

ACS DIVISION OF GEOCHEMISTRY SPRING 2001 NEWSLETTER

221st NATIONAL ACS MEETING

SAN DIEGO, CA

Message from the Chairperson:

As the new year dawns, so the Geochemistry Division Exec is once again in transition. I now retire as Chair, and in my place, George Cody takes over the reins. Peggy O'Day is now Program Chair, and it gives me great pleasure to welcome Bill Landing onboard as the new Program-Chair Elect.

The year 2000 was a challenging year for the division. Behind the scenes, the Exec was involved in complex negotiations with the ACS concerning the division's E-Journal "***Geochemical Transactions***." We in the Exec wanted to ensure that it is as simple as possible to subscribe to this journal, preferably via the membership renewal process. After much discussion, a compromise acceptable to both the Geochemistry Division and the ACS was arrived upon. I wish to take this opportunity to thank my colleagues on the Exec for their support and help with this issue, and also the staff at ACS who helped us reach this agreement.

Looking forward to events in 2001, we have one of the best programs the Division has ever organized at the San Diego National Meeting. The general theme of the meeting is on Biogeochemistry, with over 150 oral presentations, but this meeting will also see the inaugural presentation of the Geochemistry Division Medal. The Geochemistry Division will be celebrating its 20th anniversary at this national meeting. As part of the celebration the Division is hosting an Anniversary Dinner, which will be held at the Birch Aquarium, part of the Scripps Institution of Oceanography, on Tuesday, April 3rd 2001. I hope that everyone attending the meeting will be able to join us at this event, which I am sure will be a lot of fun.

Finally, it is traditional that the Chair should end the report with a "Call to Arms." The Geochemistry Division is run entirely by volunteers. We are always happy to see fresh faces get involved, whether that be through organizing a symposium or standing for election on the Exec.

If you have any ideas for symposia topics, please contact Peggy O'Day. With the new online tools ACS has available, organizing a symposium has never been easier! Alternatively, if you are interested in helping out with the Exec, contact George Cody.

See you in San Diego!

Andy Bishop
Chairperson

Electronic Projection at National Meetings

At the recent Division Leadership Conference, the ACS Committee on Meetings and Expositions announced that electronic projection will be available in ALL meeting rooms for the upcoming National Meeting in San Diego.

The committee's plan is to use San Diego as a trial for offering this service. Each meeting room will be equipped with a projector that is connected to an IBM-compatible PC. These PC's will be equipped with floppy and CD drives. It is unclear at this time whether or not the PC's will have ZIP drives, or whether there will be a provision for individual speakers to connect their portable computers to the projectors. In the event of problems, ACS has indicated that there will be provisions for making transparencies in the "audiovisual preview rooms" normally located in each facility.

Many of those involved with National Meetings have been requesting this service for sometime. Previously, individual divisions would have to pay on the order of \$400-\$600/day for a single electronic projector. Whether or not this service continues to be provided by ACS after San Diego may depend greatly on the success of this "trial run". Presenters and session chairs are supposed to be contacted regarding specific arrangements before the meeting.

Call for Papers

RS•C
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Geochemical Transactions, published by the Royal Society of Chemistry in collaboration with the Division of Geochemistry of the American Chemical Society, is an electronic journal for the rapid publication of high impact articles from all areas of geochemistry.

Making full use of the latest web-based technology, Geochemical Transactions enables you to publish '3D' interactive figures, movies, etc., as well as allowing unrestricted use of colour. Use of the electronic medium from start to finish also results in very rapid times to publication. The journal is fully archived.



Submissions for Geochemical Transactions are now being sought, for example, in the following areas:

- Organic geochemistry
- Inorganic geochemistry
- Aquatic geochemistry
- Marine chemistry and chemical oceanography
- Biogeochemical investigations of organic, inorganic and biogeochemical processes
- Molecular and isotopic analyses
- Chemical and elemental cycles
- Geochemical aspects of global change
- Instrumental or analytical techniques applying to the above
- Numeric or computational models of geochemical processes

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Submissions can be sent via e-mail to the Managing Editor at geochem@rsc.org or via the web site at

www.rsc.org/geochem

The web site also contains further details, including instructions for authors, etc

Geochemical Transactions:

Geochemical Transactions, the new electronic journal published by the Royal Society of Chemistry in collaboration with the Division of Geochemistry of the American Chemical Society, was launched successfully in March 2000. The journal is devoted to publication of articles in all areas of geochemical research, including organic and inorganic geochemistry, biogeochemistry, aquatic and marine chemistry, chemical and elemental cycles, numerical and computational modeling, and instrumental and analytical techniques. Several articles have been published to date, with many more in the works.

I would like to invite all members and affiliates to check out the journal website (<http://www.rsc.org/geochem>) for information on subscription and submission of articles. Please consider submitting a manuscript to **Geochemical Transactions**. Remember, it's your journal, and its continued success depends on your support, both by publishing in it, and by subscribing to it. Also, please encourage your institutional libraries to subscribe to **Geochemical Transactions**.

Scott Wood, Editor
Geochemical Transactions

Report from the Treasurer/Editor:

I am pleased to inform our members that the Division is in reasonable financial shape. In the near future, we will begin accepting credit cards for dues, **Geochemical Transactions** subscriptions, and other services. The goal is to make membership in the division more convenient for you!

In the not too distant future we are considering going to an all-electronic newsletter. Other ACS divisions, such as ENVR, have recently done so. The advantage is that this allows us to put more of our resources into programming for our members.

One mechanism members can use to help us provide high-quality programming, while keeping dues low, is to apply for ACS PRF type SE (Scientific Education) grants when they organize symposia at major meetings. ACS PRF type SE grants of up to \$2,000 are available to help defray the travel costs of invited foreign speakers at major symposia in North America. **The application is short, and the Division Treasurer takes care of much of the work!** You can find out about ACS PRF type SE grants at the following website: www.acs.org/80/prf/index.html

John C. Schaumloffel
Treasurer/Editor

Geochemistry Medal To Be Awarded in San Diego

The American Chemical Society Division of Geochemistry will present the GEOC Medal to its first recipient, Frank J. Millero, at the 221st ACS National Meeting in San Diego, April 1-5, 2001. This biennial award for outstanding accomplishment in geochemistry consists of a bronze medallion plus \$2,000.

Millero received a B.S. degree in chemistry from the Ohio State University in 1961, and M.S. and Ph.D. degrees in physical chemistry from Carnegie-Mellon University in 1964 and 1965. After work as a physical chemist with ESSO Research and Engineering Co., he joined the University of Miami in 1996.

A GEOC Medal Award Symposium will precede the GEOC Medal award ceremony. The symposium and award ceremony will be followed by an informal social gathering, sponsored by the Division. Symposium lectures on metal-inorganic ligand interactions (R.H. Byrne), metal-organic ligand interactions (G.W. Luther III) and the biogeochemical significance of metal-ligand interactions (K.W. Bruland) will precede the symposium's final presentation, by Frank J. Millero, on metal-ligand interaction models in natural waters. The symposium presentations are listed on page 26.

Future ACS National Meetings

Chicago: August 26-30, 2001

Orlando: April 7-11, 2002

Boston: September 8-12, 2002

Upcoming 2001 Regional ACS Meetings

Mid-Atlantic: May 30th

Central/Great Lakes: June 11th

Northwest: June 14th

Northeast: June 24th

Southeast: September 23rd

Midwest: October 10th

Southwest: October 17th

Western: October 28th

GEOC 20th Anniversary Dinner !

Please join us for Dinner in San Diego as we celebrate the Division's 20th Anniversary. The Dinner will be held on Tuesday, April 3rd 2001, following the GEOC Medal Symposium and General Business meeting as part of the Division's program at the San Diego National meeting. The venue we have selected is the Birch Aquarium, part of the Scripps Institution of Oceanography. The Aquarium is reputed to be one of the finest venues in San Diego. The price of the tickets for this event is \$42/person, which includes bus transportation from the Convention Center to the Aquarium and back. Tickets can be purchased in advance with the Meeting Registration, and will also be available at the meeting (unless sold out).

Please join with you colleagues and friends as we celebrate 20 years of Service to the Geochemical Community and acknowledge those who have made it all possible!

Menu: Birch Combo Buffet

~Carving Station~

*Carved to order Top Sirloin Beef, Au Jus
Turkey Breast with Cranberry
Rosemary Red Potatoes
Carrots a La Orange
Classic Caesar Salad with Petite Rolls
and Mini Croissants*

~Pasta Station~

*Tri Color Cheese Tortellini
Penne Pasta Primavera
Meatless Marinara Sauce,
Classic Alfredo and Basil Pesto
Garlic Bread and Bread Sticks*

~Dessert~

*Petite size Cobbler bars in Peach, Raspberry & Apple
Includes Iced Tea or Lemonade and Iced Water
Starbucks Coffee and Tea available upon request*

~Acknowledgement~

On behalf of the members and affiliates of the Division of Geochemistry, the Executive Committee of the Division would like to express our sincere appreciation to Scripps Institute of Oceanography, which has generously donated \$1000 towards the cost of the Division's 20th Anniversary Dinner.

Upcoming GEOC Symposia for the 222nd NATIONAL MEETING in Chicago, IL.

Electronic Abstract Deadline: April 30, 2001

Surface Reactivity and Catalysis in Geological Systems. Organizers: Martin Schoonen, SUNY Stony Brook, and Daniel Strongin, Temple University. Co-sponsored with Colloid and Surface Chemistry Division.

Spectroscopic Characterization of Metal Contaminants in Natural Systems. Organizer: Martine Duff, Savannah River Ecology Laboratory.

Contaminant Geochemistry in the Hanford Vadose Zone. Organizers: Sam Traina, Ohio State University, and Calvin Ainsworth, Pacific Northwest National Laboratory.

Future ACS Geochemistry Division Programming

Too often in the past, the Geochemistry programming at the National Meetings has been random, with little synergy between the different symposia. Long-range planning has also been limited.

In an attempt to build better sets of symposia, the Geochemistry Division will in future invite symposia around concentrated themes. This does not mean to say we will no longer welcome unsolicited topic suggestions, these we will always be very happy to accept. But by moving towards more organized, and offering more longer range programming we will be able to offer more dynamic meetings, attracting a wider range of geochemists from around the world.

We welcome a dialogue on the types of themes you would like to see covered. Peggy O'Day (Program Chair) is responsible for long-range programming, and would be happy to hear your suggestions (Email: oday@asu.edu).



ABSTRACTS FOR THE 221ST NATIONAL MEETING

CHEMICAL REACTIVITY OF AROMATIC AND SULFUR CONTAINING AROMATIC HYDROCARBONS IN NATURAL SYSTEMS: I

OCCURRENCE AND ORIGIN OF NON-LIGNIN AROMATIC MOIETIES IN KEROGENS

Claude Largeau, Sylvie Derenne, Pierre Metzger, Thierry Mongenot, and Armelle Riboulleau, Laboratoire de Chimie Bioorganique et Organique Physique, CNRS/ENSCP, 11 rue P. et M. Curie, Paris cedex 05 75231, France, Fax: 33143257975, clargeau@ext.jussieu.fr

It is well documented that aromatic moieties in kerogens often correspond to lignin-related units which originate from a selective preservation-type pathway. However, other sources and/or pathways are responsible for the occurrence of aromatic moieties in kerogens as reflected by the large diversity in chemical structure and thermal behaviour encountered in some aromatic-rich samples. This will be illustrated by several examples concerned with such kerogens of various geological age and geographic location formed via either selective preservation or natural sulphurization, including Kukersite (Ordovician, Estonia), Orbagnoux Laminites (Kimmeridgian, France) and Kashpir oil shale (Volgian, Russia). The nature of the biomolecules, including lipidic and proteinaceous materials, which acted as precursors of these aromatic moieties in kerogens will also be discussed.

COMPUTATIONAL CHEMICAL INVESTIGATION INTO THE FIRST STEPS OF ISORENIERATENE DIAGENESIS

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Isorenieratene is a carotenoid exclusively synthesised by green sulfur bacteria. Due to the highly specific habitat of these organisms, sulfur-rich anoxic water layers in the photic zone, isorenieratene and its diagenetic products are useful biomarkers in palaeoenvironmental studies. In sediments, isorenieratene undergoes various diagenetic alterations leading to a wide range of tetracyclic, aromatic and hydrogenated compounds. This makes reconstruction of the diagenetic pathway from observed isorenieratene derivatives virtually impossible. For this reason, we have performed a computational chemical study into the first isorenieratene cyclisation steps, using a newly developed method, a reactive force field, which allows simulation of bond rearrangements in large molecules. By this means, we managed to identify the first steps of the isorenieratene diagenetic pathway. Furthermore, we can now to estimate the effects of temperature on competing reaction mechanisms, enabling us to draw more detailed information from the distribution of isorenieratene derivatives in sediments.

NON-COVALENT INTERACTIONS BETWEEN PAHS AND HUMIC SUBSTANCES AS DETERMINED BY ADVANCED NMR METHODS

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Polycyclic aromatic hydrocarbons are well known to associate with humic substances in the environment. The associative interactions can be measured by sorption studies in batch experiments, but there are few methods that can describe the chemical or physical interactions that take place. Our group has been employing NMR methods to evaluate the sorption mechanism. Using ¹³C-labeled PAHs synthesized with the label at one or two sites and ¹³C NMR spectroscopy, we can discern the nature of non-covalent interactions by changes in chemical shifts and spin dynamics. Furthermore, 2-dimensional NMR experiments highlighting multiple quantum coherences and nuclear Overhauser effects allow us to discern the proximity of spin labels to humic structures. A new technique diffusion-ordered spectroscopy (DOSY) allows us to evaluate whether the labeled PAH associates with certain humic structures.

MOLECULAR-LEVEL RADIOCARBON ANALYSIS OF PERYLENE IN AQUATIC SEDIMENTS: PRELIMINARY RESULTS

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Perylene is found in sediments from remote lakes, urban harbors, and the open ocean. It is a unique polycyclic aromatic hydrocarbon because it has both anthropogenic and natural sources, including fossil fuels, fallout of partially-combusted organic matter, and in situ diagenetic reactions. Molecular-level radiocarbon measurements of perylene can provide insight into its carbon origin and, hence, aid in apportioning sources and identifying precursors of in situ reactions. Preliminary results of perylene isolated from surface sediments from New York and New Jersey Harbor, Baltimore Harbor, and Siskiwit Lake reveal a wide range of radiocarbon abundances [expressed in terms of fraction modern (Fm)]. Perylene from New York and New Jersey Harbor and Baltimore Harbor are dominated by a fossil carbon origin, with an Fm of 0.0694 and 0.2848, respectively. However, perylene from Siskiwit Lake is composted mostly of modern carbon (Fm=0.8804). These preliminary results are promising and pave the way for quantitative apportionment of this compound.

OXIDATIVE COUPLING OF HYDROXYLATED AROMATIC COMPOUNDS IN NATURAL SYSTEMS

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Hydroxylated aromatic compounds (HACs) are common contaminants of subsurface environments and oxidative coupling may be the dominant process in their fate and transport in such systems. In the presence of suitable catalysts, HACs may couple with: i) themselves; ii) dissolved organic molecules (DOM); and/or iii) surface functional groups associated with soil/sediment organic matter (SOM). These reactions may lead to sequestration of HACs by incorporation into SOM matrices and/or formation of dispersed polymers having enhanced sorption tendencies. Such oxidative coupling reactions were studied in a large experimental matrix of different SOMs, a wide range of concentrations of HACs, and mineral and enzymatic catalysts in batch and continuous-flow systems. The experimental results reveal that sorption, desorption and sequestration of HACs is controlled by the dynamics of coupling interactions. The rate, extent and nature of these reactions appear to be strongly influenced by the chemical structure (i.e., diagenesis) of SOM and catalyst activity.

SORPTION OF PHENANTHRENE TO COMPONENTS OF PLANT CUTICLES

Ashish P. Deshmukh, Myrna J. Salloum, Joseph R. Sachleben, and Patrick G. Hatcher, Department of Chemistry, The Ohio State University, 100, W. 18th Ave., Columbus, OH 43210, Fax: 614-688-4906, deshmukh.2@osu.edu

Plant leaf cuticles are composed of degradable and resistant aliphatic biopolymers, which make significant contributions to terrestrial organic matter. These aliphatic substrates have high partition coefficients for hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs). The present work has been aimed at studying sorption of phenanthrene and determining its interactions with cuticular components

isolated from the *Agave americana* leaves. ¹³C labeled methyl phenanthrene was used as a probe in NMR experiments for determining molecular level interactions. The presence of rigid and flexible polymethylene chains was confirmed from ¹³C and ¹H spin-lattice relaxation time (T₁) measurements, and variable temperature CPMAS. Phenanthrene molecules preferentially associated with the methylenic carbon atoms in the biopolymers as determined from heteronuclear correlation NMR experiments. The solvent extracted cuticular membrane (R1), which contains both cutin and cutan biopolymers had the highest sorption capacity (K_d=42,478), due to the presence of flexible chains in cutin.

TOXIC INHIBITION OF ACETOCLASTIC METHANOGENESIS IN CRUDE OIL- AND CREOSOTE-CONTAMINATED AQUIFERS

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Studies of methanogenic zones in hydrocarbon-contaminated groundwater indicated that acetoclastic methanogenesis is inhibited near non-aqueous sources. At one location close to crude oil, hydrogen- and formate-utilizing methanogens were found at concentrations one hundred times more than that of acetoclasts. Toxicity assays using crude oil-contaminated acetate, hydrogen, and formate solutions showed that acetate utilizers were inhibited by the crude oil. These results indicate that acetoclastic methanogenesis is inhibited near crude oil. At a creosote site, concentrations of volatile acids increase near the source, then taper off within 100m. Creosote toxicity assays indicated that acetate utilizers were inhibited at lower concentrations than formate and hydrogen utilizers were. The observed high volatile acid concentrations are likely from the inhibition of acetoclasts. The results from these two sites suggest that elevated volatile acid concentrations at a site could be related to the degree of toxic inhibition.

SOLID-STATE NMR CHARACTERIZATION OF POLLUTANT-SOIL ORGANIC MATTER INTERACTIONS: PYRENE SORPTION TO CUTICULAR MATERIALS

Joseph R Sachleben¹, Benny Chefetz², Ashish P Deshmukh³, and Patrick G Hatcher³. (1) Campus Chemical Instrument Center, The Ohio State University, 100, W. 18th Ave, Columbus, OH 43210, Fax: 614-688-4906, jsachleb@chemistry.ohio-state.edu, (2) Department of Chemistry, Ohio State University, (3) Department of Chemistry, The Ohio State University

Cuticular materials such as cutin and cutan can make up significant portions of some soils. Characterizing the sorption of pollutants, such as pyrene, to these soil components is a critical step in understanding the physical processes occurring in real soils. We probed the interaction between pyrene and several cuticular materials with one- and two-dimensional solid-state nuclear magnetic resonance (1D and 2D NMR) spectroscopy. We found that the ¹³C longitudinal relaxation time (T₁) of pyrene decreases significantly from that of crystalline pyrene upon sorption to both tomato fruit cutin and *Agave americana* cutan, indicating that the pyrene is mobile upon sorption. Magic angle spinning experiments at low spinning frequencies (2-4kHz) demonstrates that this motion can be either isotropic or anisotropic depending upon the cuticular material to which the pyrene is sorbed. 2D Heteronuclear correlation experiments elucidate the interactions between the soil organic matter and the pollutant. These experiments are allowing the development of models of sorption of hydrophobic pollutants to cuticular materials.

BIOGEOCHEMISTRY OF TERRESTRIAL ORGANIC MATTER: I

FUNGAL BIODEGRADATION OF WOOD IN SOIL CONTACT

Jody Jellison¹, Barry Goodell², Jon Connolly¹, Walter Shortle³, Cynthia Fuller¹, Andrea Ostrofsky¹, Claudia Jasalavich¹, Aria Amirbahman⁴, Timothy Filley⁵, and Stephen S. Kelley⁶. (1) Biological Sciences Dept, University of Maine, 160 Hitchner Hall, Orono, ME 04469, Fax: 207-581-2969, jellison@maine.maine.edu, (2) Wood Science and Technology, University of Maine, (3) US Forest Service, (4) Environmental Engineering, University of Maine, (5) Department of Earth and Atmospheric Sciences, Purdue University, (6) National Renewable Energy Laboratory

White and brown rot fungi are the principle agents involved in the biodegradation of coarse woody debris in the temperate forest ecosystem. The chemical and biochemical mechanisms involved in fungal biodegradation of wood will be briefly reviewed, including the roles of oxalic acid, iron, metal chelators and degradative enzymes in the decay process. Degradative fungi dramatically change the chemical characteristics of the wood and can be shown to influence the pH of the microenvironment, and to translocate cations including Ca, Mg, Fe, Mn, Cu, Zn, Co and Cd from the soil into the degrading wood substrate. A brief overview will also be given of methods used for quantification and identification of degradative microorganisms in wood.

OXIDATION MECHANISM OF WHITE ROT AND BROWN ROT FUNGI

Tünde Mester¹, Katia Ambert-Balay¹, Elisa Varela², Simone Ciofi-Baffoni², Lucia Banci², Daniel Jones¹, and Ming Tien¹. (1) Department of Biochemistry and Molecular Biology, Pennsylvania State University, University Park, PA 16807, mxt3@psu.edu, (2) Department of Chemistry, University of Florence

Our most recent studies on white rot fungal lignin degradation has focused on the mechanism of lignin peroxidase-catalyzed oxidation of a tetrameric lignin model compounds. A nonphenolic tetrameric model containing b-O-4 linkages was synthesized and its oxidation products from fungal wild type and recombinant (wild type and mutated) lignin peroxidase were identified. Incubation of the model compound with either fungal lignin peroxidase isozymes H2 or H8 under steady state conditions resulted in the formation of four carbonyl products. These results are consistent with lignin peroxidase having an exposed active site capable of directly interacting with the lignin polymer without the advent of low molecular weight mediators. We have also initiated studies on the mechanism of brown rot lignocellulose degradation. In accord with prevailing hypothesis, we have investigated the role of oxalate and dimethoxybenzoquinone in hydroxyl radical formation. Our results indicate that the effect of oxalate on hydroxyl radical formation is highly concentration dependent. It facilitates hydroxyl radical formation at low concentration but inhibits at high concentration. The mechanistic details of this effect will be discussed.

ROLE OF FUNGI IN NUTRIENT CYCLING IN FORESTS

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Forest trees fix atmospheric carbon mostly as lignified cellulose in wood. Trees mature and die; lignified cellulose is decomposed by wood-decay fungi (mineralization); and decomposing wood temporarily becomes part organic matter overlying mineral soil yielding essential elements, e.g. Ca, K, Mg, by weathering. Experiments using Sr (Ca analog) indicated the capacity of a wood-decay fungus to "weather" inorganic Sr carbonate, transport Sr, and incorporate Sr into the biomineral Ca oxalate. This work links mineralization, weathering, transport, and biomineral formation in forests to wood-decay fungi. Time-course studies of decomposing spruce stems indicated calcium in freshly fallen wood was retained in an exchangeable form and enriched in biominerals after 8 yr. Examination of this material using ¹³C-labeled tetramethylammonium

hydroxide thermochemolysis indicated that exchangeable calcium increased as the ratio of acid/aldehyde increased in oxidized side-chains of lignin residues.

DEGRADATION OF LIGNIN IN GYMNOSPERM WOODS BY WOOD-ROT FUNGI AS OBSERVED BY ¹³C-LABELLED TMAH THERMOCHEMOLYSIS

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The chemistry imparted to lignin through fungal-mediated decomposition of wood in standing trees and coarse woody debris has profound impact on carbon preservation and export, metal mobility, and subsequent bacterial utilization of degraded wood residues in forest ecosystems. Additionally, the nature of fungal degradative chemistry will influence the ability to identify and measure lignin-derived organic matter exported as DOM. In this study ¹³C-labeled tetramethylammonium hydroxide thermochemolysis was used for molecular characterization of lignin from gymnosperm woods degraded in long-term (4-8 month) laboratory inoculation experiments by various white-rot, brown-rot, and soft-rot fungi. Relationships between overall mass loss, polysaccharide depletion, and lignin demethylation and oxidation within and among these three important wood-rot groups will be discussed.

STRUCTURAL CHARACTERIZATION OF TERRESTRIALLY DERIVED ORGANIC MATTER USING QUANTITATIVE TMAH THERMOCHEMOLYSIS GC-MS

Scott W. Frazier¹, Patrick G. Hatcher¹, Louis A. Kaplan², and Fred Cannon³. (1) Department of Chemistry, The Ohio State University, 120W. 18th Avenue - Box 259, Columbus, OH 43210, frazier.114@osu.edu, (2) Stroud Water Research Center, (3) The Pennsylvania State University

Tetramethylammonium hydroxide (TMAH) thermochemolysis GC-MS is a relatively new technique that has been used to investigate the structural composition of various biopolymers and humic substances. To this point TMAH GC-MS has been utilized mostly for qualitative comparisons. Here we evaluate a methodology for the quantitative application of TMAH GC-MS to organic matter using an internal standard approach. The quantitative TMAH GC-MS procedure has been applied to degraded lignin and dissolved organic matter (DOM) samples. The terrestrial contributions to DOM were investigated based on the lignin-derived and fatty acid TMAH product distribution. Structural changes incurred upon DOM samples from microbial degradation were investigated using plug-flow bioreactors and TMAH GC-MS. TMAH GC-MS can potentially provide more information with less effort than that obtained using other degradative techniques.

THERMOCHEMOLYSIS REACTIONS OF TETRAMETHYLAMMONIUM HYDROXIDE WITH TANNINS: ORIGINS OF METHOXYBENZENES AND METHOXYTOLUENES

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Thermochemolysis/methylation (TCM) using tetramethylammonium hydroxide (TMAH) of aquatic humic substances (AHS) isolated from groundwater and surface water gives products containing high abundances of methoxybenzenes and methoxytoluenes. These mixtures are strikingly similar to those obtained from TCM of samples of eucalypt tannins, suggesting that these types of tannins contributed significantly to the AHS. We have now carried out TCM on a range of model compounds, primarily chosen to represent moieties in tannins, in an attempt to determine the full range of products which may be formed from these sources. We found that aromatic carboxylic acids with hydroxyl groups at the *o*- or *p*- position undergo some decarboxylation to form methoxybenzenes. For example, gallic acid (3,4,5-trihydroxybenzoic acid), a common component of tannins, produced a high abundance of 1,2,3-trimethoxybenzene, and in some cases methoxytoluenes were also produced from benzenecarboxylic acids. TCM of the flavanoids, quercetin and pelargonidin, produced significant concentrations of 1,3,5-trimethoxybenzene and 2,4,6-trimethoxytoluene, which are amongst the most abundant compounds in TCM product mixtures from both AHS and eucalypt tannins. We therefore conclude that our AHS samples contain significant tannin input.

