B11A-06 0930h

Putative Mineral-Specific Proteins Synthesized by the Metal Reducing Bacterium *Shewanella oneidensis*

Brian H. Lower[1] (540-231-8575; blower@vt.edu)

Michael F. Hochella[1] (hochella@vt.edu)

Steven K. Lower[2] (lower.9@osu.edu)

[1]Virginia Tech, Department of Geological Sciences, Blacksburg, VA 24061, United States

[2]Ohio State University, Department of Geological Sciences, Columbus, OH 43210, United States

For over three billion years the Earth has been home to millions of different species of prokaryotic organisms. The life and propagation of many of these microbial cells has relied on intimate contact with mineral surfaces (e.g., the use of metal oxides as terminal electron acceptors). An interface is formed at the junction of a bacterium and a mineral surface that is, by its very nature, nanoscale in size. The process of natural selection has shaped bacteria such that they are masters of the art of synthesizing fully functional structures and utilizing properties that exist only at the nanometer scale. We have begun to explore the bacterium-mineral interface to determine precisely how fundamental, nanoscale forces guide and are themselves modulated by a cell's expression of outer membrane proteins localized at a mineral surface. Recent work in our laboratory suggests that a species of dissimilatory metal reducing bacteria expresses proteins that have a high affinity for specific mineral phases. Using biological force microscopy (BFM), we have discovered that one such organism, *Shewanella oneidensis*, appears to recognize the surface of iron hydroxides - versus isostructural aluminum hydroxide counterparts - such that it produces and/or localizes putative mineral-specific proteins at the interface with goethite (FeOOH). These particular high molecular weight proteins are expressed only under anaerobic conditions, when the Fe(III) in the mineral phase is expected to serve as the microorganism's terminal electron acceptor. Protein expression patterns provided by two-dimensional gel electrophoresis confirm that specific, high molecular weight proteins are targeted to the outer membrane of *S. oneidensis* when Fe(III) is provided as a terminal electron acceptor. The results suggest that these proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron oxide binding and/or Fe(III) reduction. If this is the case, than it is possible that the evolution of dissimilatory iron-reducing bacteria like *Shewanella*, could have been, at least in part, driven by the binding/reduction ability of certain proteins to specific mineral phases.

B11A-07 0945h

Modeling the Influence of Transport on Chemical Reactivity in Microbial Membranes: Mineral Precipitation/Dissolution Reactions.

Andrew Robert Felmy[1] (509-376-4079; ar.felmy@pnl.gov)

Chongxuan Liu[1] (509-376-0129; chongxuan.liu@pnl.gov)

Susan Clark[2] (sb.clark@wsu.edu)

Tjerk Straatsma[1] (tp.straatsma@pnl.gov)

James Rustad[3] (rustad@geology.ucdavis.edu)

[1]Pacific Northwest National Laboratory, Mail Stop K8-96 PO Box 999, Richland, WA 99352, United States

[2]Department of Chemistry Washington State University, One SE Stadium Way, Pullman, WA 99164-4630, United States

[3]Department of Geology University of California-Davis, One Shields Avenue, Davis, CA 95616, United States

It has long been known that microorganisms can alter the chemical composition of their immediate surroundings and influence such processes as ion uptake or adsorption and mineral precipitation dissolution. However, only recently have molecular imaging and molecular modeling capabilities been developed that begin to shed light on the nature of these processes at the nm to um scale at the surface of bacterial membranes. In this presentation we will show the results of recent molecular simulations of microbial surface reactions and describe our efforts to develop accurate non-equilibrium thermodynamic models for the microbial surface that can describe ion uptake and surface induced mineral precipitation. The thermodynamic models include the influence of the bacterial electrical double layer on the uptake of ions from solution and the removal, or exclusion, of ions from the surface of the cell, non-equilibrium diffusion and chemical reaction within the membrane, as well as a new thermodynamic approach to representing ion activities within the microbial membrane. In the latter case, the variability in the water content within the microbial membrane has a significant influence on the calculated mineral saturation indices. In such cases, we will propose the use of recently developed mixed solvent-electrolyte formalisms. Recent experimental data for mixed-solvent electrolyte systems will also be presented to demonstrate the potential impact of the variable water content on calculated ion activities within the membrane.

