the effects of diagenesis on oxygen isotope compositions of fossil enamel. First, we demonstrate that current tests designed to evaluate the effects of apatite diagenesis are not adapted to detect any process of isotopic alteration of enamel. Then, we propose a set of mass balance equations to quantify oxygen isotope offsets resulting from diagenetic alteration that are recorded in carbonate and phosphate apatite. These equations may be applied successfully when combined with intra-tooth sampling and oxygen isotope analyses of hypsodont teeth. Our method is applied to two case studies in Chad and Afghanistan and reveals that the mode (microbially-mediated versus inorganic) and intensity of isotopic alteration of carbonate and phosphate of apatite is highly variable. Mass balance calculations indicate that the impact of diagenesis could be as high as 3 ‰ in some enamel samples and is also responsible for a decrease in intra-individual variations up to 1 ‰. The reconstitution of large temporal- or spatial-scale paleoclimates based on $\delta^{18}\text{O}_\text{p}$ analyses cannot be considered as valid so far if enamel has been affected by microbial activity.

GEOC 134: Sulfur isotopes in ancient proteins

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Recent advances in continuous flow mass spectrometry now permit the measurement of sulphur isotopes in low sulphur content organics. In this paper I will summarise the utility of measuring sulphur isotopes in ancient proteins (especially bone collagen and hair keratin), particularly for reconstructing past human and animal diets and migrations. Results from modern feeding experiments as well as archaeological and palaeontological samples will be presented.

GEOC 135: Development of new models for dietary reconstruction based on bulk and compound specific $\delta^{13}\text{C}$ analysis of diet and consumer tissues

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Mathematical modelling of the bulk and compound-specific $\delta^{13}\text{C}$ values of tissues from rats and pigs subjected to isotopically-controlled feeding experiments demonstrated similar linear correlations between dietary and bone components, however conflicting absolute values were observed. We hypothesize that this discrepancy is a result of fundamental metabolic differences between different species of animal. In order to investigate how different digestive physiologies and metabolisms affect specific diet-to-tissue fractionations, a pilot study was undertaken combining both bulk and compound specific $\delta^{13}\text{C}$ measurements of tissues from a program of controlled animal feeding experiments using ruminant and monogastric species. The careful selection of a sufficiently comprehensive range of tissues (bone, adipose tissue, muscle, skin, liver, kidney, spleen, blood, breath CO_2 , faeces, urine, methane and stomach/digestive tract contents) allowed mathematical modelling of the isotopic relationship between diet and consumer tissues at the bulk and molecular level.

GEOC 136: Effects of hydrolysis on the d13C values of individual amino acids derived from polypeptides and proteins

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This study investigates the effects of hydrolysis on the d13C values of individual amino acids (IAAs) derived from modern and ancient bone collagen. All IAAs were derivatised to their trifluoroacetyl/isopropyl esters for d13C determination using gas chromatography/combustion/isotope ratio mass spectrometry. Modern rat (MBCs; n=20) and ancient ovi-caprine and bovine (ABCs; n=27) bone collagen samples were studied where the d13C value of twelve out of its eighteen constituent amino acids were determined. Estimated bulk MBC and ABC d13C values were calculated from constituent amino acid d13C values using mass balance. Calculated bulk bone collagen d13C values were shown to correlate extremely well with measured bone collagen values for both modern and ancient samples, where R²=0.91 and 0.84, respectively. These results demonstrate that the experimental procedures employed in the acid hydrolytic cleavage of peptides or proteins to their constituent amino acids does not involve significant isotopic fractionation.

GEOC 137: Unraveling the stable carbon isotope signature of bone collagen

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The d13C values of individual amino acids from the bone collagen of rats raised on isotopically and nutritionally defined diets were determined to investigate the dietary macronutrients utilised in the synthesis of bone protein. Compound specific d13C values were obtained using gas chromatography/combustion/isotope ratio mass spectrometry of amino acids as their trifluoroacetyl/isopropyl ester derivatives. The essential amino acids were shown to be directly routed from dietary protein to collagen with only a small isotopic fractionation (ecollAA-dietAA ca. 2-3‰), believed to result from assimilation and transport processes. By comparison, the d13C values of the non-essential amino acids were shown to incorporate up to ca. 90% of the carbon from the non-protein or energy macronutrients of the diet. This study reveals for the first time on a molecular level how different dietary macronutrients are utilised in the synthesis of specific building block amino acids in bone collagen.

GEOC 138: Geochemical classification of crude oils

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Crude oils vary widely in many relevant properties. However, closer analysis reveals that many of these properties are fundamentally and naturally related. Statistical analysis of a very large collection of crude oil assays suggest that crude oils can be classified according to geochemical concepts. A 3-D classification system has been developed which uses permutations of simple crude properties to define the position of a single crude in a universe of all potential crude oils. It has been found that practically all crude oils can be grouped in statistically significant clusters in this 3-D universe. The position of these clusters and the observed trends are highly correlated with the geochemical concepts of kerogen type, chemical type and maturity. Many crude properties vary in logical and expected ways when viewed in this framework. Both physical properties and processing behaviour of new crudes can be predicted once their position in the classification system has been determined. The advantages of this approach will be illustrated by several examples from the downstream business: a) prediction of crude oil properties on the basis of very limited data (crude oil selection and valuation) b) understanding the chemistry of heavy oil components, including compatibility of asphaltenes in blends c) identification and abatement of nuisance properties (e.g. fouling and corrosion)

GEOC 139: Asphaltene solubility and aggregation

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Asphaltenes are the toluene-soluble, heptane or pentane-insoluble fraction of petroleum fluids. Asphaltenes are recognized to be remarkably polydisperse in polarity, aromaticity, and chemical functionality, and yet have many universal features: they are strongly surface-active at both oil-water and oil-solid interfaces, they are marginally stable in solution and are prone to precipitation and deposition, and they aggregate strongly in solution. We have studied the solubility properties of asphaltenes from a variety of crude sources and used the fractional solubility of asphaltenes in model solvents as a means of separating asphaltenes into sub-fractions with markedly different properties. We present in this talk "distribution functions" of asphaltene properties based on this differential solubility method, as well as some of the aggregation properties as probed by small angle neutron scattering and vapor pressure osmometry. Our results clearly indicate that the molecular architecture of asphaltenes is one of open inter-connected aromatic rings, which helps to explain many of the more recent observations on asphaltenes, in contrast to the oft-cited "island" model in which asphaltenes are depicted as very large fused ring structures.

GEOC 140: Demulsifying asphaltene-stabilized emulsions in crude oils: The synergies between asphaltene stabilizers and demulsifier agents

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Asphaltenes are known to stabilize water-in-oil emulsions making it more difficult to demulsify and desalt crude oils. Insufficiently demulsified or desalted crude oil can lead to process upsets in the operation of desalters and separator vessels. Asphaltene stability and the methods used in predicting them have been correlated to the ease of demulsification. Three case studies are presented that show the effects of chemical demulsifiers used alone and in combination with asphaltene stabilizers on the efficiency of demulsification operations. The data shows that the asphaltene stabilizer-demulsifier combination does a better job at demulsifying crude oils with asphaltene stabilized emulsions than when demulsifiers are used alone. While the data shows the action of the asphaltene stabilizer-demulsifier combination is crude specific, a careful choice of such combinations through initial testing can go a long way at solving troublesome asphaltene stabilized emulsion problems in both refineries and oilfield production operations.

GEOC 141: Characterization of asphaltenes from chemical-treated oils

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Asphaltenes are typically defined by solubility as benzene soluble and pentane or heptane insoluble. The asphaltenes are believed to exist in the oil as a colloidal suspension, and are stabilized by resins adsorbed on their surface. These higher molecular weight components of crude oil are normally in equilibrium at reservoir condition. As crude oil is produced this equilibrium may be disrupted by a number of factors including pressure reductions, crude oil chemical composition changes, introduction of miscible gases and liquids, mixing with diluents and other oils, and during acid stimulation, hot oiling and other oilfield operations. The upset of the colloidal system may result in irreversible flocculation of asphaltenes. The deposition and precipitation of flocculated asphaltenes can severely reduce the permeability of the reservoir, cause formation damage and can also plug-up the wellbore and tubing.

Asphaltene inhibitors have been used to prevent asphaltene precipitation/deposition problems in the field. Study of asphaltenes precipitated with heptane from chemically treated crude oil and the untreated crude oil were undertaken in order to show main features, which differentiate them. The asphaltene samples are characterized by GPC, elemental analysis, ¹H and ¹³C NMR spectroscopy, metal content and total acid number. The results generated from this study hopefully will provide more insights on how the inhibitors interact with asphaltenes and thus lead to the development of the next generation asphaltene inhibitors.

