MIDWEST

GEOBIO 2013

GEOBIOLOGY SYMPOSIUM

The second annual MWGB symposium

held Saturday, September 28, 2013
at Indiana University-Purdue Unviersity Indianapolis
Campus Center, 4th floor, rooms 450 A and B
420 University Blvd, Indianapolis, IN 46202

Symposium Sponsors support was generously provided by

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Welcome to the second annual Midwest Geobiology Symposium!

The Midwest Geobiology Symposium is an opportunity for undergraduate students, graduate students, and postdocs to share their research with the regional geobiology community. We hope this will become an annual event bringing together students, faculty, and researchers from Midwestern colleges, universities, and research institutions.

Geobiology is an interdisciplinary research field that focuses on the coevolution of Life and the Earth. It encompasses diverse fields such as geology, geochemistry, biology, microbiology, chemistry, oceanography, climate science, and engineering.

The Midwest Geobiology Symposium provides a venue for the regional geobiology community to discover the recent advances occurring in our respective laboratories, to provide critical feedback to ongoing research, and foster collaboration and new research directions. We encourage the participation of researchers at all levels.

We are excited to host the symposium in Indianapolis. This year, the symposium has ninety participants from twenty institutions hailing from nine states across the Midwest. We've scheduled some events at local venues to show you a bit of what Indianapolis has to offer and the IUPUI Campus Center will be ideal location for the symposium.

Sincerely,

Greg Druschel and Bill Gilhooly

Department of Earth Sciences
Indiana University-Purdue University Indianapolis

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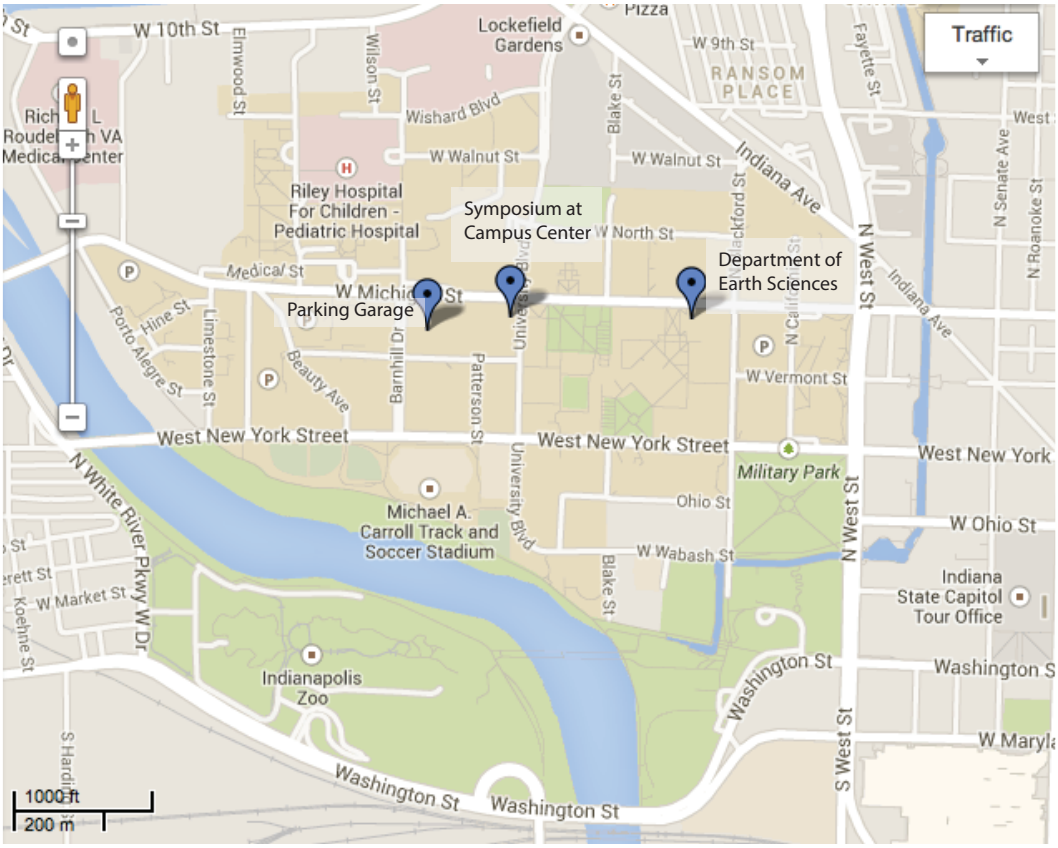
Wireless Internet Service for Visitors

AT&T offers free of charge wireless to visitors on the IUPUI campus. To connect, make sure your device's wireless networking (Wi-Fi) is turned on, and select the "attwifi" SSID. You may need to start your web browser to finish authenticating to AT&T.

Symposium Directions

The symposium will be held on the IUPUI campus at the Campus Center (420 University Blvd, Indianapolis, IN 46202) on the 4th floor, rooms 450 A and B.

Symposium parking is available in the Vermont Street Parking Garage located next to the Campus Center. A limited number of parking passes are available.



