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From Atoms to Organisms (and Back):
Rates and Mechanisms of
Geochemical Processes

October 15 & 16, 2000
Gaithersburg, MD

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FORWARD

“From Atoms to Organisms (and Back): Rates and Mechanisms of Geochemical Processes” is the eighth in a series of Geosciences Research Program Symposia dating from 1995. These symposia are topically focused meetings for principal investigators in the program and provide opportunities for our investigators to give presentations to one another and to discuss their Office of Basic Energy Sciences’ supported research. Dr. David Cole of Oak Ridge National Laboratory has kindly agreed to serve as host of the meeting, although we have come together in Gaithersburg, Maryland rather than Tennessee. Dr. Henry Shaw has taken the lead in planning the symposium at headquarters. I would like to thank both Dave and Henry for their hard work in making this meeting possible. This meeting also serves to present the accomplishments of the program to our colleagues in other DOE offices and other Federal agencies in the Washington area. In addition to the recognition the symposium gives to all of the investigators, we traditionally also recognize one outstanding contribution from a DOE Laboratory Project and one from a University Project. The outstanding contributions are selected by our session chairpersons. We are fortunate to have as guest session co-chairs Professor Zachary Sharp from the University of New Mexico, Prof. R. Lawrence Edwards from the University of Minnesota, Professor Steve Macko from the University of Virginia and Professor Henry Ehrlich from Rensselaer Polytechnic Institute. They join our Principal Investigator co-chairs Dr. Jean Whelan of Woods Hole Oceanographic Institute, Dr. Susan Brantley from Penn State University, Dr. Mike Murrell of Los Alamos National Laboratory, and Dr. John Zachara of Pacific Northwest National Laboratory. For their efforts on behalf of the investigators I thank them all. We are looking forward to an outstanding series of presentations.

Nicholas B. Woodward, Manager
Geosciences Research Program
Office of Basic Energy Sciences
U.S. Department of Energy

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Gaithersburg, MD  
October 15-16, 2000

Sunday, October 15, 2000

8:00-8:30  Registration; Morning Refreshments
8:30 – 8:40  Welcome; Introduction – Nicholas Woodward

Weathering, Mineral Dissolution/Precipitation, and Microbial Systems, Part I  
Chairpersons: Henry Ehrlich and Mike Murrell

8:40  R. A. Berner  Yale University  
“Plants, Weathering and Paleo-O2”

9:00  S. L. Brantley  Pennsylvania State University  
“Surface Chemistry and Reactivity of Na Aluminosilicate Glass and Crystal”

9:20  G. A. Waychunas  Lawrence Berkeley National Laboratory  
“Formation and Structure of Iron-Rich Oxyhydroxide Nanometer Coatings: Comparison of Laboratory-Produced and Aquifer-Seeded Samples”

9:40  J.J DeYoreo  Lawrence Livermore National Laboratory  
“Selective Binding of Chiral Amino Acids to the Atomic Steps of Calcite: A Model for Control of Biomineral Growth”

10:00  BREAK

10:20  L. E. Hersman  Los Alamos National Laboratory  
“Microbial Dissolution of Fe(III) (Hydr)Oxides”

10:40  P. A. Maurice  Notre Dame University  
“Microbially Mediated Dissolution of Kaolinite”

11:00  L. E. Hersman  Los Alamos National Laboratory  
“Dissolution of Al-Goethites in the Presence of Siderophore and Oxalate Ligands”  (for Cervini-Silva & Sposito, Univ. California, Berkeley)

11:20  C. J. Tadanier  Virginia Polytechnic Institute & State Univ.  
“Microbial Community Acquisition of Nutrients from Mineral Surfaces”

11:40  DISCUSSION
12:00  LUNCH
Weathering, Mineral Dissolution/Precipitation, and Microbial Systems, Part II
Chairpersons: Steve Macko and Sue Brantley

1:20 M. E. Conrad Lawrence Berkeley National Laboratory
“Metabolic Factors Affecting Carbon Isotope Fractionation by
Methane-Oxidizing Bacteria”

1:40 J. F. Banfield University of Wisconsin
“The Process by Which Sulfate-Reducing Bacteria Bomineralize ZnS:
Implications for Metal Distributions in the Environment”

2:00 J. M. Zachara Pacific Northwest Laboratory
“Biomineralization Associated with Bacterial Fe(III)-Oxide Reduction”

2:20 A. R. Felmy Pacific Northwest Laboratory
“Modeling of the Electric Double Layer on Microbial Surfaces:
Equilibrium and Non-Equilibrium Treatments”

2:40 T. P. Straatsma Pacific Northwest Laboratory
“Molecular Modeling of Geochemical Reactions at Microbial
Membranes”

3:00 BREAK

Hydrocarbon Systems I: Theoretical, Experimental and Mechanistic Studies
Chairpersons: Stephen Macko and Sue Brantley

3:20 H. C. Helgeson University of California, Berkeley
“Calculation of the Effect of Diagenetic Deoxygenation of Immature
Kerogen in the Oil Generation Potential of Hydrocarbon Source Rocks”

3:40 A. V. Plyasunov Washington University
“A New Approach for Correlating/Predicting Thermodynamic Functions
of Aqueous Nonelectrolytes at T-P Parameters of Hydrothermal
Processes”

4:00 J. S. Seewald Woods Hole Oceanographic Institute
“Laboratory Constraints on the Stability of Petroleum at Elevated
Temperatures: Implications for the Origin of Natural Gas”

4:20 M. A. Vairavanurthy Brookhaven National Laboratory
“Geochemical Formation and Transformation of Sulfur and Nitrogen
Bound to Macromolecular Organic Matter”

4:40 F. Mango Rice University
“The Evidence for Catalytic Natural Gas”

5:00 DISCUSSION

5:30 ADJOURN
Monday, October 16, 2000

Hydrocarbon Systems II: Paleomagnetic and Isotopic Studies of Natural Systems
Chairpersons: Zach Sharp and John Zachara

8:20  A. Schimmelmann  Indiana University  
      “Isotopically Labile Organic Hydrogen in Thermal Maturation of Organic Matter”

8:40  R. D. Elmore  University of Oklahoma  
      “Paleomagnetic Dating of Burial/Clay Diagenesis”

9:00  B. M. Kennedy  Lawrence Berkeley National Laboratory  
      “The Sources of Air-Like Noble Gases in Hydrocarbon Reservoirs”

9:20  T. Torgersen  University of Connecticut  
      “Noble Gas Evolution in Hydrocarbon Fields: Secondary Migration Processes and End-Member Characterization”

9:40  J. Whelan  Woods Hole Oceanographic Institution  
      “Toward Measurement of On-Going In Situ Upward Gas, Oil, and Water Movement in the Gulf of Mexico”

10:00 BREAK

Isotopic and Elemental Geochemistry, I
Chairperson: Zach Sharp and John Zachara

10:20  G. N. Hanson  State University of New York, Stony Brook  
       “High Precision Radiometric Dating of Sedimentary Materials”

10:40  B. M. Kennedy  Lawrence Berkeley National Laboratory  
       “Measurement of Reaction Rates in Natural Fluid-Rock Systems Using Sr and U isotopes”  (for D. DePaolo)

11:00  M. Harrison  University of California, Los Angeles  
       “The Application of High Spatial Resolution Isotope Geochemical Methods to Understand the Origin and Evolution of Geologic Energy Sources”

11:20  M. T. Murrell  Los Alamos National Laboratory  
       “Uranium Series Concordance Studies”

11:40 DISCUSSION

12:00 LUNCH
Isotopic and Elemental Geochemistry, II
Chairperson: Larry Edwards and Jean Whelan

1:20  M. W. Caffee      Lawrence Livermore National Laboratory
      “Collaborative Research: Studies for Surface Exposure Dating in
Geomorphology”

1:40  J. N. Christensen   Lawrence Berkeley National Laboratory
      “The Next Generation: Research Prospects for Multi-Collector ICP Source
Mass Spectrometry”

2:00  L. R. Riciputi    Oak Ridge National Laboratory
      “Oxygen Isotope Behavior in Feldspars during Fluid-Rock Interaction”

2:20  J. W. Valley       University of Wisconsin
      “Oxygen Isotopes in Zircon”

2:40  BREAK

3:00  S. C. B. Myneni    Princeton University
      “Spectroscopic Evidence for H-Bonding Networks in Liquid Water
and Its Relevance to Aqueous and Interfacial Reactions”

3:20  J. Horita          Oak Ridge National Laboratory
      “New Mechanisms and Variables in Isotope Partitioning”

3:40  D. R. Cole         Oak Ridge National Laboratory
      “Isotopic Fractionation in Oxide and Carbonate Systems: Inorganic and
Microbial Pathways”

4:00  DISCUSSION & WRAP UP

4:30  Meeting with outside reviewers (by invitation only)

5:30  No-Host “Refreshments” in Hilton Hotel bar

6:30  Banquet, Hilton Hotel
The Process by Which Sulfate-Reducing Bacteria Biomineralize ZnS: Implications for Metal Distributions in the Environment

Matthias Labrenz¹, Gregory K. Druschel¹, Tamara Thomsen-Ebert², Susan A. Welch¹, and Jillian F. Banfield¹

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Extremely abundant, micron-scale, spherical aggregates of ZnS particles are forming within natural biofilms collected from flooded tunnels within an abandoned carbonate-hosted Pb,Zn mine in southwestern Wisconsin. High-resolution transmission electron microscopic characterization revealed that the ~ 2-5 nm diameter particles that comprise the ZnS aggregates are sphalerite. The biofilm zinc concentration is about 106 times that of associated groundwater (0.09 - 1.1 ppm Zn).

Analysis of SSU rRNA gene sequences amplified from organisms in the biofilms revealed a variety of sulfate-reducing bacteria (SRB), all of which group within the family Desulfobacteriaceae. In situ hybridization of oligonucleotide probes specific for this SRB group to cells in environmental samples confirmed the predominance of SRB in the biofilms and verified the association of Desulfobacteriaceae with ZnS aggregates. Molecular studies also showed that the biofilms contain other microorganisms, including aerobic sulfide oxidizing bacteria. Thus, ZnS biomineralization occurs in anaerobic regions of a stratified microbial community.

Using geochemical modeling, we demonstrate that ZnS is the first sulfide to form as groundwater solutions become reduced. The calculations verify that an essentially monophase ZnS product is expected while sulfide concentrations are buffered at low values by sphalerite precipitation. Although the groundwater Zn concentration is low, slow fluid flow ensures continual Zn supply, thus continual sulfide extraction and ongoing sphalerite deposition. Because SRB of the Desulfobacteriaceae family are relatively aerotolerant, they are able to live (and thus release sulfide) in the moderately reducing environment consistent with exclusive ZnS precipitation. This represents the first characterization of low-temperature, biologically mediated sphalerite precipitation from dilute natural solutions, and the first report of in vivo bacterial ZnS ore formation.