GEOC 142: Methods for selecting asphaltene inhibitors and new insights into inhibitor mechanisms

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The stability of asphaltenes in petroleum crude oils and the crudes' propensity to precipitate and deposit asphaltenes were determined using four stability tests - the Asphaltenes-Resins Ratio; the Colloidal Instability Index; the Oliensis Spot Test and the Live Oil Depressurization Test.

Three tests used in selecting asphaltene inhibitors were then performed on the oils to determine which inhibitors inhibit asphaltene precipitation and deposition better. The tests - the heptane precipitation test, the asphaltene precipitation detection test, and the live oil deposition test -

were carried out at varying inhibitor concentration and with inhibitors of varying performance. The high-pressure live oil deposition test was found to predict the performance of the inhibitors better than the dead-oil heptane precipitation test and the asphaltene precipitation detection test. The live oil deposition test though is complex and expensive, mimics conditions in the wellbore better.

The inhibitor selection tests are discussed in detail including procedures, performance, reliability and cost benefits. Data will be presented to show how these tests explain the mechanisms of asphaltene inhibition and the behavior of asphaltene inhibitors. And how these tests can be used to distinguish an asphaltene inhibitor from an asphaltene dispersant.

GEOC 143: Potential of bound biomarkers released via hydropyrolysis for characterizing pyrobitumens and tar mats

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Hydropyrolysis (pyrolysis assisted by high hydrogen gas pressures) is an emerging technique that provides reliable bound biomarker profiles for severely biodegraded oils, contaminated cores and oil-field solids (tar mats and pyrobitumens) where the conventional free biomarker approach often fails. Hydropyrolysis tests on an extremely mature pyrobitumen (mean vitrinite reflectance greater than 2.0 and a carbon aromaticity of ca. 90%) have generated recognisable hopane and sterane profiles that matched closely those obtained for the extremely small quantity of residual bitumen present. Thus, it is reasonable to assume that the bitumen present was the precursor, via cross-linking reactions, of the largely DCM-insoluble pyrobitumen. Analysis of further pyrobitumens and a number of tar mats will be described to demonstrate how the information on the bound biomarkers released via hydropyrolysis facilitate correlations with oils and source rocks.

GEOC 144: Simple method for accurate determination of asphaltene precipitation

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A simple laboratory method was developed to measure the asphaltene related crude oil precipitation in situ. This proprietary method was based on the structural evolution of the key components in an asphaltene containing crude oil that drives the system from a solution state to the flocculation state and followed with sedimentation. The proposed method uses a measurable parameter, which uniquely relates to the structural change, to monitor the subtle changes of the solution structure. In this way, one can unambiguously determine the thermodynamic evolution of the system. In this presentation we introduce a novel experimental method that allows us to interactively measure the structural changes of the petroleum colloid. The resulting parameter, referred to as the gamma parameter, provides information about the thermodynamic state. Furrial crude oil was used as the model system. Furrial crude oil is notorious of causing well plugging if not well treated. In the laboratory we used heptane as the precipitant to initiate precipitation and applied the method described above to interactively monitor the structural evolution. Good correlation was obtained between the precipitation kinetics and the structural evolution. We believe this method can be used for fast and reasonably accurate laboratory screening for asphaltene dispersant and other field chemicals.

GEOC 145: The search for geologically aged nucleic acids

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DNA is a relatively weak molecule, comparatively speaking, yet under certain conditions it persists in the fossil record, despite what in vitro chemistry predicts. While most fossil remains do not contain DNA, museum specimens can be screened for the presence of conditions that would be conducive for nucleic acid preservation by measuring the extent of amino acid racemization and by looking at the extent of protein hydrolysis by pyrolysis gas chromatography mass spectrometry. Results from these types of analyses suggest that the preservation of DNA is linked to the cold temperatures as well as aridity at a site rather than its age. Chemical analyses of coprolites from extinct herbivores from the late Pleistocene, as well as Archaic Native Americans, show the presence of compounds derived from the Maillard reaction. These types of reactions appear to be important in sequestering labile molecules, such as DNA, in the fossil record for times longer than one might expect.

GEOC 146: Degradation of STRs in calcified tissue: Possibilities and limits

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STRs have been a useful tool in molecular biology, and related disciplines, for more than a decade. The possibility to combine several loci for individual identification, and to use such system on degraded material, has certainly been of the greatest importance in forensic sciences, and the variability and high mutation frequency in some STR systems have been useful in evolutionary studies. Here we set out to test this hypothesis. On a material consisting of human teeth from different time periods (a few decades to several hundred years), we type and sequence two STRs (D3S1358, D5S818), one nuclear fragment (amelogenin, although not the fragment with the deletion), and a mtDNA fragment (part of HVR1). All markers were typed and sequenced from all extracts. The nuclear fragment as well as the mtDNA fragment was real time PCR quantitated, and the STRs were amplified and gel electrophoresis typed. Although we certainly recognise that there is a big difference in stability and stutter effects among different STRs, we believe that this study provides data on the upper limit of STR use in highly degraded material, since the two STR systems used are considered fairly robust (non is a di-nucleotide system). The data reveals at what point calcified tissue reaches a degree of degradation where no STRs, in comparison to other markers, is of no usage any more.

GEOC 147: On the way to an understanding of DNA preservation in bone

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So far, analysis of DNA in fossils older than roughly 40,000 years remained unsuccessful and analysis of DNA in younger fossils encounters numerous technical difficulties that compromise the reliability of these studies. We are developing palaeogenetic approaches in two directions: (i) We develop novel PCR techniques that render DNA analyses in Holocene fossils more reliable. (ii) Our studies of much older fossils have shown that DNA can persist in "molecular niches" in an insoluble, matrix-associated form, which cannot be extracted, purified and amplified. To understand the taphonomic factors leading to DNA preservation and to develop new analysis methods adapted to the particular DNA chemistry in old fossils, we are now aiming at understanding, via a multidisciplinary approach, if and how different biopolymers are preserved in a series of fossil bones from the present back to half-a-million years.

GEOC 148: Ancient DNA and paleopathology: A case study from ancient Greece

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This research aimed to determine whether the skeletal condition porotic hyperostosis can be used as a reliable indicator of thalassaemia in skeletons from Neolithic and Bronze Age Greece. Polymerase chain reactions (PCR) were developed to allow the amplification of six mutations of the b-globin gene which are known to cause b-thalassaemia. Bone samples from Early Neolithic to late Bronze Age (6000-1600BC) contexts have been assessed for ancient human DNA. In this paper I will discuss some of the problems associated with this process and present some prospects for ancient DNA research in Greece. As a result of this research into palaeodisease it has been possible to form a number of conclusions about the feasibility of such studies. The remaining sections of this paper will discuss some of the critical points that should be considered in relation to ancient DNA studies of disease, both when designing projects and assessing past work.

GEOC 149: Comparison between silica-based methods for the extraction of DNA from human bones from 18th to mid-19th century London

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We directly compared five different silica-based methods for their efficiency at extracting DNA from human bones. The five samples, from two sites in London, were dated to the 18th to mid-19th century. Polymerase chain reactions (PCRs) were directed at two mitochondrial and one nuclear loci, all specific to humans. It was found that methods that used commercially available silica columns were more efficient than methods that used a silica slurry. Extraction with Qiagen QIAquick columns and the Qiagen QIAamp DNA Mini Kit were equally efficient, though we recommend the former as this method involves fewer steps thus reducing the contamination risk.

GEOC 150: The amber of El Dorado

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The legend of El Dorado (literally 'the golden one' or 'the golden man') has its origins in the stories brought back to Europe by 16th century conquistadores returning from expeditions to the New World. The historical basis of these reports lies in Musica Indian ceremonies which took place at Lake Guatavita, located in what is now central Colombia and the 'gilded man' around which these ceremonies were centered. During these ceremonies, which amounted to the inauguration of a new 'king', the heir, anointed with sticky resin and coated with gold dust, cast various types of valuables into the lake as offerings to a local deity. Other ceremonies involving casting offerings into the lake also took place at other times, resulting over time in a considerable accumulation of artifacts.

Beginning with the conquistadores, various groups have attempted to recover materials from the lake bed - with varying degrees of success. The artifacts which have been recovered include a significant number of resinous beads. To more rigorously establish their nature, and in an effort to establish the provenance of the materials used for their manufacture, we have analyzed a set of these beads by pyrolysis-gas chromatography-mass spectrometry. The results indicate that those beads that are resinous in nature are fabricated from a Class Ib amber; that is, they are derived from natural resins based on polymers of regular labdanoid diterpenes. Although numerous Central and South American ambers are known, Class Ib ambers have not previously been reported in either the geologic or archeological record of these regions. This raises intriguing possibilities regarding the origins of these artifacts, with both archeological and geochemical implications.