B11B MCC: 3014 Monday 0800h

Geologic Aspects of Carbon and Other Biogeochemical Cycles I *(joint with A, H, OS, PP, GC)*

Presiding: **E Barrera,** National Science Foundation**; D Sahagian,** University of New Hampshire

B11B-01 0800h

Neoproterozoic Seawater Sulfur Isotopes and the Evolution of Microbial Sulfur Species

Matthew T Hurtgen[1] (814.865.1178; mhurtgen@geosc.psu.edu)

Michael A Arthur[1] (arthur@geosc.psu.edu)

[1]Penn State Astrobiology Research Center and Department of Geosciences, Pennsylvania State University, University Park, PA 16802, United States

Canfield and Teske (1996) proposed that an increase in the variability of $\delta^{34}S_{pyrite}$ sometime in the Neoproterozoic−along with a corresponding increase in the isotopic difference between sulfate and pyrite ($\Delta^{34}S$)−resulted from a fundamental shift in the biogeochemical cycling of sulfur, facilitated by changes in the oxidation-state of the Earth's surface. They proposed that an increase in the depth of oxygenation of the surface ocean triggered the evolution of a non-photosynthetic sulfide-oxidizing bacteria and that these bacteria, in consortium with a host of microbes associated with the oxidative part of the sulfur cycle, were responsible for the increase in $\Delta^{34}S$ to values greater than 46 $^{o}/_{oo}$. However, $\Delta^{34}S$ values have been poorly constrained for the Neoproterozoic because the S isotopic composition of seawater sulfate has been largely unknown. In this study, we have reconstructed the S isotopic evolution of Neoproterozoic seawater sulfate by analyzing the isotopic composition of trace sulfate extracted from carbonates collected in South Australia, Namibia and Death Valley, CA. Our results indicate that Neoproterozoic $\Delta^{34}S$ values between ∼800 to 570 Ma were less than 46 $^{o}/_{oo}$ and that the apparent increase in $\delta^{34}S_{pyrite}$ variability during this time resulted from an ocean with low sulfate concentrations and rapidly evolving $\delta^{34}S_{sulfate}$−likely a consequence of severe late Neoproterozoic glacial events. Therefore, it is difficult to argue using S isotopes that a non-photosynthetic sulfide-oxidizing bacteria evolved at this time. Furthermore, we speculate that the evolution of a non-photosynthetic sulfide-oxidizing bacteria was not necessary for disproportionation reactions to operate. Rather, we argue that intermediate S species and disproportionation reactions were likely occurring through much of the Proterozoic and that the overall low $\Delta^{34}S$ is simply a function of more efficient pyrite burial in an ocean with fewer oxidants and low sulfate concentrations.

B11B-02 0815h

Active Microbial Methane Production and Organic Matter Degradation in a Devonian Black Shale

Anna M Martini[1] (ammartini@amherst.edu)

Steven T Petsch[2] (spetsch@geo.umass.edu)

Klaus Nuesslein[3] (nusslein@microbio.umass.edu)

Jennifer C McIntosh[4] (jmcintos@j.imap.itd.umich.edu)

[1]Dept. of Geology, Amherst College, P.O. Box 5000, Amherst, MA 01002, United States

[2]Dept. of Geosciences, University of Massachusetts-Amherst, 611 N. Pleasant St., Amherst, MA 01003, United States

[3]Dept. of Microbiology, 639 N. Pleasant St., Amherst, MA 01003, United States

[4]Dept. of Geological Sciences, University of Michigan, 425 E. University Ave., Ann Arbor, MI 48109, United States