MOLECULAR SPECTROSCOPIC INVESTIGATIONS INTO MICROBIAL DEGRADATION OF PLANTS

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Solid State Nuclear Magnetic Resonance (NMR) spectroscopy (¹³C) and Carbon X-ray Absorption Near Edge Spectroscopy (C-XANES) are powerful analytical tools for investigations into the quantitative chemical and physical changes that occur in wood vascular tissue upon degradation by fungal micro-organisms. As a demonstration, we present the results of a study of samples degraded by the brown rot fungi, *P. placenta* and *G. trabeum*. These organisms preferentially metabolize structural polysaccharides. Solid state ¹³C NMR spectroscopy provides quantification of the loss cellulose and hemicellulose that occurs with progressive degradation. Detailed analysis of spectral intensity in the lignin regions reveals the systematic loss of the methyl group from methoxy groups. The solid state NMR data suggest similar chemistry operating in the case of both organisms, albeit with different apparent degradation rates. C-XANES and soft X-ray microscopy [utilizing contrast derived from variation in intensity of absorption associated with the lignin derived aromatic carbon's 1s-p* transition (E=285 eV)] point to strikingly different modes of attack. In addition to fungal microorganisms we will discuss data derived from studies of other organisms and other types of wood.

INCORPORATION OF INORGANIC NITROGEN INTO HUMIFIED ORGANIC MATTER AS REVEALED BY SOLID-STATE 2-D ¹⁵N ¹³C NMR SPECTROSCOPY

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During the last years, solid-state ¹⁵N NMR spectroscopy has been demonstrated to be a powerful tool to reveal the nature of organic nitrogen in humified material. Most of the published solid-state ¹⁵N NMR spectra showed their main but broad signal intensity in the chemical shift region, most tentatively assigned to amide-N. However, due to the broadness of this signal, some intensity of pyrrole- or indole-type N may be hidden by the dominant amide-N signal. In order to achieve a more precise assignment, solid-state 2-D NMR spectroscopy, correlating ¹⁵N intensity with ¹³C signals was only recently introduced into humic substance research. In the present study this technique was applied to ¹³C-enriched plant material that was incubated up to 9.5 months after addition of ¹⁵N-enriched potassium nitrate. In this study it was intended to reveal which carbon functions will be responsible for the immobilization of inorganic nitrogen during humification.

CHEMICAL REACTIVITY OF AROMATIC AND SULFUR CONTAINING AROMATIC HYDROCARBONS IN NATURAL SYSTEMS: II

ANALYSIS OF PAHS IN ENVIRONMENTAL MATRICES: QUALITATIVE AND QUANTITATIVE APPROACHES

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds, and are common constituents of crude oils and source rocks in which they have been generated by the thermal maturation of organic matter during its burial in sedimentary basins. PAHs are also present in recent environments where their sources are various. It is currently assumed that they essentially derive from pyrolytic origins, either anthropogenic, i. e. high temperature combustion processes, or natural, i.e. natural fires. However, PAHs are also introduced into the environment through contamination by crude oils or refinery products (petrogenic origin) and they can also derive from natural precursors like triterpenoids, pigments, steroids... (diagenetic origin). PAHs are known to be mutagenic and carcinogenic compounds. Their study is then of ecotoxicological interest. They are often minor components present in complex matrices. It is then important in order to study them to develop reliable and precise analytical protocols. This work will thus present an overview dealing with various analytical approaches. Trace quantitative analysis of contaminants in complex matrices still presents some difficulties. During the last decade, the accuracy and the reliability of such measurements have increased. Improvements in extraction, purification and analysis have been performed. It has been possible to develop QA/QC approach partly due to the development of reference materials. The global schematic analytical protocol developed for the analysis of PAHs comprises several steps: extraction, purification and quantification. The work presented here will deal with all these aspects. It will first expose the necessity to perform sophisticated purification steps (high performance liquid chromatography...). Moreover if we consider the complexity of the mixtures to be analyzed, it is important to develop tools allowing a correct identification of compounds and allowing to differentiate between isomers. In this respect, the use of liquid crystalline phase will be discussed. The quantitative aspect of the PAH analysis will then be illustrated. Finally, recent analytical developments such as high temperature gas chromatography or gas chromatography/isotope ratio mass spectrometry, dealing with these compounds, will be exposed.

SEPARATION OF SULFUR HETEROCYCLES

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In the study of the sulfur-containing components in materials like petroleum, combustion residues, and environmental samples, it is frequently desirable to be able to separate these from the non-sulfur compounds. There are two principle ways to do this for the polycyclic aromatic sulfur heterocycles (PASH), namely the oxidation to the sulfones followed by a column-chromatographic separation from the non-polar hydrocarbons, and liquid chromatography on supports containing heavy metal ions. In the latter case mainly palladium in various forms has been used. The details of these schemes will be discussed and their merits detailed and compared.

IMPROVED CHARACTERIZATION OF AROMATIC HYDROCARBONS IN OILS THROUGH SEPARATION OF ORGANO-SULPHUR COMPOUNDS

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Organo-sulphur aromatic compounds in oils are known to cause a number of environmental problems upon refining and also to impede precise analysis of aromatic hydrocarbons. Such an analysis is especially important due to the role of these compounds on oil thermal stability. So as to get a better insight in the composition of aromatic hydrocarbons in oil, separation from organo-sulphur compounds is required. This can be achieved through oxidation of organo-sulphur compounds into sulfones followed by column chromatography separation. This method was perfected on model compounds to determine reaction conditions and yield and to examine (i) the behaviour of aromatic hydrocarbons upon this oxidation and (ii) the effect of steric hindrance. The aromatic fraction of two oils of different maturity stages was then submitted to this oxidation and analysis of the resulting aromatic hydrocarbons and organo-sulphur compounds was performed by GC/MS.

DEVELOPMENT OF NEW TECHNIQUES IN THE FIELD OF QUANTITATIVE AND ISOTOPIC ANALYSES OF AROMATIC AND SULFUR-AROMATIC COMPOUNDS IN WATER SAMPLES : POTENTIAL FOR PETROLEUM AND ENVIRONMENTAL GEOCHEMISTRY

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This study shows comparative results of quantitative as well as carbon and hydrogen isotopic measurements of BTEX, methanol and tetrahydrothiophene in water. Extractions are done by SPME as well as static and dynamic head-space techniques. Quantifications are performed by GC and GC-MS with a method using several deuterated internal standards. On-line specific compound isotopic measurements are performed by GC-C-IRMS for carbon and by the newly developed GC-TC-IRMS for hydrogen. For BTEX compounds, detection limits down to 10 ppt are reached, whereas concentration limits as low as 20 ppb are required for carbon and hydrogen isotopic measurements. This kind of analytical geochemistry approach proves useful in both the petroleum geochemistry field (e.g. oil proximity indicators in formation water) and the environmental one (e.g. detection, quantification, origin, biodegradation of organic pollutants in aquifers as well as waste and drinking waters).

APPLICATION OF MASS SPECTROMETRY AND GROUP TYPE ANALYSIS TO OILS OF DIFFERENT GEOCHEMICAL ORIGINS

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Group Type Analysis (GTA) was performed using solid probe-high resolution-mass spectrometry on different fractions of crude oils (topped oil, maltenes, total and sub-fractions of aromatics) in order to evaluate the potential of this quantitative method for Organic Geochemistry applications. Six crude oils, derived from the three main types of organic matter, selected because of their different chemical composition and sulfur content were analysed. Detailed analytical description of aromatic structures were obtained. Due to the complexity of aromatic structures in crude oils, a pure aromatic fraction and even better, aromatic sub-fractions allowed us, on the one hand, to decrease overlappings between different chemical families (sulfur-containing and non-sulfur-containing aromatics) and, on the other hand, to assign aromatic structures to families in a better way (for example balance between naphtho-diaromatic and/or phenanthrene). But, when using pure fractions, some critical points arose mainly due to the alkylaromatics and sulfur compounds and the high/low boiling point molecules (bp \leq 280 °C and bp \geq 600 °C). These different points were considered and an application procedure is proposed together with its limitations. Possible improvements and

adjustments of this method are suggested. The results, obtained by integration of the different FGTA analysis of aromatic subfractions, are consistent with the expected composition of the selected oils regarding to their geochemical origin.

HYDROCARBON ANALYSIS BY GC-FI-TIME-OF-FLIGHT MASS SPECTROMETRY: COMBINATION OF BOILING POINT SEPARATION, SOFT IONIZATION, AND ACCURATE MASS MEASUREMENT

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Hydrocarbon characterization by mass spectrometry has been the subject of study over the past fifty years. Numerous methods have been developed based on high and low resolution mass spectrometry using a wide range of ionization techniques. Combinations of mass spectrometry and chromatography have been very successful in resolving isomers and compound types that cannot be resolved easily by mass spectrometry alone. Field Ionization (FI) is a preferred ionization method for hydrocarbon analysis because it generates molecular ions for both aromatic and saturate hydrocarbons. Traditionally, FI has been difficult to use in high resolution mode because of the lack of sensitivity and stability, and the problem become more acute when used in conjunction with chromatography. Time-of-Flight (TOF) mass spectrometry, which has made significant progress in recent years, has potential to analyze ions generated by FI with good precision and sensitivity. We recently explored GC-FI-TOF mass spectrometry for analysis of hydrocarbon mixtures. Accurate mass (RMS error < 3 mDa) with an elevated resolving power (RP>5000(FWHM)) has been achieved for FI across a wide mass range (15-650 Da). The combination of boiling point separation and accurate mass analysis of molecular-ion-only mass spectra allowed us to elucidate petroleum crude composition (paraffins and heteroatomic molecules) at a new detailed level with a faster speed.

BIOGEOCHEMISTRY OF TERRESTRIAL ORGANIC MATTER: II

INVESTIGATION OF THE CHAIN LENGTH AND CHEMICAL CONSTITUTION OF INDIVIDUAL CONDENSED TANNINS BY MALDI-TOF MASS SPECTROMETRY AND THE CORRELATION WITH THEIR PROTEIN BINDING AFFINITY

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Condensed tannins are ubiquitous polyphenolic compounds in nature, mainly occurring in leaves and stems from higher plants. Condensed tannins released from senescing plant organic matter (leaf litter) may affect the nitrogen availability in soils by complexation and immobilisation of proteins, an important nitrogen source in soils. It is supposed that the protein binding affinity highly depends on the polymer chain length and the chemical structure of tannins. Due to the difficulty in analysing individual polymer chains, analytical methods mostly give average molecular characteristics. Therefore, we studied extracted tannin polymers from different tree species (*Salix alba*, *Picea abies*, *Fagus sylvatica*, *Tilia cordata*) by MALDI-TOF mass spectrometry and could obtain not only an average chain length, but also the distribution of individual chains and their chemical constitution. We can demonstrate that different chain length distributions are responsible for differences observed in protein binding affinities.

CHEMICAL AND SPECTROSCOPIC STUDY OF THE BIODEGRADATION OF LIGNIN IN FOREST SOILS AFFECTED BY NITROGEN DEPOSITION

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Lignin is generally the most recalcitrant component in plant litter, and its decomposition regulates that of the total organic matter (OM) in forest soils. Its biodegradation is controlled by the concentration of N available for the soil biomass, a parameter affected by N deposition caused by anthropogenic emissions. The chemical and structural features of forest soil OM were followed according to N content of soil. The OM was characterized in the humus layer and mineral soil of 15 spruce sites using specific analyses for lignin and polysaccharides, hydrolyzable-N quantification and solid-state ¹³C and ¹⁵N nuclear magnetic resonance (NMR). The effect of N content on lignin degradation was negative in the mineral soil layer and positive in the humus layer. Some differences in the quality of OM from the different sites were underlined with NMR spectroscopy.

CHANGES OBSERVED BY NMR AND PYROLYSIS GC/MS OF HARVARD FOREST SOILS AND THEIR ASSOCIATED PLANT COMPONENTS CAUSED BY TEN YEARS OF HEAVY NITROGEN FERTILIZATION

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Samples from canopy-to-soil stratigraphic profiles were collected from the Harvard Forest Chronic N plots during 1989 to 1999 and analyzed by solid-state ¹³C and ¹⁵N NMR and pyrolysis GC/MS to determine the effects of heavy N fertilization over time. DOM collected in 1997 from underground lysimeters was also analyzed. ¹³C NMR spectra from all samples contain predominantly signals associated with paraffinic (0-45 ppm) and carbohydrate (60-90 ppm) structures and low amounts of aromatic (90-160 ppm) structures. ¹⁵N NMR spectra reveal primarily signals associated with amide structures that imply existence of refractory proteinaceous materials. The mineral soil samples exhibit minor amounts of aromatic structures, suggesting little contribution of lignin structures to the organic matter. Primary changes observed in each set of the canopy-to-soil profiles were a loss of carbohydrates and a persistence of the paraffinic carbon regions of the NMR spectra. N fertilization affected leaf growth and litter decomposition in the various soil horizons.

PRESERVATION OF PROTEINACEOUS MATERIALS IN NATURAL ENVIRONMENTS

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Proteins, the most abundant nitrogen-containing substances in many organisms, traditionally have been considered relatively labile and are quickly degraded in environmental systems. However, recent studies have suggested that part of this "labile carbon and nitrogen pool" can be preserved and subsequently sequestered. In this study the chemical nature of organic nitrogen in a Coorongite sample is analyzed by NMR spectroscopy, pyrolysis GC-MS, and TMAH thermochemolysis GC-MS. The results show that the organic nitrogen in the Coorongite primarily exists in proteinaceous forms. By simulating an encapsulation process, we suggest that the proteinaceous material in the Coorongite has survived diagenesis via trapping within the refractory aliphatic structural network of the sample.

MOLECULAR TURNOVER RATES OF SOIL ORGANIC MATTER

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Soil organic matter (SOM) plays a major role in the terrestrial carbon cycle. However, the turnover rates of SOM at the molecular level are only poorly understood. Therefore we applied analytical pyrolysis in combination with compound specific isotope ratio mass spectrometry (Py-GC/MS-IRMS) to soil organic matter from fields naturally labeled with isotopically "heavy" maize plants. The difference in $\delta^{13}\text{C}$ -values between pyrolysis products from soil C of the labeled and control fields identifies the fraction of new carbon. Hence, mean residence times can be calculated for molecular fragments of soil organic matter. Unexpected low mean residence times were found for lignin from fresh plant material. In contrast carbohydrates from SOM had high mean residence times of about 50 years. As these carbohydrates are newly formed in soil, this indicates new mechanisms for the stabilization of SOM.

CONTRIBUTION OF LIGNIN AND POLYSACCHARIDES TO THE REFRACTORY CARBON POOL, AS STUDIED IN C-DEPLETED ARABLE SOILS

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Our aim was to assess the contribution of lignin and non-cellulosic polysaccharides to the refractory OC pool in arable soils. We analyzed particle-size fractions of soils from two contrasting treatments established in long-term agroecosystem experiments, i.e. fertilized plots and unmanured plots. The C-depleted plots are depleted in OC compared with the fertilized counterparts, and thus are assumed to be enriched in refractory C compounds. Lignin does not accumulate within the refractory C pool. In contrast, in fine particle-size fractions (< 6 μm) polysaccharides seem to be stabilized and contribute to the refractory C. The ratio of hexoses-to-pentoses indicated a dominant contribution of microbial sugars in the fine fractions.

$^{13}\text{C}/^{12}\text{C}$ RATIOS OF PLANT-DERIVED N-ALKANES IN SOIL PARTICLE-SIZE FRACTIONS

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Soil organic carbon can be labelled by cultivation of C4 plants, e.g. maize, on soils which have been previously cropped with isotopically distinct C3 plants. Particle-size fractions from soils cultivated 23 years either with maize or wheat have been analysed for C and N contents, and for $\delta^{13}\text{C}$ values of plant-derived n-alkanes (C29, C31). The amount of maize-derived C of organic components has been calculated by isotope balance. After 23 years of maize cropping, $\delta^{13}\text{C}$ values of alkanes from the same soil sample increase with particle size. The results have two implications. First, the input of leaf wax alkanes into the soil is occurring preferentially via large particles. Second, in a same soil sample, the C31 alkane from the 200-2000 micrometer particle-size fraction is younger than C31 alkane from the 50-200 micrometer and 0-50 micrometer fractions. In this respect, ^{13}C analysis represents a method of relative dating of individual compounds.

WHICH SUBSTANCES CONTRIBUTE SIGNIFICANTLY TO THE ENRICHMENT OF NON-EXTRACTABLE ALKYL CARBON STRUCTURES DURING LITTER DECOMPOSITION AND HUMIFICATION IN SOILS?

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^{13}C NMR spectroscopic studies of forest soil profiles revealed that unknown alkyl carbon compounds with rigid structures accumulate during litter decomposition and humification. We could show that hopanoids, a family of pentacyclic triterpenes, do not contribute significantly to this phenomenon because of their small concentrations. The chemical characterisation of insoluble alkyl carbon compounds until now was confined essentially to NMR and pyrolysis techniques. In our study we try to isolate these substances from soils by chemical degradation reactions to identify and quantify them by GC-MS. By the combination of spectroscopic and wet chemical methods we want to achieve informations about their structures, their absolute concentrations and their behavior under different pedogenetic conditions in forest soil profiles.

INVESTIGATING POPULATIONS OF METHANE OXIDISING BACTERIA USING COMPOUND-SPECIFIC STABLE ISOTOPE TECHNIQUES

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Methane oxidation by soil bacteria is an important sink of methane, either oxidising high concentrations of methane produced in anaerobic environments before entering the atmosphere or by removing ambient levels of methane directly from the atmosphere. Microorganisms responsible for oxidising methane at these two concentrations are termed low and high affinity methanotrophs, respectively. High affinity methanotrophs can not be cultured and therefore little is known about their microbiology. In this investigation stable isotopic pulse-chasing is used to label phospholipid fatty acids (PLFAs) produced by methanotrophic bacteria. Gas chromatography/combustion/isotope ratio mass spectrometry was used to provide a PLFA 'fingerprint' of the microorganisms metabolising the labelled substrate. This fingerprint was then used to identify and compare methane oxidising bacterial populations in soils. Incubation of soil with both labelled methane and carbon dioxide allowed the question of autotrophic bacteria also being involved in methane oxidation, to begin to be addressed.

MICROBIAL MOLECULAR MARKERS IN AQUATIC BIOGEOCHEMICAL CYCLES: I

POLYMER ASSEMBLY AND CARBON CYCLING IN THE OCEAN

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The ocean plays a major role in global biogeochemical carbon cycling as it holds one of the most important reservoirs of organic carbon on earth. Two parallel biological systems linked by a polymer system interact in the ocean to process about 50% of the photosynthetic activity that cycles atmospheric CO₂ in our planet. A fuel source bioreactor, fed by solar energy, and a sink bioreactor that burns this fuel generating new biomass that is then recycled as new fuel. Fuels released by these bioreactors are polymeric in nature. The energy pipeline between source and sink is a dynamic transport system consisting of self-assembling marine biopolymers. DOC polymers are not directly available to microorganisms. Bacteria feed principally on colloidal-nanometer and micron-size polymer networks. The spontaneous assembly of DOC biopolymers into microscopic gels has changed the way that oceanographers think about processes linking the microbial loop and biological

pump to the rest of the biosphere and the geosphere. The missing functional bridge allowing microorganisms to access the rich substrate of DOC polymers is the subject of this talk.

CONTRASTING ENZYME ACTIVITIES AND SUBSTRATE SPECIFICITIES IN SEAWATER AND SEDIMENTS: A REFLECTION OF MICROBIAL COMMUNITY COMPOSITION?

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To use substrates such as proteins, lipid complexes, and polysaccharides, some fraction of a microbial community must produce the specific extracellular enzymes required to hydrolyze a substrate to sizes small enough to be transported into bacterial cells. Recent studies have suggested that the composition of microbial communities may differ fundamentally between sediments and seawater. In order to investigate possible functional differences between microbial communities in these environments, extracellular enzyme activities and specificities were measured using six structurally-distinct polysaccharides as substrates at three field sites. All six polysaccharides were hydrolyzed in sediments, at rates differing by factors of ca. 10-100. In seawater, in contrast, three of the six polysaccharides-including the polysaccharide most rapidly hydrolyzed in sediments-were not measurably hydrolyzed. Restrictions in enzyme activities and/or expression among water column microbial communities could profoundly affect the rate and nature of carbon cycling in marine systems.

INVESTIGATIONS OF BACTERIALLY DERIVED CELLULAR MATERIAL AT THE SUB-MICRON SCALE

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The cycling and preservation of organic matter within the oceans are crucial steps in the global carbon cycle. Although the vast majority of marine organic carbon is originally produced by photosynthesizing organisms in the upper ocean, preservation of this carbon takes place only in sediments often located thousands of meters below the oceans surface. It has been estimated that only about 1 organic carbon molecule out of every 1000 produced is preserved within marine sediments. At present, what is known about the decomposition pathways of individual bacterial remnants within sinking matter has been elucidated by examining molecular biomarkers, which make up a small percentage of the total material. We have initiated a study of individual particles and cellular wall material in sinking organic matter using scanning transmission x-ray microscopy. Preliminary results suggest that bacterial cell wall remnants undergo a significant change in character as they sink through the water column, becoming more enriched in acid moieties.

MYCOSPORINES IN THE ENVIRONMENT: THEIR ANALYSIS AND IMPLICATIONS

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Mycosporines are secondary metabolites with marine (mycosporine-like amino acids; MAAs) and terrestrial (mycosporines and non-mycosporines) origins. Mycosporines function as sunscreen agents against UV radiation and can be 2% of the dry weight within organisms. Mycosporines and MAAs are composed of cyclohexenone and cycloheximine ring structures conjugated to an amino acid subunit and, in some instances, linked to various carbohydrates. The unavailability of commercial standards has made characterization of these compounds in the environment problematic. Therefore, we have implemented mass spectral methods to analyze mycosporines. Using LC/MS and LC/MS/MS techniques we found mycosporine-glutaminol-glucoside in several strains of rock encrusting black yeasts. In the marine environment, almost all divisions of photosynthetic algae produce several structurally distinct MAAs which are trophically transferred through the food chain. Marine phytoplankton also 'leak' MAAs into the dissolved phase decreasing UV penetration through the water column. Hence, mass spectral tools has allowed for the characterization of mycosporines.

LIPID BIOMARKERS FROM MARINE CAULOBACTERIA AS TOOLS TO STUDY DETAIL CARBON FLOW

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Caulobacteria are prosthecate bacteria and often specialized for oligotrophic environments. In a polyphasic approach, including lipid analysis, the taxonomy of marine isolates belonging morphologically to this type of bacteria was clarified. Their polar lipids were studied by chromatographic and spectroscopic methods. Using tandem mass spectrometry individual phospho- and sulfolipids were analyzed and their structures elucidated. The distribution of the different types of polar lipids, especially of the sulfoquinovosyl-, glucuronotaurine amide- and phosphatidyl-glucopyranosyl-diacylglycerols, led to the identification of three different groups of these bacteria corresponding to the genera *Brevundimonas*, *Maricaulis* and *Hyphomonast* together with some outliers belonging to undescribed genera. Isotopic ratio mass spectrometry of these biomarkers in combination with ¹³C labeled compounds can be applied to monitor the activity of this group of bacteria in microbial communities. Because caulobacteria are found in practically any type of seawater this can be a useful method to measure their role in biogeochemical cycles.

SHIFTS IN MICROBIAL COMPOSITION AND CONTRIBUTION TO MACROMOLECULAR DISSOLVED ORGANIC MATTER IN EXPERIMENTAL MESOCOSMS

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A series of experimental mesocosms were established with multiple treatments to compare changes in microbial community composition growing on a diverse array of DOM substrates. Microbial contributions and modifications of high molecular weight DOM (UDOM - > 1 kDa) were also examined. Aged coastal seawater within 220L mesocosms was amended with 1 μ M phosphate, a microbial consortia and a series of DOM treatments: 1) control, 2) glucose + free amino acids and 3) protein. Two additional mesocosms contained diatom-excreted DOM (plus phosphate and microbial consortia additions) with one of the tanks also amended with protein. DOM was consumed rapidly by the microbial community within all but the control mesocosm. Following the initial rapid consumption of DOM, UDOM-C continued to decline within the algal DOM mesocosms, but increased slightly in other tanks. Bacterial contributions to UDOM were observed, specifically as branched fatty acids and D-amino acid enantiomers. Shifts in D/L amino acid ratios and lipid biomarkers indicated changing community structure.

AMINO ACID D/L-ENANTIOMERS AS INDICATORS OF IN SITU PRODUCTION BACTERIAL CELL WALLS IN MARINE SEDIMENTS

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Although it is always assumed a priori that sedimentary amino acids are derived from settling organic matter, part of the amino acids might be synthesized in situ by living bacteria in the sediment. Application of diagenetic models to sedimentary amino acid concentration profiles, generally considered as an important tool to evaluate organic matter degradability, would thus result in erroneous estimations of amino acid degradation rates when bacterially derived amino acids are not taken into account. The analysis of D- and L-amino acid enantiomers has been used to study the potential production of bacterial cell wall material enriched in D-amino acids in samples from the northwestern European continental slope. D-amino acid concentrations were corrected for the contribution of racemization. From reported D/L amino acid ratios in peptidoglycan, the main structural components of bacterial cell walls, it was calculated that bacterial cell wall-associated amino acids account for a significant portion of the amino acids in the sediments.