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GEOC 151: Black magic from the Blackland: A systematic approach to Egyptian mummification?

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Despite a long held fascination with ancient Egyptian mummies, surprisingly little is known about the so-called 'art' of mummification. This is particularly true of the types of organic preservatives and unguents employed in the process, with little attention paid to their practical or indeed ritual role. Yet mummification clearly combined the practical considerations of body preservation with ritualistic concerns. With the extent of the ancient embalmers' skills and knowledge still uncertain, was the choice of organic materials a reflection of their physical and chemical properties and were there known benefits for cadaver survival? Sequential TD-GC/MS and Py-GC/MS, and GC/MS were employed to characterise and identify these organic materials, with the results revealing notable differences in the use and nature of these agents depending on their proximity to the body. Their choice and application would also seem to reflect the extent of the preservative role they would play.

GEOC 152: New lipid biomarkers for ancient mycobacterial disease

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Tuberculosis (TB) and leprosy are among the oldest diseases to afflict Humankind and evidence for infection can be found in the archaeological skeletal record, using analysis of DNA and mycolic acid biomarkers. These investigations can help decipher the evolution and interrelation of these two diseases. The sensitive analysis of TB mycolic acids (e.g. 1) has been successfully carried out by fluorescence HPLC of anthrilmethyl esters, but the procedure is time-consuming and the derivatives are labile. Preliminary studies have shown the presence of components of

phthiocerol dimycocerosate (PDIM) waxes from *Mycobacterium tuberculosis*. This communication describes a new derivatisation and analysis protocol for hydrolysates of ancient bones. Pentafluorobenzyl esters are prepared from mycolic (I) and mycocerosic (II) acids and these derivatives are separated from each other and underivatized phthiocerols (III). Mycocerosate derivatives are analysed by negative ion-chemical ionisation GC-MS and related methods are being developed for the other components.

GEOC 153: Biomarker for cyanobacteria

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Cyanobacteria "fix" nitrogen and carbon and are usually primary successors in marginal locations. The cyanobacterial fossil record is among the oldest, possibly reaching back 3500 M years. Their archaeological significance lies in the fact that their largely biologically un-reworked presence in sediments indicates an ancient desert environment, where sustained plant cultivation sufficient to support a human population would be achievable. A variety of molecules have been suggested as biomarkers for the cyanobacteria; monomethyl- and dimethyl-alkanes, pentacyclic triterpanes and (poly)sulphide cross-linked C14-C24 hydrocarbon chains, but none of these is a true biomarker for the cyanobacteria.

Bacterial pigments are usually products of a series of condensation reactions. A cyanobacterial pigment, scytonemin, abundantly produced in response to UV-A and -B irradiation, is required for bacterial crust development. It is not susceptible to photodegradation or desiccation, though concentrations fall with crust development. Data will be presented from our studies examining its early diagenetic fate.

GEOC 154: Asphaltene character and deposition

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Deposition of asphaltene constituents in the reservoir and during petroleum production, transportation, and refining has had an adverse effect on production and refining activities in many parts of the world. Deposits in reservoir rocks, recovery equipment, storage vessels, and pipelines have significant process implications. Because of their high molecular weight and polar nature, the asphaltene constituents have gained attention as the major compound types responsible for such effects. And such hindrance on production and processing has made the asphaltene fraction one of the most studied materials in petroleum science and technology. While studies about the variations of the molecular structures of asphaltene constituents are well documented, the behavior of these constituents in oil systems is less well documented and has not been investigated to the same extent. Understanding asphaltene character, phase behavior, and the factors contributing to the acceleration of deposition from solution is essential if these deposition effects are to be mitigated. Variables that are known to affect asphaltene phase transitions and cause flocculation (with subsequent separation from the crude oil) are changes in crude oil composition, temperature, pressure, crude oil thermal and electrical conductivity, viscosity, and flow characteristics. In this presentation, the causes and effects of phase transitions of asphaltene constituents in crude oil systems will be illustrated and the continuing need for future research will be addressed.

GEOC 155: Effects of acidizing agents on the stability of asphaltenes and their implications for formation damage

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Acidizing of wells is a common practice in petroleum production. Because of the propensity of acids to destabilize asphaltenes however, acidizing could potentially lead to formation damage in producing wells. The effects of some common acids and commercial acidizing agents on the asphaltene precipitation tendencies of some crude oils were studied. As expected, results show that the acids tend to precipitate asphaltenes from the crude oils. The effect however, was more severe for oils with higher asphaltene content, or very unstable asphaltenes. The parameters that influence the acid-destabilization of asphaltenes are discussed in detail. The use of asphaltene inhibitors as an antidote to acid destabilization of asphaltenes was explored.

GEOC 156: Concepts for paraffin deposition prediction

Klaus Weispfennig, Baker Petrolite, 12645 West Airport, Sugar Land, TX 77478

Many operators are faced with the problems inherent to paraffin deposition. These problems may be found at the end of low cost remediation such as solvent and/or solvent/dispersant treatments for on- and offshore operation, but may also encompass coiled tubing approaches or explicit deposit cutting of subsea wellbores. They may be so severe that pipeline abandonment remains as the only "viable" alternative. This presentation looks at the various prediction approaches that have been taken to gain insight into the paraffin deposition process, to understand its dominant mechanisms, to learn from shortcomings and to provide some ideas for possible incorporation into existing prediction routines. While the process of paraffin deposition is typically described by mechanisms of diffusion within the viscous sublayer or correlated via transport coefficients, little is known about the influence of shear on the deposition amount. Comprehensive flow loop tests may provide some insight into parameters of influence for the process but how well can we isolate or back-calculate physical effects in order to gain insight into their individual contributions to the overall process. Can we really transfer this problem to the laboratory to exploit the benefits of small-scale testing, are our predictions adequate, to what extent does the rheological behavior complicate the problem, do we need to consider other approaches to incorporate turbulence effects? These are just a few of the questions raised.

GEOC 157: Pipeline wax deposition models and model for removal of wax by pigging: Comparison between model predictions and operational experience

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Wax deposition simulations have been performed for two fields in the North Sea: One gas condensate and one stabilized single phase oil pipeline. The results have been compared with the available operational experience from these pipelines. Three different wax deposition models in a transient multiphase pipeline flow simulator have been used for the simulations. The basic differences between the three models are their approach for modelling the mass transfer of dissolved wax components between the bulk flow and the wall. In addition, a pigging model has been tested, taking into account the effects of wax deposit removal from the wall. The models are presented. Simulation results are compared to field data and discussed. A good agreement with field data is generally achieved for the single phase oil system, while for the gas condensate pipeline, there are indications that two of the wax deposition models overpredict the wax deposition rate.

GEOC 158: Occurrence of high molecular weight monomethyl- and dimethylalkanes (C40+) in crude oils and wax deposits

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High molecular weight (HMW) alkanes (C40+) are associated with crystallization and deposition related problems encountered during oil production, transportation, or storage, and are composed of complex mixtures of n-alkanes, methylbranched alkanes, and alkylcycloalkanes. These compounds are ubiquitous in oils and sometimes represent significant fractions of the whole oil. Methylbranched alkanes may comprise as much as 40% of HMW alkanes and alkylcycloalkanes represent up to 35% of C40+ compounds. An enrichment of methylbranched- and alkylcyclo-alkanes can influence the crystallization behavior of waxes. Thus, a more comprehensive understanding of these compounds is essential for establishing a more reliable wax crystallization model. To date, HMW monomethyl- and dimethyl-alkanes have only been reported up to C45 in recent sedimentary organic matter, and as high as C55 in insect surface lipids. This paper will focus on the occurrence of three homologous series of HMW monomethyl- and dimethyl-alkanes in crude oils and wax deposits (C40-C60), and discuss their significance and possible sources/origins.

GEOC 159: Regular solution approach to modeling solid precipitation from crude oil

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Wax and asphaltene precipitations have caused problems in petroleum industry. One of the ways to mitigate the problems is to have a model that can predict the conditions where the precipitation occurs and the amount of solid precipitated at different condition. Several models have been proposed in the past. However, models are for either wax or asphaltene precipitation. Moreover, the previously proposed models usually

involve the use of fitting parameters to match the calculated results to the experimental values. The incorporation of fitting parameters limits the predictive capability of the models. Therefore, it will be useful to have a predictive model that can describe the precipitation of both wax and asphaltene. This work has been focused on developing a model for predicting both wax precipitation as a function of temperature and asphaltene precipitation as a function of solvent added. The data for the model input were obtained extensively using experimental techniques such as TBP distillation, solvent extraction, HPLC, HTGC, SEC, and RI measurement. While the data for model validation were obtained using FTIR and cold finger solid deposition techniques.