Microorganisms employ many novel strategies to derive energy and obtain nutrients, and in doing so alter the chemistry of their environments in ways that are significant for formation and transformation of geologic materials. One such strategy is natural gas generation in sedimentary basins. Previous research has shown that stable isotopic signatures of CH_4, CO_2 and H_2O in formation waters of gas-producing black shales indicate a microbial origin for several economically viable natural gas reserves. However, these signatures leave several intriguing issues unaddressed, including the identity of the organisms and their metabolic roles and impacts on mineral, isotopic and biomarker signatures. We hypothesize that the extreme reducing conditions required for sedimentary basin methanogenesis are simply the end product of a cascade of microbial processes, initiated by anaerobic respiration of shale organic matter through NO_3, SO_4 and/or Fe(III) reduction, secondary processing of anaerobe biomass by fermentative organisms yielding volatile fatty acids and H_2, and ultimately CO_2 reduction and/or acetate fermentation to produce CH_4. This research holds importance for the several aspects of the geochemical carbon cycle. It describes anaerobic hydrocarbon degradation leading to methanogenesis in a sedimentary basin; in many instances this activity has generated economically viable reserves of natural gas. It also provides a benchmark detailing how post-depositional microbial activity in rocks may confound and overprint ancient biosignatures. Interpretation of past environmental conditions depends on molecular and isotopic signatures contained in ancient sedimentary rocks, separated from signatures of metabolically similar modern microbiota living in sedimentary basins. In addition, this research sheds light on an unrecognized and thus unconstrained source of reduced gases to Earth's atmosphere, important for understanding the rates and controls on carbon cycling through geologic time.

B11B-03 0830h

Natural Variations of δ^{30}Si Values During 4 Million Years of Progressive Basalt Weathering, Hawaii

Karen Ziegler[1] (805-893-5859; kziegler@geog.ucsb.edu)

Oliver A Chadwick[1] (805-893-4223)

Mark A Brzezinski[2] (805-893-8605)

Eugene F Kelly[3] (970-491-6881)

[1]Dept. of Geography, University of California, Santa Barbara, CA 93106, United States

[2]Dept. of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, CA 93106, United States

[3]Dept. of Soil and Crop Sciences, Colorado State University, Ft. Collins, CO 80523, United States

Terrestrial silicate weathering rates and processes are important for studies of modern and paleo-climate. Recently, Si isotope geochemistry has shed light on Si cycling in marine systems, which is directly linked to the terrestrial Si cycle as nearly 80% of the Si is supplied by continental run-off water. Understanding the terrestrial Si-isotope geochemistry is crucial for a more comprehensive understanding of the global Si cycle. Weathering of primary minerals in the pedosphere releases Si that can be incorporated into secondary minerals or leached into rivers and oceans. These are active Earth surface processes that are dependent on local climate and regional tectonics. If we understand how these processes impact soil formation we can interpret present soil properties in the context of past controls on weathering systems. Few direct tracers of weathering status exist; we most commonly use Sr isotopes to track silicate weathering, but it would be far more useful to use Si isotopes. Here we present the results of the first systematic effort to understand the variations of natural abundances of Si isotopes along a soil development gradient. We find that Si isotopes in soils are a promising indicator of weathering status in terrestrial systems and the rivers that drain them. Isotopic data from rock, secondary soil minerals and soil water from 5 soil pits along a 4.1 Ma basaltic weathering chronosequence on Hawaii demonstrate large and systematic variations of δ^{30}Si values. Unweathered basalt has a δ^{30}Si value of -0.5$^{o}/_{oo}$. Initial weathering leaches most of the Si from the top meter of soil, and converts the remaining Si into amorphous soil clay minerals. Bulk soil from >30 cm depth has δ^{30}Si values 0.5$^{o}/_{oo}$ more negative than fresh basalt. Soil water simultaneously evolves toward more positive δ^{30}Si values, leading to a Si-isotopic difference between solid and aqueous Si of 2.1$^{o}/_{oo}$. As weathering progresses, primary minerals are exhausted, and secondary amorphous minerals are transformed into crystalline phases. This second stage of mineral transformation produces even more negative $\delta^{30}Si_{bulksoil}$ signatures. Repeated transformation cycles cause the Si-isotopic ratios of both soil minerals and soil water to move in parallel towards more negative values. The oldest soil has a δ^{30}Si composition 2.1$^{o}/_{oo}$ more negative than that of fresh basalt, but still displays a 2.3$^{o}/_{oo}$ solid-aqueous difference. The top 30 cm of older soils contain atmospheric dust that