Program of events Saturday, September 28, 2013

8:30 am: Arrival and Breakfast

Oral Session I

10:00 am Brett Baker, University of Michigan, *Massive genomic reconstruction of cosmopolitan marine sediment microbial communities*

10:20 am Ben Harrison, University of Minnesota, *Characterization of microbial populations across geochemical and lithological boundaries in urban lake sediments under environmental change in Minneapolis-St. Paul*

10:40 am Brandon Briggs, Miami University, *Microbial Carbon and Nitrogen Cycles in Qinghai Lake Tibetan Plateau China*

11:20 am Dan Kekacs, Ohio State University, *Microbial Transformation of Hydraulic Fracturing Chemical Additives*

11:40 am Sarah Keenan, University of Tennessee, *Visualizing the early diagenesis of bone*

12:00 pm Shannon Flynn, University of Notre Dame, *Modeling Bacterial Metal Toxicity using a Surface Complexation Approach*

12:30 pm: Lunch

Oral Session II

1:30 pm Meghan Wagner, University of Central Michigan, *Redox Chemistry of West Antarctic Peninsula Margin Surface Sediments*

1:50 pm Fotios Kafantaris, Indiana University-Purdue University Indianapolis, *Geochemical dynamics in Yellowstone Springs: Sulfur chemistry changes at seconds-scale temporal resolution*

2:10 pm Thuy An, Indiana University, *Isolation of a new genus of sulfate reducing bacteria from water extracted from a coal bed*

2:30 pm Ted Flynn, Argonne National Laboratory, *The preferential reduction of elemental sulfur by metal-reducing bacteria under alkaline conditions*

3:20 pm Catherine Rose, Washington University in St. Louis, *Deciphering Earth History: Mapping the spatial distribution and speciation of sulfur in Ordovician carbonates*

3:40 pm Abigail E. Asangba, University of Illinois at Urbana-Champaign, *Reconstruction Of Ancient Microbial Biodiversity And Metabolism From Fossil Travertine*

4:00 pm Jeremy Fein, University of Notre Dame, *Keynote: Using surface complexation modeling to quantify bioavailability of metals to bacteria*

4:30 pm: Poster Session and Reception

7:00 pm: Conference Dinner

Keynote Presentation

Using surface complexation modeling to quantify bioavailability of metals to bacteria

JEREMY B. FEIN
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Determining the controls on metal bioavailability is crucial in order to understand the geomicrobiology of geologic systems with high metal concentrations, such as acid mine systems or contaminated soils, and in order to optimize bioremediation strategies aimed at remediating those types of systems. In addition, the controls on the rates of several environmentally significant metabolic processes, such as mercury methylation or bacterial reduction/oxidation of metals, are poorly understood. The key to improved models of all of these geomicrobiological processes is the ability to quantitatively model bacterial metal bioavailability. Metal adsorption onto bacterial cell walls represents the first interaction of a metal with the cell, and for this reason we hypothesize that accessibility of the metal to the cell is directly related to, and can be predicted by, cell wall metal speciation.

In the research that will be discussed, we test the hypothesis that bacterial surface speciation and concentration of heavy metals controls the bioavailability of those metals. Previous models of metal bioavailability (e.g., the Biotic Ligand Model) characterize metal binding onto a wide range of organisms using a generic, unspecified metal-binding biotic ligand that does not account for the many complexities of metal adsorption reactions onto biological surfaces. These models often fail because of these overlooked complexities in adsorption reactions. Over the past 15 years, we have learned much about the mechanisms involved in metal binding onto bacterial cell walls, and have developed quantitative surface complexation models based primarily on x-ray absorption spectroscopy and bulk adsorption measurements.

In this presentation, I will review my group's work to improve surface complexation models of bacterial metal binding, and to use those models to quantify the controls on the bioavailability of aqueous metals to bacteria. We have shown that bacterial chemotactic response and the enzymatic reduction of U(VI) are two examples of adsorption-controlled processes. The extent and rate of both of these processes can be directly related to the concentration of metal adsorbed onto the bacterial cell wall. Therefore, improving the sophistication and accuracy of surface complexation models of metal adsorption onto bacteria will lead to improved quantitative models of bacterial processes in realistic complex systems.

Abstracts (in alphabetical order of presenting author's last name)

Isolation of a new genus of sulfate reducing bacteria from water extracted from a coal bed

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Coal beds are anoxic subsurface environments with a unique range of aromatic and aliphatic compounds. Understanding microbial carbon metabolism in coal beds may be important for stimulating methane production. Although some studies have examined coalbed community structure using culture-independent methods, few reports have focused on the isolation and physiological characterization of microorganisms from coal or water extracted from coal beds. It is not unlikely that communities with unique metabolic properties have evolved over time due to constant exposure to the unique chemical composition of coal and the generally anoxic environment in coal beds. Our objective was to isolate and characterize microorganisms from coal beds to determine if long-term exposure to unique subsurface coal environments has selected novel microorganisms.