Our results demonstrate that coupled geochemical and microbial processes can efficiently strip Zn from solutions with sub-ppm-level Zn contents. Geochemical calculations indicate that this process should also occur in solutions with the composition of seawater. These results are significant from the point of view of bioremediation because this process reduces aqueous Zn concentrations to well below acceptable levels for drinking water (the drinking water standard is 5 ppm). The microbial precipitation reactions probably underpin mine waste remediation strategies that utilize natural or artificial wetlands. The process also may be relevant to formation of some ore deposits. The paragenesis of Mississippi Valley-type and the large stratiform sediment-hosted ore deposits is complex. However, some aspects appear to be consistent with microbially-mediated ZnS (as well as PbS and the well accepted FeS) precipitation.
Plants, Weathering and Paleo-O$_2$

Robert A. Berner$^1$ and David Beerling$^2$

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$^2$Dept. of Animal and Plant Sciences, University of Sheffield, Sheffield S10 2TN, UK

A carbon and sulfur isotope mass balance model has been constructed for calculating the variation of atmospheric O$_2$ over Phanerozoic time. In order to obtain realistic O$_2$ levels, rapid sediment recycling and O$_2$-dependent isotope fractionation have been employed by the modeling. The dependence of isotope fractionation on O$_2$ is based, for carbon, on the results of laboratory photosynthesis experiments and, for sulfur, on the observed relation between oxidation/reduction recycling and S-isotope fractionation during early diagenetic pyrite formation. The range of fractionations used in the modeling agrees with measurements of Phanerozoic sediments by others.

Results, derived from extensive sensitivity analysis, suggest that there was a positive excursion of O$_2$ to levels as high as 35% during the Permo-Carboniferous. High O$_2$ at this time agrees with independent modeling, based on the abundances of organic matter and pyrite in sediments, and with the occurrence of giant insects at that time. Paleocological modeling calculations show that at the independently estimated level of CO$_2$ for this time (about 450ppm), the O$_2$/CO$_2$ ratio was not sufficiently high to adversely affect global productivity or carbon storage. The cause of the excursion is believed to be the rise of vascular land plants and the consequent increased production of O$_2$ by the burial in sediments of lignin-rich organic matter that was resistant to biological decomposition.
Surface Chemistry and Reactivity of Na Aluminosilicate Glass and Crystal


The Pennsylvania State University, University Park, PA 16802.

One problem with investigating the rate of dissolution of plagioclase feldspars is the presence of exsolution in all known plagioclase crystals. Given the similarity between glass and crystal dissolution rates for albite measured in our laboratory, plagioclase glass might be a better substrate for investigation than plagioclase crystal. However, in plagioclase, Al content changes with Ca content. Therefore, to investigate the effect of Al/Si ratio on aluminosilicate dissolution without either the added complications of changing Na/Ca ratio or the presence of exsolution lamellae and other planar defects found in all plagioclase crystals, three glasses with variable Al/Si, NaAlSi3O8, NaAlSi2O6, and NaAlSiO4, were synthesized. These three glasses are also of interest because they have mineral analogues: albite, jadeite, and nepheline respectively.

Many similarities in dissolution behavior between plagioclase crystals and this suite of glasses were observed: 1) dissolution was slowest at near-neutral pH and increased under acid and basic conditions 2) dissolution rate at all pH values increased with increasing Al/Si ratio 3) after acid leaching, the extent of Al-depletion of the altered surface as measured by XPS or SIMS increased with increasing Al/Si ratio from Al/Si = 0.3 (albite) to 0.5 (jadeite), but then decreased in nepheline (Al/Si = 1.0), which dissolved stoichiometrically. In contrast to some published discussions of plagioclase dissolution, log (rate) increased almost linearly with Al content, and n, the slope of the log (rate) versus pH curve at low pH, varied smoothly from albite to jadeite to nepheline (= - 0.3, -0.6, -1.0 respectively). Differences in topography developed on dissolved glass and crystal surfaces may also exist. For example, the fractal dimension of the surface of albite glass and crystal observed by AFM differs after leaching. Defects in the crystalline samples may also lead to etch pitting or etching of through-going pores in some feldspar phases.

The transition states for all these aluminosilicates may consist of a protonated AlOSi linkage at low pH, and a deprotonated Si terminal group at high pH. To investigate possible rate-controlling surface species, both NMR spectroscopy and molecular orbital calculations have been initiated. Preliminary molecular simulations have been conducted to assess the possible formation of 5- and 6-fold Al on aluminosilicate surfaces from the 4-fold Al in the bulk mineral structure. NMR observations also document the presence of octahedral aluminum on some leached samples. Integration of molecular scale calculations and spectroscopic observations with observed patterns in reactivity should yield better insights into dissolution mechanisms for aluminosilicate phases.
OBJECTIVES: The surface exposure dating method using in-situ-produced cosmogenic nuclides has become a widely utilized tool in Quaternary Geology. However, as applications expand to new areas, the demand grows to provide more precision in exposure ages and to enable the dating of new lithologies from more widely varied geological settings. The objectives of our project are to better understand the systematics for the production of cosmogenic nuclides in terrestrial surface samples, to extend surface exposure dating to new rock types, and to make new nuclides available as surface exposure dating tools. In addition, we work on developing new methods, such as simultaneous interpretation of multiple nuclides, for the use of cosmogenic nuclides to date and characterize Quaternary surfaces.

PROGRESS AND ANTICIPATED RESULTS: Olivine: We focus on developing techniques for dating olivine. The removal of meteoric $^{10}\text{Be}$ and reducing the concentration of intrinsic Al, Ca, and Mn in the olivine in order to facilitate $^{26}\text{Al}$, $^{41}\text{Ca}$, $^{53}\text{Mn}$ measurement, respectively, are critical components of this work. The isolated olivine contains numerous µm-size chromite and glass inclusions that are enriched relative to the olivine itself in Al and Ca. We have developed a chemical method that is able to selectively leach these constituents out of the olivine. Because the olivine crystal structure is not as tight as that of quartz, removal of meteoric $^{10}\text{Be}$ is more difficult and considerable effort has had to be devoted to this problem. In order to verify that meteoric $^{10}\text{Be}$ can be totally removed, we have applied the procedures developed to a young volcanic lava sample from Kilauea, Hawaii that erupted in 1840. Surprisingly we obtained a $^{10}\text{Be}$ concentration of $1.6 \times 10^5$ atoms/g olivine, which is much higher than expected from in situ production. There are two possibilities for the high $^{10}\text{Be}$: 1) meteoric $^{10}\text{Be}$ has diffused into the olivine crystal and has not been removed by our leaching procedures; 2) contaminant $^{10}\text{Be}$, i.e., $^{10}\text{Be}$ not produced in-situ by cosmic rays, has been incorporated into the olivine crystal during crystallization. Conceivably this contaminant could have been scavenged from local rock during the emplacement of the basalt. If the latter is the case, it may imply alteration of the upwelling melts during Hawaiian volcanic activity.

$^{14}\text{C}$: We continue to work on development of a method for determining in situ $^{14}\text{C}$ in geologic samples. $^{14}\text{C}$ can be produced by cosmic ray interactions with quartz in a similar fashion to $^{10}\text{Be}$, $^{26}\text{Al}$ and $^{21}\text{Ne}$. To attack this problem we are developing a step-wise heating technique to separate in-situ $^{14}\text{C}$ from meteoric $^{14}\text{C}$. The extraction line has been constructed at LLNL. This system has been fully tested and C recovery throughout the entire system shown to be >90%. Blank tests performed on samples spiked with dead carbon have shown that we can now melt 20 g of quartz and extract carbon with a blank of approximately $2-3 \times 10^5$ atoms of $^{14}\text{C}$. The next series of tests will be performed on heavily shielded samples collected from deep in the Homestake mine in South Dakota and $^{14}\text{C}$ saturated quartz from high elevation in Antarctica. These samples will allow us to test the effectiveness with which we can remove meteoric $^{14}\text{C}$, to
determine the blank levels of our extraction line when it is heated with actual samples, and to ascertain the extraction efficiency with different stepwise temperature extraction procedures.

**Theoretical Calculations:** The computer code MCNPX has been installed at Los Alamos. It combines the latest version of the high-energy production and transport code LAHET (which now includes the FLUKA89 routine for interactions of particles with energies >5 GeV) and the low-energy neutron transport code MCNP4B. The FLUKA routine will allow much better calculations for low geomagnetic latitudes, where cosmic ray particles need energies as high as 17 GeV to reach the Earth’s atmosphere. Cross sections for neutron-induced reactions continue to be measured, compiled, and evaluated. Work is being done with Drs. M. Imamura and J. Sisterson on irradiating samples with high-energy neutrons and on measuring nuclides made in these samples. These cross sections and MCNPX-calculated fluxes will be used to calculate the production rates of cosmogenic for a variety of exposure conditions.
Dissolution of Al-Goethites in the Presence of Siderophore and Oxalate Ligands

Javiera Cervini-Silva and Garrison Sposito

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Microorganisms and higher plants produce siderophores to facilitate the solubilization and uptake of Fe in aerobic environments. The mechanism for Fe acquisition by siderophores (e.g., desferrioxiamine, DFO) relies on the selectivity of these ligands for Fe(III) to form very stable complexes ($K_{Fe(III)-DFO}=10^{30.6}$). In addition, aerobic organisms may enhance the dissolution of iron oxides by secreting organic ligands of smaller size and lower molecular mass (e.g., oxalate). Yet little is known about how these mechanisms of Fe acquisition interrelate to each other.

Goethite is one of the most common iron-bearing minerals found in soils. Al-goethites ($Fe_{1-X}Al_XOOH$) form in soils as result of the isomorphic substitution of octahedral Fe$^{3+}$ by Al$^{3+}$ from the soil solution. Variations in Al-for-Fe substitution alter crystal size, texture, multidomainicity, surface area, and other structural properties that could influence rates and mechanisms of dissolution. Our study examines the effect of Al substitution on the steady-state dissolution of goethite by DFO and oxalate at pH 5.

Continuous-flow stirred-tank reactors were used to study the dissolution of Al-goethites containing 0 to 10-mol% Al. The composition of the influent solution was 0.01 M NaClO$_4$, 5mM MES buffer, DFO (0-1000 μM), oxalate (0-1000μM), with the pH value was adjusted to 5. The system was covered with aluminum foil at room temperature (20 ± 2°C). The Fe concentration in the effluent solution was determined using ICP-AES at emission wavelength 259.9 nm.

Our studies show that DFO and oxalate both promote the dissolution of Al-goethite. In the presence of DFO, Al-goethites with low Al substitution (mol% Al < 2.5) showed dissolution rates varying from 2 to 94 nmol/g/h, whereas Al-goethites with higher Al content (mol% Al > 3) showed dissolution rates up to 1 μmol/g/h. The addition of oxalate enhanced the dissolution rate observed in the presence of DFO, regardless of Al content.