masks Si-isotopic weathering signatures. δ^{30}Si values of these soils of around -0.5$^o/_{oo}$ are more positive than those from deeper horizons. The top 0-5 cm of the soils show slightly lower $\delta^{30}Si_{bulksoil}$ values due to the presence of biogenic opal (phytoliths). Our data show that weathering and clay mineral and phytolith formation creates large natural Si-isotope variations, and confirm that secondary phases are a sink for negative Si isotopes. They also suggest that water from young, tectonically active areas will be of relatively high δ^{30}Si values, whereas water from old, stable continents will have relatively low values. Such a distribution is substantiated by the few, globally distributed river data.

B11B-04 0845h

Effects of Climate Change and Anthropogenic Organic Carbon Inputs on the Carbonate Mineral-Pore Water System

Andreas J Andersson[1] (808-9563285; aj@soest.hawaii.edu)

Fred T Mackenzie[1] (808-9566344; fredm@soest.hawaii.edu)

[1]Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, 1000 Pope Rd., Honolulu, HI 96822, United States

Future projections suggest that atmospheric CO_2 and organic matter deposition to the sediments of the coastal zone are likely to increase because of anthropogenic activities. Consequently, carbonate saturation state of surface ocean waters and sediment pore waters are likely to decline owing to increased invasion of atmospheric CO_2 and increased deposition and subsequent remineralization of organic matter within the sediment-pore water system, respectively. As a result of changes in the carbon chemistry of surface waters, marine calcareous organisms may have difficulty calcifying. Ultimately decreasing saturation states could lead to dissolution of calcareous sediments. In fact, dissolution of metastable carbonate minerals has been proposed as a mechanism to restore changes in surface water saturation state and pH owing to increased invasion of atmospheric CO_2, preventing any negative impacts on marine biogenic calcification. In addition, such changes in the carbon chemistry of the sediment-pore water system could have implications for the carbonate composition and reactivity of contemporary calcareous sediments. Numerical simulations based on the physical-biogeochemical box model *SOCM* (Shallow-water Ocean Carbonate Model) show that dissolution of sedimentary carbonate minerals could increase during the 21^{st} century, but will not result in the production of sufficient alkalinity to buffer the carbon chemistry of the surface ocean water against rising atmospheric CO_2. The carbonate saturation state of the sediment pore water is not significantly affected by changes in carbon chemistry of the overlying surface water, but is strongly controlled by microbial oxidation of organic matter within the sediment-pore water system. In the standard simulation of *SOCM*, the flux of DIC owing to remineralization of organic matter increased by 2.4% between 1700 and 2100. During the same period, cumulative dissolution of magnesian calcite minerals corresponded to approximately 6% of the total magnesian calcite mass present within the sediments at the initial conditions. Sensitivity analysis indicates that the extent of dissolution is mainly driven by remineralization of organic matter rather than carbonate reaction kinetics. Numerical results suggest that the dissolved carbonate ion activity of the pore water is controlled by a metastable equilibrium with the most soluble solid carbonate phase present within the sediments. Consequently, during early solutional diagenetic modifications on the seafloor owing to natural or anthropogenic processes, dissolution of carbonate minerals follows a sequence based on mineral stability, progressively leading to removal of the more soluble phases until the most stable phases remain. In the current simulation, the composition of magnesian calcite at metastable equilibrium with the pore water changed from 21 mol% Mg to 14 mol% Mg. Future decrease in average pore water saturation state is likely to alter this metastable equilibrium and could affect the average composition and rates of precipitation of carbonate cements in contemporary shallow-water sediments.