Co-produced water was anoxically collected from an active coalbed methane gas well in New Lebanon, Sullivan County, Indiana on December 3rd 2010. Microbial inocula from co-produced water were prepared by sterile, anoxic filtration of water using 0.2 μm pore size filters. Filter membranes with cells were then used to establish anaerobic enrichments for a variety of aromatic and aliphatic compounds under various electron acceptor conditions. Community analysis based on cloning 16S rRNA genes of a consortium of benzoate-oxidizing iron- and sulfate- reducing bacteria revealed the presence of both iron reducing bacteria (IRBs) and sulfate reducing bacteria (SRBs). A SRB was then isolated in pure culture using an agar dilution series. Based on the 1417bp 16S rRNA sequence of the isolate, the closest cultured phylogenetic relative of the new isolate was *Desulfarculus baarsii* DSM 2075 with only 92% 16S rDNA sequence similarity. Therefore, we propose this isolate (strain SCBM) as a new genus of SRB. Some of the closest relatives of SCBM in the NCBI database were uncultured bacterial clones extracted from coalbed water in China. This indicates that the unique anaerobic coal environment may have enriched SCBM and that such bacteria may be important members of the microbial community involved in carbon metabolism in coal beds. We have characterized this new isolate using phase contrast microscopy, scanning electron microscopy, and transmission electron microscopy. The results show that SCBM is vibrio-shaped and motile with a single polar flagellum. Preliminary data of substrate utilization range experiments show that, under sulfate reducing conditions, SCBM has the ability to use formate, acetate, pyruvate, butyrate, furmarate, and succinate as an electron donor and carbon source. Moreover, it could autotrophically grow using hydrogen and carbon dioxide. Current efforts are underway to determine the range of aliphatic and aromatic electron donors and electron acceptors that can be used by this isolate, and the roles of this microorganism in carbon biotransformation pathways under anaerobic conditions in coalbeds.

Our isolation of a new genus of sulfate reducing, benzoate-oxidizing bacteria as part of our research supports our hypothesis that long-term exposure to subsurface coal environments has selected for novel organisms. Coal environments may be an untapped source of unique microorganisms that expand our knowledge of the subsurface microbial community.

Reconstruction Of Ancient Microbial Biodiversity And Metabolism From Fossil Travertine

ABIGAIL E. ASANGBA[1*], YIRAN DONG[1], JOHN LINDO[2], RIPAN S. MALHI[2,3], ANNELEEN FOUBERT[4], RUDY SWENNEN[5], MEHMET OZKUL[6], BRUCE W. FOUKE[1,3,7]
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Abstract: A virtually unexplored frontier in the study of life in extreme environments is the extraction of genetic and environmental information directly from microbes entombed in calcium carbonate ($CaCO_3$) crystals in the geological record. An environmental metagenomic study has been initiated to systematically track the fate of microbial gene sequences, lipids and other "biomarkers" during the fossilization and diagenesis of Pleistocene terrestrial hot-spring travertine in Yellowstone National Park and the Pamukkale region of Turkey. The Mammoth Hot Springs corridor of Yellowstone contains thermal springs (73ºC) that are actively and rapidly (mm's/day) precipitating travertine, as well as a complete time-series of travertine deposits that extend back to the Pleistocene (~33 ka). Comparative samples have been collected from quarries in the Denizli Basin (700-900 ka). The goal is to quantitatively track the preservation of these biomolecules through geological time, across specific sequences of down-flow travertine depositional facies and use this information to accurately reconstruct the identity, activity and ecology of the ancient microbes and their hot-spring environments. Analyses are being conducted of biomarkers extracted from bulk rock (cm's in diameter) as well as micro-drilled samples (mm in diameter). Each travertine sample is first being quantitatively screened (optically and geochemically) to determine the extent and fabric of water-rock alteration. Biomass has been successfully extracted from 10 mm-diameter fluid inclusions in primary crystals, as well as inter-crystalline deposits, and is undergoing metagenomic sequencing.

Massive genomic reconstruction of cosmopolitan marine sediment microbial communities

Brett J. Baker, Cassandre Sara Lazar, Gregory J. Dick, Kai-Uwe Hinrichs, and Andreas Teske

Marine sediments contain a large portion of the planet's biomass and thus, microbial communities in them constitute a large component of the global biogeochemical cycling. The vast majority of microorganisms present below the seafloor are uncultured and their metabolisms are unknown. Several uncultured archaeal lineages, namely Miscellaneous Crenarchaeotal Groups (MCG), are ubiquitous and often abundant in anoxic sediments throughout the world. To resolve the metabolic capabilities of sediment communities we obtained plunger sediment cores from the White Oak River (North Carolina) estuary in October 2010. We employed massive high-throughput genomic sequencing of three sites at multiple depth multiple depths within the sulfate-rich, sulfate-methane transition (SMTZ) and methanogenic zones. Genomic assembly and binning from each of these zones has yield an unprecedented number (>120) of genomes belonging to uncultured sediment phyla. Among these genomes are several that belong to candidate divisions of Archaea and Bacteria, such as MCG, TMEG, SM2F11, WS3, OP8, TM6, SAR202, and OD1. Despite isotopic evidence of biogenic derived methane the deeper layers do not contain any currently known methanogens. Ongoing reconstruction of metabolic pathways present in these genomes is revealing the key ecological populations involved in sulfur, carbon and nitrogen cycling. This study is the first to reconstruct the genomes of numerous widespread sediment microbes and will dramatically expand our understanding of these mysterious groups.