This study is part of a collaborative research project with Larry Hersman and Patricia Maurice.
The Next Generation: Research Prospects for Multi-Collector ICP Source Mass Spectrometry

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Multi-collector ICP mass spectrometry (MC-ICPMS) represents a new class of mass spectrometer that was first developed in the early 1990’s by VG Elemental (the Plasma 54) (1). MC-ICPMS combines the high ionization efficiency of an Ar plasma source with the high precision isotope ratio measurement capability of a magnetic-sector multi-collector mass analyzer (2). Early work demonstrated that high precision isotopic measurement of Sr, Nd, Hf, Pb and U of solution samples were possible. Results by various workers have expanded to include high precision isotopic measurements of Fe, Cu, Zn, Ge, Cd, In, Sn, Te, W, Th which had proved difficult or intractable to measurement by standard thermal ionization mass spectrometry (TIMS) (3). It has also been demonstrated that high precision isotopic measurements (e.g. of Sr, Pb, W, Hf, U, Th) can be made in situ using laser ablation sampling (4). The capabilities of MC-ICPMS have opened up new areas for study in isotope geochemistry, from paleoceanography (5) to early solar system history (6). This potential has been enhanced by the introduction of a second generation MC-ICPMS’s which have new capabilities and greater sensitivity, the Nu Plasma, VG Elemental’s Axiom and the IsoProbe by Micromass Ltd. The Center for Isotope Geochemistry at LBNL and UC Berkeley has recently acquired an IsoProbe. This instrument is a single focusing magnetic sector instrument that utilizes a RF-only hexapole collision cell. The collision cell provides both energy focusing and the ability to virtually eliminate the Ar-based isobaric interferences that are intrinsic to other MC-ICPMS instruments. This facilitates the isotopic measurement of elements such as Fe, Ca, and Se, which suffer from Ar-based isobaric interferences.

Examples of DOE related topics expected to be investigated with the CIG IsoProbe include: (1) exploration of Fe isotopic effects as a monitor of oceanic biological productivity and CO2 drawdown, both in the modern ocean and as a paleoceanographic proxy (2) the secular Ca isotopic record of the oceans and its possible use as a probe of the link through atmospheric CO2 concentration between biological productivity of the ocean and continental weathering processes (3) the measurement of U, Sr, Ca and Nd isotopic composition of groundwater and rock samples as tracers fluid-rock interaction.

Isotopic Fractionation in Iron Oxide and Iron Carbonate Systems: Inorganic and Microbial Pathways

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Despite the improvements in analytical, experimental, and computational methods, there are still a significant number of rock-forming minerals for which isotopic fractionation data are lacking or in disagreement. This is particularly true for iron oxides (magnetite, hematite) and iron carbonates (siderite). Knowledge of the oxygen and carbon isotope fractionation factors for the system magnetite-siderite-H₂O-HCO₃⁻ can be used as geothermometers or to determine the sources of fluids and/or gases in natural systems. We have measured the oxygen isotope fractionation factors (1000 ln α₀⁻mag-H₂O) over a wide temperature range (25-800°C), whereas oxygen and carbon isotope fractionation factors between siderite and H₂O (±HCO₃⁻) were determined at much lower temperatures (15-75°C).

We used a number of reaction pathways to facilitate isotopic exchange between the solid and fluid. For magnetite these included: (a) oxidation of pure iron powder in either pure water or dilute NaCl solution at NiNiO, (b) reduction of hematite through reaction with water or dilute acetic acid (HAc) at NiNiO, (c) reaction of water or dilute NaCl with fine-grained magnetite at NiNiO, and (d) inorganic or microbial-mediated precipitation from solution. Experiments conducted at 300°C and above utilized the first three reaction pathways, whereas the precipitation pathways were used exclusively below 100°C. At high temperatures, the partial isotopic exchange method of Northrop and Clayton (1966) was used to determined “reversed” isotopic fractionation. Isotopic fractionation involving siderite was investigated only at low temperatures. Effective use of HAC was limited to temperatures up to about 400°C, whereas magnetite-H₂O and hematite-H₂O isotopic exchange became prohibitively slow below about 400°C. Inorganic precipitation of magnetite involved slowly titrating a solution of either KNO₃/KOH into a solution of FeCl₂ or a NaOH solution into a solution of FeSO₄ and FeCl₃ (with the Fe[II]:Fe[III] ratio appropriate for magnetite). Magnetite and/or siderite precipitation were also facilitated by using iron-reducing bacteria grown in a variety of cultures containing Fe [III] oxyhydroxide as the electron acceptor and either CO₂/H₂ or organic acids as electron donors. Each run product was characterized by XRD, SEM, and on a limited basis HRTEM and Mössbauer. Examination by SEM indicates the formation of well-crystallized octahedra and dodecahedra of magnetite with grain sizes as large as 100-200 micrometers, particularly in experiments where dilute HAc was used.

The most consistently well-behaved results were obtained from magnetite-0.5 m NaCl experiments conducted between 500 and 800°C. Fractionation factors in this temperature range agree well with those cited in the literature. Between 450 and 300°C, we observe an apparent minimum of about -8.5‰ in 1000 ln α₀⁻mag-H₂O, which is at odds with theoretically predicted values. At lower temperatures (25-90°C), we observe 1000lnα₀⁻mag-H₂O values of between 2 and -4‰ for both the inorganic and microbially mediated pathways. These values are more positive than theoretical or empirical estimates previously described. Temperature-dependent oxygen and
carbon isotope fractionation factors between biogenic siderite and H\textsubscript{2}O are very similar in magnitude to those reported from inorganically precipitated siderite-H\textsubscript{2}O fractionation studies. Isotope fractionation factors were not isotopically reversed in these low temperature experiments so attainment of equilibrium is subject to debate.
Metabolic Factors Affecting Carbon Isotope Fractionation by Methane-Oxidizing Bacteria

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Methane-oxidizing bacteria play a key role in the global CH\textsubscript{4} cycle and stable isotope measurements of CH\textsubscript{4} are potentially one of the most useful techniques for studying that role. However, carbon isotope fractionation factors reported for bacterial oxidation of CH\textsubscript{4} span a large range of values (\(\Delta_{\text{CH}_4\text{CO}_2} = 1.007 - 1.031\)). To determine the cause of this variability, we conducted a series of experiments designed to isolate the effects of different metabolic factors on the size of the carbon isotopic fractionation expressed by methanotrophic bacteria.

The results of our experiments indicate that the key factor governing the magnitude of isotope fractionation is the concentration of organisms in the culture. At cell densities less than 0.1 mg/l, \(\Delta_{\text{CH}_4\text{CH}_3\text{OH}}\) is greater than 1.03, while at cell densities greater than 0.7 mg/l, \(\Delta_{\text{CH}_4\text{CH}_3\text{OH}}\) decreases to approximately 1.005. At low cell densities, the concentration of the enzyme used to catalyze the conversion of dissolved CH\textsubscript{4} to CH\textsubscript{3}OH, MMO, is low and limits the rate of methane oxidation. During exponential growth, the rate of CH\textsubscript{4} oxidation increases significantly and becomes partially limited by diffusion CH\textsubscript{4} from the gaseous to dissolved state. This effect is independent of the form of MMO expressed by the bacteria (soluble versus particulate) or the metabolic pathway utilized to assimilate carbon (RuMP versus serine).

We did find that the metabolic pathway has a large effect on the \(\delta^{13}C\) values of biomass and CO\textsubscript{2} produced by the organisms. Type I methanotrophs (those utilizing the RuMP pathway) produce biomass with the same \(\delta^{13}C\) value as the CO\textsubscript{2}, whereas Type II methanotrophs (those using the serine pathway) produce biomass with \(\delta^{13}C\) values approximately 16\%\textsubscript{e} higher than the CO\textsubscript{2}. These effects are independent of the magnitude of the carbon isotope fractionation caused by the conversion of CH\textsubscript{4} to CH\textsubscript{3}OH. We suggest that the difference between the \(\delta^{13}C\) values of the biomass and CO\textsubscript{2} produced by the Type II organisms are due to carbon isotope fractionation associated with assimilation of CO\textsubscript{2} during cell growth (no CO\textsubscript{2} is utilized for the RuMP pathway).
Measurement of Reaction Rates in Natural Fluid-Rock Systems Using Sr and U Isotopes

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A major need of the DOE, and indeed a major objective of geochemistry, is to be able to predict the transport of chemical constituents in fluids in the Earth. This comes into play in environmental remediation, geothermal and fossil energy resources, climate change science, and nuclear waste isolation. One of the weak points in constructing models for reactive chemical transport is in the prediction of fluid-solid reaction rates, particularly for dissolution and precipitation reactions. Fluid-solid reaction rates are important independent of fluid transport, for issues such as corrosion rates and weathering. Formulations can be made using kinetic theory, but it is a seemingly ubiquitous occurrence that other factors, some presumably involving mineral surfaces and others involving transport limitations on various scales, alter the predicted reaction rate by up to several orders of magnitude. One means of addressing this issue is through the microscopic study of mineral surfaces, and substantial effort is now being made to do this using synchrotron radiation. A complementary and necessary approach, which we have taken, is to use isotopic tracers (primarily Sr, but also U and Nd) to determine fluid-solid exchange rates in various natural situations. The isotopic methods characterize the reaction rates in the system at the scale of the "reaction length," which can be anywhere from a few centimeters to hundreds of meters depending on the element used and the natural environment. The ultimate objective will be to understand the microscopic, pore scale, and mesoscale characteristics of natural systems that have been characterized in terms of "field scale" measures of reaction rates. However, an intermediate goal is to establish empirically the natural range of fluid-solid reaction rates, because if the range is limited and there are systematic variations, then a useful tool will be in hand.

To determine reaction rates, the Sr and U isotopic composition of fluids and rocks have been measured in saturated zone groundwater, vadose zone groundwater, geothermal systems, deep-sea pore fluids, and in metamorphic rocks. The groundwater and geothermal systems are advective, the fluid velocities are meters to 100's of meters per year (less in the vadose zone), and the reaction lengths for Sr are in the range of km's to hundreds of km. In deep sea pore fluids and metamorphic systems, the transport in the fluid phase is mainly by diffusion; the reaction lengths vary from 10's of cm to 10's of meters. To determine the rates, the groundwater flow velocity (or fluid phase diffusivity) must be constrained. Uncertainties in these values are typically less than a factor of ±3. Deduced fluid-solid exchange rates correspond to mineral dissolution time constants (grams dissolved/gram/yr) in the range 3 x 10⁸ yr⁻¹ for the slowest low temperature systems to about 10⁻⁶ yr⁻¹ for the fastest high temperature systems (at 500 - 600°C). The rates are not highly variable, show a significant but relatively weak temperature dependence, and are 2 to 8 orders of magnitude smaller than typical laboratory rates measured far from equilibrium. In some cases, empirically inferred rates combined with isotopic measurements can serve to constrain groundwater flow velocities; this is particularly useful for cases where the velocities are very small, such as the vadose zone at Yucca Mountain. The differing reaction lengths for different elements (e.g., Sr and O; or Sr and Nd) in the same system can also be exploited to extract information on the mesoscale hydrology (e.g., fracture spacing) of some fluid-rock systems.
Selective Binding of Chiral Amino Acids to the Atomic Steps of Calcite: A Model for Control of Biomineral Growth

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Since the emergence of life on Earth, organisms have directed the crystallization of inorganic ions from solution to form minerals that meet specific biological needs. Through selective introduction of peptides and proteins, living organisms deterministically modify nucleation, growth kinetics, surface morphologies, and facet stability. In the process, they produce nanophase materials, single-crystals, and multi-layer composites for diverse functions.