GEOC 160: Bioapatite carbon isotope ratios used to distinguish sheep from goats in the archaeological record in C4 plants environments

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Distinguishing sheep from goats archaeological bones using morphology has proven difficult. In C4 grass environments, the identification could be accomplished using carbon isotopes, due to differences in the feeding habits of sheep and goats. Sheep are grazers whereas goats are mixed feeders. Carbon isotope ratios of herbivore bones is related to that of the plants in their diet. Most bushes are C3 plants, and C3 and C4 plants differ greatly in their carbon isotope ratios ($\delta^{13}\text{C}$). Therefore in C4 grass environments pure grazers (C4 plants eaters) can be distinguished from mixed feeders (C3+C4 plants eaters) by their $\delta^{13}\text{C}$. Intra-tooth sequential sampling was performed on modern sheep and goat teeth from Kenya. Results of the isotope analysis of enamel bioapatite confirm that in that environment, sheep and goats are clearly distinguishable using this criteria, both in the $\delta^{13}\text{C}$ values and their pattern of seasonal variation. Biases related to elevation are discussed.

GEOC 161: High-resolution profiles of late Paleolithic fish otoliths: Reconstruction of seasonality of capture and paleoenvironmental conditions in Upper Egypt

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Determining the seasonality of paleoenvironmental conditions as well as resource and site use is an integral part of understanding human prehistoric adaptive strategies. Sequential oxygen and carbon isotopic profiles acquired from animal hard tissues represent a powerful tool for reconstructing 1) the seasonal variations of the physical and chemical environment, 2) the animal's life history and 3) the time of harvesting. However, accurate sampling procedures on accretionary biogenic structures are necessary to produce seasonal time-resolution records. Fish otoliths represent a complete chronological record from the birth to the death. The late Paleolithic site of Madhadma in Upper Egypt provided hundred of well-preserved otoliths of Tilapia (*Oreochromis niloticus*). We generated high-resolution isotopic profiles to reconstruct the seasonality of fishing and to get more complete insight into the arid climate and high flood paleohydrological conditions of the Nile during the late Pleistocene in this region.

GEOC 162: Investigating ancient climate through analysis of stable isotopes from fossil tooth enamel

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Inferences about ancient climates are often made based upon general assemblages of plants and animals within a particular fossil site. Computerized models have also been developed to investigate climate, especially changes since the last glacial maximum. Few quantitative techniques are available to test these interpretations. New studies examining stable isotopes collected from fossilized teeth of horse and bison allow direct testing of modeled or inferred climate patterns. Tooth enamel preserves a record of changes in $\delta^{13}\text{C}$ (from diet) and $\delta^{18}\text{O}$ (from surface water). A single third molar records these changes over a period of 18 months (Bison) to three years (Equus). Seasonal changes in temperature, rainfall, and diet can be interpreted from serial data collected from these teeth. Season of birth may also be inferred. Further studies of different mammal groups may provide insights into ancient climates for which we have no other method for investigation.

GEOC 163: Old lipids and the sea: Using cholesterol as a paleodietary proxy for extinct marine mammals

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Effective conservation of marine mammal populations requires establishing baseline ecological knowledge for species prior to human contact or exploitation. However, this type of information is often difficult to gather from fossil specimens or historical accounts. To reconstruct the diets of extinct marine mammal populations, we employed compound specific isotope analysis of cholesterol extracted from Holocene and mid Miocene fossil bones. Carbon isotope values were then compared to modern marine mammal values for interpretation. Fossil bone carbon isotope values differed significantly among species collected from a given locality (ranging from -24.8‰ to -12.9‰), and differences in values among extinct marine species were comparable to patterns observed within values for modern species, supporting our interpretation that original cholesterol is preserved. Therefore, we conclude that original lipids can be preserved in fossil bone and provide a viable paleodietary proxy for studies of extinct marine mammals.

GEOC 164: Vessels to environment via compound-specific stable isotope analysis

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Compound-specific stable carbon isotope values of the major fatty acids (C16:0 and C18:0) have been used to classify absorbed lipid residues preserved in archaeological pottery. These classifications are based on metabolic and dietary differences recorded in the $\delta^{13}\text{C}$ values of the fatty acid components of animal fats, thus allowing the different fats of the major domesticates to be distinguished (e.g. ruminant adipose, ruminant dairy and porcine adipose fats). In this paper we discuss the possibilities for the wider use of these stable isotope data, addressing aspects of human and environmental impact on animal husbandry. Reliable interpretation of the data obtained requires consideration to be given to such factors as: (i) the processing of mixtures of commodities; (ii) dietary differences, e.g. C3, C4 and marine; and (iii) atmospheric CO_2 effects. Applications of this approach are demonstrated with examples drawn from a range of British and Near Eastern sites.

GEOC 165: Bulk and compound-specific stable light isotopic ratios in recent and archaeological resins: Can we detect the transport of resins in antiquity?

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Evidence for the trade of resins in archaeological contexts relies on indirect evidence, including the modern distribution of resin-producing plants, their ancient distribution from pollen records and provenanced artefacts associated with the resin. However, studies of modern and fossil resins show that their original isotopic composition is retained and that variations exist with latitude. It is likely that resin transported from areas of different isotopic signature may be identifiable. A pilot study is underway to measure isotopic ratios, including bulk measurement of D/H, $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$, and for selected samples, compound specific $^{13}\text{C}/^{12}\text{C}$ ratios. After examining modern resins from known locations, two archaeological case studies are planned. These will examine *Pistacia* sp. resin from Canaanite amphorae imported into Egypt from known geographical locations in the Eastern Mediterranean during the Late Bronze Age, and *Pinus* sp. resin lining Roman amphorae sherds imported to Britain from Southern France and Spain.

GEOC 166: Collection and isotopic analysis of mud gases: Past, present, and future

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Isotopic analysis of mud gases has become an integral component of hydrocarbon exploration for many major oil companies. A variety of different methods and containers have evolved over the years for collection and shipment of these samples. The pros and cons of the various sampling containers are evaluated. Isotopic analysis methods have also evolved. Traditional dual-inlet mass spectrometry still provides the most reliable results, but online GC-Combustion-Mass Spectrometry allows for more rapid analysis of smaller samples at acceptable precision levels. Despite the advances that have been made, delays in shipping samples, which must often be identified as "hazardous materials," have limited the applicability of mud gas isotope logging (MGIL) in some areas. Soon to be launched are deployable, remote isotope laboratory systems. These new logging tools are sufficiently robust and reliable to allow isotope laboratories to be set up in close proximity to the main drilling areas.

GEOC 167: Mud gas isotope logging applications in GoM drilling operations: Methodology and concepts

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Advances in sampling and analytical techniques now permit the isotopic analysis of very small amounts of hydrocarbon gases in air that are collected from the circulating mud stream during drilling. A recently developed technique termed Mud Gas Isotope Logging (MGIL) has found considerable application and continued success in GoM hydrocarbon exploration. MGIL helps validate hydrocarbon-charged intervals identified by standard mud gas or wireline techniques, assess vertical reservoir compartmentalization, and identifies possible bypassed or low-resistivity pays. Benefits for regional GoM exploration are assessment of sealing intervals, charge history, and thermal maturity of hydrocarbons. In this talk we examine the fundamental application of MGIL to GoM exploration, including strengths and limitations. Introduced also, are future MGIL advances set to debut in 2003.

GEOC 168: Using headspace gas data to understand petroleum fluid distributions in the Gulf of Mexico and other sedimentary basins

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Cuttings headspace gas is an old technique enjoying a new lease of life. Its original usage was to attempt to establish maturation profiles, given the traditional view that fine-grained rocks are "impermeable"; thus the gases are regarded as in-situ. Modern concepts of petroleum migration, however, involve vertical migration through fine-grained sequences. Therefore, in young, cold sedimentary sequences where the mudrocks are well below the thermal stress levels required for significant petroleum generation, headspace gas data are now used to map migration pathways and "fronts".

We show that, integrated with other available geochemical data, a headspace gas composition and isotope profile is a powerful tool providing important information on the migration style (lateral vs. vertical migration). In some cases, where subsurface fluid samples are not collected, and the source rock is not drilled, cuttings headspace gas may be the only geochemical data collected from a well, yet it can provide critical information where data from flowline / mud gas is ambiguous.