Magnetic Susceptibility and Microbial Communities in Hydrocarbon-Contaminated Sediments

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Oil spills are an everyday occurrence and may become a long-lasting problem when large quantities of hydrocarbons escape into the environment. Some of the contamination may be cleaned up by physcial means, but in many cases, the oil becomes inaccessible, and the only solution for its elimination is biodegradation. In the past, hydrocarbon bioremediation was monitored by geochemical and microbiological testing. However, geophysical methods such as magnetic susceptibility (MS) may also be used to assess hydrocarbon bioremediation. Two sediment cores, one contaminated and one uncontaminated with hydrocarbons, were acquired from a field site in Bemidji, Minnesota. First, MS was measured with a Bartington MS probe. Then molecular microbiological methods such as denaturing gradient gel electrophoresis (DGGE), polymerase chain reaction (PCR), and the construction of 16S clone libraries were used to assess the microbial communities and diversity in the two cores. The results showed that MS was higher in contaminated sediments, particularly above the water table and at the oil plume resting on the water table where the highest peak in MS occurred. In addition, there was more microbial diversity in the contaminated core, where bioremediation was occurring. Iron-reducing bacteria were found above the water table, in an elevated area of MS. At the peak of highest MS, syntrophic bacteria and methanogenic archaea were the predominant members of the community, showing the oil plume was undergoing methanogenesis. In conclusion, since high MS was coincident with bioremedial microbiological communities, this geophysical method may be a suitable tool to assess hydrocarbon bioremediation, since it is less expensive and less time-consuming than traditional chemical and biological methods.

Connecting zinc partitioning and isotope fractionation during Fe(II)-catalyzed recrystallization of Fe(III) oxide minerals

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Fe(III) oxide minerals are abundant in soil, sedimentary, and aquatic systems [1]. Biogeochemical processes often cycle iron between the Fe(II) and Fe(III) redox states and play an important role in elemental cycles and the fate of trace metals in groundwater [2]. This cycling creates conditions where aqueous Fe(II) and solid Fe(III) oxide minerals coexist. Recent work has shown that these two forms of iron can undergo a series of secondary, abiotic reactions involving oxidative Fe(II) adsorption, electron transfer through the mineral, and reductive dissolution of Fe(III) at a spatially separate surface site. These reactions may cause the complete self-recrystallization of crystalline, thermodynamically stable iron oxide minerals such as goethite (alpha-FeOOH) and hematite (alpha-Fe_2O_3) [3-5]. It has been demonstrated that during this recrystallization process trace metals such as Zn may be incorporated into the structure of iron oxides via overgrowth in surface regions undergoing oxidative Fe(II) adsorption and may be released from the structure to aqueous solution in regions of a mineral surface undergoing reductive dissolution [6,7].

Zinc is vital for most living organisms and, it is integral to various biological processes and plays a role in enzymes and regulatory proteins. As a micronutrient, zinc is utilized in many microbrial processes, including methanogensis and methane oxidation, key process affecting natural gas formation, organic matter degradation in anaerobic soils and sediments, and the concentrations of greenhouse gases in the atmosphere. Zinc is also the second most abundant transition metal in seawater and is often used as a nutrient proxy in modern and ancient oceans. Metal availability limited by uptake by iron oxides is thought to have affected the rate of methanogenesis, and thus the evolution of the atmosphere and oceans, in the geologic past. In addition, zinc is a water and soil contaminant associated with mining and industrial activities [6,8,9]. In order to understand the processes affecting the availability and cycling of zinc in modern and ancient aquatic systems it is critical to identify the occurrence and extent of zinc repartitioning into iron oxides. While this is straightforward in model laboratory systems, in natural aquatic systems and samples from the rock record identifying this phenomenon is challenging.

Prior to this investigation, isotopic fractionations associated with trace metal incorporation during iron cycling have been unknown, and this research thus investigates whether such processes produce a stable isotope fractionation in trace metals such as zinc. In order to identify such fractionations, it is important to know the fraction of solid-associated metal incorporated into the mineral. Since this information cannot be provided by mass balance and chemical extraction approaches, this investigation is combining X-ray Absorption Fine-Structure (XAFS) spectroscopy and isotpic analyses utilizing a multi-collector inductively coupld plasma mass spectrometer (MC-ICP-MS). The coupling of these tools allows for the investiagtion of any fractionation of Zn isotopes observed during trace metal adsorption or incorporation. This investigation utilizes XAFS spectroscoy to quantify Zn incocorpration into the Fe(III) oxide minerals goethite and hematite during Fe(II)-catalyzed recrystallization and will also identify coordination changes that occur upon incorporation which is especially relavent for zinc which has been shown to be octahedrally coordinated in solution but tetrahedrally coordinated when incorporated into hematite. This information is required to interpret any observed isotopic fractionations of Zn during these processes because heavier isotopes tend to preferentially partition into stronger bonding environments (i.e., increased covalent character, lower coordination number, shorter bond length). The effects of Fe(II) concentration, pH, Fe(III) oxide mineral structure, and reaction time on the partitioning of Zn during the dynamic self-recrystallization of Fe(III) oxide minerals are being investigated, and this research will further our understanding of processes that modify the availability and fate of trace metals and provide a foundation for using stable isotope ratios to identify the occurrence of metal incorporation in modern and ancient aquatic systems.