A number of investigations have shown that the protein fractions associated with mineralizing parts of organisms plays a primary role in controlling carbonate formation. In general, those found in carbonate biominerals are marked by the common presence of acidic amino acid residues, particularly aspartic acid (ASP). Consequently, the calcium carbonate-amino acid system provides an attractive model for investigating biomineralization.

To understand the physical controls of amino acids on calcite growth, we have examined the growth and dissolution of single crystal calcite in amino acid-bearing solutions using in-situ atomic force microscopy (AFM), nucleation on self-assembled monolayers (SAM), bulk growth experiments, surface spectroscopy and crystallographic modeling. Our results show that the binding of individual amino acids to single atomic steps on the calcite surface results in many features observed in biomineralized systems, such as preferential binding and stabilization of non-equilibrium facets. We also find that binding of amino acid enantiomers breaks the crystal symmetry and induces the emergence of chiral structures. From the chiral behavior and the crystal symmetry, we show that the amino acid binding must involve multiple sites on the calcite surface as well as multiple functional groups on the amino acid molecule. Using bulk crystals nucleated on organic templates, we show a logical (but rarely illustrated) link between changes in elemental step motion and macroscopic crystal shape. From these shapes we construct the modified 2D Wulff plot for the {104} face in the Asp-bearing system and show that the amino acid has a pronounced effect on the step-edge free energy. In contrast, examination of the dependence of elementary step speed on amino acid concentration indicates that the organic fraction has little effect on step kinetics. From bulk and surface spectroscopic analysis, we find that Asp is not present within the bulk of the crystals, nor is it adsorbed in any appreciable amount on the {104} face. Using molecular modeling, we predict that binding to the steps is preferred over binding to the {104} face and that L- and D-Asp exhibit distinct binding energies in a way that that matches the symmetry observed during the growth experiments. Based on these results we propose that the modification of calcite growth by acidic amino acids results from changes to the calcite surface and step free energies in response to enantio-specific binding to the individual step risers. This conclusion suggests that the concept of stereochemical recognition commonly used to describe the interaction of organic growth modifiers with biomineral surfaces can be recast in terms of surfactant activity, establishing an important step
towards understanding how the more complex peptides and proteins found in living organisms act to control carbonate mineralization.
Paleomagnetic Dating of Burial/Clay Diagenesis

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Paleomagnetic dating using chemical remanent magnetizations (CRMs) can provide valuable information on the absolute timing of diagenetic events. For example, CRMs in altered rocks around conduits for flow can be used to date the fluid migration and associated rock/fluid interactions. The origin of widespread CRMs, however, is problematic and it is not clear what diagenetic process is being dated. Most of these CRMs occur in rocks that have not been altered by externally derived fluids thus the CRM must be related to a diagenetic remagnetization mechanism other than fluids. We have been testing burial diagenesis of clays as a remagnetization mechanism for such widespread CRMs. Results from Mesozoic carbonates in the Vocontian Trough in SE-France support the hypothesized acquisition of a CRM during burial diagenesis of smectite. Where smectite has been altered to other clays, the carbonates are characterized by a prefolding, but secondary, normal polarity CRM throughout the basin based on fold, conglomerate, and reversal tests. At sites with partial alteration, the CRM is absent or weakly developed, and where the clays show no evidence for burial alteration, the units are characterized by a primary magnetization. CRM intensity varies inversely with the amount of smectite. Geochemical data indicate that orogenic-type fluids are not an agent of remagnetization. Results from Jurassic sedimentary rock on Skye, Scotland, are also consistent with a connection between clay diagenesis and magnetite authigenesis. In north Skye, where detrital smectite is abundant, the rocks contain a weak magnetization. The same age rock in south Skye, where the clays have been altered to illite by hydrothermal heating and fluids, contain a multi-component CRM residing in magnetite and pyrrhotite. The CRM was acquired in the early Tertiary, which is consistent with the timing of the hydrothermal activity that caused the alteration. Based on these studies, we conclude that diagenesis of smectite is a likely remagnetization mechanism and that paleomagnetic analysis can be used to date this event.
Modeling the Electrical Double Layer on Microbial Surfaces: Equilibrium and Non-Equilibrium Treatments

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Microbial surfaces can develop a significant net surface charge as the result of the protonation/deprotonation of carboxylic acid, phosphate and other functional groups. This net charge results in the formation of an electrical double layer that can significantly affect the uptake of metal and other ions as well as the attachment of microbes to charged mineral surfaces.

In the development of the equilibrium model, a numerical solution to the Poisson-Boltzman equation is presented which is valid for an arbitrary mixture of electrolyte ions. This model was then used to calculate the surface potential, Donnan potential, and ion concentration profiles for semipermeable microbial membranes. These calculations showed that in dilute solutions (I<0.01M), typical of subsurface groundwaters, previous models of surface potential development were in significant error since they were based upon fixed 1:1 electrolyte concentrations and could not consider all ions present in solution. This fact, coupled with the knowledge that many environmentally important bacteria develop a relatively high surface charge, can lead to the concentration of cations at the microbial surface by factors as high as 10,000 (see Figure 1) and to the development of a diffuse electrical double layer that can extend significant distances away from the microbial surface. Such double layer effects could be important factors in microbial metal uptake and surface precipitation or redox processes.

![Figure 1.](image-url)

In the non-equilibrium treatment, a numerical finite difference model is developed for solution of the Nernst-Planck-Smoluchowski equation for spherical particles applicable to the nanoscale with sharp gradients generated by electrostatic forces. The results of these modeling calculations show that molecular diffusion can be an extremely effective process at the nanoscale and that even the high cation concentration effects calculated for microbial surfaces can be achieved in relatively rapid time frames (i.e., <0.2 sec.). In addition, there is a corresponding anion exclusion, owing to the net negative charge. This non-equilibrium effect of crossing ion...
gradients can create an intermediate zone, which is high in both attracted cations and excluded anions. Implications of this effect as regards bio-induced precipitation/dissolution reactions are discussed.
High Precision Radiometric Dating of Sedimentary Materials

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We have shown that it is possible to obtain U-Pb ages for soil calcite in late Paleozoic and early Mesozoic sedimentary rocks with uncertainties of 1 Ma (Rasbury et al., 1997; Wang et al., 1998). As reported here marine cement, evaporite calcite, lake calcite, swamp calcite and spring calcite can also be used for high precision U-Pb dating. For example, a Miocene spring calcite (tufa) gives a U-Pb age with an uncertainty of 0.4 Ma.

The Middle Miocene Barstow Fm. Rainbow Basin, Mojave Block, So. California:
U-Pb ages of a lacustrine tufa show great potential for improving time resolution in terrestrial sections. The range in $^{238}\text{U}/^{204}\text{Pb}$ of 4000 provides enough spread in the Pb isotopic ratios to precisely define the $^{238}\text{U}-^{206}\text{Pb}$ isochron. The concordant U-Pb age of a tufa deposit that occurs in the middle member of the Barstow Fm. at Owl Canyon is 14.7 ± 0.4 Ma. The tufa is composed of alternating bands of fibrous and micritic calcite, with higher and lower uranium concentrations respectively. The fibrous calcite exhibits a gradual increase in the concentration of uranium in the outward growth direction of the calcite with a homogeneous dull luminescence under cathodoluminescence. These observations are consistent with cyclic mixing of varying proportions of U-poor and Ca-rich water from springs and U-rich and Ca-poor evaporative lake water during the precipitation of the tufa. Mono Lake tufa deposition is a modern analogue.

Late Paleozoic Lacustrine and Palustrine Carbonates, Appalachian Basin, SE Ohio:
The Upper Paleozoic strata of the Appalachian Basin of southeastern Ohio are cyclic and mostly non-marine with sparse biostratigraphic controls that make correlation with marine sections difficult. Paleontologic evidence is insufficient to definitely place the Pennsylvanian–Permian boundary. Rather, the location of the boundary is based on the correlation of cycles from the mid-continent and incursions of rare marine units in the basin. U-Pb analyses of the Freeport Limestone, a lacustrine limestone that is considered Desmoisnian, give a concordant age of 302 ± 2 Ma. Our previous estimates (Rasbury et al., 1998) suggest that the Pennsylvanian-Permian boundary is 302 ± 2 Ma and that the Desmoisnian-Virgilian boundary is 307 ± 3 Ma. Thus, it appears that correlation of the late Paleozoic terrestrial units of the Appalachian Basin is within a few million years of the marine stratigraphic section of the mid-continent.

Late Paleozoic Marine Cements and Calcite from Evaporite Deposits:
Marine aragonite (now calcite) cements are common in the late Paleozoic. U-Pb results from the early Permian (Wolfcampian) Laborcita Formation from the Sacramento Mountains produce an age of 304 ± 2 Ma. The algal mounds that include these cements were deposited directly above the Carboniferous-Permian boundary based on fusulinid biostratigraphy. Rasbury et al., (1998) suggest that the age of this boundary is 301 ± 2 Ma. Thus the age of the cements appears to provide the time of sedimentation. A similar marine cement sample from the Tansil equivalent of the Capitan Limestone from the Guadalupe Mountains of the Delaware Basin gives a U-Pb age of 262 ± 5 Ma. This age is consistent with a U-Pb zircon age of 265 ± 0.3 Ma from an ash near the base of the Capitan Limestone (Bowring et al., 1998). The Delaware Basin has a thick succession of evaporates including the Castile Formation, a finely layered unit of gypsum, halite and calcite, which is thought to be earliest Ochoan based on Sr stratigraphy, i.e., about 260 Ma.
Concordant U-Pb ages for the calcite are 251 ± 2 Ma suggesting a 10 million year discrepancy. Such a discrepancy is not surprising since the latest Permian units are evaporites and redbeds without marine fossils. More work is necessary to understand the discrepancy between our ages and the Sr stratigraphy.