CHEMICAL REACTIVITY OF AROMATIC AND SULFUR CONTAINING AROMATIC HYDROCARBONS IN NATURAL SYSTEMS: III

NORMAL PHASE SEPARATION OF AROMATIC COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ON CHARGE TRANSFER COLUMNS: COMPARISON ON STANDARD MIXTURES AND AROMATICS FROM NARROW CUTS OF BOSCAN AND ARJUNA CRUDE OILS

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Compositional kinetic schemes of kerogen and oil cracking used for petroleum system modelling require the quantitative evaluation of hydrocarbon structural families, since structural characteristics influence thermal stability. Mass spectrometry with response factors on fragments or molecular ions is generally performed for this quantification. Although this analysis is correctly achieved for saturates, quantification of aromatics from oils and source rock extracts is still a difficult problem since it is complicated by the presence of several molecular ions from different structural families at the same nominal mass. We propose to perform quantification by using high performance liquid chromatography coupled to mass spectrometry of molecular ions, the prerequisite being an efficient separation of interfering aromatic families. The ability of charge transfer phases for separating aromatics according to their number of pi electrons, independently of their alkylation degree, is shown here both on reference compounds and on different narrow cuts of crude oils.

13C ANALYSIS OF PAH : A NEW DIMENSION IN SOURCE ASSESSMENT STUDIES

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Among various chemical contaminants, the pollution caused by Polycyclic Aromatic Hydrocarbons (PAHs) has led over recent years to numerous studies on the origin, distribution and fate of PAHs in the environment. The sources of these compounds are numerous. It is currently assumed that they are mainly of a pyrolytic origin. Besides this origin, PAHs are introduced in the environment through contamination by crude oils, coal tar or various refinery products (petrogenic origin). They can also be derived from biogenic precursors like terpenes, pigments and steroids (diagenetic origin). It is important to study the biogeochemical cycles of PAHs as these compounds show mutagenic and carcinogenic properties. Nevertheless, the elucidation of PAH source and behaviour can be problematic. Indeed these studies are based on PAH molecular fingerprints or concentration ratios. Physical, chemical and microbial transformations can alter the characteristics of many sources during transport and deposition. Alternative methods are thus very desirable. In that prospect, GC-C-IRMS (gas chromatography/ combustion / isotope ratio mass spectrometry) can be a complementary technique of source apportionment. The measurement by GC-C-IRMS of isotopic composition of individual PAHs in conjunction to a molecular approach add a new dimension to biogeochemical studies and provides the geochemist with a powerful tool to study the fate and the origin of the organic matter. In this paper we will present this technique and the specific problems related to the analysis of PAHs by GC/IRMS (sample preparation, oxydation of PAHs, chromatographic resolution). Two applications will be presented : (i) we will discuss the use of GC/IRMS to quantitatively source apportion methylphenanthrenes in petroleum contaminated sediments; (ii) we will discuss the use of GC/IRMS to follow the contamination of the French Atlantic coast by the heavy fuel released by the ERIKA tanker in December 1999.

ANALYSIS OF TOTAL SULFUR AND SPECIATION OF SULFUR COMPOUNDS BY HYPHENATED TECHNIQUES

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Under environmental pressures to reduce sulfur levels in automotive fuels, new lower levels were set by European Commission. In Europe, since the 1st January 2000, maximum sulfur level in gasoline is 0.0150 % (w/w) and 0.0350 % (w/w) for diesel. In 2005, they will be both 0.0050 % (w/w). What will be the next specifications after? 0.0010 % (w/w) or less? Which techniques could be used to measure total sulfur at these different levels of concentration with a good level of precision (WDXRF, EDXRF, UVF...)? Which normalized methods could be used? This paper describes the state of the art for the analysis of sulfur in petroleum products and what kinds of techniques and normalized methods could be used (Result of the last Round Robin test organized in Europe in 2000 by CEN TC19 working group 27). In order to reduce the level of sulfur in petroleum products for the future specifications, research center like the IFP has been working for many years to develop hydrodesulfurization units and catalysts. In the same way our analytical laboratories develop methods in order to help the understanding of the mechanisms involved in the removal of sulfur during the treatment. This paper presents hyphenated techniques in gas chromatography able to analyze sulfur in petroleum products (GC-AED, SCD, PFPD) like gasoline and diesel (analysis of the feeds and hydrotreated products, speciation of refractory sulfur compounds).

RESOLVING MULTIPLE SOURCES OF THE PETROGENIC HYDROCARBON BACKGROUND IN BENTHIC SEDIMENTS OF PRINCE WILLIAM SOUND, ALASKA

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Petrogenic hydrocarbons, including polycyclic aromatic hydrocarbons (PAH), derived from a Tertiary petroleum province in the eastern Gulf of Alaska, dominate the hydrocarbon background in benthic sediments of Prince William Sound. Contributors include seep oil residues and organic shales and coals having a wide range of thermal maturities. Identification and quantification of these sources, required because of presumed differences in PAH bioavailability, were accomplished through a research program containing five elements. These include: (1) geology and physiography of the region, (2) sampling of all major probable hydrocarbon contributors, (3) organic petrography and grain-size analysis of the sediments, (4) precise quantitative analysis for organic carbon and the PAH, saturate biomarkers, and aromatic steroids at ppb and sub-ppb concentrations, and (5) statistical analysis of the chemical data including elemental mass balance constraints. Results show that the organic shales and seep oil residues are major contributors whereas the coal contribution is minor.

BIODEGRADATION OF LIGNITE IN LIGNITE-CONTAINING MINE SOILS

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In mine soils lignite can be present in addition to recent organic matter derived from plant material. Its biochemical reactivity and role in the soil carbon cycle is unknown. The aim of this study was to examine the fate of lignite carbon and associated decomposition processes in soils. Lignite-containing mine soils of different age with and without recent organic matter contribution were incubated for 16 months and the carbon mineralization monitored. ¹⁴C activity measurements were carried out to determine the lignite contribution to the CO₂ emission, the microbial biomass and the humic acid fraction. Lignite carbon was decomposed during the whole incubation period, it was partly mineralized and partly incorporated in the soil microbial biomass. A higher portion of lignite can be extracted as humic acid with increasing soil development, indicating that the residual lignite in the soil is oxidized during biodegradation.

BIODEGRADATION BY MICROBIAL MATS OF ALKYLATED AROMATIC HYDROCARBONS FROM PETROGENIC ORIGIN

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Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental contaminants. The PAH contribution in the environment is essentially from pyrolytic sources and from petrogenic origin. This contamination represents a serious risk to environment and human health because of carcinogenic properties of certain PAHs and PAH metabolites. It becomes important to study the PAH behaviour in the environment. Their persistence is due to their low water solubility, so they become rapidly associated with sediments where the microbiological degradation represents the major process of PAH transformation. Hydrocarbon-degrading bacteria can use PAHs as carbon and energy source. The PAH degradation can also depend on the number of aromatic rings. The aim of the work presented here was to study the bacterial degradation of petrogenic PAHs (naphthalenes, phenanthrenes and dibenzothiophenes) by bacterial mats. Indeed recent studies have shown that these bacterial mats can play an important role in bioremediation of areas polluted by petroleum. During the Gulf War in 1991, bacterial mats have grown on petroleum-contaminated areas and have completely degraded hydrocarbons (Krupp et al., 1996). In the present study, a bacterial mat coming from a petroleum chronic-contaminated area (Gulf of Fos in the south Mediterranean coast of France near petroleum terminals) has been used in microcosm studies to evaluate the capabilities of these organisms to degrade PAHs.

BIODEGRADATION AND BIOREMEDIATION OF PETROLEUM AND PETROLEUM-DERIVED COMPOUNDS: WATER TRANSPORTATION, SOLUBILITY, AND EMULSIFICATION INFLUENCE: AN OVERVIEW AND STUDY

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The present study and overview of the importance of transportation and solubilization of hydrophobic organic compounds to the rates of biodegradation is mainly related to aquatic environments. However, for comparison soil remediation is briefly reviewed. We stress the difference between soil microbiota and both planktonic and benthic marine organisms. We present the various emulsifying agents and transporting media important for benthic contact with petroleum and other organic contaminants. Based on our experiments we conclude that the bioavailability of oil and hence the sequence of bioremediation depends on the above-discussed parameters as well as the diversity of the biomass. In cases where the polar aromatics (PAHs) and sulfur containing (thiophenic) compounds are more bioavailable to the microbial community, the biodegradation of these is faster than the normal hydrocarbons. Furthermore, bacterial species that are not involved directly in the alteration of the organic contaminants could facilitate the biodegradation by the formation of bioemulsifiers.

REACTIVITY AND BIOLOGICAL ACTIVITY OF PAH ON RESPIRABLE PARTICULATES

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Certain polyaromatic hydrocarbons (PAH) have been linked to cancer. Ambient air particulates contain many organic molecules including PAH. The host matrix may play a pivotal role in the atmospheric reactions of PAH. The reactivity of benzo[a]pyrene towards NO₂ and O₃ on several different supports was measured using infrared spectroscopy. The ability of these particulates to induce the expression of an endothelial adhesion molecule, ICAM-1, was measured using a human umbilical vein endothelial cell line and a human macrophage culture system. The mutagenicity of these particulates was studied on the chinese hamster ovary cell line AS52. The cytotoxicity of the particles was found to be dose dependent and caused an increase in the mutation frequency when compared to controls. These results demonstrate that the reactivity of PAH at the solid/gas interface varies with the support and the composition of particulates can contribute to the biological effects.

BIOGEOCHEMISTRY OF TERRESTRIAL ORGANIC MATTER: III

CONTROLS ON FORMATION AND DEGRADATION OF SOIL ORGANIC CARBON

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Formation of soil organic C occurs primarily through decomposition of plant material. Once plant C enters the soil, it is stabilized biochemically, physically, and chemically. In this study we relate residence time of carbon in soil fractions to shifts in microbial populations and physical protection mechanisms. The $\delta^{13}\text{C}$ values of soil fractions from ^{13}C -labeled experiments indicate C-pools with distinct turnover rates, microbial biomass (0.5 - 2 y), slow (10's y) and stable (100-1000 y). Approximately 60% of organic C is respired as CO_2 during the initial degradation by the soil microbial population. Changes in the composition in the microbial community towards fungi can decrease the amount of C respired as CO_2 . Soils with high clay content increased retention of organic C and incorporation into aggregates by 20%. Microbial biomass C is generally comprised of proteins and amino acids with the first byproducts of microbial decomposition appearing as unsaturated aliphatics as determined by 2-D NMR. The microbial products become part of the slow C pool, which is C that is physically protected within soil particles and biochemically resistant to degradation. Recent C incorporated into the slow pool is associated with soil aggregates > 250 μm . The C associated with aggregates < 53 μm is biochemically and chemically stabilized; however the nature of these organic C compounds is not completely defined. Disturbance of the soil in cultivated agricultural systems leads to loss of large soil aggregates, increased microbial respiration, and the subsequent loss of protected C.

13C AND 14C: DEPLETION OF GRASSES GROWING IN URBAN AREAS CONTAMINATED BY FOSSIL-FUEL CO₂

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The increasing use of fossil fuels during the past century has introduced huge amounts of fossil CO_2 in the terrestrial environment. Since fossil fuel derived CO_2 is ^{13}C -depleted relative to atmospheric CO_2 , plant carbon can be used to monitor diffuse input of fossil fuel CO_2 in modern ecosystems (e.g. Marino and Mc Elroy, *Nature*, 1991, 349, 127-131). Here, we measured ^{13}C content and ^{14}C -age of grasses growing in pristine and urban environments in France : 16 samples in Paris and 8 samples in pristine rural areas about 350 miles eastward, westward and southward from Paris. The results show that urban grasses are strikingly depleted in ^{13}C and ^{14}C , thus giving evidence for a notable input of fossil fuel C.

DIRECT IDENTIFICATION AND RADIOCARBON DATING OF MICRO-CHAR IN SOILS

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Black carbon (BC) is produced by vegetation fires and fossil fuel combustion and resides in many black soils. BC made up 15 to 45 percent of the soil organic carbon in sub-surface horizons (20-40 cm) of several German soils. Here we focus on the nanometer morphology and structure and ^{14}C -age, applying a suite of complementary methods: high resolution transmission microscopy (HRTEM) combined with electron energy loss spectroscopy (EELS), energy dispersive X-ray (EDX) analysis and Raman spectroscopy, and radiocarbon dating of the BC via ^{14}C accelerator mass spectroscopy (AMS). Results show that BC-composition may vary drastically within one particle, e. g. ratios organic carbon-to-oxygen changed from 4 to 100 within less than a micrometer. BC-crystallinity generally is small and very variable with stacks of 1 to 4 basic structural units. We detected two coexisting forms of BC, i. e. amorphous char-BC probably being the solid residue of the burned biomass, and highly graphitized, onion-like soot-BC derived from extensive recombination of small free radicals within flames. The BC is 1150 to 4500 carbon-14 years old, and up to 3322 years older than bulk soil organic carbon. Summarizing, micro-char in soils was quantified and identified unambiguously and it persisted for millennia in the soils studied here. If similar patterns hold true for other dark colored soils then BC in soils could be a significant sink in the global carbon cycle.

SORPTION OF DISSOLVED ORGANIC MATTER TO SOIL PARTICLE SURFACES: WHAT HAPPENS WITH THE CARBON?

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Sorption of organic matter (OM) to minerals have repeatedly been shown to be a major process in the stabilization of OM in soils and sediments. However, sorptive stabilization leads not to an infinite accumulation of OM and often a steady state equilibrium of carbon input and carbon output exists. In soil systems, it appears that the major output pathway of carbon that entered the mineral soil horizons as dissolved organic matter (DOM) is production of CO_2 and not leaching of DOM. But there are also indications that OM in solution is only sparingly degradable and that interactions with surfaces are required for a higher mineralization rate. Such surfaces could be biofilms adhering on minerals, and there is experimental evidence that pulses of DOM enhance the heterotrophic activity of the biofilm community. In our talk, we discuss the possible consequences of the competition of DOM sorption to pure mineral surfaces and to biofilm surfaces for carbon cycling. We propose that this competition is crucial for the fate of carbon in soils and sediments and present possible methodological approaches to proof this hypothesis.

SEASONAL CONTROL ON THE PRODUCTION OF DISSOLVED ORGANIC CARBON AND NUTRIENTS IN THE FOREST FLOOR

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Seasonal variations in the concentrations of dissolved organic carbon and nutrients (N, P, and S) in soil and stream water are well documented. There are indications that these variations result from changes in the microbial activity, especially in the organic layers of forests. In our presentation we provide further evidence for a microbial control on the production of dissolved organic carbon and nutrients in forest floors by analyses of biomolecular markers such as lignin-degradation products, acid and neutral sugars, and amino sugars. In addition, these analyses and supplementary NMR spectroscopic measurements indicate the seasonal impact on the production of dissolved organic carbon and nutrients to result in strong alteration in the chemical composition (e.g., acidity, aromaticity, dispersity) and, thus, in the functional behavior in aqueous systems, soils, and sediments.

FACTORS CONTROLLING THE NATURE AND REACTIVITY OF AQUATIC HUMIC SUBSTANCES

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Source materials, watershed chemistry, oxidative processes and hydrology exert strong influences on the nature and reactivity of aquatic humic substances. This class of organic compounds originates from the degradation and leaching of organic detritus and is transported by surface water and groundwater. The chemical characteristics of humic substances are influenced by the nature of source materials and the biogeochemical processes involved in carbon cycling within terrestrial and aquatic systems. These processes include allochthonous flow of organic carbon from the watershed, autochthonous carbon fixation by algae and aquatic plants, transformation and degradation of both autochthonous and allochthonous organic material by heterotrophic microbial activity, transport of particulate organic material to the sediments, remobilization of organic matter from the sediments, geochemical interactions, and photodegradation by UV light. In this paper, insights gained from studies of the factors that control the nature and reactivity aquatic humic substances from diverse environments will be presented.

APPLICATION OF FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY TO THE STRUCTURAL CHARACTERIZATION OF TERRESTRIAL ORGANIC MATERIAL

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The structural characterization of complex mixtures such as terrestrial organic material has been elusive to date because of insufficient compound resolution with conventional techniques. Using an electrospray ionization (ESI) source coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), we have been able to resolve individual compounds within humic and fulvic acid mixtures (mass resolving power: approx. 80,000). We have examined two samples in detail: dissolved organic matter (primarily fulvic acids) from Suwannee River, GA, and humic acids from a degraded wood from Mt. Rainier, WA. With appropriate instrument and sample conditions, the mass spectra of these complex mixtures were compared to determine common compounds and their relative concentrations. The mixtures were compared to appropriate standards to determine potential sources of different compound classes. With this technique, our ability to determine molecular formulas for individual compounds as well as determine their potential source has been substantially improved.

MICROBIAL MOLECULAR MARKERS IN AQUATIC BIOGEOCHEMICAL CYCLES: II

USING CHEMICAL CHARACTERIZATION TO DETERMINE SOURCES OF DOM TO THE MARINE ENVIRONMENT

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Chemical characterization is crucial to our understanding of the importance of marine DOM. Recent studies show that the high molecular weight (HMW) fraction of DOM is homogenous, with polysaccharides dominating the surface ocean reservoir. These polysaccharides (termed acylated polysaccharides (APS)) consist primarily of seven neutral sugars (15-20% C in surface waters), and acetylated amino sugars (20-25% C). APS decrease from approximately 55% of HMW C in surface waters to 25% in deep waters, suggesting a surface ocean source. Initial laboratory studies show that polysaccharides similar to APS are produced by different species of algae. However, microbial sources for these compounds have remained largely unexplored. Currently, we are investigating the ability of individual species of bacteria to produce APS in culture. Furthermore, we are studying the structure and sources of marine DON, which appears to consist of amino sugars in surface waters and refractory proteins in deep waters.

DISSOLVED ORGANIC CARBON IN ENDEAVOR SEGMENT OF JUAN DE FUCA RIDGE

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Seafloor hydrothermal vent systems host a rich diversity of life over a wide range of temperatures and pressures. Circulation through marine vent systems therefore has the potential to cause concentration changes in dissolved organic substances through microbial and abiotic interactions. These dissolved organic substances would likely be augmented and altered in distinct chemical patterns. To examine these processes, water samples were collected from both high temperature and low temperature vents at the Endeavor Segment of the Juan de Fuca Ridge during June-July and September, 2000. We also collected low temperature samples throughout four different time series ranging from 24 hours to 4 days. Ongoing measurements of the dissolved organic carbon (DOC) content of these samples help to constrain the fluxes and reaction histories of dissolved organic matter in these contrasting hydrothermal systems.

TRACING THE ROUTING AND SYNTHESIS OF AMINO ACIDS USING GAS CHROMATOGRAPHY-COMBUSTION-ISOTOPE RATIO MASS SPECTROMETRY IN PALAEODIETARY RECONSTRUCTION

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There is increasing interest in the application of compound-specific stable isotope approaches to palaeodietary reconstruction since they overcome problems associated with bulk analyses, e.g. contamination and biases in weighted averages. Compound-specific approaches also allow insights into the routing of dietary components to consumer tissues unobtainable from bulk isotope values. The utility of this approach is demonstrated through stable isotope analyses of the tissues of rats raised on isotopically and nutritionally defined diets. Amino acids were derivatised to trifluoroacetyl/isopropyl (TFA/IP) esters and carbon isotope values obtained using GC-C-IRMS. Correction factors were applied to each amino acid and errors arising from the derivatisation procedure determined. Carbon isotope values were obtained for thirteen of the common amino acids allowing incorporation of dietary amino acids into tissues to be detected and degrees of enrichment to be determined. Non-essential amino acids were statistically more enriched in ¹³C than the essential amino acids, relative to diet.

STABLE CARBON ISOTOPIC FRACTIONATION IN THE MARINE COPEPOD TEMORA LONGICORNIS

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To establish ¹³C fractionation effects between zooplankton and their diet, and the influence of grazing and egestion on ¹³C contents of particulate organic carbon (POC), a series of mesocosm experiments have been performed. For well-fed copepods (*T.longicornis*) the total body was found to be enriched in ¹³C by 1.3-2.3 ‰ and the respired CO₂ was enriched in ¹³C by 0.8 ‰ compared to the bulk material in the diet.

Faecal pellets, were highly depleted in ^{13}C by 4.3-11.3‰, which is in isotopic mass balance with the enriched body tissue and respiratory carbon (Klein Breteler et al., 2000). Compound specific isotopic analyses indicated that lipids (sterols and alkenones) were isotopically light, but equally light in algae, copepods and faecal matter (Grice et al., 1998). In particular, the $\delta^{13}\text{C}$ of cholesterol, bears the $\delta^{13}\text{C}$ signature of its dietary sterol, indicating no significant carbon isotopic fractionation effects occur when the copepod modifies sterols in its diet (Grice et al., 1998). Furthermore, the ratio of long-chain alkenones and their $\delta^{13}\text{C}$ in *I. Galbana* were identical to those egested in faecal material. In faecal pellets of copepod, the residual matter after lipid extraction was significantly depleted in ^{13}C by about 16 ‰ compared to the residual material of the diet. Pyrolysis indicated that proteins and some chitin were the major constituents (Klein Breteler et al., 2000). Further experiments have shown rates of change of the $\delta^{13}\text{C}$ values are different between non-lipids and lipids, attributed to differences in the utilisation and turnover of components. Our results suggest biosynthesis of amino acids as a major cause of isotopic fractionation in *T. longicornis*. The low $\delta^{13}\text{C}$ value of faecal pellets adds another variable, confounding the stable carbon isotopic signal in the pelagic food-chain. In contrast to POC, on a molecular level our results indicate that lipids are conservative tracers of the $\delta^{13}\text{C}$ value of phytoplankton upon which zooplankton feed (Grice et al. 1998). Therefore, when tracing flows of carbon within and through the pelagic food chain and to sedimentary organic matter, it is recommended to use the $\delta^{13}\text{C}$ value of lipids such as sterols and steranes derived from eukaryotic sterols.

DETECTING BIOCHEMICAL PATHWAYS AND TAXONOMIC GROUPS WITH ISOTOPES: SOME EXAMPLES USING AMINO ACIDS

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Although the pathways of intermediate metabolism are fairly stereotypical in most organisms, many taxa employ different means to the same end when it comes to some of the minor reaction pathways. A good example of this can be seen in the synthesis of amino acids from TCA cycle intermediates, where at least three different enzymes can catalyze the anapleurotic fixation of inorganic carbon to either pyruvate or phosphoenolpyruvate to replenish the supply of TCA cycle intermediates drawn off for amino acid synthesis. Each of these enzymes has a different isotope effect, and the fractionations expressed at specific carbon positions within their amino acid and related biochemical products preserve the evidence of the enzymatic pathway employed. Examination of a number of microbial and higher taxa shows that different autotrophic and heterotrophic taxa, and perhaps even different bacteria strains, may be distinguished based upon the intramolecular isotopic composition of their amino acids.

EXAMINATION OF CARBON ISOTOPIC FRACTIONATION IN AMINO ACIDS TO INVESTIGATE MICROBIAL METABOLISM

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MOLECULAR TRACERS OF ORGANIC NITROGEN SOURCES IN THE SEA: DEL ^{15}N AND ^{13}C COMPOSITION OF AMINO ACIDS IN DISSOLVED AND PARTICULATE ORGANIC MATTER FROM THE EQUATORIAL PACIFIC

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Oligotrophic ocean food webs are dominated by prokaryotes, which may represent both the dominant producers and consumers in many environments where nitrogen is a key limiting resource. Understanding the origins and cycling of organic nitrogen remains a central issue in oceanography, in particular in view of evidence that novel N-fixing prokaryotes may be key players in such systems. Most identifiable organic nitrogen is present as amino acids, however traditional molecular-level amino acid analysis has limited ability to distinguish sources. Stable isotopic fractionations of amino acids, by contrast, show large and characteristic relative fractionation patterns, and these patterns may have the potential to discriminate proteinaceous sources in the environment. We present here the first stable carbon and nitrogen isotopic compositions of individual amino acids from both dissolved and particulate material in the Equatorial Pacific, focusing in particular on the potential ability of this approach to distinguish prokaryotic from eukaryotic nitrogenous material

SEASONAL AND DIEL DETERMINANTS OF THE ISOTOPIC COMPOSITION OF ORGANIC MATTER IN A FRESHWATER WETLAND

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A study of the isotopic composition of organic matter was conducted in a freshwater marsh over seasonal and diel time scales to determine the sources of dissolved organic matter (DOM). Carbon isotopic composition of particulate organic matter (POM) ranged seasonally from -35‰ to -25‰ while change in DOM was more significant over daily time scales (-28 to -22‰). The carbon isotopic composition of individual amino acids in DOM revealed diel and seasonal change related to phytoplankton and bacteria contributions. Diel changes in the carbon isotopic composition of phenylalanine were similar in both DOM and POM, however they were different for isoleucine measured in these two pools. This disparity suggests a decoupling of the pools indicating a larger bacterial contribution at night. The isotopic composition of DOM suggests it is more closely linked to phytoplankton and bacteria during the summer, and more likely the result of diagenetic processes in the spring and fall.

CHEMICAL REACTIVITY OF AROMATIC AND SULFUR CONTAINING AROMATIC HYDROCARBONS IN NATURAL SYSTEMS: IV

EXPERIMENTAL STUDY OF THE REACTIONS OF OH RADICALS WITH POLYCYCLIC AROMATIC HYDROCARBONS ADSORBED ON GRAPHITE PARTICLES

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants, present in every compartments of the environment : soils and sediments, marine and continental waters, atmospheric phase and biota. In order to improve our knowledge of their biogeochemical cycles, the study of each compartment appears essential. More precisely, the study of the atmospheric phase is of primary importance to elucidate their long-range transport and their photochemical reactivity. Due to their physico-chemical properties and their major way of formation (pyrolytic one), PAHs are mostly present in the atmospheric phase adsorbed on fine particles that form the respirable part of the atmospheric aerosol. In the atmospheric phase, adsorbed PAHs are subjected to various degradation processes which can modify their structures and their physico-chemical properties. The most important process is the photo-oxidation, with various atmospheric oxidants (OH and NO_x radicals, ozone, ...). As the corresponding oxidation products may be much more toxic than the parent PAHs, their determination and the elucidation of photo-oxidation mechanisms are essential. Few information on the chemical and photochemical degradation of adsorbed PAHs is available. The purpose of the present work is to present the first results obtained on a new experimental apparatus developed in Bordeaux to study the photo-oxidation of PAHs in the

heterogeneous phase (at the gas-particle interface). A discharge-flow reactor, coupled with laser induced fluorescence detector, has been developed and tested with different PAHs, like phenanthrene, anthracene, benzo[e]pyrene and fluoranthene. The work has dealt firstly with the study of their reactions with OH radicals, graphite being chosen in a first part as a model of atmospheric particles. Photo-oxydation products have been tentatively identified by HPLC and GC/MS.