(1) Kappler & Straub (2005) *Rev. Mineral. Geochem.* 59, 85-108. (2) Webber et al. (2006) *Nat. Rev. Microbiol.* 4, 752-764. (3) Catalano et al. (2010) *Geochim. Cosmochim. Acta.* 74, 1498-1512. (4) Williams & Scherer (2004) *Environ. Sci. Technol.* 38, 4782-4790. (5) Yanina & Rosso (2008) *Science.* 320, 218-222. (6) Frierdich et al. (2011) *Geology* 39, 1083-1086. (7) Frierdich & Catalano (2012) *Environ. Sci. Technol.* 46, 1519-1526. (8) Konhauser et al. (2009) *Nature* 458, 750-753. (9) Johnson et al. (2008) *Rev. Earth & Planetary Sci.* 36, 457-493.

Testing biological sources of variability in leaf wax D/H

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Leaf waxes record information about environmental growth conditions and are commonly used as proxies for reconstructing paleoclimate. Plants synthesize these protective leaf waxes during a process that involves incorporating hydrogen atoms from environmental water into waxy lipids, such as long chain ($> C_{20}$) *n*-alkanes and alkanoic acids. Hydrogen exists as two stable isotopes in nature: ^{2}H (also called Deuterium, or D) and ^{1}H. The relative ratio of these isotopes (D/H) in environmental water varies chiefly through variations in the hydrologic cycle. Because hydrogen atoms in leaf waxes are sourced from environmental water, the D/H of leaf waxes varies with water input.

Long-chain plant lipids are recalcitrant on geologic time scales. It is expected that sedimentary accumulations of leaf waxes will record changes in D/H of leaf waxes and environmental water over time. Initial studies demonstrate relationships between D/H of lipid biomarkers and D/H of their respective source waters in modern systems [1]. However, leaf waxes do not perfectly record D/H of environmental water. Rather, D/H from leaf waxes are offset from source water due to biological and other effects that are not fully established. Identification of the biological factors that control isotope signatures in modern environments is critical to confidently interpret the stable isotope record preserved in plant lipids.

To further develop the application of leaf waxes as a paleohydrology proxy, we are conducting a systematic study to examine differences in D/H of leaf waxes, environmental water, and leaf water of tropical plants. Plant specimens are collected from the Climatron at the Missouri Botanical Garden (St. Louis, MO), the Kampong National Tropical Botanical Garden (Miami, FL), and the Fairchild Tropical Botanic Garden (Miami, FL). Sampling methods test for biological variation across plants of different habits (e.g. shrubs, grasses, woody) and phylogenetic placement in order to determine whether systematic variations in D/H can be identified.

(1) Sachse, D., Billalut, I., Bowen, G. J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., et al. (2012). Molecular Paleohydrology: Interpreting the Hydrogen-Isotopic Composition of Lipid Biomarkers from Photosynthesizing Organisms. *Annual Review of Earth and Planetary Sciences, 40*(1), 221-249.

Characterization of Microaerophilic Fe(II)-Oxidation Utilizing *Marinobacter* from the Soudan Iron Mine

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Fe(II)-oxidizing bacteria act as important agents of environmental change and have significant influence on industry and infrastructure by contributing to the cycling of iron, sulfur, nitrogen, oxygen, and manganese. The microbial facilitated oxidation of Fe(II) to Fe(III) results in corrosion and biofouling of municipal water distribution systems as well as water-associated industrial structures. Despite a long and persistent scientific interest in the Fe(II)-oxidizing bacteria, little biochemical and genetic analysis has been conducted regarding this metabolism due to the particular requirements for their cultivation. Here we demonstrate light-independent, microaerophilic Fe(II)-oxidation at neutral pH by *Marinobacter* sp. strain JG233, isolated from the Soudan Iron Mine in Northern Minnesota. Unlike many of the current model organisms for microaerophilic Fe(II)-oxidation, JG233 grows heterotrophically to high cell densities on a variety of carbon sources, and is genetically tractable. Genetic tractability was demonstrated through the targeted deletion of the flagellin gene cluster, resulting in a motility deficient strain. Growth occurred at temperatures ranging from 2-37ºC, with an optimum temperature of 30ºC, and NaCl concentrations from 1-13%, with an optimum of 7%. JG233 tolerates a pH range of 5-10 with an optimum of 6, and is able to grow anaerobically respiring nitrate to nitrite. The 16S rDNA sequence of JG233 shares a 99.02% sequence identity with *Marinobacter guinea*, and a 98.8% sequence identity to *Marinobacter adhaerens* strain HP15. JG233 may utilize an uncharacterized mechanism of Fe(II)-oxidation, as the draft genome of JG233 does not contain homologs to proteins shown to be involved either in the oxidation or reduction of iron in other systems. *Marinobacter* strain JG233 represents a distinct model for the study of microaerophilic Fe(II)-oxidation at neutral pH as it is genetically tractable and capable of heterotrophic growth; traits previously unavailable in microaerophilic Fe(II)-oxidation models.