References:
The Application of High Spatial Resolution Isotope Geochemical Methods to Understanding the Origin and Evolution of Geological Energy Sources

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Understanding the rates and mechanisms involved in the formation of exploitable geological energy sources, including fossil fuel, geothermal, and fissionable materials, requires knowledge of the age of origin and subsequent thermal history of the system over geological time. In the past year, we have coupled application of the ion microprobe and ⁴⁰Ar/³⁹Ar thermochronometry to: (1) assess the thermal and diagenetic histories of sedimentary basins (southern San Joaquin basin, central California); (2) study the intrusion history and thermal evolution of a young geothermal system (Geysers steam field, northern California) to resolve fundamental questions regarding its origin; and (3) develop tools to investigate the stability of uraninite in the presence of fluid and radiation effects to better understand the nature of unconformity-type uranium deposits (Athabasca Basin). Some of these efforts require significant developmental work to make meaningful progress. In particular, we have found it necessary to develop a robust ion microprobe calibration for isotope ratio analysis of oxygen and carbon isotopes of complex carbonate compositions to in order to investigate rock-fluid interactions. Similar developments have been required to study the U-Pb and oxygen isotopic systematics of uraninites and associated phases.

In our study of the adjacent producing fields within the southern San Joaquin basin, we have been able to resolve C- and O-isotopic compositions of multiple generations of calcite, dolomite, and Fe dolomite cements at the ca. 10-µm scale and with ± 0.5 ‰ precision. Such observations are vital for determining the cementation histories needed to assess the evolution of petroleum reservoirs. Similarly, we have been able to establish granitoid emplacement and the subsequent thermal evolution in the Geysers geothermal field with sufficient precision (± 25°C, ± 50 ka) to constrain quantitative thermal models. Likewise, integrated high spatial resolution and precision U-Pb and O-isotopic studies of stratiform uraninites permit the alteration history of these bodies to be studied in unprecedented fashion. Finally, our research bears directly upon efforts to understand the geochemistry of potential reservoirs appropriate for subsurface sequestration of carbon dioxide. Measurement of the carbon and oxygen isotopic composition of phases that incorporate CO₂ is among the most fundamental geochemical tools for investigating the processes that govern the mass balance of this component between atmospheric, hydrospheric, and crustal reservoirs. Since carbonate precipitation represents a key terrestrial sink, development of techniques to improve the accuracy and precision of measurements of carbon and oxygen isotopic ratios obtainable at the micron scale is clearly warranted. Hence, while our proposal does not explicitly target the issue of subsurface CO₂ sequestration, we consider our ongoing efforts to develop a robust ion microprobe calibration for in situ isotope ratio analysis of oxygen and carbon isotopes of complex carbonate compositions to be an allied effort.
Ample evidence indicates that large amounts of CO2 are produced during diagenetic deoxygenation and hydrogenation of kerogen as it reacts with H2O during burial of source rocks in the upper part of sedimentary basins (Price and Wenger, 2000), which is consistent with the overall irreversible hydrolytic disproportionation reaction represented by

\[
1057 \text{C}_{515}\text{H}_{596}\text{O}_{72(c)} + 16,598 \text{H}_2\text{O}_{(l)} \rightarrow 1256 \text{C}_{406}\text{H}_{528}\text{O}_{19(c)} + 34,419 \text{CO}_2(g),
\]

\[
(oxygenated kerogen) \quad (quasi-deoxygenated kerogen)
\]

where the subscripts (c), (l), and (g) refer to the crystalline, liquid, and gas states, respectively. This reaction corresponds to the sum of two half-reactions after cross multiplying by the reaction coefficients for \(H_2(g)\); i.e.,

\[
1057 (\text{C}_{515}\text{H}_{596}\text{O}_{72(c)} + 958 \text{H}_2\text{O}_{(l)} \rightarrow 515 \text{CO}_2(g) + 1256 \text{H}_2(g)) \quad (2)
\]

and

\[
1256 (406 \text{CO}_2(g) + 1057 \text{H}_2(g) \rightarrow \text{C}_{406}\text{H}_{528}\text{O}_{19(c)} + 793 \text{H}_2\text{O}_{(l)}).
\]

Reaction (1) is favored in relatively shallow or otherwise uncompacted source rocks with high porosities and permeabilities which are open to interstitial flow of water into the rock in response to the escape of \(\text{CO}_2(g)\) produced by the reaction. Under these conditions, for every mole of \(\text{H}_2\text{O}\) that enters the source rock and is consumed by reaction (1), \(\sim\) 2 moles of \(\text{CO}_2\) are produced by combining the mole of oxygen derived from \(\text{H}_2\text{O}\) with \(\sim\) 2 moles of carbon and \(\sim\) 3 moles of oxygen extracted from the immature oxygen-rich reactant (\(\text{C}_{515}\text{H}_{596}\text{O}_{72(c)}\)). In the process, 2 moles of hydrogen derived from \(\text{H}_2\text{O}\) are consumed by conversion of 0.064 moles of the reactant kerogen to \(\sim\) 0.076 moles of \(\text{C}_{406}\text{H}_{528}\text{O}_{19(c)}\). As the reaction proceeds and all of the \(\text{C}_{515}\text{H}_{596}\text{O}_{72(c)}\) kerogen is converted to \(\text{C}_{406}\text{H}_{528}\text{O}_{19(c)}\), the weight percent hydrogen in the kerogen increases by \(\sim\) 23 percent from \(\sim\) 7.5 to \(\sim\) 9.3 percent of the kerogen, which corresponds to a huge increase in the oil generation potential of the source rock!
Microbial Dissolution of Fe(III)(hydr)oxides

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In aerobic environments, microorganisms are faced with approximately ten orders of magnitude discrepancy between available Fe (~$10^{-17}$ M) and their metabolic requirement (~$10^{-7}$ M). In contrast to facultative anaerobic environments, where dissimilatory iron reducing bacteria (DIRB) are often abundant, few studies have detailed microbial interactions with Fe(III)(hydr)oxides in aerobic environments. In order to understand better acquisition of Fe from Fe(III)(hydr)oxides, we investigated the production of siderophore and Fe(III) reduction by a strict aerobe in the presence of synthetic hematite as a source of Fe. Pseudomonas mendocina grew best when Fe was supplied as FeEDTA (approximately $1.8 \times 10^8$ CFU mL⁻¹), grew abundantly when Fe was supplied as hematite (approximately $1.2 \times 10^8$ CFU mL⁻¹), and grew poorly when Fe was withheld from the medium (approximately $5.5 \times 10^7$ CFU mL⁻¹). As expected, negligible siderophore was produced per cell when Fe was supplied as FeEDTA and more siderophore was produced in the hematite flasks than in the controls. Thus, growth on and the production of siderophore in the presence of hematite present compelling evidence that siderophore was produced as a mechanism to acquire Fe from hematite. For the Fe reduction experiments, Fe reduction by components of the supernatant fluid was induced weakly when Fe was supplied as hematite or as FeEDTA, but much more when the cells were cultured under extreme Fe deprivation. In fact, 16 times as much Fe reduction occurred in the controls than for either of the FeEDTA or hematite amendments.

In a second study, P. mendocina was grown in batch culture with hematite, goethite, or ferrihydrite as Fe sources. P. mendocina obtained Fe from these minerals in the following order: goethite > hematite > ferrihydrite, exerting $3.2 \times 10^{16}$, $3.9 \times 10^{16}$, or $5.5 \times 10^{16}$ cell h (μmol Fe)⁻¹ kcal⁻¹ to obtain the Fe, respectively. Furthermore, Fe dissolution for each of the minerals appears to have occurred in excess, as evidenced by the growth of P. mendocina in the medium above the sediments. These results demonstrate that an aerobic microorganism is able to obtain Fe for growth from different insoluble Fe minerals, with varying dissolution rates.

Our results are in contrast to the long held assumptions that Fe acquisition was facilitated solely by siderophores and provides a new perspective regarding microbial interactions with Fe bearing minerals.
Isotope partitioning among different phases and species under natural conditions is controlled by (1) path/rate-dependent kinetic processes and (2) equilibrium reactions. The former involves heterogeneous reactions catalyzed by mineral and microbial surfaces, which facilitate otherwise extremely slow chemical and isotopic exchange reactions at low temperatures. Equilibrium partitioning, attainable generally only after prolonged duration of catalyzed or non-catalyzed reactions, is determined by a few thermodynamic variables, most notably by temperature. Our programs on experimental isotope geochemistry at Oak Ridge National Laboratory have demonstrated that (a) reactions that have been considered too slow to proceed measurably under natural conditions can be facilitated by analogs of natural materials, resulting in large kinetic isotope effects or the attainment of isotopic equilibrium in short periods of time, and (b) in addition to temperature, pressure and fluid composition are important variables in determining equilibrium isotope partitioning between aqueous fluids and other coexisting phases (e.g., minerals, vapor).

It was demonstrated that a Ni-Fe alloy similar to awaruite and Ni catalyst catalyzed chemical and isotopic exchange reactions between CO$_2$ and CH$_4$ at relatively low temperatures. Abiogenic methane hydrothermally formed from dissolved CO$_2$ under reducing conditions at 200-300ºC has low $\delta^{13}$C values ($\leq-25\%e$), which are indistinguishable from natural microbial and thermogenic methane. The carbon isotope equilibrium between CO$_2$ and CH$_4$ was readily attained in the presence of a Ni catalyst at 200-600ºC. These results underline the potential roles of transition metals in nature as “geocatalysts.”

Our experimental investigations demonstrated unambiguously that pressure and fluid composition affect significantly equilibrium isotope partitioning in the systems mineral-water and water liquid-vapor even at elevated temperatures up to 600ºC (“isotope pressure and salt effects”). Theoretical calculations and simulations suggest that these isotope effects are due largely to changes in the structure and properties of water caused by the increase of pressure and the presence of solutes. These two variables are in some cases as important as temperature, which has been considered a sole variable in equilibrium isotope partitioning. Some discrepancies in experimental results from the literature can be reconciled by taking into account these two effects. The newly obtained knowledge on fundamental aspects of the mechanisms and variables of isotope partitioning has far-reaching implications to isotope geochemistry and cosmochemistry, because pressure and fluid composition vary widely, and because there are many potential natural catalytic materials.
The Sources of Air-Like Noble Gases in Hydrocarbon Reservoirs

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Noble gases associated with sub-surface fluids have a variety of sources, identified through their unique isotopic compositions and relative abundance patterns. In hydrocarbon systems, the primary sources are (a) radiogenic noble gases (\textsuperscript{4}He, \textsuperscript{40}Ar, \textsuperscript{21}Ne, \textsuperscript{131-136}Xe) produced either in the deep crust or locally in the reservoir and/or source rock and (b) non-radiogenic noble gases originally from the atmosphere. Although mantle noble gases are sometimes found in these systems, typically the radiogenic and atmospheric components dominate.

The atmospheric component is identified primarily by isotopic composition and by relative gas abundances (\textit{e.g.}, Ne/Kr/Xe/Ar), determined from the abundances of non-radiogenic isotopes, typically \textsuperscript{20,22}Ne, \textsuperscript{36}Ar, \textsuperscript{84}Kr, and \textsuperscript{130}Xe. It is generally assumed that the source for all atmospheric noble gases in subsurface fluids is air-saturated sea, meteoric or connate water (1). Evidence for water-derived noble gases in hydrocarbon systems is extensive and provides strong support that water plays an important role in hydrocarbon systems. However, evidence has surfaced suggesting that the hydrocarbons themselves are also a source of atmospheric derived noble gases (2) with a relative abundance pattern that is highly enriched in the heavy noble gases (Kr and Xe). \textsuperscript{130}Xe/\textsuperscript{36}Ar enrichment factors up to \~600 relative to air have been observed (2). This component cannot be derived from air saturated water by distillation and/or solubility driven equilibration with oil, gas, or oil-gas systems, as suggested by (1). Instead, we believe this fractionated air component is derived from the petroleum source rock. Support for this hypothesis is provided by laboratory studies of noble gases in carbon-rich and petroleum source rocks (3,4).