GEOCHEMISTRY OF ABIETANE HYDROCARBONS IN A SOLID WASTE LANDFILL

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A series of hydrocarbon derivatives of abietic acid were determined in a municipal solid waste landfill using gas chromatography/mass spectrometry. The concentration of abietane hydrocarbons in the upper (aerobic) part of the landfill was very modest, while in the underlying anaerobic part they were among the most prominent hydrocarbon constituents. The hydrocarbon fraction of the soils below the landfill contained almost exclusively abietane hydrocarbons, including fichelite, abietane and abietamonoene as the predominant species as well as the final product of their aromatization – retene. The total concentration of abietane hydrocarbons in the soil was much higher than that in the solid waste, reaching up to 100 mg/kg. Detailed vertical profiles of abietane hydrocarbons in the landfill and underlying soils suggested that they are intensively formed under methanogenic conditions in the lower parts of the landfill. Their mobility in soils seems to be rather restricted due to the adsorption.

EFFECT OF HEAVY METALS ON THE BIODEGRADATION OF 14C-PHENANTHRENE IN SOILS

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The natural attenuation of polycyclic aromatic hydrocarbons (PAHs) in industrially polluted soils maybe affected by co-contaminants. Therefore, the aim of this study is to assess, in microcosm experiments, the effect of metals on the biodegradation of phenanthrene, a three-ring PAH. Three soils are selected according to their time exposure to the metal contamination (uncontaminated -control, 3 days or 20 years). The mineralization of phenanthrene in the recently metal contaminated soil reaches 2,5% of the phenanthrene, and is significantly lower than that observed for the other soils (at least 8%). These results indicate a potential toxicity of bioavailable metals towards the PAH degrading microorganisms. In addition, analyses of phenanthrene metabolites, using HPLC and GC-MS, indicate that degradation starts rapidly, but continues slowly (half-life>200 days). This work demonstrates the effects of metals on the biodegradation of phenanthrene in soils, its persistence and therefore potential threat to human health.

ELEMENTARY AND BULK REACTION PATHS FOR THE THERMAL CRACKING

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The prediction of aromatic hydrocarbons thermal stability in natural surroundings is a subject of high interest for both geochemistry and environmental sciences. A major problem to complete such predictions arises from the complexity of the aromatic fraction in oils. In this presentation, we will describe a strategy to generate bulk reaction networks, specific to aromatic compounds, involving constraints from elementary processes. This methodology is based on a double interpretation of pyrolysis experiments (global vs. molecular scales) on isolated compounds, coupled with molecular modeling techniques. The current knowledge towards elementary cracking processes involving aromatics heavier than toluene or ethyl-benzene still remains limited, mainly for two reasons: a lack of experimental data, that would show the thermal behavior of polyaromatic structures when submitted to pyrolysis, and their poor thermochemical characterization. Both reasons can partly be related to the difficulties encountered to observe and quantify individually aromatic compounds. Nevertheless, some work was already done on the thermal reactivity of aromatic hydrocarbons. At the scale of elementary mechanisms, a major issue of these studies was to emphasize, at least, the influence of the initiation step on the global rate of decomposition of aromatics. Aromatic compounds, depending on their structure, may indeed follow different initiation paths, which partly explains the large variety of reactivity of aromatic fractions in oils, compared to saturates. For instance, the reactivity of a methylated aromatic and that of its ethylated counterpart should be reversed between laboratory and natural conditions, because thermal decomposition does not initiate through the same process. Another possible approach to the prediction of aromatic hydrocarbon thermal stability is to establish bulk reaction networks, involving a limited number of reactions (2 or 3) and a limited number of chemical classes. Although they are much less precise than complex reaction networks, global kinetic schemes are more useful, and usually they lead to predictions which are consistent with field data, as soon as apparent rate parameters can be constrained and validated by a complex approach.

GENERATION AND DESTRUCTION OF AROMATIC SULFUR COMPOUNDS AND ITS IMPLICATION OF OIL CRACKING UNDER RESERVOIR CONDITIONS

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Aromatic sulfur compounds are important species for oil properties. Their concentration changes have been correlated with organic input, oil maturity, and viscosity and API gravity. To understand how their relative concentration changes with maturity, we have done extensive pyrolysis studies under close system conditions with and without the presence of reservoir rocks that contain clay. Sulfur compounds were classified in three groups: thiophenes (T), benzothiophenes (BT) and dibenzothiophenes (DBT). In order to derive kinetics of thermal alteration of aromatic sulfur compounds, we have done two heating rates of pyrolysis (10C/hour, and 1C/hour). With the increase of thermal maturity of oil, abundance of BT and DBT will initially and then decrease with pyrolysis temperature. The increase of BT and DBT appears to result from thermal cracking of asphaltene compounds. The decrease of BT and DBT with temperature is mainly due to thermal degradation of aromatic compounds. Kinetics of both generation and destruction of BT and DBT have been derived. The derived kinetics can be used to calibrate thermal alteration of oil under reservoir conditions.

COMPARISON OF THE GENERATION AND DEGRADATION RATES OF SATURATED AND AROMATIC HYDROCARBONS IN GEOLOGICAL CONDITIONS

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The purpose of the work is to determine the generation and degradation rates of saturated and aromatic hydrocarbons in order to compare their window stability in geological conditions. Kerogens originate from the 3 main types of organic matter were artificially matures in open and closed pyrolysis systems and generations rates were calculated for the n-C12 and n-C24 alkanes and for the toluene, the sum of the 3 xylenes isomers and the methylthiophene. For secondary cracking, 4 model compounds were selected: the n-C25, the 9-methylphenanthrene (9-MPh), the 1-methylpyrene (1-MPyr) and the dodecylbenzene and each of them was pyrolyzed in closed system and corresponding kinetic parameters were calculated. Results show that the dodecylbenzene is first degraded in laboratory conditions, then the n-C25 and the two methylated are the most stable compounds. However, in geological conditions, although DDB is still the less stable compound, the two methylated aromatics are less stable than the n-C25 ; under isothermal conditions these aromatic compounds are degraded below 190C whereas the n-C25 just starts to be degraded. Consequently, the aromatic window, whatever the kerogen type, is much narrow than the saturate one in geological conditions.

BIOGEOCHEMISTRY OF TERRESTRIAL ORGANIC MATTER: IV

ACCUMULATION AND RECYCLING OF CARBON, PHOSPHORUS, AND SULFUR IN SEDIMENTS FROM CONTAMINATED AND PRISTINE SITES IN THE FLORIDA EVERGLADES

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The Everglades, Florida is a vast wetland ecosystem that is accumulating carbon as peat. Peat thickness varies from only a few cm to more than 3 m, and consists of an accumulation of macrophyte remains and microbial organic matter. Parts of the northern Everglades are heavily contaminated with phosphorus and sulfur from agricultural runoff. The excess phosphorus has stimulated emergent macrophyte productivity in the contaminated areas, and eutrophic-adapted macrophytes (cattails) have displaced the native, oligotrophic-adapted macrophytes (sawgrass) here. Accumulation rates for both total phosphorus and organic carbon are about 100 x higher at the phosphorus-contaminated sites compared to pristine areas of the Everglades. Sulfur accumulation rates in sediments are about 5 x higher at contaminated versus pristine sites, largely from reaction of H₂S with peat. Rates of carbon and phosphorus recycling in sediments are also higher at contaminated sites, reflecting higher rates of decomposition of organic matter from cattail compared to sawgrass. Overall, carbon and phosphorus accumulation exceeds recycling by 5 x at contaminated sites and 2 x at pristine sites. Results are significant for protective wetlands constructed on old agricultural land, which grow primarily eutrophic cattail vegetation.

GEOCHEMICAL TRANSFORMATION OF ORGANIC SULFUR COMPOUNDS: ROLE OF BIRNESSITE CATALYSIS

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The heteroatom sulfur intimately interacts in the geochemical transformation of organic matter in soils and sediments. While there is significant contribution of organic sulfur compounds to soils and sediments from the original biological organic matter, the dominant fraction of sedimentary organic sulfur is generated through abiotic reactions of inorganic sulfur nucleophiles with functionalized organic matter. Major types of organic sulfur compounds in soils and sediments include thiols, organic sulfides, di- and poly-sulfides, thiophenes, sulfonates and ester-linked sulfate. Thiols constitute a major type of organic sulfur in the early stages of organic matter transformation, generated biotically from the microbial degradation of sulfur-containing biochemicals and abiotically through reactions of sulfur nucleophiles (e.g. H₂S) with functionalized organic molecules. Abiotic reactions involving polysulfide ions represent a major pathway for forming organic polysulfides. Although it is believed that the heterocyclic thiophenic compounds are generated chemically, the exact mechanisms are not clear. Our results suggest that geochemical catalysis involving mineral particles, for example birnessite(-MnO₂), could be important for forming this class of molecules. We used 3-mercaptpropionic acid (3-MPA) as a simple model to understand the transformations of thiols mediated by birnessite. Sulfur XANES spectroscopy and mass spectrometry gave information of reaction products. The disulfide was the main product when the thiol was reacted alone with birnessite. However, in the presence of catechol, an important lignin derivative, a thiophenic end product was formed. Evidence suggests that the mechanism involves ring cleavage of catechol forming unsaturated products followed by reaction with 3-MPA. Our results illustrate the importance of mineral catalysis in the transformation of organic sulfur compounds in the geosphere.

UNDERSTANDING THE SOURCES OF DISSOLVED ORGANIC CARBON IN THE SACRAMENTO-SAN JOAQUIN RIVER DELTA, CALIFORNIA, USA

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Intensive irrigated agriculture on peat soils in the Sacramento-San Joaquin River Delta has resulted in widespread oxidation of soils, and subsidence of land surface well below sea level. Consequently, to prevent flooding, irrigation and precipitation waters containing large quantities of soil-derived DOC must be pumped continuously from much of this region into river waters. It is widely believed that this soil-derived DOC represents the major Delta source of DOC, elevating DOC concentrations by 40-45% over that found inflowing to the Delta. However, the emerging picture from regional and source specific studies garnering information on DOC composition from analytical techniques such as ¹³C-NMR, SUVA, and compound-specific isotopic analysis indicates that the composition of DOC in Delta waters is not consistent with the simple addition of peat soil-derived material to river water. Evidence of contributions from other potential sources such as wetlands and in-channel productivity will be presented.

TERRESTRIAL ORGANIC MATTER CYCLING ON THE INNER LOUISIANA SHELF

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The cycling of particulate terrestrial organic matter (OM) on the inner Louisiana Shelf was examined using carbon isotopic, mineral surface area, and biomarker analyses. Fine sediment particles comprising the Atchafalaya "mud stream" appear to play an important role in the distribution of terrestrial OM along the coast. Stable and radioactive carbon isotopic values, and lignin content and composition indicate that two 'pools' of terrestrial OM are exported by this river system: fresh, C3 plant debris that is preferentially deposited near the river, and degraded, soil OM that is exported farther offshore. Terrestrial organic carbon burial in the study area accounts for 10% of the riverine OC discharge. A significant portion of terrestrial OM (47%) and much of the marine OM (up to 80%) appears to be degraded before burial. There is also substantial lignin loss, but the relative importance of sorting versus degradation is unclear.

FACTORS INFLUENCING THE TRANSPORT OF KEROGEN IN THE EEL RIVER SEDIMENTARY SYSTEM

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Half of the particulate organic carbon delivered to the oceans by rivers draining uplifted sedimentary terrains may be kerogen. The fate of kerogen as it is uplifted, eroded and transported to the shelf is dependent partially on watershed processes. In the Eel River system most of the clay-sized sediment is produced via the mass wasting of the Jurassic-Tertiary Franciscan Complex mélange. The organic carbon in these sedimentary rocks appears to be a Type III kerogen. Modern C is added to the clay (<4µm) fraction in vegetated topsoils. However, the kerogen dominates as the source of C in the clay fraction on the middle shelf because gully wall erosion, earthflows and slides cut through soil profiles and deliver predominantly unmodified material to the river. Factors that influence hillslope erosion, such as uplift rate, rock shear strength and land use, are thus expected to control the flux of ancient C from watersheds.

MOLECULAR PALEONTOLOGY: TRACING THE EVOLUTIONARY ROOTS OF ANGIOSPERMS USING THE MOLECULAR FOSSIL OLEANANE

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The earliest complete evidence for angiosperms (flowering plants) is from Early Cretaceous (ca 130 million years before present) fossils. Yet, angiosperms are the dominant plant group today, outpacing more ancient clades like conifers and ferns. Among seed plants the pentacyclic triterpene oleanane and related compounds appear specific for angiosperms, and angiosperm diversification from E. Cretaceous to Miocene (ca 5 mybp) correlates with oleanane occurrence and abundance in sediments. Our work also has shown that oleanane is lacking from a wide range of plant fossils, but is found in the Permian gigantopterids and Lower Cretaceous bennettitaleans, in addition to angiosperms. Phylogenetically, bennettitaleans belong to the anthophytes, a clade of living and fossil seed plants that also includes Pentoxiales, Gnetales and angiosperms, based on their morphological characters. However, recent molecular (rRNA) data suggests Gnetales belong to the conifers. Interestingly, pyrolysis of five living Gnetales species by did not produce oleanane.

EFFECTS OF FOSSIL FUNGAL INFECTION ON LIPID EXTRACT COMPOSITION OF HIGHER PLANTS REMAINS

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The lipid fraction extracted from uninfected shoots of a fossil conifer, *Frenelopsis alata*, was analysed by GC/MS, and compared with shoots of the same conifer infected by extinct epiphyllous fungi, so as to study the effects of fungal infection on the chemical composition of extracts from higher plant remains. The extracts from the uninfected shoots appeared to be composed of (i) classical constituents of higher plant lipids, (ii) elemental sulphur and (iii) substantial amounts of terpenoids characteristic of conifers. Comparison of this extract with that of fungi-infected shoots revealed, in addition to the aforementioned compounds, the presence of substantial amounts of functionalized benzoic compounds that were interpreted as degradation products of lignin by fungi. These results give preliminary indications on the conspicuous influence on the composition of extracts from fossil plants that can be associated with fungal infection.

NEW INSIGHTS ON THE DIAGENESIS OF DITERPENES

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Key diterpene skeletons biosynthesized by all plants include the tetracyclic structures beyerene and kaurene, and other common diterpenes widely found in plants include tricyclic diterpenes such as abietenes, pimarenes and rimuenes. However, these compounds are not commonly reported as biomarkers. One reason is the intervention of diagenesis. We conducted laboratory experiments in which geomimetic pathways for the diagenesis of abietene, pimarene, kaurene and beyerene were investigated. The wide array of hydrocarbon products formed in these experiments are found in oils from around the world. This work demonstrates the instability of compounds such as kaurene, fichtelite, and abietene compared to rearranged, stereoisomeric, and partially degraded products formed during diagenesis. As a consequence, some of the parent diterpane structures that are common to plants are relatively rare in ancient sediments and oil while a large number of diterpanes that still require structure elucidation are ubiquitous in geological samples.

SURFACE COMPLEXATION MODELS: A BRIDGE BETWEEN SPECTROSCOPY AND FATE AND TRANSPORT: I

COMPARISON OF SURFACE COMPLEXATION MODELS FOR METAL ADSORPTION WITH SPECTROSCOPIC STUDIES

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Surface complexation models of metal adsorption on oxide surfaces in electrolyte solutions are of the greatest value when applied to experimental data referring to a wide range of ionic strengths, electrolyte types, and surface coverage. The triple-layer model (TLM) is well-suited to analyse such data to establish metal speciation on oxide surfaces. X-ray spectroscopic and diffraction studies can also be interpreted in terms of surface speciation. In the present study, the results of extensive TLM analyses of Ca adsorption on a variety of minerals, and of Cd and Pb adsorption on goethite, under a wide range of ionic strengths and surface coverages, are compared with published X-ray spectroscopic and diffraction studies of alkaline earth, Cd and Pb adsorption. In many regards, the two approaches yield consistent results, but much more work for the two approaches on the same samples is needed.

DO SURFACE COMPLEXATION MODELS SCALE FROM THE MOLECULAR LEVEL TO THE MACROSCOPIC LEVEL

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Ion adsorption on metal(hydr)oxides is strongly affected by both chemical and electrostatic interaction. The various surface complexation models, which have been developed, take both factors into account. Recently we have discovered that the pH dependence of ion binding on oxides is primarily determined by the electrostatic interaction, which is determined by the position of the adsorbed charge in the interface, which is different for the various models. In the CD-MUSIC model the charge of a specifically bound ion is not treated as a point charge, at the scale of

the interface, but is distributed over the surface and the Stern layer (BS approach). We will show how the charge distribution is related to the structure of adsorbed species, allowing a direct link between surface spectroscopy and macroscopic thermodynamic ion adsorption modeling. The choice of the model is crucial if the goal is to link spectroscopy with thermodynamics for ion adsorption.

INFLUENCE OF DIELECTRIC CONSTANT ON METAL SURFACE COMPLEXATION

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Criscenti and Sverjensky demonstrated that, within the context of the extended triple-layer model, transition and heavy metal adsorption onto oxides such as goethite and gibbsite from NaCl, NaNO₃, and NaClO₄ solutions can be described by surface complexes involving the electrolyte anion. However, the preferential formation of metal-electrolyte anion complexes such as >SOHCdNO₃⁺ and >SOHCdClO₄⁺ at the mineral surface has not been thoroughly examined. One variable that may influence metal surface complexation is the dielectric constant at the mineral/water interface. The dielectric constant of water decreases near a mineral/water interface due to the ordering of water molecules and this decrease may favor ion-pairing. The long-range effects of solvation on metal-anion complexation energies are examined using ab initio calculations and varying the dielectric constant within a polarizable continuum model.

APPLICATION OF X-RAY ABSORPTION SPECTROSCOPY TO SURFACE COMPLEXATION MODELING OF SINGLE AND BI-SOLUTE METAL ION ADSORPTION

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Substantial research has been directed toward developing mechanistic models capable of describing sorption reaction phenomena over a range of field-scale behavior. These efforts have led to the development of modeling approaches that attempt to depict the reaction of solutes with mineral surfaces using molecular spectroscopy. In this research, macroscopic data for divalent metal ion sorption to ferrihydrite were used in conjunction with X-ray absorption spectroscopy (XAS) data to estimate surface complexation model (SCM) parameters. The XAS results were used to identify the types of surface complexes formed in single and bi-solute systems. SCM reactions were selected based on the XAS results, and metal ion binding constants were determined for the single-solute systems. These constants were then used to predict sorption in bi-solute systems. The modeling results show that SCMs often fail to predict bi-solute sorption.

EVALUATION OF SILICA: WATER SURFACE CHEMISTRY USING NMR SPECTROSCOPY

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We have combined traditional batch and flow-through dissolution experiments, multinuclear nuclear magnetic resonance (NMR) spectroscopy, and surface complexation modeling to re-evaluate amorphous silica reactivity as a function of solution pH and reaction affinity in NaCl and CsCl solutions. ²⁹Si cross-polarization NMR results show that silanol surface complexes decrease with increasing pH. ²³Na and ¹³³Cs NMR results show that the alkali cations form outer-sphere surface complexes and that the concentration of these complexes increases with increasing pH. We have described the silica-water surface chemistry using both the triple-layer and the constant capacitance models and constants derived from solution analyses alone do not fit our experimental data. Our data suggest that changes in surface speciation are driven by solution pH and to a lesser extent alkali concentrations, and not by reaction time or saturation state.

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STRONTIUM SORPTION TO MINERAL SURFACES: A DISCUSSION OF THE IMPORTANCE OF SURFACE CHARGE FOR OUTER-SPHERE SORPTION

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Surface complexation models require the sorption of outer-sphere complexes to be dependent on the electrostatic properties of mineral surfaces. Comparison of strontium sorption to amorphous silica, kaolinite, and goethite question this requirement and question surface acidity constants measured from acid-base titrations. These minerals show similar strontium sorption as a function of pH, but have distinct surface charge properties. The largest fraction of sorbed strontium on these phases is present as outer-sphere complexes that retain their primary hydration sheath as identified by EXAFS analyses of more than 20 samples from pH 4 to 10. Strontium sorption to amorphous silica can be modeled as an outer-sphere complex using new surface acidity and capacitance constants determined by nuclear magnetic resonance spectroscopy (see Maxwell et al., this session). If we extend our approach to strontium sorption to goethite and kaolinite surfaces, our model results are not consistent with surface acidity constants derived from acid – base titrations and with our strontium EXAFS data.

IN SITU SPECTROSCOPIC STUDIES OF SULFATE AND BORATE ADSORPTION MECHANISMS ON IRON OXIDES: IMPLICATIONS FOR SURFACE COMPLEXATION MODELING

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Understanding and predicting adsorption reactions at the mineral-water interface is an important area of geochemical research. Typically, in situ spectroscopy is used to determine adsorption mechanisms, while surface complexation modeling is applied to describe the extent of adsorption over a range of pH and surface loading. As surface complexation models become more sophisticated, it becomes increasingly important to refine them with results from complementary spectroscopic studies. In this paper, the authors will present information on sulfate and borate surface complexation mechanisms on iron (III) oxides and hydroxides obtained via ATR-FTIR spectroscopy. The effect that reaction variables such as pH, ionic strength, surface loading, and sorbent structure have on adsorption mechanisms will be discussed in detail. The results will also be contrasted with predictions of adsorption mechanisms obtained from surface complexation models in the literature.

MODELING THE SURFACE COMPLEXATION PROPERTIES OF RUTILE UP TO HYDROTHERMAL CONDITIONS

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Potentiometric titrations, utilizing a hydrogen electrode concentration cell, have been conducted to quantify and rationalize the adsorption of cations and anions by rutile. In these titrations, the adsorption of di- and trivalent cations (Ca²⁺ and Nd³⁺), and anions (oxalate and sulphate) were examined in NaCl media (0.03 and 0.3M), from 25 to 250°C (125°C for oxalate). The adsorption data were modeled successfully with the classic 1pKa model and the charge distribution Multi Site Complexation (CD-MUSIC) model. In addition, the models included a three-layer representation of the electric double layer. The CD-MUSIC model permits macroscopic measurements, such as our titration data, to be reconciled with molecular spectroscopic information. Moreover, the CD-MUSIC model describes the affinity of ions for various types of surface hydroxyl groups on a mineral surface. In modeling the Ca²⁺ adsorption data, the bonding configuration was constrained by recent complementary X-Ray standing wave measurements.

CHEMICAL REACTIVITY OF AROMATIC AND SULFUR CONTAINING AROMATIC HYDROCARBONS IN NATURAL SYSTEMS: V

APPLICATION OF TRIAROMATIC STEROIDS AS AGE-RELATED BIOMARKERS

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Triaromatic 23,24-dimethylcholestanes (TA-DMD) are most likely derived from 23,24-dimethylcholesterols in dinoflagellates and possibly haptophytes. Therefore, parameters based on TA-DMD might be applied to distinguish Paleozoic from Mesozoic (and younger) oils and rocks, dinoflagellate and haptophyte records (Triassic and younger). Parameters based on dinosteranes and TA-dinosteroids, also derived from dinoflagellates, have been shown to display this utility. This study shows the distribution of the TA-DMD in source rocks and oil samples with a wide ranging age distribution from the Proterozoic through the Mesozoic and compares the results to TA-dinosteroids in the same samples. The TA-DMD occur in all marine (and many lacustrine) source rocks and oil samples of Jurassic and Cretaceous age and are rarely detected in Permian and older ones, which demonstrates their potential application as age-diagnostic indicators to distinguish Paleozoic and Mesozoic sources. TA-DMD and TA-dinosteroids data in the same samples are compared.

ELEMENTS ON REFRACTORY SULFUR COMPOUNDS AFTER HYDROTREATMENT OF VACUUM RESIDUE

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Atmospheric or Vacuum residues coming from distillation of crude oil have the highest sulfur concentration. Sulfur entities are mainly located in heavy polyaromatic structures such as asphaltenes and resins. These sulfur compounds and their reactivity are not well known. Hydrotreatment experiments have been conducted using a fixed bed reactor and Hydrodesulfurization / Hydrodemetallation (HDS/HDM) catalyst. Liquid chromatography separation, elementary analysis have been carried out on the effluents. Location of the most refractory sulfur to hydrotreatment have been examined and the kinetics of desulfurization have been investigated. Results have pointed out several HDS rates depending on the compound classes. These sulfur species are predominantly found in the heaviest resins and aromatics.

RECONSTRUCTING THE GEOLOGICAL HISTORY OF AUSTRALIAN CRUDE OILS USING AROMATIC HYDROCARBONS

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The distributions of methylated naphthalenes in crude oils carry within them detailed information regarding the geological history of the oils. The effects of thermal stress, mixing, biodegradation and migration contamination all leave recognisable imprints, which can be deconvoluted. An extended suite of crude oils from several locations in Australia was analysed for their methylated naphthalene content. It was shown that three ratios of selected isomers, each reflecting the same underlying sedimentary reactions, are linearly related to each other when thermal stress has been the only factor controlling the distribution of methylated naphthalenes. This internal consistency allows for an assessment of maturity independent of source, age and location of the crude oil. When the relationships between the three ratios are not linear, secondary processes such as mixing, biodegradation or migration contamination have affected the crude oil. Close examination of the distribution of methylated naphthalenes can reveal the extent to which either of these processes has affected the oil. The application of this approach is demonstrated using several case studies of oils from Australian petroleum systems.