Testing the NADPH hypothesis for lipid D/H ratios

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The measurement of the hydrogen isotopic composition (D/H) of lipids is common in organic geochemistry, and has widespread application in paleoclimate (Sachse et al., 2012), biogeochemistry (Li et al., 2009), and petroleum geochemistry (Schimmelmann et al., 2006). Lipids derive their hydrogen from environmental water, but their D/H ratio is mediated by isotopic fractionation between water and lipid. Recently, a biochemical mechanism has been proposed to account for this fractionation, suggesting that lipid D/H is controlled by the D/H of hydride transferred to lipid from intracellular NADPH (Zhang et al., 2009). This hypothesis is supported by the observation that in many bacterial strains, lipid D/H varies as a function of central carbon metabolism. The pathways of central carbon metabolism are responsible for most NADPH production, and therefore lipid D/H varies in concert with the carbon source (Zhang et al., 2009).

Our laboratory is undertaking a set of experiments designed to test this hypothesis, by imposing strong deuterium depletion on intracellular NADPH while holding the carbon source invariant. To accomplish this, we use engineered strains with a perturbed mechanism of NADPH production. Our model organism is *Methylobacterium extorquens* AM1, a bacterium that is capable of growth on C1 compounds such as methanol, during which its growth is limited by its supply of reducing power (i.e. NADPH; Strovas and Lidstrom, 2009). During growth on methanol, NADPH derives from methylene tetrahydromethanopterin dehydrogenase, an intermediate step of the H_4MPT pathway that oxidizes formaldehyde to formate. We will measure the D/H ratio of lipid in this strain, which is expected to reflect this mode of NADPH production, and to show depletion relative to water similar to that observed in other organisms grown on C1 compounds.

We plan to compare this D/H ratio to that of an engineered strain of *Methylobacterium* in which the H_4MPT pathway has been inactivated and replaced by a non-orthologous glutathione-dependent pathway from *Paracoccus denitrificans* that produces NADH but not NADPH (Chou et al., 2011). Because carbon metabolism does not produce NADPH in this strain, reducing power is severely limited. Instead of deriving from carbon metabolism, NADPH in this strain derives from transhydrogenation of $NADP^+$ by the reaction

$$NADP^+ + NADH \leftrightarrow NADPH + NAD^+,$$

a reaction that is catalysed by nucleotide transhydrogenase (encoded by *pntAB*). The isotope effect associated with transhydrogenases is extremely large (800‰ to 3500‰; Jackson et al., 1999; Zhang et al., 2009), resulting in a low expected D/H ratio of the hydride transferred to lipid from NADPH. An observed severe depletion in lipids of the engineered strain will support the hypothesis of Zhang et al. (2009). We also plan to measure D/H depletion in a third, evolved engineered strain, in which a mutation has arisen in the promoter region of *pntAB*, upregulating expression of transhydrogenase (Chou et al., 2011).

By comparing these strains, we aim to disconnect the mechanism of NADPH production from carbon metabolism, testing the hypothesis that the production mechanism of NADPH controls lipid D/H. By comparing multiple strains in which the production of NADPH via transhydrogenase is variably regulated we hope that we can glean additional information about the effect of intracellular NADPH residence time on lipid D/H.

References

Chou, H.-H., Chiu, H.-C., Delaney Nigel, F., Segrè, D., Marx, C.J., 2011. Diminishing returns epistasis among beneficial mutations decelerates adaptation. Science 332, 1190-1192.

Jackson, J.B., Peake, S.J., White, S.A., 1999. Structure and mechanism of proton-translocating transhydrogenase. FEBS Letters 464, 1-8.

Li, C., Sessions Alex, L., Kinnaman, F.S., Valentine, D.L., 2009. Hydrogen-isotopic variability in lipids from Santa Barbara basin sediments. Geochimica et Cosmochimica Acta 73, 4803-4823.

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., Magill, C.R., McInerney, F.A., van der Meer, M.T.J., Polissar, P., Robins, R.J., Sachs, J.P., Schmidt, H.-L., Sessions, A.L., White, J.W.C., West, J.B., Kahmen, A., 2012. Molecular Paleohydrology: Interpreting the Hydrogen-Isotopic Composition of Lipid Biomarkers from Photosynthesizing Organisms. Annual Review of Earth and Planetary Sciences 40, 221-249.

Schimmelmann, A., Sessions Alex, L., Mastalerz, M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagensis and thermal maturation. Annual Reviews of Earth and Planetary Sciences 34, 501-533.

Strovas, T.J., Lidstrom, M.E., 2009. Population heterogeneity in *Methylobacterium extorquens* AM1. Microbiology 155, 2040-2048.

Zhang, X., Gillespie, A.L., Sessions, A.L., 2009. Large D/H variations in bacterial lipids reflect central metabolic pathways. Proceedings of the National Academy of Sciences 106, 12580-12586.