We now have evidence for a third air-like noble gas component, identified by an unusual Ne/Kr/Xe/Ar relative abundance pattern that is unlike air saturated water or the highly fractionated source rock component. Systematic field-wide trends in noble gas compositions suggest that this third air-like component may be derived from the reservoir sediments. Understanding the formation and occurrence of these atmospheric noble gas sources and their interaction with oil and natural gas systems will lead to a better understanding of the processes and scales related to primary and secondary migration, basin scale fluid movement, gain or loss of secondary porosity, and biodegradation.

The Evidence for Catalytic Natural Gas

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Light hydrocarbons (LHs, C_1 - C_9) are traditionally viewed as the thermal products of decomposing organic sediments. However, serious contradictions persist. Thermal gas generated in the laboratory, for example, does not resemble natural gas. LHs may be formed catalytically, however, by the transition metals in organic sediments (Ni, V, Fe, and Co) and evidence supporting this view continues to mount:

Thermal decomposition of crude oil (200°C, weeks) gives a product dominated by cyclopentanes with little or no gas, a composition unlike natural LHs.


Natural LHs exhibit the characteristics of catalytic products, in particular a proportionality between isomers:

\[
\frac{(xy_i)}{(x,y)} = \alpha
\]

(where x and x_i are isomers; y and y_i are isomers that are structurally similar to x and x_i; and \(\alpha\) is a constant). It holds for all oils, at all concentrations (0.001 to 10 % LH in total oil). The correlations approach 0.99, the strongest yet reported for LHs.

GOR (gas-to-oil ratio) is correlated \(r^2 = 0.75\) to the oil concentrations of four LHs (2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane). This relationship is consistent with a catalytic reaction in which LH concentrations increase with oil maturity approaching thermodynamic equilibrium in the process.

These results suggest three phases of oil & gas generation in sedimentary basins:

1) Thermal generation of immature oil with no gas. The LHs are dominated by cyclopentanes with cyclopentane/cyclohexane ratios far from thermodynamic equilibrium.

2) The catalytic generation of mature oil and natural gas. The LHs are dominated by cyclohexanes with cyclopentane/cyclohexane ratios approaching thermodynamic equilibrium.

3) The catalytic conversion of oil to wet gas and wet gas to dry gas.
Microbially Mediated Dissolution of Kaolinite

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Previous research by our group has shown that aerobic Pseudomonas mendocina bacteria are able to acquire Fe from Fe(III)(hydr)oxides by enhancing mineral dissolution through a variety of mechanisms. Unlike dissimilatory Fe reducing bacteria (DIRB), which require mM concentrations of Fe, the P. mendocina require only μM concentrations. These observations led us to hypothesize that the bacteria may be able to acquire Fe present in even trace quantities in association with clay minerals such as kaolinite.

To test this hypothesis, we began by characterizing a suite of natural kaolinite samples with variable Fe content. Characterization methods included: atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and potentiometry. We then chose several end-member kaolinite samples, in terms of surface Fe content and crystalline order, for use in abiotic and microbially mediated dissolution experiments.

Microbially mediated kaolinite dissolution experiments were conducted under Fe-limited conditions. Because the study system was Fe limited, the bacteria were only able to grow to levels above those of kaolinite-free controls by obtaining Fe from the solid phase. Substantial enhanced growth of the bacteria was observed in the presence of kaolinite. We further observed that the bacteria significantly enhanced rates of Al and Si release from the kaolinite. These results indicate that clays which contain even trace quantities of Fe need to be considered as additional sources of Fe in aerobic environments and suggest that microbial processes may exert important but until now largely overlooked influences on the dissolution rates of clays.

Our ongoing research focuses on determining the mechanisms of microbially mediated kaolinite dissolution. For example, we observed substantial production of siderophores in the presence of the kaolinite. We are therefore conducting dissolution experiments in the presence of several natural and synthetic siderophores, including siderophores produced by the P. mendocina bacteria. We shall present this preliminary research, along with plans for future mechanistic studies.

We thank J. Fulghum (Kent State Univ.) for assistance with XPS analysis and R. Pruett (IMERYS Corp.) and P. Schroeder (Univ. of Georgia) for natural kaolinite samples.
Uranium Series Concordance Studies

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Objectives: The goal of this project is to provide unique information on the behavior of U-series members in the environment using improved capabilities for Quaternary dating.

Project Description: Uranium-series disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements have typically been made by decay counting; however, there are considerable advantages in using mass spectrometric techniques. We have previously used BES funding to develop such techniques. The general goal of the current project is to apply mass spectrometric methods to answer basic questions in Quaternary dating and geochemistry. Emphasis is placed on a multi-element concordia approach. This work provides information on the recent evolution of magmatic systems and also has application to natural hazard risk assessment, paleoclimate studies, and the carbon cycle.

Results: A number of projects are ongoing including studies to determine: 1) the residence time of Hawaiian magmas at different stages of volcano evolution and in different settings in the same volcano; 2) the spatial and temporal evolution of travertines in central Italy and Nevada; 3) temporal and spatial evolution of MORB at the Northern Gorda Ridge, the Axial Valley of the Mid-Atlantic Ridge, and the EPR; and 4) ventilation ages for deep-ocean water, both presently and during the past glacial maximum using U-series dates for deep-sea corals.

Here we highlight our U-series dating results for ice samples. Improved radiometric dating methods for polar ice are needed to improve correlation of paleoenvironmental records from the cryosphere with other media, and for basic studies in glaciology and the terrestrial history of meteorites. Such methods would be of greatest utility for older ice deposits where radiocarbon dating or counting layers are not possible. We have applied uranium-series disequilibria techniques to age-date near-surface ice samples from Allan Hills, Antarctica, an ablation area known for its abundance of old meteorites. Prior studies (Fireman, 1986) on dusty samples based on alpha spectrometry and a recoil model for uranium series nuclides dissolved in ice suggested an old 325 ka age for ice from this area. However, our results for three Allan Hills samples failed to confirm these results based on alpha spectrometry. Our mass spectrometric data are most consistent with a young age for these ice samples, with their large U-series disequilibria inherited from precipitation. These data suggest that dating large samples of polar ice based on U-series disequilibria inherited from precipitation may be feasible. We are presently applying these techniques to date extremely dusty ice found at the base of the GISP2 ice core, thought to have an age of >150 ka based on ice accumulation models. These results should further constrain U-series techniques for dating dusty polar ice and provide valuable age constraints for a section of ice core that is not precisely dated by other techniques.
Spectroscopic Evidence for H-bonding Networks in Liquid Water & Its Relevance to Aqueous and Interfacial Reactions

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The hydrogen bond (H-bond) in liquid water holds the key to its peculiar behavior, with implications for geological, biological and chemical processes. In liquid water, the dynamical motion of atoms at the picosecond time-scale causes the H-bonds to break and reform resulting in a statistical distribution of different coordinations for the water molecules. We developed soft x-ray spectroscopy methods for studying the structural environment of H-bonded configurations in water and other related systems, and examined them using the high-resolution Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the oxygen K-absorption edge. Since the x-ray absorption process is faster than a femtosecond, it allows probing of the molecular orbital structure of frozen, local geometries of water molecules. Our results indicate that the electronic structure of liquid water is significantly different from that of the solid and gaseous forms, with a pronounced pre-edge feature below the main absorption edge. Theoretical calculations of these spectra suggest that this feature originate from specific configurations of water, for which the H-bonding is unsaturated and strongly asymmetric. Our results show that an unsaturated H-bonding environment exists for a significant fraction of water molecules in liquid water. Although x-ray and neutron scattering and vibrational spectroscopy have been used to understand the nature of water structure, the x-ray spectroscopy provided unique information on the electronic structure of liquid water. We extended these studies to understand the nature of H-bonding interactions in natural organic molecules and between organic-molecules and liquid water. Our current investigations are focused on understanding the nature of water and organic molecules at the interfaces.
A New Approach for Correlating/Predicting Thermodynamic Functions of Aqueous Nonelectrolytes at T-P Parameters of Hydrothermal Processes

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Recently we proposed a new model to correlate the standard thermodynamic properties of aqueous nonelectrolytes over extended density and temperature (up to 1300-1500 K) range (Plyasunov et al., 2000a,b). This model is a result of cooperation between geochemists, physico-chemists and chemical engineers. The model starts with the semiempirical correlation for the standard (at infinite dilution) partial molar volumes of aqueous neutral species, suggested by the fluctuation solution theory and the necessity to transform into the virial equation of state at low densities. Thermodynamic manipulations yield analytic expressions for the standard partial molar Gibbs energy, enthalpy and heat capacity. Examples of applications of this model to correlate properties of aqueous inorganic and organic neutral species at elevated temperatures and pressures will be given and discussed. Future directions of research include the extension of this model to a large variety of aqueous organic compounds through the group contribution techniques, attempts to correlate properties of strongly polar substances, such as an aqueous silica, neutral ionic pairs and, perhaps, neutral hydroxo complexes of heavy metals. If successful, results will be useful for many applications in geochemistry and technology.
Oxygen Isotope Behavior in Feldspar During Fluid-Rock Interaction

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In-situ microscale oxygen isotope analysis of feldspar is an attractive method of investigating fluid-rock interactions from the atomic to crustal scale due to its ubiquitous occurrence in the earth’s crust, its stability over a wide range of conditions (<100°C to >600°C), and its well characterized isotopic fractionation and diffusion rates. Secondary ion mass spectrometry (SIMS) is an excellent technique to investigate microscale isotopic variations in feldspar in both low and moderate temperature settings because of its high spatial resolution (10-30 μm diameter spots, 1-4 μm deep), essentially constant mass bias correction for all feldspar compositions, and relatively high precision (0.5 - 1‰ δ18O).

We have documented a large range in feldspar δ18O values (+8 to -15‰) in feldspars from the Boehls Butte Anorthosite altered at temperatures >500°C, indicating variably intensive interaction with meteoric fluids. Systematic gradients of over 15‰ are preserved from the rim to the core of large (~1mm) andesine grains in contact with fine-grained (50-100 μm) anorthite grains in one sample, with the other three analyzed samples displaying less variability (5-8‰).