AROMATIC MOITIES DISTRIBUTION IN AROMATICS AND NSO COMPOUNDS FROM CRUDE OIL BEFORE AND AFTER HYDRODESULFURIZATION PROCESS

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In order to protect earth atmosphere, refineries are more and more requested to reduce the sulfur content of distillation cuts for gas oil and fuel production. The purpose of the work was to compare sulfur balance in vacuum residue coming from distillation of crude oil submitted to hydrodesulfurization process in order to identify refractory sulfur aromatic structures. For that purpose, aromatics, resins and asphaltenes isolated from both the initial and the desulfurized oils were submitted to moderate pyrolysis in closed system where the temperature/time ranged from 300 to 375°C and from 1 to 72h respectively. Total mass and atomic balances (C, H and S) were performed together with molecular identification of the main aromatic and S-aromatic structures by GC-MS. Results show that resins are the major compounds generated from asphaltenes which, when they undergo secondary cracking, generate aromatics and S-aromatics as major fractions. During the hydrodesulfurization process, beside H₂S production, the distribution of the aromatic products generated from asphaltenes and resins are significantly different. Consequently, this chemical process not only reduces the residual sulfur content of the aromatic and NSO fractions in the oil recovered after hydrotreatment but also leads to new aromatic and S-aromatic compounds which are more difficult to be removed. The molecular identification of these new aromatic compounds will allow to adjust the hydrotreatment conditions and catalyst development with the objective of a very deep desulfurization of the vacuum residue used as fuel.

THERMODYNAMIC CONSTRAINTS ON THE FORMATION AND EVOLUTION OF SULFUR-CONTAINING AROMATIC COMPOUNDS IN PETROLEUM SYSTEMS

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The organic sulfur compounds present in immature oils and bitumens are primarily alkylthiolanes, alkylthianes and alkylthiophenes, whereas most of the organic sulfur present in mature crude oils is accounted for by methylated benzothiophenes and dibenzothiophenes (Orr and Sinninghe Damsté, 1990). The standard molal thermodynamic properties and heat capacity power function coefficients of these predominant compounds as well as other organic sulfur compounds in the liquid state have been estimated by combining calorimetric data reported in the literature together with group contributions taken from Richard and Helgeson (1998). Theoretical calculations using these thermodynamic properties provide constraints on the transformations undergone by organic sulfur compounds as a result of the increase in temperature and pressure, as well as the variations in H₂ and H₂S fugacities with depth in sedimentary basins.

GENERATION OF HYDROCARBON GAS FROM COAL AND ITS RELATION TO CARBON ISOTOPE FRACTIONATION

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A variety of low-mature, dry coals was pyrolysed in an open-system, temperature programmed device, on-line coupled to a combined gas chromatograph / isotope ratio mass spectrometer (GC-IRMS). No significant differences occurred with respect to the generation dynamics of C₁ to C₃ hydrocarbons from coals of different geological age and geographic origin. Likewise, stable carbon isotope signatures of the hydrocarbons displayed very similar trends. The mineral matrix of sediments containing coaly organic matter had no significant influence on hydrocarbon gas generation and related isotope fractionation. These findings justified to establish a general model of gas generation based on primary cleavage reactions from coal. This model is based on a variety of distinct types of chemical reactions contributing to the generation of methane, ethane, and propane. Each type of reaction is characterised by an individual isotope ratio of the precursor, by a range of activation energies, and by a specific kinetic isotope effect. As a consequence, a reaction kinetic model is proposed based on sets of parallel first-order reactions describing the generation and isotope fractionation of C₁ to C₃ hydrocarbons from coaly organic matter.

INVESTIGATION INTO TENTATIVE PRECURSORS OF RESERVOIR PYROBITUMEN

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Pyrobitumen is solid insoluble bitumen originating from the thermal degradation of liquid oil. Prospecting for petroleum in deep, hot reservoirs increases the risk that the reservoir will contain pyrobitumen, acting as a porosity and permeability-reducing cement, therefore highly detrimental to reservoir quality. Due to its relatively low density, it also leads to incorrect wireline log estimates of the oil in place. The aim of this work was to determine the potential of an immature, heavy, type II oil and of its constituents to form pyrobitumen. Closed system pyrolysis was used to artificially mature a sample of Boscan oil (Venezuela) at temperatures from 300-500°C for 4 hours and the insoluble residue recovered and weighed to calculate the amount of "pyrobitumen" produced. Samples of the oil were fractionated into saturate, aromatic, resin, and asphaltene (SARA) components. Part of the aromatic fraction was further divided by preparative HPLC into mono + di-aromatics and tri + polyaromatics and pyrolysed under the same conditions. At 500°C all fractions produced pyrobitumen although asphaltenes yield more insoluble residue (72%wt) compared to the saturates (19%wt). In addition the asphaltenes and resins produced pyrobitumen at lower temperature than the aromatics and saturates. The tri + polyaromatic aromatic fraction produces more pyrobitumen (46%) than the light aromatics (33%). The insoluble pyrolysates were analysed by photonic microscopy to determine their reflectance, by dark field mode transmission electron microscopy to image their microtexture and by X-ray diffraction to measure the extent of the aromatic domains formed. This work shows that whilst pyrobitumen is a natural consequence of thermal cracking disproportionation, the amount of pyrobitumen produced and its physico-chemical properties are strongly dependent on the oil composition.

ADVANCES IN STABLE ISOTOPE BIOGEOCHEMISTRY: NEW DEVELOPMENTS AND APPROACHES

LIQUID-CHROMATOGRAPHY ISOTOPE-RATIO-MASS-SPECTROMETRY VIA A MOVING WIRE INTERFACE

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We are continuing development of the moving-wire interface originally described by Brand and Dobberstein (1996, *Isotopes Environ. Health Stud* 32, 275-283). Liquid samples are coated onto a 0.25-mm Ni wire either continuously (~0.1 mL/min H₂O from a capillary) or periodically (~1-mL droplet deposited via a syringe). The sample is dried onto the wire and combusted at 800°C. ¹³C/¹²C ratios of the resulting CO₂ are measured via isotope-ratio-monitoring. The accuracy of the system has been previously demonstrated for sugars dissolved in pure MeOH and H₂O. However, we find that combustion of organo-phosphorous compounds (nucleic acids) or sugars in aqueous phosphate buffers results in low CO₂ yields and anomalously enriched ^{d13}C values due to incomplete combustion. Current research is focused on 1) improving combustion of refractory compounds and 2) reducing the C blank of the Ni wire. Preliminary analyses of nucleosides, nucleotides, and bulk RNA extracts using both the moving-wire system and an elemental analyzer produce ^{d13}C results with precision < 0.2 permil and accuracy < 1.0 permil between methods for samples containing 10 mg of carbon. Results from RNA extracts of collected and cultured organisms should be available for the conference.

COMPOUND SPECIFIC STABLE ISOTOPE CHARACTERISATION OF VOLATILE FATTY ACIDS (C₂ - C₆)

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Acetate, the C₂ volatile fatty acid (VFA), can be formed by thermal degradation of organic matter and organic fluids, but is usually a penultimate end member in the anaerobic degradation of organic matter by bacterial consortia, and is thus found in a variety of environment: hot springs, deep and shallow marine sea sediments, peatlands, landfill sites, oil reservoirs, animal and human guts. Measurement of turnover rates and associated isotopic composition (primarily ^{d13}C) from porewaters and sediment sampled at appropriate timescales in the field provide insight e.g. on carbon mass balance, without the need for laboratory simulations. While compound specific (CS) ^{d13}C measurements of acetate and associated VFA are possible by solid phase micro-extraction, this technique depends on equilibrium absorption of the acetate to the microfibre and is not suitable for the low concentrations of acetate that are found in several environments. For such situations, we have developed a solid phase extraction technique, which concentrates the VFA from a sample size of ~ 10 ml of liquid, to a volume of solvent sufficiently small to allow accurate measurement of ^{d13}C by GC-IRMS. This concentration technique may also produce samples suitable for CS ^{d13}C analyses, or for concentrating separate components for CS ¹⁴C dating.

FLOW CYTOMETRIC RETRIEVAL OF IN SITU D13C SIGNATURES OF ALGAL POPULATIONS USING PYROLYSIS-GC-IRMS

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Here we demonstrate that individual phototrophic populations can be probed directly for their in situ d13C signature by means of a compound-specific isotope-ratio analysis of cellular fatty acids volatilized from flow cytometrically sorted cells using in-line pyrolytic methylation. This novel methodology greatly improved the resolution in discriminating and tracing differential carbon pathways existing at the base of the pelagic food web of Lake Loosdrecht. Our approach revealed a permanent coexistence of phytoplankton groups differing by 6 to 8 ‰ in d13C with cyanobacterial species always depleted in 13C relative to eukaryotic algae. Predominant members of micro- and mesozooplankton were shown to reflect this isotopic difference as the result of preferential grazing. Flow cytometric retrieval of d13C signatures applied in conjunction with 13C-carbonate labeling of lake phytoplankton also enabled assessments of population-specific in situ growth rates. Diatoms and green algae, although comprising least abundant phototrophs in the lake, exhibited rates up to 9-fold higher than growth rates recorded for cyanobacterial species. The coexistence of phytoplankton groups widely different in d13C as well as in standing stock and population turnover time has important implications for the interpretation of carbon transfer in pelagic food webs.

COMPOUND-SPECIFIC STABLE CARBON ISOTOPES: THE EFFECT OF BIOSYNTHETIC PATHWAYS

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The interpretations of stable carbon isotopic compositions of sedimentary lipids have for the most part relied on culture studies of organisms. Two steps are important in this respect: Firstly the fractionation of 13C from inorganic carbon to the fixation site within the cell and secondly subsequent fractionation from the fixed carbon to the compounds of interest. For the last step, only a few pioneering studies on the fractionation patterns of lipid biosynthesis have been done and a number of empirical observations on stable carbon isotopic compositions of different compounds classes have been reported, some of them predating the advent of irm-GCMS. Here we present for a number of organisms (algae, bacteria and plants) the results of different types of analysis aimed at a better understanding of the effects of biosynthetic pathways on the stable carbon isotopic composition of lipids. This involved the development of several novel techniques to enable the determination of stable carbon isotopic compositions of storage products, such as sugars and polyhydroxy alkanolic acids, and the intramolecular distributions of 13C in isoprenoids. The results show that biosynthetic pathways can have dramatic effects on the 13C-contents of individual compounds, causing significant dispersity and thus complicating the interpretation of stable carbon isotopic compositions of sedimentary compounds.

HIGH PRECISION ISOTOPE RATIO FINGERPRINTING OF ETHANOL AND OTHER COMMERCIAL MOLECULES AND MATERIALS

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The potential of the isotope ratios of C, H, O, N to provide definitive characterization of natural products has long been recognized. While stable isotope ratio mass spectrometry (IRMS) is the most accurate and precise way of measuring these ratios, the utility of IRMS for characterization of chromatographically separated molecules has until recently been limited to 13C/12C and 15N/14N. Recent technological developments now allow the direct measurement of 18O/16O and D/H in molecules that have been resolved by capillary GC. Isotope ratios can be used to define isotopically distinctive end members and have been used to characterize high energy explosives (TNT), drugs of abuse (cocaine, heroin), and performance enhancing drugs (testosterone). The more isotopes that can be brought to bear on a problem, the better the chances of unambiguous identification are. The ability to measure multiple isotope ratios in a single molecule allows "stable isotope fingerprinting" of a wide variety of molecules. Three isotope ratios from a single compound can be measured in a variety of commercially important molecules, including ethanol and flavor compounds (e.g. benzaldehyde, vanillin, linalool) with the application being to determine their origin in an effort to detect adulteration or substitution. The measurement of 13C, 18O, and D in the ethanol molecule is under intensive investigation, because IRMS provides an attractive alternative to existing NMR techniques. The ethanol-bearing sample is sampled by a GC autosampler using headspace sampling techniques, and the capillary GC resolves ethanol from water and congeners.

OXYGEN-DEUTERIUM ISOTOPIC MEASUREMENTS USING A VARIETY OF PYROLYSIS METHODS: IRMS CONTINUOUS FLOW TECHNIQUES

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The technique of interfacing an Elemental Analyser or Gas Chromatograph to a stable isotope ratio mass spectrometer has, since their inception, proved to be remarkable versatile analytical tools for the measurement of carbon and nitrogen isotopes across a wide application base. By 1994 sulphur was added to the Elemental Analyser list and more recently those of oxygen and hydrogen have started to be analysed. The analysis of oxygen and hydrogen involved a departure from the normal flash combustion mode of operation to one of pyrolytic thermal decomposition of the sample. This work describes the application of the technique to the measurement of hydrogen and oxygen isotopes across an extensive range of sample types. Samples such as chlorinated hydrocarbons, water, simple organic samples, such as cellulose, phosphates, nitrates etc were measured using a variety of pyrolysis reactor configurations and temperatures. Results will be presented and, where appropriate, comparisons made of the results from the same samples but using alternative pyrolysis techniques.

SENSITIVE DETECTION OF STABLE ISOTOPES IN GEOCHEMISTRY USING MULTI-PHOTON LASER WAVE-MIXING SPECTROSCOPY

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Many analytical applications in geochemistry rely on precise measurement of isotopes and isotope ratios using a mass spectrometric method. Multiphoton laser wave mixing is presented as a sensitive isotope-capable optical method without the use of a mass analyzer. By using counter propagating input laser beams, laser wave-mixing spectroscopy yields sub-Doppler spectral resolution that is suitable for isotope ratio measurements and hyperfine structure analysis. Laser wave mixing also offers high spatial resolution, minimum interferences, excellent detection sensitivity and relatively low cost. Unlike mass spectrometer based methods, wave mixing offers unambiguous isotope measurements.

ON-LINE DETERMINATION OF D18O IN SILICATES, CARBONATES AND OTHER INORGANIC SUBSTANCES: FIRST RESULTS

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Common EA-IRMS couplings have failed in quantitatively converting carbonate- or silicate-oxygen to CO with/without adding 'catalysts'. From theoretical calculations a minimum temperature of ~2000°C for converting silicate-O to CO is known. Hence, fluorination is preferred for d18O measurements of inorganic oxides. O2 and after conversion CO2 can be used as measuring gas. We tried to determine the d18O values of inorganic oxide samples using the TC/EA-IRMS with fluorine-containing additives to achieve a quantitative yield. The volatile fluorine-substances cannot be adapted to the weighing procedure necessary for TC/EA-IRMS analysis. We have tested a CF-polymer as a non-hygroscopic fluorine-containing 'catalyst'. Apart from CO we identified other product gases interfering with d18O determination. We installed a trap for cryogenic purification of the reactor effluent prior to GC-separation. With the CF-polymer we observed quantitative CO-yields. Accuracy (1-3 %) and precision (0.6 %) of d18O values should be improved further to make the method attractive.

SURFACE COMPLEXATION MODELS: A BRIDGE BETWEEN SPECTROSCOPY AND FATE AND TRANSPORT: II

SURFACE COMPLEXATION EFFECTS IN BACTERIAL METAL REDUCTION

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Bacterial metal reduction has gained recognition as a dominant factor in geochemical metal cycling. While the physiology of this process is understood, the importance of the aqueous chemistry is not as well characterized. This work describes laboratory cultures of *Shewanella putrefaciens*, a bacterium which grows anaerobically by reducing insoluble manganese oxides. Cultures were grown in a well-defined minimal medium free of competing trace metals and chelating agents. Chemical analysis indicated that the rate at which reduced manganese appeared in solution varied strongly as either the phosphate or the sulfate concentration was elevated. Electron microscopy indicated that 50-nm sized particles were in contact with the organisms, and associated electron energy-loss spectroscopy identified these particles as the initial manganese oxides, without adsorbed precipitates. These measurements differ strongly from those seen in sterile controls, particularly in a high phosphate environment. These data indicate that organisms play a complex role in controlling their microenvironment.

COMPETITIVE SORPTION OF CU AND PB TO HEMATITE AND FULVIC ACID – HEMATITE COMPLEXES: TESTING THE LINEAR ADDITIVITY APPROACH

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Application of surface complexation models to complex sorbent materials requires that possible interactions between different sorbent phases are understood. In this study, we investigated the sorption of protons, Cu(II), and Pb(II) to colloidal hematite and purified humic and fulvic acids by titration and batch techniques. The experimental data were modelled using a surface complexation model for hematite and the NICA-Donnan model for fulvic and humic acids. Metal sorption experiments with hematite in the presence of fulvic acid were then predicted based on the composite additivity approach and compared with experimental results. At pH < 6, most of the fulvic acid was adsorbed to the hematite surface, resulting in increased Cu(II) sorption. At pH > 6, increasing concentrations of fulvic acid remained in solution, resulting in decreased Cu(II) sorption. The additive model predicted these general trends qualitatively. However, the amount of Cu(II) or Pb(II) sorbed was consistently underestimated at low pH values, indicating that the system may not behave strictly additive as assumed in the composite additivity model.

CATALYTIC EFFECTS OF GOETHITE ON CHROMIUM(VI) REDUCTION BY HYDROGEN SULFIDE IN ANAEROBIC AQUEOUS PHASE

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Cr(VI) reduction by hydrogen sulfide with/without goethite under anaerobic condition was investigated. Experimental data show that the reduction rate was strongly dependent on the initial concentrations of both Cr(VI) and sulfide, as well as the amount of goethite. In the presence of goethite (0.33g/L, pH=8.45), the observed kinetic constant was about 5 times higher than that without goethite. Increasing surface area of goethite or decreasing initial Cr(VI) concentration resulted in higher observed rate constant. The catalytic effect of goethite may arise from the adsorption of reactants on the surface and/or the ferrous iron generated by the reductive dissolution of goethite.

RATES OF URANIUM(VI) SORPTION AND SURFACE PRECIPITATION ON MINERAL SURFACES

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The fate and transport of uranium contamination can be significantly influenced by reactions occurring at mineral surfaces. Characterization of uranium associated with the surfaces of the iron oxide goethite coupled with macroscopic measurements of uranium partitioning between the sorbed and aqueous phases has demonstrated the transformation from sorption-control to precipitation-control of dissolved uranium concentrations. Rates of uranium adsorption and desorption have been measured on goethite and the clay mineral montmorillonite. Desorption from mineral surfaces occurs rapidly when initiated by perturbation of equilibrium conditions and also near equilibrium as measured by isotope exchange. As uranium concentrations increase, a surface precipitate characteristic of the uranyl oxide hydrate schoepite forms; however, at low levels of supersaturation the heterogeneous nucleation of the precipitate may be kinetically hindered. In a meta-stable state which persisted for more than a month, dissolved uranium concentrations were controlled by sorption even when in excess of the solubility limit.

IRON XAS OF REDUCED ESTUARINE SEDIMENTS AND GEOCHEMICAL MODELING OF POREWATER: SEDIMENT REACTIONS

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We combined iron synchrotron X-ray absorption spectroscopy (XAS) with bulk porewater and sediment analyses of reduced estuarine sediments from Naval Air Station Alameda (CA) to quantify processes and rates of iron redox transformations below the sediment-water interface. Analyses of iron XAS data collected on core sediments indicate a sulfide fraction dominated by pyrite and an oxide fraction dominated by Fe-bearing detrital minerals, probably phyllosilicates. Minor iron phases (<10 atom-% Fe) such as iron oxyhydroxides and amorphous FeS were not identified in the spectra. The relative proportion of Fe-sulfide to Fe-oxide and total iron concentrations increased with depth to ~10 cm below the sediment-water interface, reflecting porewater exchange with surface waters and removal of iron from solution as pyrite under reduced conditions. Deeper sediments (at 55 cm) showed a relatively higher proportion of Fe-oxide to Fe-sulfide and lower total iron

concentrations than shallower sediments. This probably results from differences in initial iron concentrations and indicates that Fe-bearing detrital minerals did not dissolve significantly since burial (~50 years).

REACTION-BASED MODEL FOR COMPETITIVE SORPTION AND TRANSPORT OF CD AND ZN IN SOILS

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Predicting the mobility of heavy metals in soils requires an accurate competitive sorption for model heavy metals and major cations. Heavy metals in soils can be sorbed by cation exchange and specific adsorption to clay minerals, oxides, and soil organic matter. In this study, we investigated the sorption of Cd²⁺ and Zn²⁺ in the presence of Ca²⁺, Mg²⁺, and Na⁺ in an acidic soil material. A competitive sorption model for Cd²⁺ and Zn²⁺ was formulated based on cation exchange reactions and specific adsorption reactions to sites with high affinity for Cd²⁺ and Zn²⁺. The model accurately described Cd²⁺ and Zn²⁺ sorption over several orders of magnitude in solution concentrations of Cd, Zn, and Ca. Coupled to a transport code, the model correctly predicted the breakthrough curves of Cd, Zn, and Ca in multicomponent column transport experiments. The applicability of the model for predicting heavy metal release and transport in contaminated soils will be discussed.

CESIUM MIGRATION IN HANFORD SEDIMENTS

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¹³⁷Cs is a significant contaminant in many high-level nuclear wastes (HLW) in the United States, Canada, Europe, and the former Soviet Union. While Cs⁺ is known to sorb strongly to the mica and clay fraction of soils, there is evidence at the Hanford nuclear site in the United States of enhanced migration of Cs⁺ in the vadose zone below leaking HLW tanks. The HLW at Hanford is dominated by high concentrations of NaNO₃ and it is thought that some of the reduced retardation of Cs⁺ may be the result of competition with Na⁺. In addition, competition from K⁺ may also be important in reducing Cs⁺ retardation. A composite of Hanford sediment has been studied previously by Zachara et al (2000) who found evidence for at least two exchange sites with differing affinities for Cs⁺ versus Na⁺ and K⁺: 1) a high affinity site believed to be frayed edge sites on micas, and 2) a relatively lower affinity site on expandable clays. Here we report on flow-through column experiments carried out using the same Hanford sediment and influent concentrations of 10⁻⁴ M CsI. The column experiments indicate retardations of 42 and 7.8 for 1 and 5 M NaNO₃ influent concentrations respectively. Premodeling using the code CRUNCH (Steefel, 2000) based on batch-derived parameters predicts observed breakthrough curves within 15%. Column experiments carried out at flow rates which differ by a factor of 5 give the same bulk retardation, suggesting kinetic effects are not important at these time scales and chemical conditions.

SIMULATING REACTIVE TRANSPORT OF RADIOUCLIDES AT THE NTS USING NON-ELECTROSTATIC SURFACE COMPLEXATION

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A database of non-electrostatic surface complexation (NEM-SC) constants for Am, Eu, Sm, Np, Pu, Cs and Sr sorption to FeOH (iron oxide), CaOH (calcite), and AlOH and SiOH (aluminosilicate) reactive sites and for participation in several ion exchange (IE) reactions was developed. The reaction constants were derived from both laboratory sorption experiments and published sorption data. The sorption reactions are being used to model the reactive transport of radionuclides away from underground nuclear tests at the Nevada Test Site. Though the NEM is the most simplified surface complexation model, it is able to adequately predict RN sorption in single mineral batch, mixed sediment batch, and flow through sorption experiments. Given the mineralogic and hydrologic complexity of the natural environment and the uncertainty of the various SC parameters controlling sorption, the NEM may very well be the most appropriate surface complexation model for describing contaminant migration in complex natural environments.

GEOCHEMISTRY DIVISION MEDAL SYMPOSIUM IN HONOR OF DR. FRANK MILLERO: THE IMPORTANCE OF METAL-LIGAND INTERACTIONS IN NATURAL WATERS

INORGANIC SPECIATION IN NATURAL WATERS

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Due to improvements in thermodynamic data, and chemical models based on such data, speciation calculations are now performed routinely as a means of understanding and predicting environmental chemical behavior. Speciation calculations are important because different forms of a given element have different properties. Thus, as one example, the speciation of iron is studied as a means of assessing the bioavailability of this important element. In other cases, speciation studies are important not because of direct biological implications but because observations of chemical distributions in conjunction with an understanding of elemental speciation can be used to better understand important biogeochemical processes. In this regard, as an example, the comparative chemistries of yttrium and the rare earths can be used to assess the general characteristics of scavenging (adsorptive removal) processes in the oceans. In such cases, where comparative chemistries and comparative distributions are involved, substantial precision in comparative speciation characterizations is required. A particularly outstanding example of the importance of chemical speciation is embodied in the marine CO₂ system, where speciation calculations partition total carbon into the forms responsible for air/sea exchange (CO₂), mineral dissolution and precipitation reactions (carbonate), and acid neutralizing capacity (bicarbonate and carbonate). The robust model linking the various components of the marine CO₂ system creates a particularly stringent requirement for equilibrium constant accuracy. This presentation reviews progress in chemical speciation modeling over the last third of the 20th century. In addition to examining the status of current inorganic speciation models appropriate to natural waters, this presentation highlights a variety of problems in speciation models that should be addressed in future studies.

METAL ORGANIC COMPLEXATION IN THE ENVIRONMENT

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In the last two decades much progress has been made on metal organic complexation in freshwater and marine systems using voltammetric techniques. Most work has centered on the use of anodic stripping voltammetry (ASV) and competitive ligand equilibration with cathodic stripping voltammetry (CLE-CSV) to obtain conditional equilibrium constant data. More recently a kinetic approach has been used to derive formation and dissociation constants and conditional equilibrium constant data. These data along with known model compounds are giving an indication of what the unknown natural ligands are that bind metals such as Fe(III), Zn(II) and Cu(II). Field and laboratory data will be used to show that metal organic complexation is key to metal speciation and how organisms can acquire metals. Recent work using mass spectrometry for structure elucidation will also be used to show the significance of strong metal sulfide complexation in the environment.

POTENTIAL CONSEQUENCES OF METAL:NATURAL ORGANIC LIGAND COMPLEXES IN THE MARINE ENVIRONMENT

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There is recent evidence that complexation of trace metals with natural organic ligands plays an important role in their marine chemistry, in particular for iron, zinc and copper. The chemical speciation in surface waters of these three trace metals is dominated by complexation with natural organic ligands. The fact that these trace metals exist as organic chelates can influence their roles as either limiting nutrients or toxic metals in the marine environment. Activities of micro-organisms at the molecular, cellular, community and ecosystem levels are influenced by the chemical speciation of these trace metals. The existence of organic complexes can also influence concentrations, cycling and residence times of these trace metals in marine environments. Examples of the consequences of such metal-organic ligand complexes will be presented.

SPECIATION OF METALS IN NATURAL WATERS

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The form or speciation of a metal in natural waters can change its kinetic and thermodynamic properties. The form of a metal in solution can affect its toxicity and solubility. Ionic interaction models that can be used to determine the activity and speciation of divalent and trivalent metals in seawater and other natural elements will be discussed. The model is able to consider the interactions of metals with major and minor inorganic anions as a function of temperature (0 to 50°C), ionic strength (0 to 6M) and pH (1 to 13). Recently it has been shown that many divalent metals are complexed with organic ligands. Although the composition of these ligands is not known, a number of workers have used voltammetry to determine the concentration of the ligand [Ln] and the stability constant (KML) for the formation of the organic complexes (ML). These results have been added to our inorganic speciation model. The model can be used to examine the competition of inorganic and organic ligands for divalent metals as a function of ionic strength. The importance of organic ligands in controlling the solubility of Fe(III) in seawater will be discussed.