Microbial Carbon and Nitrogen Cycles in Qinghai Lake, Tibetan Plateau, China

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Saline lakes on the Tibetan Plateau are sensitive indicators to enviornmental change and the microbial response can either amplify or negate further change by altering the carbon and nitrogen cycles. Therefore, an Illumina metagenomic and metatranscriptomic dataset was created to provide baseline knowledge on the major metabolic pathways related to late-summer carbon and nitrogen cycling. Water samples were collected from the high elevation (3196 m), saline (12.5 g L^{-1}) Qinghai Lake. Bacteria dominated both the DNA (98%) and cDNA (58%) samples; however, a substantial amount (42%) of the cDNA reads was assigned to Eukaryota. Annotated reads depicted an autotrophic to heterotrophic carbon cycle. The DNA sample was dominated by autotrophic *Cyanobacteria* (mainly *Synechococcus*, 41.7% of the reads). In contrast, heterotrophic *Proteobacteria* (mainly *Gammaproteobacteria*, 20% of the reads) dominated the cDNA sample. Aerobic respiration was the most abundant heterotrophic pathway consistent with the dissolved oxygen in the lake water (8.9 ppm). In addition, annotated reads related to the nitrogen cycle identified the potential for N_2-fixation; however, no N_2-fixation transcripts were detected in the cDNA sample. N_2-fixation was likely inhibited by the presence of both nitrate and nitrite (0.39 and 0.13 mg L^{-1}, respectively). Aqueous ammonia was below detection limits and the assimilation of ammonia into organic molecules was the most active pathway. Transcripts of glutamine synthetase (*glnA*) were detected from both *Verrucomicrobia* and *Bacteroidetes*. In addition, nitrite reductases, both DNA and cDNA, were annotated within the *Bacteroidetes, Verrucomicrobia, Planctomycetes, Alphaproteobacteria, Betaproteobacteria*, and a fungus. These data show that the microbial communities in Qinghai Lake are involved in the carbon and nitrogen cycle, and provide baseline information on the microbial response to environmental change.

Tracking the Geochemical Trends in Transgressive Lithofacies Superjacent to Late Middle Pennsylvanian Coals (Carbondale Group) from Southern Indiana

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Two cores from southern Indiana that each contains a transgressive lithofacies sequence superjacent to coal seams were sampled for bulk geochemistry and stable isotopes. The geochemistry is expected to track environmental changes stemming from Late Pennsylvanian Midcontinent Seaway (LPMS) waters that inundated paleo-southern Indiana peat swamps. Capturing and documenting the changing geochemical parameters over this sequence (coal to black shale to grey shale) may reflect the influence of sulfate-rich marine waters flooding reduced organic-rich equatorial paludal environments. Geochemical upsection trends in both cores reveal changes in both the initial redox condition of the water column as well as changing bottom water redox conditions through time (TS%, C/S, Fe_T/S, TOC, Mo/TOC, Metal Inventories), offshore to nearshore trends in sediment deposition (Th/U, C/N, $\delta^{13}C$, Metal Inventories), large-scale differences in both the type and volume of the organics being deposited (TOC, $\delta^{13}C$, C/N), and differing rates of seawater renewal to the area from the West (Mo/TOC, Metal inventories). Side-by-side comparisons reveal similar upsection trends in most redox sensitive metal values (V, Ni, Mo, Cr, Fe, etc.), overall TOC, and in both the range and trends of $\delta^{13}C$. However, marked differences are seen in several parameters over the flooding interval: an increase in overall metal inventories in Core 3 relative to Core 2; an interval in Core 3 that contains significant pyrite enrichment containing high C/N, TS %, and Fe_T/Al; and several enriched ^{13}C values in the black shale of Core 3 that are not present in Core 2; all of these indicate that the water chemistry of the transgressive sequence differs perhaps due to a change in the paleoenvironmental conditions at the time of deposition. Developing an understanding of how these events took place on both a macro and micro scale is vital to understanding marine transgressions and inform our depositional models for organic matter sequestration into economically viable shales.

Isotopic evidence for anaerobic oxidation of methane in a small, ice covered arctic lake

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Methane (CH_4) is a potent radiative greenhouse gas, with arctic lakes contributing 6-16% of the annual CH_4 flux to the atmosphere[1]. Despite the abundance of lakes in the arctic, and the recognized importance of methane cycling to climate change and the global carbon cycle, little is known about CH_4 cycling within Arctic lakes, especially the importance of anaerobic oxidation of methane (AOM). The majority of CH_4 is produced within anoxic lake sediments by methanogenic archaea utilizing two main pathways: carbon dioxide (CO_2) reduction and acetate (CH_3COOH) fermentation. Both processes produce CH_4 that is depleted in ^{13}C via kinetic isotope effects, with $\delta^{13}C_{CH4}$ as negative as -110‰ for CO_2 reduction and -50 to -65‰ for CH_3COOH feremntation[2]. Hydrogen isotope effects during CH_3COOH fermentation cause large deuterium (D) depletions (δD_{CH4} = -531‰), whereas the D/H discrimination for CO_2 reduction is significantly less (δD_{CH4}=-170 to -250‰). Approximately 30-99% of CH_4 that reaches oxygenated sedments or water is consumed by CH_4-oxidizing methanotrophic bacteria. Under anoxic conditions, anaerobic oxidation of methane can also occur by utilizing alternative terminal electron acceptors other than dissolved oxygen. Stable isotope fractionation associated with CH_4 oxidation leads to ^{13}C depletion of produced CO_2 and ^{13}C enrichment in the residual CH_4[2]. Microbial communites involved in sulfate reduction, denitrificiation, and iron and manganese reduction have been linked to AOM processes in both freshwater and marine environments. Studies on methane production and consumption in freshwater lakes have rarely focused on AOM, with only a handful of documented examples. Furthur study of AOM is critical in assessing the relative importance of physical and biological processes controling methane emissions from freshwater lakes.