B11B-05 0900h

Geochemical Short Circuits: How Recycled Ancient Organic Matter Impacts the Biogeochemical Carbon Cycle

Steven T Petsch[1] (spetsch@geo.umass.edu)

Peter A Raymond[2] (peter.raymond@yale.edu)

Brett E Longworth[1] (brettl@geo.umass.edu)

[1]Dept. Geosciences, University of Massachusetts-Amherst, 611 N. Pleasant St., Amherst, MA 01003, United States

[2]School of Forestry and Env. Studies, Yale University, 205 Prospect St., New Haven, CT 06511, United States

Biogeochemists have commonly simplified the geological carbon cycle into fluxes between three carbon reservoirs, namely transfers between dissolved inorganic carbon and organic matter, and dissolved inorganic carbon and carbonate minerals. Using these simplifications a remarkably degree of understanding has developed regarding the pace and character of carbon cycling through geologic time. Isotope ratios in ancient carbonate minerals and organic materials can be understood as the result of specific changes in carbon fluxes and reservoir masses in the geologic past. Because formation and oxidation of organic matter directly involve the gases CO_2 and O_2, reconstructions of the geologic history of the carbon cycle lead towards information about the evolution of Earth's atmosphere, greenhouse conditions, and climate change. There is need to constrain the transformations of ancient sedimentary organic matter during rock weathering and riverine transport. A growing body of evidence suggests that these processes are less straightforward and more susceptible to biological activity than can be accommodated in simple models of the geologic carbon cycle. It has been shown that organic matter in sedimentary rocks provides a substrate for the growth of heterotrophic organisms during rock weathering and in the subsurface. Other studies have revealed that rivers draining ancient sedimentary rocks transport highly aged organic carbon to the oceans. Still other research has revealed that this aged organic matter is partially degraded by river and estuarine heterotrophs. Taken together, these efforts reveal that understanding of this key component of the geologic expression of carbon biogeochemistry, namely the transport and transformations of organic carbon between storage in sedimentary rock reservoirs and delivery to the ocean/atmosphere system as inorganic carbon, is less than complete. Building on several small case studies from rivers draining the eastern U.S. and entering the Mid Atlantic Bight, this study explores the possible impacts of ancient organic matter delivery to the oceans on diverse features and processes such as marine carbon pools and turnover rates; net carbon sequestration on land and delivery of terrigenous carbon to the oceans; global organic matter oxidation rates and influence on atmospheric composition; and isotope ratios of marine dissolved inorganic carbon through geologic time.

B11B-06 0915h

Carbon cycle dynamics in the geologic record: Speleothems as a source for new biogeochemical and paleoclimate information

Amy Frappier[1] (A.frappier@unh.edu)

Dork Sahagian[1] (dork.sahagian@unh.edu)

[1]CCRC/EOS & Earth Sci., University of New Hapmshire, Durham, NH 03824

Many of the key outstanding questions in paleoclimate and biogeochemical cycles involve terrestrial ecosystems. Caves provide an important depositional environment for sedimentary archives of past and present terrestrial environmental changes. Until recently, the tools available to the research community have been appropriate for coarse resolution studies, but have been inadequate to address other important questions such as: 1. How have climate changes affect ecosystem carbon cycling in the past? 2. What is the role of tropical ecosystems in climate change and the global carbon cycle? 3. How does disturbance affect below ground carbon processing and export to groundwater? Recent developments in the use of speleothems as a tool for carbon cycle and paleoclimate studies have opened the door for a fresh look at these perennial questions. Our recent carbon isotopic study of a speleothem from Belize indicates that terrestrial carbon cycling may be more sensitive to interannual climatic variability such as El Nino-Southern Oscillation (ENSO) than previously thought. In this case, the geologic record has revealed carbon cycle sensitivity to climate forcing that has not been instrumentally observable over the same period. A number of other studies have revealed intriguing correlations between the speleothem carbon isotopic record and various Earth system processes such as millennial scale climate variations and land use history. These results suggest that our understanding of speleothems as a biogeochemical tool remains largely unexplored. In order to better understand the utility of the speleothem carbon isotopic record, we are conducting a modern process study at the Belize cave site. This will enable us to calibrate the record preserved in speleothems for exploration of past carbon cycle behavior. Our initial analysis suggests that speleothems faithfully record variations in terrestrial ecosystem biogeochemical processes that are measurable in real time, and are thus a valuable research tool with considerable untapped potential.