ADVANCES IN STABLE ISOTOPE BIOGEOCHEMISTRY: COMPOUND SPECIFIC APPLICATIONS

METHODICAL INVESTIGATIONS ON D13C ANALYSIS OF AMINO ACID ENANTIOMERS WITH GC-C-IRMS AND APPLICATION IN SOIL SCIENCE

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The application of a combined gas chromatography - combustion - isotope ratio mass spectrometry (GC-C-IRMS) method for stable carbon isotope analysis of amino acid enantiomers in soil samples is presented. Triplicate d 13C analyses of pentafluoropropionyl (PFFA) isopropyl ester derivatives of 27 amino acid enantiomers revealed that discrimination during derivatisation is minimal and reproducible. Thus, correcting for the d 13C signal of underivatized amino acid enantiomers is possible for all investigated amino acid enantiomers. The detection limit approached 0.3 ng for some amino acid enantiomers in the splitless mode. The linearity in the range between 0.3 and 10 ng was acceptable for all amino acids except for D-aspartic acid in the splitless mode. In the split-mode, however, linearity was not confirmed, and detection limit exceeded 10 ng injection amount. Operating the GC-C-IRMS system in the split-mode is therefore not recommended. First results on the compound specific d 13C signature of soil-inherent amino acid enantiomers will be discussed.

TWO STRATEGIES TO ENHANCE THE VOLATILITY OF NON-POLAR AND AROMATIC AMINO ACIDS WITHOUT THE ADDITION OF EXTRANEEOUS CARBON FOR HIGH PRECISION ISOTOPIC ANALYSIS

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Amino acids are routinely derivatized using carbon-containing groups prior to Gas Chromatography-Continuous-flow Isotope Ratio Mass Spectrometry (GCC-IRMS) for C and N isotopic analysis. For C isotopic analyses, derivative C contaminates analyte C because the entire derivatized compound is combusted to CO₂, thus, correction procedures are required to extract the analyte isotope ratio. For N isotopic analyses, derivative C increases the ratio of carbon to nitrogen and thus the mass of CO₂ that must be cleared. We present here two strategies amino acid isotopic analysis without adding derivative C, one based on chemical reduction to amino alcohols and the other on enzymatic decarboxylation to yield alkyl amines, and a GC analysis strategy to produce acceptable chromatography using these strongly hydrogen-bonding compounds. Chemical reduction was evaluated for six non-polar amino acids: alanine, valine, leucine, isoleucine, methionine, and phenylalanine, using NaBH₄ in THF with I₂ as an electrophile. Percent recovery from the reduced reaction mixture was 60-84%, reflecting extraction efficiency. GC separation of a mixture of the six amino alcohols was achieved using a thick stationary phase (5 mm) capillary column to avoid tailing due to hydrogen bonding to the walls of the fused silica capillary. The reproducibility of GCC-IRMS determinations of amino alcohols averaged SD(d13C)=0.25±0.19‰. The absolute differences between d13C of amino acids measured by an elemental analyzer coupled to IRMS and amino alcohols measured by GCC-IRMS was d13C=0.14‰ and showed no general trend. Tyrosine and phenylalanine were decarboxylated with tyrosine decarboxylase enzyme and phenylalanine decarboxylase enzyme respectively in a mixture of 18 amino acids in acetate buffer 0.1M, pH 5.5 at 37° to tyramine and phenethylamine. Percent recovery of tyramine and phenethylamine were 95% and 96%, respectively. The reproducibility of GCC-IRMS of tyramine and phenethylamine measured by GCC-IRMS averaged SD(d15N)=0.425±0.007‰. These data indicate that both strategies will be useful for high precision isotopic when derivatization must be avoided.

INVESTIGATIONS OF TURTLE METABOLISM AND HATCHLING DEVELOPMENT USING STABLE CARBON ISOTOPE ANALYSIS OF INDIVIDUAL AMINO ACIDS

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The role of maternal diet in the survival of the next generation is not fully understood. After laying her clutch of eggs, a female turtle leaves the nest and does not return. Therefore, all energy and nutritional reserves required for the development of the hatchling and also to fuel the hatchling for the first few weeks of life must be present in the freshly laid egg. To determine the important protein requirements for successful hatchling development, we investigated the embryonic development of the red-bellied turtle (*Pseudemys rubriventris*). Chemical and stable isotope analyses of egg yolk and muscle tissue indicate rapid utilization of protein during early development. The isotope composition of the individual amino acids, isoleucine and phenylalanine, remained constant over the development period, indicating that they were not synthesized *de novo* and were obtained directly from the diet of the mother. Identification of these essential amino acids in turtles provides a means to determine the importance of specific components in the diet of the mother that are needed to ensure successful hatchling development.

INFLUENCE OF LONG-TERM FERTILIZER AND MANURE ON THE DISTRIBUTION AND 15N NATURAL ABUNDANCE VALUES OF AMINO ACIDS IN THE VERSAILLES '42 PARCELLES': PRELIMINARY RESULTS

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CARBON AND NITROGEN STABLE ISOTOPE VARIATION IN PRIMATE HAIR REFLECTS ECOLOGICAL AND DIETARY VARIATION

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In correlation with C₃ plant variation, hair d13C values in non-human primates across a wide geographic range and primate taxa monitor forest or woodland canopy cover. Species from evergreen forests have the most negative values, those from deciduous forests are intermediate, and

those from a drought afflicted forest are the least negative. Primates eating C4 plants, CAM plants, or grass-eating insects and vertebrates have hair $\delta^{13}\text{C}$ values outside the range of animals feeding solely on C3 plants. Hair $\delta^{15}\text{N}$ values from arboreal primates observed feeding on legumes are significantly lower than those of other primates, fruit-eating monkeys are intermediate, and omnivorous monkeys and prosimians have significantly more positive $\delta^{15}\text{N}$ values than the other groups. Subsections of hairs show isotopic variation within a monkey species with significant seasonal variation in diet even though analysis of total hairs showed no interindividual variation.

DISTRIBUTION AND OCCURRENCES OF TORBANITES IN PANGAEA: STABLE CARBON ISOTOPIC COMPOSITION OF BIOMARKERS RELATED TO CLIMATE

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The torbanites are a group of organic-matter-rich sediments consisting mainly of the remains of *Botryococcus braunii*, preserved in the rock record. In this study, stable carbon isotopic compositions of biomarkers and their distributions have been used to investigate the roles of eukaryotes and prokaryotes giving rise to the formation of torbanites. All samples are characterised by algaenan-derived n-alkanes indicative of *B. braunii*. Some samples contain an unusual distribution of monomethylalkanes comprised of at least 4 series (C23 to C31+, each series differing by two carbon atoms) and all samples contain a novel series of macrocyclic alkanes (C14-C33+) and methylated counterparts. The monomethylalkanes and macrocyclic alkanes have been identified by GC-MS and the co-injection of authentic standards. $\delta^{13}\text{C}$ contents of the n-alkanes are quite similar in all samples and are close to the $\delta^{13}\text{C}$ of the total organic matter, indicating algaenan represents a significant part of the organic matter. $\delta^{13}\text{C}$ of the unusual series monomethylalkanes are found to be significantly enriched in ^{13}C compared to phytoplankton derived biomarkers by up to more than 20‰. Biomarker distributions and $\delta^{13}\text{C}$ of biomarkers in torbanites allow classification into 3 groups: (i) eastern Australia (Newnes and Glen Davis) characterised by intense heterotrophic reworking of *B. braunii* biomass (ii) southern Africa and eastern Australia (Temi), intense heterotrophic reworking of *B. braunii* biomass and evidence of an active methane cycle (iii) Scotland, evidence of an active methane cycle, high relative abundance of macrocycles but no monomethylalkanes with the unusual distribution. The biomarker distributions in the two Scottish torbanites which were deposited under a tropical climate are quite different from all the other torbanites which were deposited under glacial conditions. The two Scottish torbanites do not contain monomethylalkanes with the unusual distribution. The absence of these components in Scottish torbanites might be related to the fact that these sediments were deposited under tropical conditions. Perhaps these monomethylalkanes are *B. braunii* biomarkers indicative of very cold climate conditions. The monomethylalkanes with the unusual distributions might be derived from botryals of the race A of *B. braunii*. Perhaps the race A biosynthesised botryals in high amounts in response to the extremely cold climate conditions.

COMPOUND SPECIFIC HYDROGEN ISOTOPE ANALYSIS: NEW INSIGHTS INTO GEOCHEMICAL AND BIOGEOCHEMICAL REACTION MECHANISMS

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Recent advances in continuous flow mass spectrometry have revolutionized compound specific hydrogen isotope analysis of organic compounds. Due to the larger mass difference between the heavy and light isotopes for hydrogen (^2H ; ^1H) versus carbon (^{13}C ; ^{12}C), hydrogen isotope fractionation is often significantly larger than for carbon and can provide new insight into the origin and fate of hydrocarbons in the environment. For aromatic hydrocarbons such as toluene, H isotope analysis is the key isotopic parameter indicative of biodegradation of this group of priority groundwater pollutants. Similarly, H isotope fractionation patterns examined in tandem with carbon isotope fractionation patterns are key to determining whether C1-C4 hydrocarbons found in deep groundwaters in mining environments are formed by thermal cracking versus by polymerization.

PALAEOCLIMATE RECORDS IN COMPOUND-SPECIFIC δD VALUES OF LIPID BIOMARKERS IN OMBROTROPIC PEAT

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The exploitation of biomarker stratigraphic records as climate proxies is well established in ocean and lake sediments, but not as yet in peat deposits. Recent work demonstrated variations in biomarker n-alkane distributions that correlate with vegetation changes at the bog surface through time. We now extend this work, taking advantage of recent analytical developments that make it possible to measure compound specific deuterium values for biomarkers. Initial work focused on a 40 cm peat profile from Bolton Fell Moss, Cumbria, UK. The bog vegetation is sensitive to climate changes in the past >200 years (age depth model based on ^{210}Pb dating) correlating with the global scale cooler period of the later 19th and early 20th centuries. Correlations with meteorological records suggest compound-specific δD values have potential for use as a new climate proxy. Refinements of this approach include extension to other compound classes and other bogs to obtain synchronous records.

THEORETICAL, EXPERIMENTAL, AND OBSERVATIONAL TECHNIQUES FOR HYDROTHERMAL CHEMISTRY: I

XAFS ANALYSES OF SOLUTIONS AT SUBCRITICAL AND SUPERCRITICAL CONDITIONS IN THE HYDROTHERMAL DIAMOND ANVIL CELL

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The hydrothermal diamond anvil cell (HDAC) can subject aqueous solutions to pressures up to 2500 MPa and temperatures from -190 to 1200°C. Transmission X-ray absorption fine structure (XAFS) spectra on solutions in the HDAC indicate that Zn remains in solution as ZnCl_4^{2-} complex in 1M $\text{ZnCl}_2/6\text{M NaCl}$ and as ZnBr_4^{2-} complex in 1M $\text{ZnBr}_2/6\text{M NaBr}$ aqueous solutions up to supercritical conditions. Heating the latter solution from 25 to 500°C results in a 63% reduction of waters of solvation of the ZnBr_4^{2-} complex and a similar reduction in the hydration shell of the bare Br^- ion. The hydration waters appear to be weakly hydrogen bonded to the halide ions. Feasibility tests of the fluorescence XAFS method indicate that we will be able to obtain useful spectra on solutions with concentrations in the ppm range on first-row transition elements and possibly elements as light as Cl.

SOLVATION OF INORGANIC METAL ION COMPLEXES UNDER HYDROTHERMAL CONDITIONS: NOVEL RESULTS FROM X-RAY ABSORPTION ANALYSES

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Knowledge of how the structure of complexes and interaction of ions vary as a function of temperature and pressure is important for understanding the transport and deposition of ore metals and mineral dissolution in crustal fluids. Detailed x-ray absorption spectroscopy analyses of aqueous solutions in modified hydrothermal diamond anvil cells show that chloro and bromo zinc complexes exhibit zinc-halide bond contraction at a rate up to 0.01 Å/100 °C, upon heating from 25 °C to 500 °C. Conversely, the oxygens of the La³⁺ ion hydration shell undergo bond expansion of 0.12 ± 0.03 Å in the equatorial plane while those in the tricapped trigonal prismatic sites are contracted inwards by 0.13 ± 0.03 Å upon heating in aqueous solutions from 25 °C to 300 °C. We attribute these results to hydrogen bond breaking and commensurate reduction of the outer-hydration shell waters of the complexes in sub- and supercritical aqueous solutions.

XAFS ANALYSIS OF RADIATION-INDUCED SMALL CU PARTICLE CLUSTER FORMATION IN AQUEOUS CUCL₂

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Under favorable conditions, synchrotron radiation that is used as a structural probe in gaining insight into the ion-water and ion-ion interactions of geochemical interest, can induce oxidation and/or reduction in aqueous solutions. Successive x-ray absorption fine structure (XAFS) spectra, measured from a 55 ppm CuCl₂ aqueous solution show the formation of copper clusters and their growth as a function of time of irradiation. The nearest neighbor distance of the clusters increases over irradiation time from 2.48 ± 0.02 Å to 2.55 ± 0.01 Å, indicating that the clusters approach the lattice dimensions of bulk copper. Analysis of spectra measured in the intermediate time period shows presence of a distribution of clusters that can be represented by a mixture of a small cluster (5-10 Å across) and bulk copper. The aqueous copper ions are reduced by reacting with hydrated electrons produced through hydrolysis of water by the incident radiation.

DETERMINATION OF CRITICAL TEMPERATURES OF BaCl₂-SATURATED AQUEOUS SOLUTION BY VISUAL METHOD IN A DIAMOND-ANVIL CELL

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Visual observations using a diamond-anvil cell confirm that the system BaCl₂-H₂O has two critical lines, one ending at a lower critical point and the other at an upper. We measured the two critical temperatures to be 384.3 (±0.8) °C and 471.6 (±0.8) °C respectively. The lower temperature agrees with that reported by Valyashko et al. (Dok. Akad. Nauk SSSR, 272, 390, 1983), but the upper temperature is about 13 °C lower than their reported value. They used visual observations in thick-walled silica tubes to determine the lower critical point at about 25 MPa. Because of pressure limitation of the silica tube, an autoclave procedure (a less reliable method) was used to determine the upper critical point at about 98 MPa. This limitation does not apply to the diamond-anvil cell. Additionally, the diamond-anvil cell allows for in situ sample characterization by advanced spectroscopic methods.

THERMODYNAMIC MODELS OF NATURAL FLUIDS: THEORY AND PRACTICE

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Our efforts to develop a highly accurate global model for predicting the thermodynamic properties of natural fluids are discussed. We have used free energy based equations of state (EOS) to represent the equilibrium chemistry of multicomponent aqueous systems for conditions where the brine phase is nearly incompressible. These liquid density models are in excellent agreement with solubility, osmotic, emf, etc. data for brines to high concentration and temperature (0°-250°C, saturation pressure). For compressible systems, we have developed new EOS that yield correct free energies for both liquid and vapor densities and successfully describe the large compositional changes that can occur during phase separation. They accurately extrapolate experimental measurements to regions substantially above the critical region of water. However, in the region of the critical point, special effort must be made to ensure that the model obeys universal scaling. We discuss the significant role of molecular simulations in developing natural fluid models. Simulations of Al³⁺ solvation using the AIMD first principles method show considerable bond breaking (hydration) in the solvation shell and give important insights into the structure of aqueous solutions.

HYDROGEN BONDS AT HYDROTHERMAL CONDITIONS

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High pressure changes properties of every crystal. This effect is especially pronounced in case of molecular crystals, where the molecules that constitute the crystal can significantly change their chemical and physical properties, including activity, while deformed. Although, in most of the previously published studies it was assumed that the changes in molecular geometry are so minor, that the ambient-pressure geometry of the molecule can be constrained during refinement at high pressure. This approach was to some extent justified, because the changes in bond length and angles at pressures accessible for molecular crystals (below 10GPa) are usually comparable to experimental errors. Thanks to the development of a novel technique, high-pressure single-crystal XRD with CCD detection, the observation of changes in molecular geometry became much easier. The pressure dependence of molecular and hydrogen-bond geometry will be discussed on basis of Diamond Anvil Cell experiments with urea, melamine and ice crystals.

STABILITY AND DYNAMICS OF CLATHRATE HYDRATES UNDER PRESSURE

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Clathrate hydrates are inclusion compounds with water forming the frameworks. A generally accepted theory based on the solid solution model proposed by Van der Waals and Plateeuw suggested that the stability of hydrates is due to weak van der Waals interactions between the

guests and the host water molecules and each cavity in the structure can accommodate only one guest. However, there are growing evidences from recent experiments on nitrogen hydrate and speculation on argon hydrate suggesting the possibility of multiple occupancy. Classical isobaric-isothermal molecular dynamics calculations were performed to investigate this novel phenomenon. The results show that double occupancy in the large cages of nitrogen hydrate is thermodynamically stable. In contrast, external pressure is required in order to stabilize double occupancy in argon hydrate. The dynamical properties of the guest and vibrational spectra for the nitrogen and argon hydrates were computed. The theoretical results may be helpful for the experimental characterization of double occupancy. The stability of gas hydrates under external pressure was also studied theoretically. The nature of the high pressure transition is revealed. In particular, the effects of pressure on the intermolecular vibrations of methane in several postulated and newly identified high pressure hydrate phases will be presented

MONTE CARLO GIBBS ENSEMBLE SIMULATION OF PHASE EQUILIBRIA OF THE RWK2 WATER

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A computer program, based on the Gibbs Ensemble Monte Carlo method, has been developed to simulate liquid-vapor phase equilibria of water. This method consists of three simulation steps: displacement of molecules inside phases, volume change of both phases and molecule exchange between phases. These simulation steps ensure the satisfaction of equilibrium conditions, which include internal equilibrium, equal pressure and chemical potential between phases. A special insertion technique, biased rotation insertion, is used to accelerate the exchange of molecules between liquid and vapor phase. This program can be adapted to study other thermodynamic and structural properties of water and aqueous mixtures on molecular level.

DIRECT OBSERVATIONS ON THE PHASE BEHAVIOR OF CO₂ IN HYDROTHERMAL SYSTEMS

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The issue of CO₂ miscibility in fluids is critical to understanding hydrothermal systems at high pressures and temperatures, because the evolution of CO₂ inevitably modifies the solution chemistry. However, direct experimental studies on this system have been very limited. In this study we have used an externally heated diamond anvil cell to monitor the phase behavior of in a CO₂-H₂O system. Using in-situ Raman spectroscopy, supplemented with direct optical determinations, we have explored the limits of phase immiscibility in this system. Consistent with some theoretical predictions, our experimental data indicates continuation of the 2-phase region in CO₂-H₂O system to pressures exceeding 3.5 GPa and temperatures in excess of 300 C.

BIOGEOCHEMISTRY OF ARCHEA

POLAR ETHER LIPIDS AS TAXONOMIC AND QUANTITATIVE MARKERS OF ARCHAEA

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We have been working on lipid structure analysis of various kinds of methanogenic and other Archaea. As application of lipid analysis to microbial ecological studies, quantitative and qualitative analyses of archaeal ether lipids have been developed. Low and high sensitivity HPLC analyses of core ether lipids were used for quantification of methanogenic cell biomass in certain environments. For qualitative analysis, a new simplified component parts analysis was developed. This method was first devised for chemotaxonomic purpose, but later applied to inference of groups of methanoarchaea in wastewater digester sludge. Care should be given to the application based on the recent advancement of lipid biochemistry of Archaea, since extraction yield of lipid from cells, limited availability of core lipid by acid methanolysis of aminophospholipids of Archaea, acid lability of hydroxyarchaeols and allyl ether-containing phospholipids, and the occurrence of unusual core lipids in a hyperthermophilic methanoarchaea have been uncovered.

WIDESPREAD OCCURRENCE OF STRUCTURALLY DIVERSE TETRAETHER MEMBRANE LIPIDS

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Membranes of hyperthermophilic archaea are predominantly composed of isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs) whilst those of hyperthermophilic eubacteria are partly composed of branched glycerol dialkyl ethers/ glycerol monoalkyl glycerol diethers. The structural difference from diacyl membrane lipids of non-thermophilic eukaryotes and prokaryotes apparently contributes to the thermal stability of membranes of hyperthermophiles. Recently, however, indirect evidence was reported for GDGTs in non-thermophilic Crenarchaeota, archaea genetically related to hyperthermophilic archaea but living in low temperature (<20°C) environments. Using a new analytical technique we have found in recent and ancient sediments known and newly identified isoprenoid and branched GDGTs which are far more widespread and structurally diverse than previously thought. Their distribution indicates the ubiquitous environmental presence of non-thermophilic organisms that have independently evolved from hyperthermophilic archaea and eubacteria. The structures of some GDGTs point to the occurrence of both typical archaeal and eubacterial biosynthetic pathways in single organisms. Some of the structural differences in the novel membrane lipids compared to those of hyperthermophilic counterparts are likely adaptations to low temperature environments.

COMPOUND-SPECIFIC 14C MEASUREMENTS OF ARCHAEOAL AND BACTERIAL LIPIDS FROM THE SEDIMENT: WATER INTERFACE OF SANTA BARBARA BASIN

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Non-extremophile Archaea represent a significant fraction of total prokaryotic biomass in the oceans. Four biphytanes (C₄₀ isoprenoids) derived from caldarchaeol, the major membrane lipid of Crenarchaeota, are present both in water column particulate matter and in the sediments. These biphytanes from all sample types and environments have uniformly heavy stable carbon isotope (δ¹³C) values near -20‰. This uniform ¹³C enrichment argues for an autotrophic metabolism in the Archaea, specifically one that incorporates dissolved inorganic carbon (DIC) in the form of bicarbonate rather than CO₂. Here we exploited the gradient in D¹⁴C of water column DIC in Santa Barbara Basin (SBB) to distinguish whether the archaeal lipids present in the deep SBB reflect production in ¹⁴C-enriched surface waters (~ +70‰) or in ¹⁴C-depleted deep waters (~ -105‰). Two C₄₀ isoprenoids were extracted from SBB surface sediment (0-1 cm, < 5 yr deposition). Their D¹⁴C values (-100‰, -101‰) do

not reflect either biomass production in surface waters or heterotrophic uptake of sinking euphotic zone carbon. In contrast, other bacterial lipids do reflect the consumption of fresh phytodetritus (C15 fatty acids, ~ +35%). The fatty acid carbon is only slightly ¹⁴C-depleted relative to surface waters. Lipids representing a purely eukaryotic source (phytoplanktonic sterols) have exactly the same ¹⁴C concentration as surface waters (D14C=+69 ± 14‰, n=6). Accordingly, these compound-specific radiocarbon analyses provide compelling evidence that the Archaea fix inorganic carbon within the deep Santa Barbara Basin.

DETECTION, IDENTIFICATION, AND MOLECULAR MONITORING OF ARCHAEL COMMUNITIES LOCATED ON DETERIORATED ANCIENT WALL PAINTINGS

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Efforts to control microbial growth on objects of art are ineffective without a better understanding of the microbial diversity. New DNA based techniques have been developed, which allow the identification of individual microbial species in sample material without the cultivation of the organisms. One strategy to this approach is the Denaturing Gradient Gel Electrophoresis (DGGE) of PCR-amplified gene fragments coding for rRNA [1]. It allows the separation of DNA fragments of identical length but different sequence due to their different melting behaviour in a gel system containing a gradient of denaturants. As a result, a bandpattern is obtained, which visualises the complexity of the microbial community, and in addition, individual members of the community can be identified. A second strategy to this approach is in situ hybridisation. End-labelled oligonucleotides are sufficiently sensitive to allow the specific detection of individual microbial cells directly in sample materials. Fluorescent rRNA-targeted oligonucleotide probes confer fluorescent stain specifically to cells of a phylogenetically coherent group on various taxonomic levels from species up to the kingdom level. They can be applied to samples without prior cultivation and determine the cell morphology and identity of microorganisms, their abundance and the spatial distribution in situ [2]. The presence of extremely salt tolerant and moderate halophilic bacteria has been demonstrated in wall paintings [3] where salt efflorescences on the surface is a common phenomenon. Archaea are representing a microbial domain which has not been previously considered as a potential contributor to the deterioration processes of wall painting or similar objects of art. In this work we describe the detection of Archaea in deteriorated ancient wall paintings by denaturing gradient gel electrophoresis (DGGE) of PCR-amplified DNA encoding 16S rRNA and fluorescent in situ hybridization (FISH) without prior cultivation of the organisms.

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ANAEROBIC OXIDATION OF METHANE MEDIATED BY A MICROBIAL CONSORTIUM ABOVE MARINE GAS HYDRATE

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Methane hydrate containing sediments were sampled during RV SONNE Cruise SO143-2 and SO148-1 to the Cascadia margin in August 1999 and 2000. Integrated over the upper 15cm, the sulfate reduction rates in the zone of anaerobic oxidation of methane (AOM) are >100 mmol/m²/d and represent some of the highest values ever measured in cold marine sediments. A combination of biomarker studies involving stable isotope analysis and fluorescence in situ hybridization shows that a consortium of archaea and sulfate reducing bacteria is responsible for AOM in these and other methane-rich sediments. This consortium may occur in extremely high numbers of 10¹⁰ cells per ml sediment. AOM rates were measured in parallel to sulfate reduction rates in surface and subsurface zones of methane seeping sediments. New data are presented on the distribution, activity and diversity of the archaea/SRB consortia in methane rich sediments.