δ18O_feldspar values as low as -15‰ require interaction with nearly pristine meteoric fluids. Based on the regional geologic setting and Ar-Ar and U-Pb thermochronology, alteration occurred during very rapid, nearly isothermal uplift associated with crustal extension, suggesting penetration of meteoric fluids to depths near the brittle-ductile transition (~10km). Modeling of the isotope gradients assuming diffusion from a stirred solution of limited volume into a sphere indicates that fluid-rock interaction was short-lived (<10000 yrs), and requires rapid "quenching" of diffusion to preserve the observed isotopic gradients. These results illustrate the potential of using microscale feldspar isotope disequilibrium as a geospeedometer for short-lived fluid-rock systems.

We have utilized SIMS microanalysis to study the origin of widespread K-feldspar cements in the Mt. Simon Sandstone in the mid-continent of the U.S. Average K-feldspar δ18O values of 11 samples increase systematically from +14±1‰ in the southern most, deeply buried samples to +24±2‰ in the northern most, shallow samples, with a similar trend observed for quartz overgrowths in four samples. Cathodoluminescence (CL) petrography reveals two populations of quartz overgrowths, a dark zone inner zone and a bright outer zone. Fluid inclusion (FI) studies of rare, very small (typically <3μm) inclusions in the quartz overgrowths suggests homogenization temperatures (Th) are bimodally distributed, with the majority of the inclusions falling between 60 and 100°C and the remainder, associated with brighter CL, have homogenization temperatures between 110 and 145°C. Spatial distributions suggest an average decrease of ~25°C in FI temperatures from south to north in both populations. FI from the early, dark-CL quartz overgrowths have maximum Th, consistent with temperatures predicted from burial curves (<95°C) for fluids originating in the deeper, southern part of the basin and associated with widespread K-feldspar cements formed at ~400Ma. Although our data is limited, SIMS analysis of overgrowths suggests that δ18O values decrease slightly with increasing Th, but the isotopic shift cannot be explained by changing fractionations associated with temperature shifts. Our data suggests that the regional isotopic variations in the K-feldspar
and quartz are most consistent with progressive modification of burial fluids, migrating from south to north.
Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas

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Petroleum coexists with water and minerals in subsurface sedimentary environments. In addition to acting as catalysts and confining media, inorganic sediment components may participate as reactants during organic transformations at elevated temperatures and pressures. These interactions can provide reaction pathways that regulate the stability of petroleum and result in the production of organic alteration products that constitute natural gas. Laboratory experiments are being conducted to constrain the type and extent of organic-inorganic interactions during the heating of individual aqueous hydrocarbons and crude oil in the presence of water and iron oxide and iron sulfide mineral assemblages that buffer the redox state of the chemical system.

Results from experiments containing individual aqueous hydrocarbons indicate decomposition of n-alkanes occurs via a series of sequential oxidation reactions that produce alkenes, alcohols, ketones, and organic acids as metastable intermediates that subsequently decompose to form carbon dioxide and methane. The production rate and relative abundance of individual alteration products are strongly dependent on the redox state and temperature of the system. Evaluation of the relative abundance of reaction intermediates within a thermodynamic framework indicates that some species may attain a state of reversible metastable thermodynamic equilibrium.

Experiments examining the stability of oil dissolved in water and oil existing as a separate phase floating on water indicate that aqueous oxidation reactions may play a pivotal role during the decomposition of oil in sedimentary basins. Under relatively reducing conditions, oil dissolved in water decomposes substantially faster than a separate oil phase and produces a gas that contains more carbon dioxide and a relatively methane-rich C1-C4 hydrocarbon fraction. These data are consistent with results from the single hydrocarbon experiments and suggest that organic compounds dissolved in water have access to reaction pathways that are not available in an oil phase. Accordingly, the absence of water and/or redox sensitive minerals may account for the presence of oil in a variety of environments at temperatures higher than conventional models predict. In addition, oxidative degradation of the C2+ fraction of natural gas may be responsible for the conversion of natural gas condensates to methane-rich “dry” gas.
Molecular Modeling of Geochemical Reactions at Microbial Membranes

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A computational modeling capability is being developed for the study of geochemical reactions at the outer bacterial envelope of gram-negative bacteria. This modeling capability is applied to study the molecular processes that govern microbial metal binding, microbial adsorption to mineral surfaces, and microbe mediated oxidation/reduction reactions at the bacterial exterior surface. The understanding of these mechanisms is crucial in the development of successful bioremediation strategies, in particular in dealing with the technological difficulties in the transport of bacteria to the subsurface locations where they are needed.

Lipopolysaccharides form the major constituent of the outer membrane of gram-negative bacteria, and are believed to be a key factor in these processes. In the first phase of this project, a molecular model has been developed for the rough LPS of *pseudomonas aeruginosa*, based on Hartree-Fock SCF calculations of the complete molecule at the 6-31g* level, followed by a restrained electrostatic potential (RESP) fitting procedure to obtain partial atomic charges. This charge model is used in molecular dynamics (MD) simulations of the bacterial membrane, consisting of a periodic layer of LPS molecules exposed to the exterior aqueous environment and a lipid layer exposed to the periplasmic space (Figure 1). MD simulations of the rough LPS membrane, extending over 1 ns, have been completed. The resulting trajectory is analyzed for structural and energetic factors that determine the role of LPS in processes at the cell surface. Structural properties include the degree of order in the polysaccharide core, the role of complexed ions in inter- and intra-molecular interactions, and the accessibility of ion sites for ions out of the aqueous phase. Dynamical properties include the mobility of the lipid and polysaccharide fragments of individual LPS molecules as well as collective LPS motions. Of particular interest is also the electrostatic character and availability of adsorption sites at the cell surface for adsorption to external mineral surfaces (Figure 2).
Figure 1. Molecular model of the outer bacterial membrane of *pseudomonas aeruginosa*, consisting of the exterior lipopolysaccharide and interior lipid membrane.

Figure 2. Electrostatic potential iso-contours at –1500 mV (red), 0 mV (white) and 1500 mV (blue) of the rough LPS membrane of *pseudomonas aeruginosa*. 

Microbial Community Acquisition of Nutrients from Mineral Surfaces

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Mineral surfaces act as concentrators for both organic and inorganic microbial nutrients and environmental contaminants. The bioavailability of mineral surface associated nutrients and contaminants is controlled by a complicated set of both biotically and abiotically mediated processes which occur at microbe-solution, mineral-solution, and microbe-mineral interfaces. The work described here was conducted to i) design and demonstrate use of a continuous-flow steady-state bioreactor (chemostat) for culturing microorganisms using phosphate adsorbed on goethite as a model nutrient-mineral system, ii) develop molecular biology techniques suitable for identifying and observing the spatial distribution of microbial populations enriched in chemostat experiments, and iii) apply nanotechnology to measure forces of interaction between microbes and mineral surfaces.

Microorganisms from an undisturbed acidic mineral soil were maintained in chemostat culture for 45 d, using Pi adsorbed on colloidal goethite (40 μmol P/g) as a sole phosphorous source. Glucose-mineral salts media and goethite slurry were added at equal rates to give a 4 d hydraulic retention time. After a short initial aclimation period microbial utilization of adsorbed Pi averaged 82±6 %. Microscopic examination and Gram staining of chemostat effluent showed that bacteria with motile Gram-negative rod-shaped morphology predominated, although small numbers of bacteria with other morphologies were observed initially. Fatty acid profile and 16S rDNA analyses both indicated that the dominant Gram-negative species was Burkholderia cepacia. Temperature gradient gel electrophoresis of PCR amplified chemostat effluent DNA extracts yielded 3 distinct 16S rDNA fragments. Two of these fragments have been sequenced and phylogenetically identified as B. cepacia and a Caulobacter sp.

The interfacial forces between bacteria and mineral surfaces have been measured for several bacteria-mineral systems using Biological Force Microscopy, a nanotechnology developed in our lab. Native cells are linked to an atomic force microscope cantilever, that in turn is used to measure forces between the cells and mineral surfaces. The measurements, which can be performed in solution, are quantitative down to the nanoNewton range over distances of zero (contact) to hundreds of nanometers. Bacteria-mineral systems examined include various combinations of E. coli, B. cepacia, and S. putrefaciens with goethite, graphite, muscovite, and iron and manganese (hydr)oxide surfaces.
Noble Gas Evolution in Hydrocarbon Fields: Secondary Migration Processes and End-Member Characterization

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Hydrocarbons carry an indigenous noble gas component acquired from the hydrocarbon source area. Typically, this component contains radiogenic noble gases (e.g., \(^{4}\text{He}\) and \(^{40}\text{Ar}\)) and an air-like component characterized by highly fractionated abundance patterns (\(^{136}\text{Xe}/^{36}\text{Ar}\) ratios > 600 times the ratio in air have been observed). The solubility of noble gases in hydrocarbons and water dictate that noble gases will be stripped from groundwater (air saturated water, ASW) during secondary migration and will dilute the indigenous noble gas signature in the hydrocarbon. The composition of ASW is also be modified in the carrier strata by basal fluxes and \textit{in situ} production. The degree of dilution by the modified ASW component is a function of the total amount of water with which the hydrocarbon interacts during secondary migration (water/hydrocarbon interaction ratio). Systematic trends in noble gas composition (F[Ng] and isotopic compositions vs. \(1/[^{36}\text{Ar}]\)) identify wells which produce hydrocarbons originating from common source areas and that interact with a common groundwater. Zeroth order interpretation of noble gas evolution as simple mixing can characterize noble gas composition of the source area (slope of the line) and modified groundwater with which it interacts (the intercept at \(1/[^{36}\text{Ar}]\sim0\)). Application of the concept to multiple data sets (published and unpublished) provides proof of concept and identifies distinct and readable noble gas evolution trends that are interpretable as secondary migration paths.

In the gas fields of Alberta, Canada, evolution trends defined by noble gas compositions support the hydrologically defined secondary migration flow paths of Garven (1989) and Hitchon (1984). Two groups of wells have source areas (distinct from source rock) that are characterized by very large but different enrichment factors of radiogenic \(^{4}\text{He}\) and \(^{40}\text{Ar}\) (as well as \(^{21}\text{Ne},^{136}\text{Xe}\)) that could not have been derived solely from the source rock. These large enrichments suggest that Tertiary orogeny, preceding secondary migration, degassed large volumes of old crust into the source areas. This noble gas evolution defined scenario supports a role for tectonics in the accumulation of hydrocarbons (Oliver, 1986, 1989). Noble gas evolution analysis can thus provides a fundamental constraint on models of hydrocarbon migration and emplacement.
The source of all the organic carbon in sediments and in petroleum generated from them is the organic matter from animal and plant residues originally deposited at the sediment-water interface. There has been much effort to understand the geochemical mechanisms by which this biogenic organic matter, composed mainly of biopolymers such as proteins and carbohydrates, is converted into consolidated sedimentary geopolymers. The transformations involve both biotic processes (mediated primarily by bacteria and fungi) and abiotic processes, some of which are catalyzed by minerals common in soils and sediments. During these transformations, the dominant heteroatoms, particularly sulfur and nitrogen, undergo conspicuous changes in speciation.