B11B-07 0930h

Deconvolving the Carbon Isotope Record

Benjamin S. Cramer (benjamin@dges.tohoku.ac.jp)

Institute of Geology and Paleontology, Tohoku University, Aoba, Aramaki, Sendai 980-8578, Japan

The evolution of the whole-ocean δ^{13}C value, under an assumption of steady state with respect to mass, can be modeled as:

$$\frac{d}{dt}\delta_\Sigma(t) + \frac{\delta_\Sigma(t)}{\tau_C} = \frac{1}{\tau_C}\delta_F(t)$$

where δ_Σ is the whole-ocean δ^{13}C value, τ_C is the residence time of carbon and a net instantaneous δ^{13}C forcing function is defined:

$$\delta_F = \delta_i - f_{carb}\Delta_{carb} - (1 - f_{carb})\,\Delta_{org}$$

where δ_i is the δ^{13}C value of carbon input (e.g. weathering and volcanism), f_{carb} is the fraction of carbon removed through burial of carbonates as opposed to organic carbon, and Δ_{carb} and Δ_{org} are the differences between δ_Σ and δ^{13}C values for buried carbonate and organic carbon. The solution to this differential equation is:

$$\delta_\Sigma(t) = \frac{1}{\tau_C}\int_0^t \delta_F\left(t'\right) e^{\left(-\frac{t-t'}{\tau_C}\right)} dt'$$

which can be expressed as a convolution

$$\delta_\Sigma(t) = \frac{1}{\tau_C}\delta_F\left(t'\right) \otimes e^{\left(-\frac{t-t'}{\tau_C}\right)}$$

revealing that the evolution of the whole ocean δ^{13}C value is determined by the instantaneous δ^{13}C forcing (δ_F) subjected to a causal (i.e. phase-shifting) low-pass filter whose frequency response is dependent only on the carbon residence time. One consequence of this observation is that variance in δ^{13}C records should be concentrated at wavelengths >0.1 m.y., thereby explaining the persistent appearance of cyclicity dependent on orbital eccentricity (∼0.1 and ∼0.4 m.y. periods) in δ^{13}C records. I demonstrate that an assumption of non-linear forcing of f_{carb} by orbitally-forced variations in insolation can explain most of the structure of high-resolution δ^{13}C records throughout the Cenozoic. A second consequence is that τ_C and δ_F should be separable by numerical manipulation of δ^{13}C records. Two applications are 1) estimation of the residence time of carbon at various times in the past and 2) investigation of changes in the instantaneous forcing through time.

B11B-08 0945h

Marine Respiration Ratios

Wallace Smith Broecker[1] (845-365-8413; broecker@ldeo.columbia.edu)

Taro Takahashi[1] (845-365-8537; taka@ldeo.columbia.edu)

[1]Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W/P.O. Box 1000, Palisades, NY 10964-8000, United States

Considerable confusion exists regarding the choice of numerical values for the so-called Redfield ratios. Most often quoted are those determined by Redfield himself $O_2 : C : N : P = 138 : 106 : 16 : 1$. He determined these ratios based on the bulk chemical composition of plankton as well as changes in the chemical compositions observed in deep ocean waters. Hence, these ratios represent both the net utilization by plankton in surface waters and the respiration of biogenic debris in deep waters. Only in the mid 1980s did *Takahashi and Broecker (1985)* show that the deconvolutions based on nutrient distribution in northern Atlantic employed by Redfield were strongly biased by the admixing of waters from the southern Atlantic thermocline. Based on an analysis of global set, they proposed that an O_2 to PO_4 ratio of 176±6 characterized the entire interior of the major oceans. In the early 1990s, *Anderson and Sarmiento (1994)* conducted more elaborate calculations, which confirmed this contention. Recently *Li and Peng (2002)* challenged this conclusion claiming that the O_2 to PO_4 ratios range from 176 all the way down to 116 with the median value lying close to that proposed by Redfield. If their analysis proves to be correct, it brings into serious question the use of $PO_4{}^*$ as a quasi-conservative water mass tracer. In this talk, we will strongly defend the validity of the Takahashi- Broecker value. We will also suggest that the term Redfield ratio be restricted to the original 138 : 106 : 16 : 1 values and that the revisions be referred to as respiration ratios.