LIPID BIOMARKER ANALYSIS OF METHANE CARBON CYCLING IN ANAEROBIC SEDIMENTS OF HYDRATE RIDGE, CASCADIA MARGIN

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Large deposits of exposed methane-sulfide gas hydrate have been found on the second accretionary ridge of the Cascadia convergent margin off the coast of Oregon (Hydrate Ridge, 600-800 m water depth). The area is characterized by prolific vent communities, thick bacterial mats, authigenic carbonate lithologies, and continuous expulsion of methane-rich fluids, which in part are locally derived from the decomposition of gas hydrates. During the international, multi-stage research project TECFLUX undisturbed sediment cores were recovered using a video-guided multiple corer system in August/September 1999 and August 2000. Molecular and carbon-isotopic studies on lipid biomarkers provide evidence that a large part of the methane is anaerobically oxidized in the sulfate-depleted sediments of Hydrate Ridge. The process is indicated by the high abundance of diverse archaeal (irregular isoprenoids, glycerol ethers) and bacterial biomarkers (short-chain fatty acids, short-chain alcohols) which are highly depleted in ¹³C relative to the methane carbon source (δ¹³CCH₄=-65 per mil PDB) down to -128 per mil PDB. The combination of these results with fluorescence in situ hybridization (FISH) studies provides evidence that the anaerobic oxidation of methane (AOM) is most probable mediated by a structured consortium of archaea and sulfate-reducing bacteria (SRB) living in syntrophic association. The essentially limitless reservoir of methane available to the archaea/SRB consortium in this gas hydrate environment allows the kinetic carbon isotope effect (ε_{CH₄}-biomarker) associated with AOM to be fully developed (ε_{max}=72 per mil). Without the process of AOM the escape of methane into the water column would be even greater, possibly allowing methane to enter the atmosphere.

ARCHAEL AND BACTERIAL INTERACTIONS DURING ANAEROBIC METHANE OXIDATION AT COLD SEEPS

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Recent analyses have shown that archaea mediate anaerobic methane oxidation at cold seeps in diverse marine settings, including the California margin, Hydrate Ridge, and Mediterranean mud volcanoes. At these latter settings, evidence for the role of archaea in anaerobic methane oxidation is provided by isotopically depleted archaeal biomarkers. The diversity of these biomarkers is profound and includes diethers, crocetane, PMI, and glycerol dialkyl glycerol tetraethers. These results suggest that the archaea responsible for methane oxidation represent a complex and diverse microbial community. However, organic geochemical and isotopic analyses indicate that in addition to archaea, bacteria are also significant components of this community. A wide variety of bacterial compounds were identified, including hopanoids, fatty acids, and two distinct series of novel non-isoprenoidal ether lipids. Based on their distributions, isotopic compositions, and structures, these compounds

apparently reflect several different bacterial communities, including sulphide-oxidising and sulphate-reducing bacteria. It is likely that these bacteria are vital in mediating the flow of carbon and redox potential in the sediments, maintaining thermodynamically favourable conditions for methane oxidation.

HOW METHANE-CONSUMING MICROBIAL COMMUNITIES INDUCE CARBONATE CRUST FORMATION

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Authigenic carbonate crusts formed through microbial methane oxidation are a common occurrence at seafloor cold seeps world-wide. In order to investigate the microbiological controls on dissolved carbon equilibria and carbonate mineralogy, we conducted mineralogical, stable isotope, organic geochemical and phylogenetic studies of carbonate crusts formed on submarine mud volcanoes of the eastern Mediterranean Sea. These show that carbonate crust formation is favoured by specific assemblages of methane-consuming archaea and sulphate-reducing bacteria. The crusts contain a highly diversified and previously unrecorded set of ¹³C-depleted archaeal lipid biomarkers that are produced by a diverse archaeal community composed mostly of novel groups recognised with archaeal 16S rRNA gene surveys. The presence of ¹³C-depleted bacterial biomarkers, combined with data from the bacterial rRNA gene surveys, suggest that diverse bacterial communities are also involved in anaerobic methane oxidation. The bulk chemical reactions carried out by microorganisms favor carbonate crust formation by increasing pH and carbonate alkalinity, producing supersaturation conditions with respect to carbonate minerals. Furthermore, the steep dissolved sulfate gradients produced by microbial sulfate reduction exert a strong control on carbonate mineralogy. Aragonite precipitation is thus favored near the sediment-water interface, where high sulfate concentrations inhibit the precipitation of high-Mg calcite.

MOLECULAR FOSSILS FROM ANCIENT METHANE: RELATED SETTINGS

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A large portion of methane produced in marine sediments is metabolized anaerobically before reaching the water column or the atmosphere. In addition to aerobic methanotrophy, anaerobic oxidation of methane (AOM) is estimated to account for a consumption equivalent to 5 - 20% of the annual global methane flux to the atmosphere. Field and laboratory studies as well as molecular approaches have greatly added to the knowledge on the metabolic processes fueled by methane inputs and the combined results from these studies strongly suggest that syntrophic consortia of Archaea performing reversed methanogenesis and sulfate-reducing bacteria (SRB) account for AOM in marine sediments. In methane-related deposits, lipid biomarker studies, combined with compound-specific stable carbon isotope measurements provide important information on the activity of the distinctive AOM performing consortia. Furthermore, compound structures and their isotopic signatures allow to discriminate allochthonous contributions of organic matter and supply valuable information on the impact of other significant biota thriving in the respective environments. Whereas numerous modern settings have now been explored for the presence of diagnostic, methane-related lipids, only few studies exist on ancient, pre-Quaternary deposits. Little is yet known about the paleoenvironmental significance of these compounds and both their structural as well as their isotopic preservation potentials. We here provide a review on fossil marker molecules extracted from a set of six ancient methane-related environments ranging in age from Tertiary to Jurassic (Miocene methane-derived limestones from northern Italy; Oligocene seep carbonates from two locations in Washington state, USA; Jurassic (Oxfordian) seep deposits from southern France).

BIOGEOCHEMICAL CONSEQUENCES OF DYNAMIC INTERACTIONS BETWEEN BENTHIC FAUNA, MICROBES, AND AQUATIC SEDIMENTS: I

IMPACT OF POLYCHAETES (NEREIS AND ARENICOLA) ON SEDIMENT BIOGEOCHEMISTRY IN COASTAL AREAS: PAST, PRESENT, AND FUTURE DEVELOPMENTS

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Our knowledge on sediment biogeochemistry associated with burrow structures of *Nereis* sp. and *Arenicola* sp. was limited 20 years ago. The first studies focused on solute exchange across the sediment-water interface. The results showed that these animals have significant effects on nutrient fluxes and inspired us to work on specific processes, such as nitrification and denitrification. Thus, a number of studies agreed that more than 60% of total sediment denitrification in coastal sediments can be associated with *Nereis* burrow structures. Later, the focus was, and still is, related to the mechanisms by which burrow dwellers stimulate carbon diagenesis in sediments. Among the aspects studied are: the role of mucus secretions, the role of particle entrapment and reworking, the role of electron acceptor availability, the role of organic matter age and origin, and the role of diffusion scales. We have now a solid knowledge on the mechanisms by which these animals affect decomposition processes in sediments. In the future, we may turn to molecular techniques to solve unanswered questions. It is obvious to examine the phylogeny of specific bacterial groups (e.g. sulfate reducers, nitrifiers, denitrifiers) to identify bacterial communities associated with burrows. Are they specific for this environment, and thus adapted to the physical and chemical conditions here, or are they simply migrants from other parts of the sediment environment?

FATE OF PHYTODETRITUS IN CONTINENTAL SLOPE SEDIMENTS

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The responses of the continental slope benthos to phytodetritus deposition were studied with in situ tracers. Study sites offshore of Cape Fear (I) and Cape Hatteras (III), NC were characterized by different organic C deposition rates, macrofaunal densities (III > I in both cases) and taxa. ¹³C-labeled diatoms were emplaced in plots on the seafloor at both locations. At Site I, tracer diatom was intercepted at the surface primarily by protozoa and surface-feeding annelids. Little of the diatom C penetrated below 2 cm even after 14 months. At Site III, annelids were primarily responsible for the initial uptake of tracer. Diatom C was transported to a depth of 12 cm and was found in animals collected between 5-10 cm in days. The natural organic C depositional flux is hypothesized to be the master variable that controls the fate of organic detritus via its influence on faunal densities and taxa.

ENHANCED ORGANIC MATTER REMINERALIZATION AND NUTRIENT TURNOVER BY POPULATIONS OF BURROWING SHRIMP IN YAQUINA BAY, OR

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Burrowing, or thalassinid, shrimp structure large areas of intertidal habitat of Pacific Northwest estuaries. This field study utilized a combination of anoxic incubations, porewater dialysis peepers, and benthic chambers to quantify the role of burrowing shrimp species on organic matter (OM) decomposition and nutrient fluxes across the sediment-water interface (SWI) on Idaho Flat, an intertidal sandflat in Yaquina Bay, OR. The two species studied have functionally different bioturbational effects on OM cycling and nutrient fluxes. Bioturbation by *Neotrypaea californiensis* had a more significant impact on organic carbon reaction rates whereas bioirrigation by *Upogebia pugettensis* enhanced nutrient fluxes across the SWI. The large-scale physical and chemical alteration of sediments by dense beds of these burrowing shrimp has implications for OM remineralization processes and nutrient fluxes in areas of the estuary they inhabit.

FEEDBACK IN THE BENTHIC BOUNDARY LAYER BETWEEN BACTERIA, LARGE FAUNA, CHEMISTRY, PHYSICS AND HUMAN ACTIVITIES

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Physics, chemistry and biology are inextricably connected in the benthic boundary layer. This close coupling sets up positive feedback processes in sediments. Bioturbation by metazoans oxygenates sediments and oxidises toxic sulphides. As a result, metazoans create a more favourable environment for themselves. Contrary positive feedbacks also exist, however, such as sulphide production by bacteria. Increased concentrations of toxic sulphides, reduces competition for organic carbon from metazoans. Exogenous factors such as carbon input and temperature limit these processes and direct human physical impacts are also likely to be significant: e.g. the southern North Sea is dragged over by fishing gear about 5 times per year on average. This mixes sediment layers and increases faunal mortality, therefore it is likely to be important to the state of the benthic boundary layer. Benthic feedback mechanisms and the potential role of human disturbance in determining the state of this system will be discussed.

CHEMICAL AND BIOLOGICAL IMPLICATIONS OF WATER FLOW THROUGH PERMEABLE SEDIMENTS

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Sandy marine sediments usually have very low organic content and high permeability. Paradoxically, however, oxygen concentration in pore waters is typically zero within a few mm of the sediment-water interface. We are testing the hypothesis that the low organic content of sands is due to high bacterial activity, fueled by a high rate of supply of organic substrates and oxygen as water is advected through the sediment. Laboratory experiments show that faster water flows lead to rapid removal of phytoplankton into sandy sediment and low abundance and activity of bacteria in the overlying water. At slower flow speeds, more organic matter remains in the water column and more remineralization occurs there. Bacterial activity in the sand, as measured by extracellular enzyme activity, is as high as that measured in finer-grained sediments with much higher standing stocks of organic matter.

VOLTAMMETRIC MICROELECTRODES TO INVESTIGATE THE EFFECT OF BIOTURBATION ON THE 3-D DISTRIBUTION OF REDOX SPECIES IN SEDIMENT POREWATERS

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Sediment bioturbation changes the distribution of dissolved chemical species and mixes the solid phase, ultimately increasing reaction rates near the sediment-water interface. Bioturbation also introduces spatial heterogeneities near the sediment-water interface which may invalidate the vertical gradient method for determining fluxes. To determine the effect of bioturbation in saltmarsh sediments, we have used a computer-controlled microelectrode array to measure in situ the three-dimensional distribution of the redox species O₂, Mn(II), Fe(II), and SH₂S in porewaters. As the array was lowered in the sediment, voltammograms were recorded at each electrode using a multiplexer. Such system allowed to map each depth increment around a burrow in less than three minutes.

COMPARING EFFECTS OF QUANTITY AND C-N RATIO OF ORGANIC MATTER ON MARINE BENTHIC FLUXES USING MULTIVARIATE EXPERIMENTAL DESIGN

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Import of organic matter from the pelagic zone to sediments give rise to changes in fluxes over the sediment-water interface. The aim of this study was to evaluate in what way these changes are dependent on the quantity and C-N ratio of the organic matter. Multivariate experimental evaluation makes it possible to simultaneously evaluate the effect of quantity and C-N ratio as well as their relative importance in changing benthic fluxes. We used intact sediment cores, kept at in-situ temperature in a boxcosm system especially designed for flux measurements. The organic matter added consisted of freeze-dried algae and lignin, mixed in different proportions. The two materials differed with a factor of 100 with respect to their C/N-ratios. As response parameters, benthic fluxes of nutrients, O₂, CO₂, DOC and DON were measured. Results on the magnitude, time lag and duration of the response to the organic addition will be presented, as well as an evaluation of the relative importance of quality and C-N ratio.

EXTRATERRESTRIAL ORGANIC CHEMISTRY: I

ASPECTS OF EXOGENOUS DELIVERY

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It is widely accepted that many comets and meteorites fell on the Earth early in its existence and that these extraterrestrial objects were replete with organic molecules, such as amino acids, quinones, and others. Today, certain chemical coincidences between extraterrestrial and biotic compounds, such as excesses of L-amino acids, seem to indicate that some species survived to sway the trajectory of evolution on Earth. Furthermore, isotopic enrichments in cometary and meteoritic molecules imply a non-terrestrial origin. Thus, there is a (chemical) historical sequence that connects processes that occurred in the interstellar medium five billion years ago to life on Earth and perhaps elsewhere. With

this symposium we hope to bring together talks pertaining to the abundance and formation of organic compounds in space, their processing en route to the surface of terrestrial planets, and subsequent terrestrial processing in order to gain a more comprehensive understanding of all aspects of exogenous delivery.

OBSERVATIONS OF ORGANIC MATERIAL IN THE INTERSTELLAR MEDIUM

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Carbonaceous material in the interstellar medium (ISM) takes many forms, including aliphatic (chain-like) hydrocarbons, polycyclic aromatic (ring-like) hydrocarbons, simple alcohols and other organic molecules detectable by infrared spectroscopic techniques. The evolution of interstellar grains is believed to be a cyclic process. This cycle includes the injection of dust into the diffuse (density < 100 atoms/cm³) intercloud medium from its formation site in the circumstellar shells of evolved stars, and the processing and destruction experienced by grains over time. New generations of star-formation regions (dense molecular clouds) form out of the swept-up combination of circumstellar dust and the recycled products from previous dense clouds. I will give an overview of the inventory of the dominant carbon-bearing molecules as a function of interstellar environment based on what we have learned from space- and ground-based infrared spectroscopic observations. I will discuss recent results concerning the nature of aliphatic hydrocarbons in the diffuse intercloud medium, and the production of aromatic carbonaceous dust around certain evolved hot stars.

AMINO ACIDS IN SPACE ENVIRONMENTS

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Amino acids may form by gas phase reactions in interstellar clouds, photochemical reactions in solid dust grains, or by aqueous alteration in carbonaceous meteorites. The simplest amino acid, glycine, has not been unambiguously detected in either the interstellar medium or cometary comae. Upper limits of Glycine in molecular clouds are 10⁻¹⁰ relative to H₂ and <0.005 relative to H₂O in the coma of comet Hale-Bopp. However, many amino acids have been identified in carbonaceous meteorites, and they are deuterium enriched, implying an interstellar heritage. The amino acid composition of CI chondrites is strikingly different from CM chondrites, suggesting that they originate from a different type of parent body. Recent laboratory simulations indicate that amino acids are highly susceptible to UV photodestruction and have therefore limited survivability in regions with elevated UV flux. This provides important constraints for the origin of amino acids in space and the possible exogenous delivery of such compounds to the early Earth. In this paper the current knowledge on amino acids in the interstellar medium and solar system bodies is summarized and recent laboratory studies are presented.

SUGAR-RELATED COMPOUNDS IN CARBONACEOUS METEORITES

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Carbonaceous meteorites are relatively enriched in carbon. Much of this carbon is in the form of soluble organic compounds. Absent among the biologically important compounds reported in meteorites are polyhydroxylated compounds (polyols) including sugars, sugar alcohols, sugar acids, etc. Five-carbon sugars are central to the role of contemporary nucleic acids, DNA and RNA. Glycerol, a three-carbon sugar alcohol, is a constituent of all known biological membranes. Our analyses of Murchison and Murray meteorites show that a variety of polyhydroxylated compounds are present. The identified compounds include sugar-alcohols, sugar-acids, deoxysugar-acids, and sugar di-acids. In general the compounds follow the abiotic synthesis pattern of other meteorite classes of organic compounds: decreasing abundance with increasing carbon number within a class of compounds and many, if not all, possible isomers are present at a given carbon number.

THE ORGANIC CONTENT OF THE TAGISH LAKE METEORITE

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Carbonaceous chondrites, the product of presolar and planetary abiotic processes, offer a unique record of chemical evolution. The Tagish Lake meteorite, which fell into an icy lake in the Yukon Territory in January 2000, has been classified as one of the rare CI subgroup of these chondrites. The post-impact history of this meteorite is unusual in that portions were recovered within hours of infall and frozen immediately in an airtight container. With such a collection history, samples from the meteorite may be the most pristine materials of their kind. The organic content of the meteorite has been investigated, and both its insoluble material and extractable compounds have been analyzed using LCMS separation techniques. The results will be presented and assessed in view of data already available for other carbonaceous meteorites.

MOLECULAR SPECTROSCOPIC CHARACTERIZATION OF THE ORGANIC MACROMOLECULE IN THE MURCHISON METEORITE

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The organic material in primitive chondritic meteorites has attracted considerable attention, not only because it retains a record of synthesis in the interstellar medium (ISM) and Solar Nebula, but also because it may have been an important component of the prebiotic organic material on the early Earth. The bulk of the insoluble organic matter (70-90 wt. % of the total organics) is present as a poorly characterized macromolecular material, thought to be composed of a variety of aromatic ring systems cross linked by short methylene chains, esters, sulfides and biphenyl groups. We have employed a number of solid state NMR experiments including single pulse ¹H and ¹³C (with and without ¹H decoupling), ¹⁵N and ¹³C CPMAS (with and without ¹H decoupling). In addition we have analyzed the organic residue with C- and N-XANES. The functional group information extracted from these spectroscopic data provide a basis to derive a statistically consistent molecular model for the Murchison macromolecule. Ultimately, such a model can be used as a constraint for any mechanistic scenario presented for the synthesis of the extraterrestrial macromolecular phase.

THE DEGRADATION OF COMPLEX AND REFRACTORY ORGANIC MATERIAL AS A SOURCE OF LIGHT AND VOLATILE MOLECULES: THE CASE OF EXTENDED SOURCES IN COMETS

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Laboratory irradiations of ice mixtures by UV photons or energetic particles to simulate the evolution of interstellar and cometary ices lead to the formation of a complex refractory material. We present and discuss results we have obtained when some of these refractory molecules are in

their turn irradiated or heated. Through different processes, such as thermal- and photo-degradation, the molecules in solid phase can release volatile products, which may be different than the original icy precursors and thus act as parent molecules for extended sources in comets, and indirect pathways for the production of interstellar species. Quantitative data (quantum yields, kinetic parameters) about those processes were missing to interpret observations of comets. Now, they allow us, for instance, to address the extent to which the presence of molecules like polyoxymethylene and hexamethylenetetramine in comets is relevant as an explanation for the formaldehyde and CN radical extended sources observed in several comets.

LOW TEMPERATURE ICE PHOTOCHEMISTRY AS A SOURCE OF METEORITIC AND COMETARY ORGANICS

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Ices on grains in interstellar dense molecular clouds contain a variety of simple molecules as well as aromatic molecules of various sizes. While in these clouds, the icy grains are photo-processed by ultraviolet light, producing more complex molecules. It has been proposed that interstellar ice photochemistry may be the source of the organic compounds seen in comet and asteroidal dust (IDPs) and carbonaceous meteorites. We will review published work on the photo-oxidation of aromatic molecules, and will present new results of UV photochemistry of aromatics in the presence of simple molecules at 12 K. Overall we find that low-temperature ice photochemistry is consistent with the molecules and deuterium enrichments seen in carbonaceous chondrites. Thus, perhaps molecules formed in the interstellar medium and delivered to the early Earth by IDPs may have had an influence on the evolution or origin of life.

THEORETICAL, EXPERIMENTAL, AND OBSERVATIONAL TECHNIQUES FOR HYDROTHERMAL CHEMISTRY: II

SIMULATED HYDROTHERMAL VENT STUDIES SHOULD NOT FORGET THE ARRHENIUS EQUATION!

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Several recent reports claim to have demonstrated the synthesis of organic compounds under simulated hydrothermal vent conditions. However, a critical question is whether these syntheses are really unique to hydrothermal environments. Organic reactions obey the Arrhenius equation so that the higher the temperature a reaction is carried out, the faster the reaction rate. Thus, the elevated temperatures used in hydrothermal simulation experiments likely only accelerate reactions that also take place at lower temperatures albeit at slower rates. Relevant examples are the reactions associated with petroleum formation. Petroleum is produced from sedimentary organic matter by a series of geochemical reactions that take place at temperatures between 50° to 175° C over time scales in excess of several million years. However, at hydrothermal vent temperatures of 300° to 350° C, these generation reactions are much more rapid and petroleum may be produced in periods as short as 100 years. On a global scale the amount of hydrothermal petroleum is estimated to be very small in comparison to that generated at lower temperatures. Because this type of relationship should be valid for other organic geochemical reactions, over long intervals of geologic time the yield from organic synthesis reactions at low temperatures would likely in general greatly exceed that produced under hydrothermal conditions.

GEOCHEMICAL OBSTACLES IN HYDROTHERMAL BIOPHOSPHORYLATION

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Much experimental, and theoretical work has been published, claiming to model prebiotic chemical processes that would lead to the emergence of life on

Earth. The relevance of such claims is limited by geophysical and geochemical probability. Conditions to be met may be summarized as:

- * sufficient rate of supply of source molecules, competing with their rate of destruction,
- * selective concentration of desired reactants at the exclusion of interfering species,
- * selective condensation to libraries of (nucleic acid) oligomers, without resorting to artificial activation.
- * stochastic interreaction and growth of such oligomers to sizes permitting biofunctionality and natural selection based on fitness (about 30-40 residues for ligase activity and perhaps 70-80 for replicase function).

Particular problems adhering to biogenesis proposals for submarine hydrothermal environments include the lack of substantial nitrogen sources and dilution into the receiving medium. More or less promising approaches toward elimination of these obstacles are discussed.

AN EXPERIMENTAL INVESTIGATION INTO NON-BIOLOGICAL CARBON FIXATION REACTIONS UNDER HIGH TEMPERATURE-HIGH PRESSURE CONDITIONS

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Several recent theories on the origin of life propose that hydrothermal vent systems might have been an ideal location for the emergence of Earth's first life. For carbon fixation, the reductive citrate cycle (RCC) has been invoked as a particularly advantageous route, principally as it doubles the number of CO₂ acceptors with every cycle. Of course extant organisms that utilize the RCC cycle for carbon fixation do so by employing a spectacularly complex array of biomolecular hardware. It remains difficult to see how such complexity could arise in the harsh realm of hydrothermal vents. Experiments have been run to test whether chemistry useful for carbon fixation might have spontaneously arisen from primitive hydrothermal environments. Specifically, aqueous reactions with T=150-250 °C and P=2-200 MPa were used to establish the various catabolic pathways leading to the conversion of citric acid to low molecular weight products. Second, promising (forward) synthetic pathways were then identified that use transition metal sulfides as critical catalysts.

IN-SITU MONITORING OF ORGANIC REACTIONS UNDER HYDROTHERMAL CONDITIONS

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We have explored via the hydrothermal diamond anvil cell, the depths and heights of chemical complexity and have discovered the following:

- 1) regardless of concentration, the products of citric acid and water remain miscible up to CO₂ molar concentrations of 50 %- i.e. the ternary system citric acid (+/- products)-H₂O-CO₂ remains miscible across the CO₂-H₂O join at P and T of 200 MPa and 200 C, respectively.

2) We are able to follow, via in-situ Raman spectroscopy, the catabolic reactions that degrade citric acid, through serial decarboxylations, under acidic

conditions and under high temperature and pressure conditions.

3) These methods should be applicable to many systems subject to the following caveats. Broadening of the suite of products reduces the signal to noise considerably. The proper choice of gasket material is critical-conventional gasket material used in hydrothermal diamond anvil cells tend to catalyze hydrogenation.

CATALYSIS IN PREBIOTIC SYNTHESIS: MONTMORILLONITE CATALYSIS OF RNA FORMATION

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Montmorillonite clay catalyzes the formation of RNA oligomers containing 6-15 monomer units starting from activated nucleotides in reactions performed in aqueous solution. RNAs containing up to 50 monomer units are formed in multi-step reactions. The role of the clay, the regioselectivity and the homochiral selectivity will be discussed. It is concluded that catalysis had a central role in the prebiotic syntheses leading to the origins of life on Earth.

CATALYSIS IN THE 3-D: HOW ORGANIC MOLECULES MAY BE FORMED

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Catalysis is often little more than a word to phenomenologically describe the fact that a reaction follows a certain path leading to products of unexpected kind or unexpected yield. Seldom is the mechanism known. This is particularly true for catalysis under hydrothermal conditions with minerals acting as heterogeneous catalysts. By studying MgO and olivine single crystals grown from a CO₂/H₂O-laden melt we can show (1) that these minerals are capable of dissolving CO₂ and H₂O, (2) that they convert them to reduced C and H, (3) that C and H segregate into defects such as dislocations, forming C_n protomolecules, with some C-H attached. Upon solvent extraction, these proto-molecules turn into carboxylic and dicarboxylic acids, suggesting that they had been pre-assembled in linear defects such as dislocations. This observation suggests that the interface across which long-chain fatty acid molecules are assembled extends into the 3rd dimension, with dislocations as synthesis sites.

HYDROTHERMAL PRODUCTION OF AMPHIPHILIC MOLECULES FROM PYRUVATE

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The synthesis of amphiphilic molecules capable of aqueous self-assembly into membrane-like structures, including bilayers and micelles, is an essential step in the emergence of a protocell. Mechanisms for the prebiotic synthesis and assembly of amphiphiles are thus of considerable interest. We observe amphiphile synthesis from pyruvate in a CO₂-water fluid subjected to 250°C and 2,000 atmospheres pressure for 2 hours. Principal run products include acetic acid and CO₂ (from pyruvate decarboxylation), methyl succinate (from pyruvate dimerization and subsequent decarboxylation), and a yellow-brown, chloroform-soluble fraction. This material was dried and washed in a phosphate buffer (pH=8.5), which left behind small droplets of insoluble, highly fluorescent liquid. This liquid, which appears to be surface active, separated into a fluorescent spot on a 2D TLC chromatogram, and produced numerous droplets observed by fluorescence microscopy. Studies are in progress to characterize these synthetic compounds.