We studied the sulfur and nitrogen speciation of humic substances, the presumed initially-formed geopolymeric macromolecules. Our studies reveal di- and poly-sulfide linkages to be among the dominant forms of sulfur in humic substances from various sulfur-rich locations, suggesting that the sulfur linkages play a crucial role in humification. Sulfur is incorporated into sedimentary organic matter through the reactions of H₂S and its partial oxidation intermediates generated in bacterial sulfate reduction. It is believed that di- and poly-sulfide linkages are introduced mainly through reactions of reactive polysulfides. However, since H₂S is the predominant sulfur nucleophile, thiols are expected to be the leading products of the initial incorporation of sulfur into organic matter. Thiols can undergo oxidation to form disulfides, but the pathways of oxidation in sediments are unclear. Using XANES spectroscopy to determine sulfur speciation, our results with various model thiols establish that iron oxide could be a potential oxidant for forming disulfides from thiols. Thus, the oxic-anoxic interface is probably the primary site for major transformations involving disulfide cross-linking that augments humification. The application of nitrogen k-edge XANES indicates that pyridinic nitrogen is a prominent form, along with amino and amide nitrogen, in humics and sediments. The formation of heterocyclic compounds, such as the pyridinic form, from a predominantly amino nitrogen is intriguing. Studies are in progress to comprehend the formation of heterocyclic compounds from amino acid and protein precursors.
Oxygen Isotopes in Zircon

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Zircon is a refractory mineral that is highly retentive of oxygen isotope ratio. Igneous zircons preserve the magmatic oxygen isotope ratio from the time of crystallization even through granulite facies metamorphism or intense hydrothermal alteration. Empirical determinations of oxygen diffusion coefficient indicate closure temperatures above 800°C (Peck et al., 1999). For samples that have been dated, this provides a direct link to known geologic events.

Archean zircons show a narrow range of δ18O: Jack Hills (6.2±1.0‰, Peck et al. 2000, Wilde et al. 2000); Barberton (5.5±0.7‰, Valley et al. 2000); Superior (5.7±0.6‰, King et al. 1998). In contrast, younger Grenville samples have higher and more variable values, 8.2±1.7‰ (Valley et al. 1994, Peck et al. 2000). Thus, Archean magmas have uniformly primitive, mantle-like values while the younger magmas show variable input from high δ18O sources. High values of δ18O form in low temperature processes related to sedimentation, weathering, and alteration, and indicate that supra-crustal lithologies were buried or subducted to the magma source regions and/or zones of contamination. The absence of high “S-type” oxygen isotope ratios in the Archean magmas suggests that these processes were less important in the early Earth.

Low δ18O igneous zircons have been found in rhyolites from Yellowstone (-0.4 to 5.8, Bindeman and Valley 2000a,b) and the Tiva Canyon tuff, Timber Mtn (δ18O=4.7). At Yellowstone, the low values are restricted to relatively small, post-caldera eruptions. These units have low δ18O quartz and zircon, disequilibrium Δ(Qt-Zc), and zoning of δ18O in zircon. Zircon cores are xenocrystic and normal in δ18O, while rims are low in δ18O. Estimates of zircon residence in low δ18O magma are on the order of 500-5000 years, ruling out catastrophic phreatic interactions of magma and meteoric water as have been proposed. A new model is proposed to form low δ18O rhyolites involving caldera subsidence followed by wholesale melting of the hydrothermally altered, down-dropped roof. Zircons from Yucca Mtn, near Timber Mtn also provide boundary conditions for estimating post-magmatic hydrothermal alteration. Zircons were separated from carbonate fault gouge in Trench 14. The proposal of hydrothermal zircons has lead to concerns about the proposed nuclear waste repository at Yucca Mtn. The δ18O values of zircon in carbonate gouge are similar to those from adjacent Tiva and Rainier Mesa tuffs and provide no evidence of hydrothermal activity (Bindeman and Valley 2000c).
Formation and Structure of Iron-Rich Oxyhydroxide Nanometer Coatings on Quartz: Comparison of Laboratory-Produced and Aquifer-Seeded Samples.

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Fe oxyhydroxides are potent scavengers of toxic oxyanions (arsenite, selenite, chromate) over a large pH range, and can also incorporate or sorb toxic metal cations under appropriate conditions. Recent work has shown that coatings of these materials, down to nanometer thicknesses, can be ubiquitous even in the cleanest sediments, effectively creating a large surface area sorbant that dominates mineral-water interface reactivity. This project combines three efforts to understand the nature, formation and alteration of these coatings in aquifer sediments: 1) laboratory sample preparation and characterization including both perfect single crystal surfaces and high surface area silica (Aerosil). 2) emplacement of perfect single crystal surfaces into sampling wells at aquifers where the sediments, conditions and chemistry is well described. These samples are withdrawn periodically to reveal coating formation and quartz surface degradation. 3) Characterization of coatings on natural quartz grains from these aquifers and elsewhere representing a range of formation environments. Characterization methods include synchrotron-based x-ray absorption spectroscopy in grazing incidence mode (GIXAS), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

Our work during the first half of FY 2000 was directed on analysis of the first two sets of perfect crystal samples from an aquifer sampling well at the Cape Cod site. The first samples extracted, after three months duration, did not have enough Fe for full analysis, but Fe concentrations on the surface were measured via total reflection x-ray fluorescence (TRXRF) at the Stanford Synchrotron Radiation Laboratory (SSRL), and partial GIXAS data were obtained. The six month samples had sufficient Fe in coatings for complete GIXAS and TRXRF analysis, as well as AFM imaging. TEM studies on sections of these samples are in progress at the National Center for Electron Microscopy (NCEM) at LBNL.

Our observations of initial laboratory-produced precipitates on Aerosil and on quartz r- and m-plane surfaces show a strong dependence on Fe3+ solution concentration and on dehydration. At low pH values that suppress oxyhydroxide polymerization in solution, individual inner sphere Fe3+ surface complexes dominate sorption only at coverages below 2% of a monolayer of surface silanol groups. With increased coverage, Fe oxyhydroxyl polymers form at the surface. These have hematite-like structure for r- and m-plane quartz surfaces with strong texturing such that the hematite (0001) axis is along the surface plane normal. No definite epitaxial relationship is observed suggesting either nucleation and growth on topologic (not molecular-scale) features, or nucleation in solution, possibly in locally dry areas. Drying and aging promotes polymerization (clustering and precipitation) in samples initially having only sorbed isolated complexes. This could explain how very low aqueous Fe3+ concentrations can lead to Fe3+ coating formation during drying of sediments in vadose zones. AFM images of clean m-plane surfaces show uniform terrace and step structure with step height of 2.6 Å, and terrace width of several thousand Å. The step edge is the preferred position for precipitation development and may catalyze polymerization.
Toward Measurement of On-Going \textit{In Situ} Upward Gas, Oil, and Water Movement in the Northern Gulf of Mexico

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Previous work provided evidence for on-going oil and gas injection (termed dynamic migration) into reservoirs of Eugene Island Block 330 (EI330) and areas to the south along the Louisiana Gulf Coast shelf edge and slope. Alterations to reservoired oils are produced by "gas washing", in which oil in reservoirs is "washed" with multiple volumes of upward migrating gas. Gas washing, together with oil biodegradation, is probably responsible for the hydrocarbon compositional changes that occur in some, but not all, EI330 oils on short time-scales (5-10 year). The result of gas washing working together with biodegradation is a very dynamic reservoir system where heavier n-alkanes are lost by ongoing biodegradation in the reservoir and are replaced by the lighter n-alkanes, which accompany gas washing.

Many lines of evidence indicate this on-going upward gas flow may not be restricted to the Gulf of Mexico, but might be part of a much larger phenomenon which occurs worldwide, particularly over active oil and gas generation areas in actively subsiding basins such as many of the world's major river deltas and continental margins. Even though this upward gas flow is probably very large volumetrically, it is often difficult to detect and quantify because the upward gas flow involved is highly localized and probably episodic. Here, we describe our initial research over the last few years aimed toward developing better \textit{in situ} seafloor methods for continuous detection and measurement of the gas amounts, compositions, and fluxes involved. \textit{In situ} measurements of gases would provide a crucial missing link in quantifying the importance of gas flux both at the sediment-water interface and in the subsurface - it is much easier to make these measurements at the sediment surface than in the subsurface. Furthermore, only 2\% of generated oil and gas is ever trapped in a producible reservoir, while about 54\% of the remainder is discharged at the sediment surface into the overlying ocean. Therefore, these \textit{in situ} measurements could also be important in understanding oceanic biogeochemical processes if this gas flux were delivering crucial nutrients to the ocean from deep sediment sources.

Our initial results from several recent cruises to the northern Gulf of Mexico will be described including:

1. A continuous fluorescence method for detection of oil and gas and water seepage in ocean bottom waters which may be suitable for monitoring large areas over long time periods; and

2. Initial results from \textit{in situ} gas measurements of bottom waters and sediment pore waters from two gas seep areas associated with gas hydrates in the Gulf of Mexico.
Biomineralization Associated with Bacterial Fe(III)-Oxide Reduction

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Iron(III) oxides are the primary redox buffering mineral phase in geochemical environments. Fe(III) oxides are utilized as electron acceptors by dissimilatory metal reducing bacteria (DMRB) that drive the reductive portion of the Fe-biogeochemical cycle in soils, sediments, and groundwaters. The bioreduction of Fe(III) oxides can lead to the formation of a variety of secondary mineral solids that play a key role in the solid-phase geochemical speciation of metal ions and contaminants, and in heterogeneous redox processes. Biomineralization reactions affect the thermodynamics and kinetic pathways of dissimilatory iron reduction.

The biomineralization process has been studied using fresh, aged, and heated hydrous ferric oxide (HFO). HFO is a form of poorly crystalline Fe(III) oxide that upon aging and heating transforms to more crystalline Fe(III) oxides including ferrihydrite, goethite, and hematite. We have incubated fresh and treated HFOs with *S. putrefaciens* and lactate under anoxic conditions and followed the kinetics of bioreduction and the biogenesis of secondary phases. The solution composition, CO$_2$(g) pressure, electron donor/acceptor ratio, and minor element composition of the HFO were varied to test hypotheses on biomineralization mechanisms. The identity, size, morphology, and composition of the secondary phases were studied by a combination of x-ray diffraction, variable temperature Mössbauer spectroscopy, and scanning and transmission electron microscopy. The biomineralization products included an array of fine-grained crystalline Fe(III) oxides (6-line ferrihydrite, goethite, lepidocrocite, and hematite), and Fe(II) containing solids including siderite, magnetite, green rust, and vivianite. Ours is the first report of the biogenesis of crystalline Fe(III) oxides and green rust. The results collectively support a conceptual model where the key factors governing biomineralization are the biogenic flux rate of Fe$^{2+}$, the electron/donor acceptor ratio, and the pH (influencing mineral stability and complexation to the residual oxide). A direct role of the cell surface in mineral precipitation was not observed.
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