In this paper we compare data from the Gulf of Mexico with other global systems to demonstrate application of cuttings headspace gas data in exploration and production.

GEOC 169: Comparison of subsurface gas data from different sampling methods

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Subsurface gas data, both chemical and isotopic compositions, can be acquired on samples from a variety of different methods. The latter include production, formation tests (MDTs or DSTs), rigsite mud gas logs, mud gas samples (gas tubes or bags) and canned cuttings (notably headspace gas samples). However, there has been little published work on the comparability of data acquired by these different means. In this study gas data, which were acquired from two wells in the deepwater Gulf of Mexico by four different sampling methods, are compared. The four methods are: MDTs, headspace gases, rigsite mud gas log and mud gas tubes. The results show that there are systematic differences and similarities between the sample methods in both these wells. If generally applicable, this study should assist in the interpretation of more limited gas data sets.

GEOC 170: Fluid inclusion microseeps in the Gulf of Mexico

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Fluid Inclusion Microseeps (FIMs) are identified above deep productive reservoirs in the Gulf of Mexico, and are interpreted to arise through near-vertical microseepage of light hydrocarbons followed by fluid-rock redox reactions at depth-temperature-nutrient conditions permissible for bacterial activity. Thermophilic, sulfate-reducing anaerobes are implicated. FIMs are identified and characterized using Fluid Inclusion Stratigraphy (FIS), a mass spectrometric method for mapping volatiles released from crushing rock material. Key indicator species include light hydrocarbons (generally C1-C5), CO₂, organic acids and sulfur compounds (H₂S, COS, CS₂, S₂ +/- SO₂ and thiols). Presence is non-specific to

lithology (ss, sh, cb) or degree of non-biologic diagenesis, suggesting that volatiles may in part be encapsulated within mineral products of bacterial activity, such as carbonates. FIMs typically occur to depths corresponding to present day temperatures of approximately 65-80°C. Recognition of FIS subsurface seeps in areas limited to shallow well control can be used to infer deeper prospectivity and focus exploration efforts. Analysis of approximately 200 wells from the GOM demonstrate that drilling success will be 75% in areas near FIMs, while drilling success in areas without FIMs will be 10%.

GEOC 171: Natural gas formation in petroleum systems: A different ball game in the same stadium

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The key to the definition of a Petroleum System is the identification of the source and a constraint on timing of oil formation and migration. For oils, modern geochemical techniques of oil-source correlation and kinetic analysis of kerogens provide such data with high accuracy. For natural gases, timing of gas formation and correlation to a specific source is a different ball game. In contrast to oils, gases do not form in a narrow time window but are generated over prolonged periods of millions of years and often in different time windows controlled by the subsidence of the gas kitchen. Therefore, fundamental questions of gas formation in relation to oil formation in a petroleum system can not be addressed. When did the gases migrate, before or after the oils? Are the gases related to the oils and part of the oil formation process or are they from a different source altogether? For example, we can identify up to 6 oil source rocks in the Gulf of Mexico, yet, with the exception to Norphlet gases, we cannot assign gases to any of these sources with certainty, nor do we have any clue as to the timing of gas migration other than from geological inference. However, there are now new kerogen-specific isotope calibration techniques available that allow not only an identification of the gas source but also an assessment of the timing of gas formation. With these new techniques we found that oil and gas formation are indeed entirely different "ball games" in the "Haltenbanken stadium" in the North Sea: Although the gases are associated with Upper Jurassic shale-sourced oils, we could show that they are predominantly sourced from the Lower Jurassic coals. The timing of gas formation turned out to be very different from oil formation and was critical for assessing the gas risk in this area. From this study we infer for the Gulf of Mexico with its multiple potential gas source rocks, that an isotope calibration of source rocks would clearly contribute to the understanding of gas formation and the assessment of gas risk in deep water prospects.

GEOC 172: Dynamic gas-driven petroleum systems?

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Large volumes of gas appear to have vented through a north-south transect of the offshore northern Gulf of Mexico. Even though very large quantities of gas appear to be involved, the specific sites of venting are generally highly localized at faults and fractures in the seafloor. Venting may be episodic making the actual hydrocarbon fluxes involved difficult to estimate. This venting gas causes significant changes in compositions of reservoir oils, both in the past and at the present time. This upward gas movement produces a number of interesting effects at the seafloor, including support of a prolific and diverse biological community, formation of seafloor gas hydrates, and sometimes massive disruption of the subsurface and surface sediments including ejection of fossils from older deeper sediments to the modern seafloor. In some cases, methane bubbles issuing from the seafloor appear visually to be venting directly into the atmosphere. Venting is accompanied by natural oil slicks at the sea surface which can be followed for miles. This behavior is not limited to the Gulf of Mexico - similar observations are continuing to be made in ocean basins worldwide, particularly in river deltas and on continental margins. It has recently been estimated that natural seafloor methane vents may deliver enough methane to the atmosphere to be important in global climate change.

This talk will explore the relationship between subsurface petroleum migration and surface sediment oil and gas venting which is commonly localized, volumetrically significant, episodic, rapid, and recent. Examples of gas and oil compositional and isotopic data from the Gulf of Mexico and constraints on gas and oil migration processes will be presented along with evidence of on-going vigorous localized gas venting through the seafloor. These observations raise an important fundamental question - to what extent should petroleum systems be viewed as static versus dynamic? Should this distinction make a difference in how we explore for gas and oil?

GEOC 173: Gas distribution in the Mesozoic of the eastern onshore areas, Gulf of Mexico: Louisiana, Mississippi, Alabama, and Florida

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Petroleum in the Mesozoic of the eastern onshore areas of the Gulf of Mexico (Louisiana, Mississippi, Alabama and Florida) is produced from numerous intervals and sourced from multiple source rocks. Here we focus on the two most prolific petroleum systems, driven by Oxfordian and Cenomanian-Turonian aged source rocks:

1. Numerous reservoirs have accessed petroleum from Smackover carbonate source rocks of Oxfordian age: older Oxfordian Norphlet clastics, intra-formational Smackover carbonates, Cenomanian clastics and possibly latest Cretaceous carbonates.
2. Reservoirs of Upper Cretaceous age have also accessed petroleum from the Tuscaloosa and Eutaw clastic source rocks of Cenomanian and Turonian age.

In this paper we show how vertical and lateral variations in the petroleum phase state, GOR, hydrocarbon and non-hydrocarbon gas composition can be related to the originating source rock, migration style and post-emplacement alteration processes.

GEOC 174: Evaluating geological factors responsible for generation of natural gas and pyrobitumen through pyrolysis of Smackover oil

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While some aspects of gas generation are fairly well understood, the in-situ cracking of oil to gas and pyrobitumen under geologic conditions is not. Determination of how various reservoir environments influence in-situ cracking is needed. Oil derived from Smackover source rocks was used in a series of pyrolysis experiments to evaluate the effects water presence, water chemistry, grain surface area, and grain mineralogy have on the amounts and proportionality of gas and char generated from the thermal decomposition of oil. The original oil contains 1.7wt% sulfur with an API gravity of 34.0. Isothermal pyrolysis of the oil occurred under anhydrous (no added H₂O) and hydrothermal (added H₂O) reactor conditions. The experiments were conducted at 340 to 400°C for 288 to 720 hours. Comparisons between anhydrous and hydrothermal experiments under identical temperature conditions indicate that the hydrothermal experiments generate incrementally more gas and less pyrobitumen than anhydrous experiments.

GEOC 175: Energetics of nanomaterials: The competition between polymorphism and surface energy

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Many oxides are polymorphic, often showing different structures for small particles. Examples are α - and γ -Al₂O₃ and Fe₂O₃, the TiO₂ polymorphs (rutile, anatase, and brookite), the ZrO₂ polymorphs (cubic, tetragonal, and monoclinic) and numerous manganese oxides, as well as Al and Fe oxyhydroxides. Sulfides and selenides also show polymorphism at the nanoscale. The reason for such polymorphism can be related to the competition between small (free) energies of phase transitions and differences in surface (free) energies of different polymorphs. High temperature oxide melt solution calorimetry is an excellent tool for studying these factors, and several examples are given. The energetics of the TiO₂ polymorphs (rutile, anatase, and brookite) were studied by high temperature oxide melt drop solution calorimetry. Relative to bulk rutile, bulk brookite is 0.71 ± 0.38 kJ/mol and bulk anatase is 2.61 ± 0.41 kJ/mol higher in enthalpy (this work). The surface enthalpies of rutile, brookite, and anatase are 2.2 ± 0.2 J/m², 1.0 ± 0.2 J/m², and 0.4 ± 0.1 J/m² respectively. The closely balanced energetics directly confirm the crossover in stability of nanophase polymorphs inferred by Zhang and Banfield. An amorphous sample is 24.25 ± 0.88 kJ/mol higher in enthalpy than bulk rutile. General implications for nanophase stability relations are discussed. Unanswered questions include the following.. Are more symmetric phases generally/always of lower surface energy? Do amorphous materials have smaller surface energy than crystalline? What is meant by "amorphous" at the nanoscale? Are hydrous phases (hydroxides and oxyhydroxides) of lower surface energy than anhydrous? Are there compositional or crystal chemical systematics in the energetics of polymorphism and surface energies.