BIOGEOCHEMICAL CONSEQUENCES OF DYNAMIC INTERACTIONS BETWEEN BENTHIC FAUNA, MICROBES, AND AQUATIC SEDIMENTS: II

SULFIDE CONTROL OF INFAUNAL DISTRIBUTIONS AT NORTHERN CALIFORNIA METHANE SEEPS

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Sulfide is toxic to most animals at higher concentrations (> 2mM), although it is a common constituent in marine sediment environments. At seeps, sulfate reduction fueled by methane can lead locally to extremely high hydrogen sulfide concentrations in the porewater (> 10 mM). Recent investigations off northern California (520 m) compared the geochemistry of bacterial mats and clambeds using microelectrodes. In the bacterial mat sediments, HS⁻ reaches the sediment surface and increases linearly with depth in the sediment (up to 12 mM) at 9 - 11 cm. In the clam beds, HS⁻ is present only below 3-4 cm and reaches maximum values of 2- 2.5 mM. We will relate these geochemical differences to variation in the abundance, vertical distribution and composition of macrofauna within sediments. Although both microhabitats support assemblages of small, soft-bodied invertebrates, annelids and turbellarians dominate the bacterial mats while a more diverse fauna is found within clambeds.

BIOGEOCHEMICALS AS CONTROLLING FACTORS IN THE BEHAVIOR AND GROWTH OF YOUNG-OF-THE-YEAR WINTER FLOUNDER

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The characteristic habitat of juvenile winter flounder (*Pseudopleuronectes americanus*) at the sediment-water interface subjects these fish to intense biogeochemical gradients. In the eutrophic Hudson-Raritan estuary, dissolved oxygen disappears within one fish body thickness even in sandy substrates, and overlying water column concentrations can decline from 250 mM to 10 mM in a few days. Bejda et al. (1992) showed that periodic reductions of dissolved oxygen to 70 mM retards winter flounder growth rates. We report that growth rates of field-caged fish increased with increasing sediment organic matter concentration to an intermediate maximum and then declined, presumably because of the depletion of TEAs, and the accompanying accumulation of biologically-active reduced biogeochemicals. Fish in laboratory experiments responded to declining oxygen at 100 mM (moving to more oxygenated water) and to sulfide at 15-20 μM, but not to 50 μM nitrite or 100 μM ammonium, though the fish appeared to be in distress.

MICROBIAL DEGRADATION OF ORGANIC MATTER IN DEEP-SEA SEDIMENTS: RESPONSES TO POM PULSES

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The aim of this study was to test the effect of particulate organic matter (POM) pulses of different size and composition on bacterial activity in oligotrophic and eutrophic deep-sea sediments using chitin and diatom aggregates as model POM substrates. The enrichment with such particles enhanced production rates, enzyme activities and biomasses of natural microbial assemblages from different deep-sea sites. The relation between POM input and its processing was investigated under laboratory conditions as well as in situ with benthic chamber landers. The activities of the microbial assemblages rapidly increase proportional to the amount of POM added over a wide range of substrate concentrations. The results indicate that POM additions between 0.02-0.1 mg C ml⁻¹ sediment can be degraded within two to four weeks in deep sea sediments at temperatures <4 °C and pressures of 500 bar.

EXPLORING THE ROLE OF GUT MICROBIOTA IN THE FIDDLER CRAB, UCA PUGILATOR

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We are studying the gut microbiota of the fiddler crab *Uca pugilator* to determine the role of resident microbes in the digestive physiology of the host and how the activities of the microbiota influence marsh geochemistry. Our first objective was to examine the gut lining and associated microbiota. Using scanning electron microscopy (SEM), we found the fore- and mid-gut were free from microbial attachment and the hindgut was colonized densely by rod-shaped and filamentous bacteria. Direct counts of the resident microbiota were made by separating the attached microbes, staining with 4',6-diamidino-2-phenylindole (DAPI), and counting. Anterior and posterior hindgut sections had significantly different ($p < 0.05$) densities with averages of 5.30×10^8 bacteria g⁻¹ wet tissue in the anterior hindgut and 1.37×10^9 bacteria g⁻¹ wet tissue in the posterior hindgut.

DIATOM AND BACTERIAL EXTRACELLULAR POLYMERS IN MARINE SEDIMENT STABILIZATION

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Marine sediment stability is in part due to microbial activity. Stabilized areas of sediments contain large populations of extracellular polymer-producing pennate diatoms. These polymers are believed to help form aggregates by binding to sediment particles. It is not clear which of several diatom polymers is responsible for stabilization, nor is there agreement concerning a role for bacterial polymers. By measuring the hydraulic conductivity of small bioreactors containing glass beads as sediment particle analogues, we showed that, contrary to current wisdom, the diatom motility polymers have little effect on sediment properties. Extracellular matrix polymers, which have differing solubility properties from the motility polymers, most influence sediment stability. Results with a *Navicula* sp. were similar, but not identical, to those obtained with *Amphora coffeaeformis*. In biofilms containing both diatoms and the bacterium *Pseudoalteromonas haloplanktis*-a marine sediment biofilm isolate-it appeared that diatoms control biofilm properties, not bacteria.

ROLE OF ORGANIC CARBON EXCRETION BY BULBOUS RUSH AND ITS TURNOVER AND UTILIZATION BY BACTERIA UNDER IRON PLAQUES IN EXTREMELY ACID SEDIMENTS

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Bulbous rush (*Juncus bulbosus* L.) is a pioneer species in highly acidic mining lakes of the Lusatian mining district (Eastern Germany), which are extremely low in inorganic carbon. The objective of this work was to elucidate inorganic carbon formation under iron plaques surrounding the roots of bulbous rush. The methodological approach included microscopic examination of the microbial component, stable carbon isotopes analysis and quantification of root exudation and biomass. Our results show that a rhizobacterial community is present under the iron plaque, which rapidly recycles carbon exuded by roots back to the plant. The differences in the $\delta^{13}C$ and biomass production among plants with and without iron plaque suggest that iron plaques may be important in allowing bulbous rush to maintain a positive carbon balance in the low carbon environment of acidic mining lakes.

QUANTIFYING BIOLOGICALLY INDUCED SOLUTE TRANSPORT IN AQUATIC SEDIMENTS: AN INVERSE APPROACH

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Biologically enhanced solute transport (bioirrigation) may have significant effects on sediment biogeochemistry, e.g., by supplying oxidants through flushing of macroinfaunal burrows to depths where the sediment is (in a bulk sense) highly reducing. Thus, bioirrigation may affect nutrient, electron and proton cycles by changing redox conditions, and it may enhance benthic exchange fluxes significantly. An inverse model is presented to quantify bioirrigation from measured solute and reaction rate depth profiles. The model is based on a one-dimensional nonlocal transport description, and includes Monte Carlo simulations and statistical comparison of competing model structures. It is applied to various marine environments, using several different chemical constituents. The presence of subsurface maxima in flushing intensities is detected at several locations. The approach allows an estimate of bioirrigation intensities as a function of sediment depth at sites where little is known about the type, distribution and activity of benthic organisms.

MODELING SMALL SCALE SPATIAL HETEROGENEITY IN EARLY DIAGENESIS

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Traditional sampling techniques, e.g. sediment-core squeezers or dialysis porewater samplers, provide information on sediment biogeochemistry in the vertical direction. Consequently, most currently available reactive-transport models of early diagenesis treat sediments exclusively as vertical, one-dimensional systems. However, recent technological advances, e.g. microelectrode arrays and DGT-gel samplers, reveal significant horizontal heterogeneity in aquatic sediments (e.g., associated with infaunal burrows or fecal pellets) that can only be represented adequately by multidimensional models. A promising way to incorporate spatial variability in early diagenetic models is through probability distribution functions. Such functions may for instance represent the likelihood of encountering highly reactive organic matter, or describe burrow networks in a statistical fashion. Here we show how information from benthic ecological studies can be used to establish probability functions for burrow densities, types, and sizes. Representative burrow networks can then be generated, based on which the impact of macrofauna on early diagenesis can be assessed.

EXTRATERRESTRIAL ORGANIC CHEMISTRY: II

METEORITIC AND ORGANIC MATERIAL IN THE ATMOSPHERE

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Single particle analyses of stratospheric aerosols during two NASA WB-57F missions during 1998 and 1999 have provided novel information and a means to constrain the ablation and flux of meteoritic material. Measurements in this region of the atmosphere show that approximately half of the particles contain 0.5-1.0 wt % meteoric iron by mass, requiring a total extraterrestrial influx of 11-34 Gg per year. The Na/Fe ratio in these stratospheric particles is larger and the Mg/Fe and Ca/Fe ratios smaller than in chondritic meteorites, implying the fraction of material that is ablated must lie at the low end of previous estimates. Complimentary aerosol measurements below the tropopause show that particles contain ~50% organic matter by mass, a level which cannot be explained solely by bulk solubility. These observations stimulated thought on the astrobiological implications of an inverted micelle of organic material containing meteoric components.

ENERGETIC PROCESSING OF ASTROPHYSICAL ICE ANALOGS

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Icy materials in space are subjected various forms of energy capable of inducing physical and chemical alterations, including energetic particles and ultraviolet photons. Particle irradiation and UV photolysis may be simulated in the laboratory in order to study the materials known to be present in cosmic environments. A study of the formation of organic molecules from "icy" mixtures (T ~ 20-100 K) due to both irradiation (0.8 MeV protons) and photolysis (6-10 eV) is presented here using mid-IR spectroscopy from 5000-400 cm⁻¹ (2-25 microns). The experiments described are relevant to icy mixtures as analogs of interstellar grain mantles, comets, or icy satellites. Our mixtures contain not only H₂O, but molecules such as CO, CO₂, CH₄ and CH₃OH-- all known to exist in astrophysical ices and to play important roles in the formation and evolution of organic materials. Comparisons between irradiation and photolysis results are presented.

SURVIABILITY OF SIMPLE BIOMOLECULES DURING EXTRATERRESTRIAL DELIVERY: THERMAL EFFECTS

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Whether amino acids and nucleic acid bases can be successively delivered to the Earth by the space bodies other than meteorites (i.e., comets, asteroids and interplanetary dust particles) is unclear and depends primarily on capability of the biomolecules to survive high temperatures and shock waves during atmospheric deceleration and impacts to the terrestrial surface. We focused on the effect of temperature, studying the pyrolysis of amino acids and nucleic acid bases in the interval of 400-1000 °C, in oxygen-free (N₂ or CO₂) atmosphere. The simple biomolecules exhibit rather high thermal stability: they have chances to survive to the degree of 1-10% during atmospheric entry heating of the space bodies up to 500-600 °C, even without surface protection typical for meteorites. For amino acids, we also quantified the yields of piperazine-2,5-diones (cyclic dipeptides), as well as detected other derivatives which are able to regenerate amino acids upon hydrolysis.

IN SITU SPECTROSCOPIC OBSERVATION OF CHEMICAL REACTION WITHIN VAPOR CLOUDS INDUCED BY METEORITIC IMPACTS

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Most organic matter delivered to the Earth's surface by large meteoritic bodies is thought to be destroyed on impact. However, the consequences of impact-destroyed organic matter are not understood well yet. In order to observe chemical reaction of reduced carbon in an impact vapor within an oxidizing atmosphere, we performed a series of impact experiments using carbon-rich projectiles, high-impedance metal targets, and N₂-O₂-Ar model atmospheres. The emission spectra of the impacts were monitored by high-speed spectrometers. The spectroscopic observation indicates that vaporized carbon readily reacts with atmospheric nitrogen and forms CN radicals, which are unstable in an oxidizing condition. This experimental result suggests that a carbon-rich meteoritic body vaporized in an oxidizing atmosphere may create a reducing local environment, which may help synthesizing organic matter from once destroyed meteoritic organic matter. Such re-synthesis of organic matter may increase the overall survivability of meteoritic organic matter significantly.

GENERATION OF PEPTIDES IN IMPACT EVENTS

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In order to test the viability of extraterrestrial delivery of organic compounds to the Earth via a large-object impact, we performed laboratory shock experiments using a proxy comet consisting of water (or ice) and near saturation levels of amino acids. We subjected our "comet" to well-constrained, ballistic shock events generating pressures similar to those in a low-angle comet-earth collision. Post-experiment analysis using LCMS revealed that a large fraction of the initial amino acids survived the impact event and that dominant reaction products appeared to be all possible dipeptide and cyclic dipeptide pairings of the initial amino acids. We observed distinct differences in response among the amino acids to pressure and temperature and shock pulse duration. These experiments demonstrate (1) the viability of comets to transport pristine extraterrestrial organic compounds to the Earth and (2) the potential for formation of biologically important compounds using the energy released during large-scale collisions.

AMINO ACID RACEMIZATION ON MARS

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Biomarkers such as chiral amino acids are key components in the search for evidence of past or present life on Mars. In order to assess the stability of amino acid chirality on Mars, we have calculated the time to total racemization of several amino acids based on diurnal and seasonal temperature fluctuations with latitude. Because amino acid racemization is extremely sensitive to temperature, maximum temperatures at each latitude will determine overall racemization rates. We conclude that racemization will be essentially complete on Mars for most amino acids, except at polar latitudes and at depths below the surface where temperature fluctuations are damped. These results have profound implications for the design of life detection instruments for Mars, as well as for the survival of chiral biosignatures in Martian meteorites recovered on Earth.

SELF-ASSEMBLED VESICLES OF MONOCARBOXYLIC ACIDS AND ALCOHOLS: A MODEL SYSTEM FOR MEMBRANE STRUCTURE AND FUNCTION IN EARLY CELLULAR LIFE

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Amphiphilic molecules such as monocarboxylic acids up to 12 carbons long are present in carbonaceous meteorites, and have also been synthesized by Fischer-Tropsch reactions under simulated prebiotic conditions. Similar compounds are produced photochemically in simulated interstellar/precometary ices, which can then be delivered to planetary surfaces during late accretion. It is therefore likely that amphiphilic compounds were available in the early Earth environment. We tested the possibility that such compounds could self-assemble into barrier membranes required by early cellular forms of life. Under defined conditions of pH and concentration, unbranched monocarboxylic acid 8-12 carbons in length are able to assemble into vesicular bilayer membranes. Significantly, addition of small amounts of alcohols markedly stabilized the bilayers. The vesicles provided a selective permeability barrier to ionic solutes and readily encapsulated macromolecules such as DNA. We conclude that membranous vesicles produced by mixed short-chain monocarboxylic acids and alcohols are plausible models for early cell membranes.

THEORETICAL, EXPERIMENTAL, AND OBSERVATIONAL TECHNIQUES FOR HYDROTHERMAL CHEMISTRY: III

INFLUENCE OF SUBMARINE HYDROTHERMAL ACTIVITIES ONTO THE ARCHEAN OCEAN CHEMISTRY AND ECOSYSTEM

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Archean (3.5 to 2.5 Ga) hydrothermal fossils (such as massive ores) are examined to constrain the early ecosystem and ocean chemistry. Abundant organic matter are often found in Archean massive sulfides, suggesting the strong linkage between early microbial evolution and submarine hydrothermal activities. Stable carbon isotopes of these organic matter and sulfur isotope compositions of sulfides indicate that hydrothermal methane and oceanic sulfate were extensively involved in the early ecosystem. Meanwhile, stable isotope fractionation patterns of the above samples are distinctive compared to modern counterparts. Detailed geochemical examination of Archean hydrothermal fossils supports that large amounts of hydrogen and methane were released during the seawater/rock interaction, and these fluxes into oceans were most likely causative factors for the distinctive isotope fractionation patterns. High submarine hydrothermal activities and large flux of hydrothermal components into Archean oceans maybe controlled the evolution of early ecosystem and ocean chemistry.

CORRELATING MINERALOGY OF BLACK SMOKER CHIMNEYS TO SYNCHROTRON X-RAY TOMOGRAPHY IMAGES

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Black smoker chimney structures are critical for understanding the relationship between microbiology, mineralogy, geochemistry, and fluid dynamics. Synchrotron X-ray tomography images were collected on inner and outer portions of chimney samples from the Juan de Fuca Ridge. Elemental mapping and point analysis by electron microprobe were done on 2-dimensional cross-sections of the samples, and extrapolated through the 3-dimensional tomography images. One inner sample is composed of Fe and Zn sulfide and pores lined with amorphous silica and barite. Sulfides were formed from hydrothermal fluids (~180 to 255°C). Flow of lower temperature fluid mixtures through pores precipitated amorphous silica (~60 to 172°C) and barite (~6 to 60°C). Outer samples composed of amorphous silica and barite reflect dominance of lower temperature mixtures. Tomography images show a 3-dimensional map of silica- and barite-lined pores that correlate the mineralogy to fluid composition and temperature along the flow path.

SEARCH FOR PHOTOSYNTHESIS AT DEEP-SEA HYDROTHERMAL VENTS

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Deep-sea hydrothermal vents receive no light from the sun and would therefore seem an unlikely place to find photosynthetic organisms. However, weak light, primarily black-body emission, can be found near vents (White et al. Geophys. Res. Lett. 27, 1151-1154, 2000). This raises the possibility that organisms that derive some of their cellular energy from photosynthesis may be found near vents. To test this idea, four Alvin Dives were made during July, 2000 in the Endeavor field of the Juan de Fuca ridge. Solid samples were collected from vent flanges, and water samples were taken near vents and throughout the water column, with care taken to ensure that samples were not contaminated by surface water. Samples were analyzed by microscopy, UV/Vis, fluorescence and HPLC, and cultures were inoculated. Preliminary analysis indicates that no evidence was obtained for a significant population of photosynthetic organisms near vents. Analysis of pigments and cultures indicate that chlorophyll-like pigments are ubiquitous in the ocean and that small numbers of photosynthetic organisms are present both near vents and throughout the water column.

EXPERIMENTAL EXAMINATION OF THE EFFECTS OF HYDROTHERMAL CONDITIONS ON MICROBIAL METABOLISM

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We are examining the impact of hydrothermal conditions on microbial metabolism. One of the largest hurdles in the area of microbial ecology is the inability to study a wide range of physical and chemical gradients that impact on microbial growth and viability. For example, little is known about the effect that the phase changes that are associated with hydrothermal conditions have on microbial metabolism. Utilizing pure cultures obtained from the American Type Culture Collection (ATCC) we have explored the quantification growth and in-situ interrogation of metabolism of microbes at high pressures. Here we present techniques that we have developed that will be useful for investigating how bacteria thrive under a wide range of chemical and physical extremes.

BIOGEOCHEMICAL CONSEQUENCES OF DYNAMIC INTERACTIONS BETWEEN BENTHIC FAUNA, MICROBES, AND AQUATIC SEDIMENTS: III

GEOCHEMICAL CYCLING OF ALGAL LIPIDS IN SURFACE SEDIMENTS WITH DIFFERENT BIOLOGICAL AND PHYSICAL MIXING PROCESSES

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A series of microcosm experiments (with addition of ^{13}C -labeled algae) were conducted to test the influences of physical disturbance, different macrofauna species, and no-mixing on the geochemical cycling of algal lipids. Physical stirring rapidly mixed the testing algae (initially added on the sediment-water interface) to deep depth below the oxic/anoxic boundary, which resulted in slow degradation of algal lipids. Degradation rate constants of lipids in physically-mixed cores tend to decrease with depth. Frequency of physical stirring had no impact on overall degradation of algal lipids but stimulated microbial growth. Two macrofauna species, *Paraprionospio ponnata* (polychaete) and *Ogyrides limnicola* (crustacean), showed different bioturbation behavior and thus affected algal lipid degradation and microbial growth differently. In no-mixing cores, all added algae (in top 2 mm) degraded under oxic conditions and faster than in physical mixing cores. Less microbial growth was observed in no-mixing cores relative to biological and physical mixing cases.

SEASONAL VARIATION OF DISSOLVED ORGANIC MATTER, AND OF NITROGEN, AND CARBON RECYCLING RATES, IN A COASTAL MARINE SEDIMENT

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Concentrations of dissolved organic carbon and nitrogen (DOC and DON), ammonium, nitrate and total carbonate (T-CO₂) were studied monthly during a fifteen months period in the pore water of a near-shore marine sediment. Pore water concentrations of the solutes varied seasonally with higher concentrations of DOC, NH₄⁺ and T-CO₂ in late summer and early fall. Pore water DON showed no strong seasonal trends, but concentrations were slightly higher in winter compared to summer. Fluxes across the sediment-water interface were calculated for all months from the measured pore water gradients using an apparent diffusion coefficient. The benthic fluxes of DOC, DON, NH₄⁺ and T-CO₂ showed seasonal trends with higher fluxes in the warmer period. Of the total dissolved nitrogen flux, NH₄⁺ dominated in late summer and early fall, but in spring and early summer this flux was dominated by DON. The T-CO₂ flux dominated the total dissolved carbon flux during all seasons, but in winter and early spring the differences between T-CO₂ and DOC fluxes were very small. A large part of the total annual benthic flux occurred over a short period; 68% of the dissolved nitrogen flux and 64% of the dissolved carbon flux occurred during July to October. C/N ratios in the flux of mineralization products (T-CO₂/NH₄⁺) varied during the year with higher C/N in winter (16-18) compared to other seasons (6-9). Also C/N ratios in the flux of hydrolysis products (DOC/DON) showed seasonal trends with higher C/N in the warmer periods (5-10) compared to spring (2-3). These results indicate a fractionation of C and N during degradation and that the preferential nitrogen loss occurred during the initial hydrolytic step. Benthic mass balances for carbon and nitrogen suggested that the annual recycling efficiency for organic carbon was 57% and for nitrogen 64%. Of the annual dissolved carbon flux, DOC constituted 46% and T-CO₂ 54%. Fluxes of DON, NH₄⁺ and N₂ constituted 42%, 53% and 5%, respectively, of the annual dissolved nitrogen flux. The mass balances demonstrated that the flux of DOM was an important component of carbon and nitrogen recycling in this coastal sediment.

EFFECT OF EXTRACTION METHOD ON MARINE SEDIMENT HUMIC ACID CHARACTERISTICS: IMPLICATIONS FOR THE ELUCIDATION OF CONTAMINANT BEHAVIOR

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In order to manage contaminated marine sediments, it is important to understand the chemical and biological processes that control contaminant interactions with minerals and natural organic matter. To this end, we have sought to correlate measures of contaminant behavior with a number of sediment physicochemical properties to determine what measurable aspects of the bulk sediment and sediment organic matter control or predict contaminant behavior in marine sediments. Humic acid fractions were extracted from San Diego Bay sediments under a variety of "standard" extraction conditions. Examination of yield, elemental composition and IR spectra indicated significant variations in the humic pools extracted by various methods. The question of which extractable pool of humic acid is more relevant if we are to use it in subsequent experiments to characterize or predict contaminant behavior in marine sediments will be discussed, in terms of our analytical results and current models of humic/contaminant interactions.

FATE AND REACTIVITY OF SEDIMENTARY LIPID BIOMARKERS IN BIOTURBATED MEDITERRANEAN COASTAL SEDIMENTS: A LABORATORY APPROACH

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The fate of microalgal lipid biomarkers in marine coastal sediments submitted to natural bioturbation processes was studied under laboratory conditions. Both dead phytoplanktonic cells (*Nannochloropsis salina*) and luminophores (inert fluorescent particulate tracers) were deposited at the surface of sediment cores which were then incubated (15°C, dark) for 22, 44 and 63 days. After each incubation time, sediment reworking was quantified using luminophores and concentration profiles of different specific lipid components (n-alkenes, n-alcohols, alkyl diols, sterols and fatty acids) were determined as a function of depth. The results show that, in the sediment investigated, bioturbation occurs essentially as a bio-diffusive process and has a significant impact on the qualitative and the quantitative distributions of sedimentary lipids. The diagenetic fate of the lipids varied from one (class of) compound to another indicating different potential of preservation between compound classes. For each biomarker, the comparison of the amount recovered in the entire sediment cores after incubation with the amount deposited initially at the surface allowed the determination of its degradation constant and its turn-over rate. The results suggest that repetitive oscillations of redox conditions, encountered by the sedimentary lipids during the mixing of the sediment, greatly influence the reactivity of these compounds. Results also indicate that freshly deposited lipids degrade faster than components already present in the sediment.

CONSEQUENCES OF SEDIMENT MIXING FOR THE DEPTH DISTRIBUTION OF BACTERIAL FATTY ACIDS IN INTERTIDAL SEDIMENTS

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The depth distributions of benthic foraminifera, porewater constituents (O₂, Mn²⁺) and fatty acid methyl esters (FA) were studied in intertidal sediments under in-situ conditions and after sieving, homogenization and oxic incubation. Total concentration of FA characteristic for living bacteria (C12-C19) increased with depth (0 - 6 cm) under in-situ conditions but reversed its pattern during the incubation. However, the depth-

integrated concentration remained constant. In contrast, FA characteristic for algae (C20:5w3 and C22:6w3) were almost evenly distributed at all time steps but decreased due to microbial breakdown. Oxygen and more than 90 % of living foraminifera were restricted to the uppermost millimeters at all times. The redistribution of bacterial FA is explained by the exclusion of sediment mixing. Under incubation conditions, Fe(III), Mn(IV) and SO₄²⁻ are no longer replenished to several centimeters depth while aerobic respiration increasingly dominates carbon mineralization.

QUANTITATIVE DETERMINATION OF BIOTURBATION AND BIOIRRIGATION IN COHESIVE SEDIMENTS

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Bioturbation and bioirrigation in fine-grained cohesive sediments are quantitatively described in laboratory benthic mesocosms and two field sites (Dry Tortugas, Florida, and Mississippi Sound) through the feedback processes between experimental data and computational simulations. The field and laboratory data sets include spatial distributions of redox species, burrow geometry, speciation and population of burrowing macrofauna, and spatial distribution of particle tracers. The simulations are based on a simultaneous solution of two-dimensional, diffusion-advection-reaction equations for the major sedimentary redox species. Parameters for the equations are determined, and then refined, through repetitive comparisons of simulation results and experimental data. Resulting parameters indicate that burrow walls are the host to significant amount of redox reactions, due to their increased amount of labile carbon input and microbial activities. Consequently, depths and surface areas of burrows are some of the most important controlling variables in the bulk chemical mass transfer of burrowed sediments.