GEOC 176: How does pH affect the phase stability and coarsening kinetics of TiO₂ under hydrothermal conditions?

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Hydrothermal coarsening kinetics and phase stability of nano-sized titania (85% anatase 15% brookite) in pH 1.9 to 12.5 solutions were investigated to pinpoint the growth mechanism (Ostwald ripening vs. oriented attachment, OA) and its interplay with phase stability. XRD, BET, and TEM are used to characterize size, morphology, aggregate structure, and phase weight percentages. Upon coarsening at 200 °C at pH values << ZPC (5.2) conversion of anatase and brookite to rutile correlates with increase in Ti solubility. At pH near the ZPC, the phase content remains unchanged and the crystals grow predominantly via OA. At pH >> ZPC, brookite quickly converts to anatase without rutile formation, and the size distribution increases rapidly. In regimes where there is evidence for OA, the largest crystals have symmetry-breaking morphologies, possibly explained by sequential attachment on one {101}. Results indicate interdependence of thermodynamic phase stability, growth mechanism, and the solid-solution interfacial energy.

GEOC 177: Special phase transformation and crystal growth pathways observed in nanoparticles

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Phase transformation and crystal growth in nanoparticles may happen via mechanisms distinct from those in bulk materials. We combine experimental studies of as-synthesized and hydrothermally coarsened titania (TiO₂) and zinc sulfide (ZnS) with thermodynamic and kinetic modeling and molecular dynamics (MD) simulations. The samples were characterized by transmission electron microscopy, X-ray diffraction, synchrotron X-ray absorption and scattering, and UV-vis spectroscopy. At low temperatures, phase transformation in titania nanoparticles occurs predominantly via interface nucleation at particle-particle contacts. Coarsening and crystal growth of titania nanoparticles can be described using the Smoluchowski equation. Oriented attachment-based crystal growth was common in both hydrothermal solutions and under dry conditions. MD simulation and experiment predict large structural perturbations within very fine particles, and are consistent with experimental results showing that ligand binding and aggregation can cause phase transformation without particle coarsening. Such phenomena affect surface reactivity, thus may have important roles in geochemical cycling.

GEOC 178: Oriented aggregation and chemical reactivity: The case of goethite (FeOOH) nanoparticles

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Nanoparticle growth and phase transformations are critically important to the geochemical cycling of both natural and anthropogenic chemical species. Goethite (α-FeOOH) is a common and important mineral in the biogeochemical cycle of iron and other metals at the Earth's surface. Furthermore, this mineral commonly occurs as nanoparticles in the 3-10 nm size range (e.g., Penn et al., *Geology*, 2000). High-resolution transmission electron microscopy (HRTEM) and low-temperature magnetometry of synthetic goethite nanocrystals show that when aqueous suspensions of goethite nanocrystals are aged at 90 °C, the nanocrystals grow almost exclusively by oriented aggregation of superparamagnetic 3-4 nm primary nanocrystals. Furthermore, recent work suggests that the rate of redox when using hydroquinone as the reducing agent and goethite nanoparticles as the terminal electron acceptor is strongly particle size dependent. For example, redox reactions using ~3.5 nm and ~30x350 nm goethite particles show that the rate of redox is 2-3 times faster (normalized to total surface area of the particles) in experiments using the smaller goethite nanoparticles.

GEOC 179: Retention of Cs and Sr in solid-phase products of clay mineral weathering

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Integrated macroscopic and spectroscopic studies are being conducted to elucidate the behavior of radionuclides (¹³⁷Cs/⁹⁰Sr) in the vicinity of leaking nuclear waste tanks. We are studying weathering reactions of layer silicate clays (illite, vermiculite, smectite and kaolinite) that affect contaminant sorption/coprecipitation under caustic geochemical conditions imposed by tank waste leachate (pH 14; 2 M NaNO₃ background, high Al concentrations). Dissolution of Si leads to precipitation of poorly crystalline Al and Si phases that transform to crystalline zeolites over times ranging from 24 hr to 2 yr, with concurrent impacts on kinetics of Cs and Sr sorption-desorption. The coupling of Cs/Sr uptake to mineral transformation rates (monitored using solid-state NMR, XRD, FTIR, SEM-EDX, TGA and wet chemical methods) depends on (i) the type of clay mineral and (ii) contaminant concentrations. The recalcitrance of both radionuclides to desorption increases with weathering time (consistent with Ostwald ripening) for all systems studied.

GEOC 180: Microbial formation of Fe minerals and metal-substituted magnetite nanoparticles by iron-reducing bacteria

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Crystalline metal oxides including magnetites formed by biogenic or abiotic processes are ubiquitous in subsurface environments. The objective of this research is to study the formation of crystalline extracellular Fe minerals and metal-substituted magnetites in discrete sizes from <10 to 200 nm by anaerobic microorganisms. Microorganisms isolated from extreme environments proved capable of precipitating siderite, hematite, rhodochrosite, uraninite, maghemite, vivianite, magnetite, and metal-substituted magnetites depending on the chemical milieu of their environment. Bacterially-mediated geochemical processes facilitated formation of metal-substituted magnetite nanoparticles by iron-reducing bacteria. Chemical analysis and X-ray powder diffraction analysis showed that trace metals were partitioned into biologically formed magnetite nanoparticles. Microbially facilitated formation of the metal-substituted magnetite nanoparticles at near ambient temperatures may influence the biogeochemical cycles of carbon and metals in subsurface environments as well as may expand the possible use of the specialized ferromagnetic particles.

GEOC 181: Trace element binding during structural transformation in iron oxides

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Iron (hydr)oxides often control the mobility of inorganic contaminants in soils and sediments. A poorly ordered form of ferrihydrite is commonly produced during rapid oxidation of ferrous iron at sharp redox fronts encountered during discharge of anoxic/suboxic waters into terrestrial systems. Ferrihydrite efficiently sequesters inorganic contaminants from solution during its formation. Co-precipitated As, Ni and Pb may become immobilized during transformation of ferrihydrite to more crystalline forms, such as goethite or hematite. Patterns of As, Ni and Pb partitioning to goethite or hematite in laboratory studies have been assessed. These results indicate that As and Ni may be hosted within the goethite and hematite structure leading to metal stabilization. A comparison will be made between laboratory solids and contaminated iron-rich sediments. The rates and mechanisms of metal partitioning to goethite or hematite will be assessed with respect to the long-term fate of these solid phase contaminants.

GEOC 182: Formation of nanoscale magnetite during the reduction of 2-line ferrihydrite by *Geobacter metallireducens*: Time-course changes in geochemistry, mineralogy, and reactivity with carbon tetrachloride

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Detailed time-course changes in geochemistry, mineralogy and environmental reactivity were examined during the microbial reduction of 2-line ferrihydrite by *Geobacter metallireducens*. During 50 days of incubation, Eh, pH, and the concentrations of Fe(II)(aq), acetate, and total protein were monitored. Solids were recovered periodically and characterized by X-ray diffraction, micro-Raman spectroscopy, transmission electron microscopy, and BET surface area analysis. Selected area electron diffraction (SAED) revealed a gradual spinel-ordering in the particles with no concurrent change in mean particle diameter (2-4 nm) indicating a topotactic process of nano-scale magnetite (Fe₃O₄) formation. Low Fe(II)/Fe(TOT) ratios in the early stages of spinel-ordering suggest a maghemite (γ-Fe₂O₃) precursor. A strong correlation between the pseudo-first order reaction rate (k_{obs}) for CT transformation and the surface area concentration (m²/L) of biogenic magnetite confirm a surface-mediated reaction with surface associated Fe(II) the likely agent responsible for CT reduction.

GEOC 183: Massive hydrocarbon venting with minor, constantly replenished (flow-through) retention in a 100 x 200 km area offshore Louisiana Gulf of Mexico

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A basin model with a 100 m, 5wt% TOC, HI=628 Jurassic Type II source at the top of the Louann salt, and a 30 m, 4 wt%TOC, HI=205 Eocene Type III source 3.5 km higher in the section is used to analyze distinctive patterns of hydrocarbon source and gas washing chemistry in a 100 x 200 km area in the offshore Louisiana GoM. All aspects of the chemical pattern are reproduced if the migration hydrocarbon saturation is £0.05%. About 132 Bt (billion tons) of hydrocarbons vented into the ocean over the last 20 Ma. Discovered resources are 1.4 Bt, 37 Bt are retained in source strata, and 15 Bt in migration pathways. If drawn from about 15 km (minibasin scale) the discovered resources can be supplied in the recent time intervals geologically and biologically required. Venting rates (900 tons/a) at Joliet agree closely with independent estimates from hydrate accumulation.

GEOC 184: High-resolution geochemical technology for the dissection of multiply sourced petroleum basins

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Geochemistry makes a major impact on exploration strategy when new petroleum systems or combinations of petroleum systems are documented. Prolific petroleum basins typically have multiple source rocks, and establishing these sources and their contributions, especially to mixed petroleum accumulations, can be a challenge. In mature basins, retrenching with well-established molecular and bulk analyses may be insufficient to elevate understanding of the petroleum systems to the new levels necessary to make a major impact on exploration. We investigated petroleum systems in the prolific producing basins of Mexico using high resolution geochemical technologies (HRGTs) including (1) diamondoid analysis for thermal cracking of oil to gas, (2) age-related biomarkers, (3) compound specific isotope analysis of biomarkers (CSIA-B), and (4) compound specific isotope analysis of diamondoids (CSIA-D). Results show improved delineation of oil and gas provenance in the region leading especially to new concepts in gas exploration.

GEOC 185: Gas geochemistry of the Macuspana Basin (Mexico): Thermogenic accumulations in sediments impregnated by bacterial gas

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A gas survey was performed in the Macuspana basin (South of Mexico). Two distinct gas families were identified: the family 1, represented by an homogeneous and purely thermogenic gas, associated with condensates and expelled at the end of the oil window, and the family 2, composed of a mixture between a bacterial dry gas and a thermogenic gas of high maturity. Chemical, isotopic parameters and noble gas data have provided informations about the sources, the proportions of mixing, and directions of hydrocarbon accumulation of these two families. Considering the risk associated with further oil and gas exploration in the basin, deeper parts of family 1 gas fields constitute a good target for oils accumulations, associated with already discovered dysmigrated gas and condensates. In contrast, the bacterial gas fields can be considered as a less promising target for future oil and gas exploration.

GEOC 186: Natural gas compositional trends in the northern Gulf of Mexico basin

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Isotopic and bulk compositional data for a large gas data set facilitated identification of major compositional trends in offshore areas of the US Gulf of Mexico. Gases occurring in those parts of the basin having oil sources of Jurassic age can often be compositionally distinguished from gases interpreted to have been derived from younger sources (Tertiary and Cretaceous). Deuterium isotopic compositions tend to be more negative in these gases than in gases having younger sources. Ethane and propane carbon isotopic compositions also distinguish these gases from other gases in the basin and aid in the estimation of thermal maturity.

Gases occurring in those parts of the basin having Tertiary and Cretaceous oil sources generally have similar isotopic compositions. Compositional similarities in these gases may result from a number of phenomena – for example, thermogenic-thermogenic gas mixing or a single source for the gases.

Gas compositions in individual wells tend to be similar or vary systematically as a function of reservoir depth. Regionally, gas compositions vary less systematically. This suggests local basin evolution exerts some control on gas composition.

Biogenic gases or mixed biogenic-thermogenic gases commonly occur in the basin. Gases containing a biogenic component are suggested on the basis of methane carbon isotope-gas wetness and methane deuterium-methane carbon isotope plots. The sources of biogenic gas are most likely the thick, rapidly deposited Neogene or Quaternary section containing the gas reservoirs. The amount of biogenic gas in a mixed gas can be estimated using the following relationships:

$$\text{Vol. \% Biogenic Gas} = [(\delta C1UK - \delta C1TH) / (\delta C1BIO - \delta C1TH)] * [(100 - \%C2+UK)]$$

$$\delta C1TH = 0.93 * \delta C2UK - 14.6$$

Where:

UK=unknown gas sample carbon isotopic composition

BIO=biogenic end-member methane carbon isotopic composition @ -70‰ to -75‰

TH=thermogenic end-member methane carbon isotopic composition

Gases are highly mobile components. The availability of compositional data for gases adds significantly to our ability to describe and interpret the extent and definition of petroleum systems in the Gulf of Mexico Basin.

GEOC 187: Using C1-5 compositional data to understand the origins of petroleum fluids including "biogenic" gases in the Gulf of Mexico and other sedimentary basins

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Much of the current understanding of the origins of hydrocarbon gases (methane through pentanes) in sedimentary basins has been derived from analysis of carbon and hydrogen isotopes. To date, gas compositions have not been systematically studied by geochemists, with composition often relegated to a simple "wetness" or "C2+ content"

An understanding of gas compositions is important for three reasons: (1) the commercial value of a sales gas is directly determined by its composition; (2) mixing / unmixing models using isotopes require an understanding of the relative proportions of the components (3) composition can in some cases provide critical information on the origin of a gas, in cases where the evidence from isotopes is ambiguous

In this paper we compare data from the Gulf of Mexico with other global systems to show how gas compositions, when systematically studied, can be used to provide insights into the origins of C1-C5 hydrocarbon-bearing petroleum fluids, as well as the distinction between "biogenic" and "thermogenic" gases.

GEOC 188: Survey of gases in near-surface Gulf of Mexico sediments

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For the purpose of measuring the indigenous and migrated hydrocarbons in near-surface sediments, we have taken over 7,000 piston cores in the last 6 years. More than 2,000 of these cores were extracted from Gulf of Mexico sediments. We selected exploratory coring sites based on seafloor expressions of structural anomalies seen on existing 2D or 3D seismic records. Such features are sometimes the conduits for upward migration of thermogenic hydrocarbons. Measured gases included methane, ethene, ethane, propene, propane, i-butane, n-butane, i-pentane, n-pentane, neo-pentane, and carbon dioxide. When concentrations were sufficient, stable carbon isotopic compositions of methane and other alkane gases were also measured.

The C1-C3 light hydrocarbon gases were present at measurable concentrations in all sediment samples. Although the carbon isotopic composition of methane in almost all measurable samples appeared to be biogenic, this is misleading considering molecular compositions. The high presence of the C2+ alkane gases provides compelling evidence of thermogenic gas in many samples, even though their methane isotope ratios were usually "too" light. Moreover, because ethane and propane exist in these near-surface sediments independent of any thermogenic sources, interpreting gas origin based solely on ethane or propane of 1 or 2 ppmV is problematic. The ethane/ethene ratio is much more definitive of the existence of a thermogenic component. The source of background ethane and propane is apparently connected to microbial activity, but perhaps not directly. It is more likely that bacteriogenic ethene degrades to ethane (and propene to propane) to maintain these low level concentrations in near surface sediments. Evidence for this effect will be presented.

There is a clear relationship between the isotopic compositions of ethane and propane in well gases. The samples trending toward heavier carbon are typically in association with more mature oils. This effect has been used as a maturity diagram for thermogenic gas samples. The carbon isotopic ratios for ethane and propane in sediment gases are not nearly as "linearly-trending." Whether these apparent isotopic alterations are microbial or are from other mechanisms is not clear, but some observations can still be made concerning apparent maturities.

GEOC 189: Evidence of a deep source of bacterial methane in the Gulf of Mexico continental slope

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We assess the hypothesis that bacterial methane in deep reservoirs accumulated by rapid burial of shallow bacterial methane formed via microbial activity on recent organic matter. Most bacterial methane formed in shallow sediment in the Gulf slope appears to be lost through seal failures and via rapid microbial oxidation, which results in sequestration of the carbon as geologically stable authigenic carbonate rock. Analysis of bacterial methane from sea floor seeps and vents near gas hydrate on the Gulf slope shows essentially zero modern carbon. The isotopic properties of methane in deep oil reservoirs of the Gulf slope at 3 to 4 km shows that most methane is a mixture of thermogenic and bacterial methane. We suggest that prolonged methanogenesis over considerable depth in the sedimentary section best explains our findings. The lower boundary of the microbial biosphere in the cold Gulf slope may be deeper than thought.

GEOC 190: Microbial ethane and propane production in deepwater Gulf of Mexico reservoirs

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The Plio-Pleistocene age Magnolia Field in the deepwater Gulf of Mexico Garden Banks block 783/784 provides an empirical case example of the biogenic production of ethane and propane. The $\delta^{13}C_1$ of oil-associated gases in the field vary linearly with gas wetness and range from -51 to -68‰. $\delta^{13}C_2$ and $\delta^{13}C_3$ are similarly variable and correlate strongly with that of C_1 ($R^2 \sim 0.85$). Methane $\delta^{13}C_1$ and δD values are consistent with methane generation via CO_2 -reduction. Gas composition and isotopic character covary with a number of fluid attributes that are related to anaerobic biodegradation of liquid hydrocarbons (e.g., TAN and low n-alkane depletion), suggesting that the microbes responsible for biodegradation are acting in concert with those responsible for biogenic methane, ethane and propane production. Recent hydrocarbon emplacement in the field coupled with low temperatures (<75°C) have resulted in incomplete mixing of biogenic and thermogenic gases.

GEOC 191: Overburden effect on sands deposited in the mouth bar system (case study)

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Paper focuses on detailed formation evaluation of Miocene gas bearing reservoirs in Matagorda Island field (GOM 622-23); and developing some advanced interpretation techniques that could improve drilling and well performance in other parts of Gulf of Mexico. Four rock types for the Siphonina Davisi sands were defined on the basis of similar porosity, permeability, textural and depositional characteristics, and pore throat size trends. A clear correlation has been found between the NMR response and paleofacies that also were identified on conventional log diagrams and in cores. Time stabilization tests were run on selected samples to understand the effects of hydrostatic stress on porosity and permeability. Best rocks reduce permeability from 95 to 80 %, and porosity from 92 to 94 %; B-type of rock subjected to 90-75 % alteration of initial porosity; and C-type about 60%. Low permeability rocks losing almost all measure permeability under formation conditions.

GEOC 192: Gas hydrate exploration in the Gulf of Mexico

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A number of factors make the Gulf of Mexico a prime area of interest for commercial production of gas hydrates. First, gas hydrate reaches its maximum concentration in coarse clastics, and deposition in the Gulf provides for substantial amounts of sand within the zone of hydrate stability. Second, the high gas flux rate of the Gulf of Mexico and the extensive system of migration paths should result in many reservoirs containing gas hydrate. Third, the existing infrastructure improves the economics of hydrate development through the leveraging of existing facilities. Fourth, the Gulf of Mexico enjoys a favorable political climate. Fifth, technology required for exploitation of gas hydrate is now emerging. Most current models for hydrate emplacement are derived mainly from piston cores and observations from submersibles, omitting the potential for more deeply buried hydrate concentrations. Integrating all available data yields a wealth of new exploration opportunities for offshore operators.

GEOC 193: Continuum between solid and solution complex: Nanocluster formation on sulfide minerals

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Surface complexes are often assumed to have similar structure to their solution-phase counterparts. However, spectroscopic evidence suggests that polynuclear complexes are often formed on mineral surfaces, even below concentrations required to saturate reactive surface sites. Arsenic and molybdenum, and presumably many other chalcophiles, adsorb to sulfide minerals as metal-sulfide nanoclusters on sulfide mineral surfaces. These clusters often are formed from solutions that contain no appreciable concentration of polymeric solution species. Here, we discuss the structure of these adsorption complexes, the possible driving forces for nanocluster formation in these systems, and the differences between these clusters and nanoclusters formed in solution. The surface plays a critical role in the formation of such clusters, serving as a template for organization and possibly stabilizing adsorbed complexes through the formation of bridging metal-sulfur bonds.

GEOC 194: Iron hydroxide nanoprecipitate formation and suppression on quartz surfaces

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EXAFS experiments show that sorbed ferric ions form iron hydroxide surface precipitates at surface coverages >5% monolayer on Aerosil silica. Below this coverage, precipitates form only if water is removed by evaporation. Single crystal quartz GIXAFS and AFM experiments show similar results, and indicate preferred nucleation at terrace step edges. The precipitates are highly oriented, have mean size of 1 nm, and are well described by a hematite-like structure with hematite [0001] direction normal to the quartz surface. Dissolved silica in the Fe³⁺ solution suppresses precipitation, possibly due to solution Fe³⁺-SiO₄ ion pairing. The Fe³⁺ surface complex on quartz is highly distorted, presumably due to bidentate multinuclear attachment to the stiff silicate framework. No tetrahedral Fe³⁺ is observed in precipitates formed from acidic solutions, but in basic solutions high in dissolved silica, most of the Fe³⁺ enters tetrahedral coordination either in solution complexes or on the silicate surface.

GEOC 195: Mössbauer investigations of surface-bound Fe(II)

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We are using Mössbauer Spectroscopy to investigate the structure and chemistry of FeII adsorbed on FeIII oxides as a function of (i) oxide surface, (ii) pH, and (iii) FeII concentration. Mössbauer spectra reveal the growth of magnetite nanoparticles on lepidocrocite after twelve hours of exposure to 500 μ M FeII. The formation of nanoparticles challenges our conventional thinking that adsorption is the dominant mechanism by which FeII is removed from the aqueous phase at low concentrations. The signature and fate of FeII is spectroscopically selected for by adding the aqueous FeII as ⁵⁷FeII (only ⁵⁷Fe is Mössbauer active). To avoid the underlying oxide from swamping the Mössbauer signal, the oxide is synthesized from ⁵⁶Fe. Using active and inactive Fe isotopes allows us to spectroscopically investigate the nature of FeII bound to iron oxides. The formation of Fe oxide nanoparticles has direct implications on the reactivity of surface bound FeII and its role in contaminant reduction.

GEOC 196: Influence of chemical conditions on rates of oxidation of arsenic(III) by synthetic, biogenic, and natural manganese oxides

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Oxidation of As(III) by an aquifer sediment, synthetic, and biogenic manganese oxides is being studied following observation of significant As(III) oxidation during transport in field experiments conducted in a quartz-sand aquifer under different sets of chemical conditions. In the field, faster oxidation was observed in oxic groundwater at pH 5.7 with no dissolved phosphate as compared to suboxic groundwater at pH 6.2 with dissolved (50 μ M) and adsorbed phosphate, nitrate, and higher dissolved salt concentrations. Oxidation rates observed in the field were on the same order as those observed in laboratory experiments with synthetic Mn(IV) and Mn(III) oxides. The effect of phosphate concentration and pH on the oxidation rate observed in laboratory experiments was on the same order as that observed in the field. Ongoing experiments are comparing As(III) oxidation rates by Mn oxides produced by bacterial spores to those by synthetic Mn oxides and the aquifer sediment.

GEOC 197: Molecular dynamics simulation of aqueous solutions confined in nanopores and interlayers of inorganic materials

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Aqueous fluids play an important role in the natural transformation of nano-particles, facilitating the processes of dissolution, transport, and segregation. Water can also be unwelcome in many nano-technological applications. In both cases, molecular-level understanding of the structure and dynamics of aqueous species at fluid-solid interfaces and in nano-pores is the key to understanding and predicting geochemical evolution and technical functionality of, e.g., adsorbents, ion exchangers, and filtration membranes. Here we describe molecular dynamics simulations of surface and interlayer species in several inorganic layered materials (single- and double- hydroxides, hydrous cement phases, clays) and the effects of water confinement between their layers. The substrate structure and composition strongly affect the behavior of aqueous species at the interface and in the confined nano-spaces. MD simulations, combined with NMR and IR spectroscopy, allow us to merge greatly different time and length scales in understanding and prediction of the nano-scale properties of these materials.

GEOC 198: Intimate interaction of Cu and hydrous ferric oxides determined by analytical electron microscopy

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The fate of trace elements in ecosystems is mainly governed by their interactions with submicron particles. Trapping of trace elements leads to their pre-concentration onto/into solid phases, and to a strong coupling of the cycle of trace elements and particles. In particular, to assess the behavior of copper in ecosystems, it is compulsory to understand the Cu-colloids interactions. The answer to this question requires the use of high spatial resolution microscopy. This research focuses on the interactions between trace element (Cu^{2+}) and particulate forms of Hydrous Ferric Oxides (HFO). The metal-particle interactions have been assessed by Transmission Electron Microscopy coupled with Electron Energy Loss Spectroscopy. This technique allowed us to determine : - the oxidation state of iron and copper at the nanometric scale - and the atomic ratios (Fe/O, Fe/Cu). This approach would ultimately help us to gain information on the fate of trace elements in the environment.