Here, we focus on isotopic evidence of AOM in one shallow arctic lake. Potentilla Lake is located approximately 5 km from the terminal moraine of the Russells Glacier, on the ice free margin of western Greenland. The lake occurs within a narrow valley overlying a structural shear zone, resulting in half-graben basin structure. Under open-water conditions of summers 2012 and 2013, a strongly developed thermocline and oxycline were present. Methane concentrations were at trace levels in the upper water column and incresed below 7m depth where water was completely anoxic. With decreasing [CH_4], and increasing [O_2], $\delta^{13}C_{CH4}$ became isotopically heavier upward though the water from column by ~30‰ from the sediment-water interface to the lake surface, suggesting consumption by CH_4-oxidizing methanotrophic bacteria. In winter 2013 the study site had an ice cover of ~2m overlying a completely anoxic water body. Similar to open-water conditions, methane concentrations increased with depth, suggesting oxidation of CH_4 under anoxic conditions. With increasing [CH_4], $\delta^{13}C_{CH4}$ became isotopically lighter downward through the water column, ranging from -31‰ under ice cover to -69‰ at the sediment-water interface. This shift of 38‰ in $\delta^{13}C_{CH4}$ furthur supports oxdiation in the upper but not lower part of the water column at Potentilla Lake. Analogously to $\delta^{13}C_{CH4}$, δD_{CH4} became isotopically lighter downward though the water column, raning from -48‰ under ice cover to -369‰ at the sediment-water interface. Corresponding $\delta^{13}C_{CH4}$ and δD_{CH4} from the water column display a positive linear correlation (R^2=0.96), further indicating active AOM. Sulfate concentration displays depth trends opposite to that of methane, with [$SO4^{2-}$] declining downward from 28 to 7μM. This trend of decreasing concentration with depth is observed in marine sediments where AOM is coupled to sulfate reduction (SDMO)[3]. Genomic analysis is planned to characterize the microbial community in Potentilla Lake. This work displays the first occurance of AOM linked to sulfate reduction in an arctic lake, representing a potentially critical mechanism controlling methane emissions in polar environments.

[1] Bastviken, D., 2004, Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate: Global Biogeochemical Cycles, v. 18, no. 4
[2] Whiticar, M. J., Faber, E., and Schoell, M., 1986, Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation-Isotope evidence: Geochimica et Cosmochimica Acta, v. 50, p. 693-709.
[3] Borrel, G., Jezequel, D., Biderre-Petit, C., Morel-Desrosiers, N., Morel, J. P., Peyret, P., Fonty, G., and Lehours, A. C., 2011, Production and consumption of methane in freshwater lake ecosystems: Res Microbiol, v. 162, no. 9, p. 832-847.

Microbial Organic Matter Diagenesis and Carbon Cycling within Deep-sea Antarctica Sediments

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Microorganisms mediate the majority of organic matter (OM) remineralization in marine sediments and are thus ultimately responsible for the preservation and removal of OM from the global carbon cycle. Unfortunately, the effects of climate change on these sedimentary communities and their biogeochemical pathways remain uncertain. From a marine perspective, increasing global temperatures result in the warming of ocean waters, changes of levels of primary production and fluxes of phytodetritus to the sediments below. This research investigated the microbial responses to differing OM fluxes experienced at two contrasting Antarctic settings: an offshore continental margin (sedimentation rate ~20m/Myr) and a near shore basin rich in diatomaceous sediments (sedimentation rate ~ 2cm/yr). Structural and $\delta^{13}C$ analyses of phospholipids, 454 sequencing of the SSU rRNA gene, measurements of total hydrolysable amino acids (THAA), porewater, and sedimentary geochemistry were used to characterize the interactive relationship between OM quality and resident microbial communities. Similar to most deep-sea environments, sediments of the continental margin are suggestive of refractory OM, as indicated by low THAA abundances (7 μmol g sediment^{-1} or 2% of total organic carbon (CO) in surface sediments), and relatively large abundances of non-protein amino acids β -alaine and γ -aminobutric (40% THAA in surface sediments). In contrast, sediments of the near-shore basin hold relatively labile OM, characterized by large THAA concentrations (120 μmol g sediment^{-1} or 40% of total OC in surface sediments) and relatively low amounts of β -alaine and γ –aminobutric (5% THAA in surface sediments). It is therefore reasonable that sediments of the near shore basin harbored higher bacterial cell numbers, as determined by phospholipid concentrations (~10^9 cells g^{-1}), than sediments from the continental margin (10^6-10^7 cells g^{-1}). Despite the differences of incoming OM quantity and quality, both sites appear to support heterotrophic communities as evident by $\delta^{13}C_{lipid}$ values, sequencing results, and interstitial and sedimentary geochemistry. Additionally, autotrophic activity in deeper sediments of the near shore basin is evident by increasing $\delta^{13}C_{DIC}$ values and methane concentrations with depth (maximum concentration 12.8 mM at 21.61 meters below sea floor). We hypothesized that autotrophic and methanogenic organisms are utilizing CO_2 derived from heterotrophic co-inhabitants to produce methane. Ultimately these observations imply that when increased primary production and phytodetritus fluxes create anoxic environments, labile OM preservation can occur, even when large heterotrophic microbial communities are present. Thus, anoxic sediments have the potential to be a valuable carbon sink for locations of high primary production, and could play an important role in regulating global ocean chemistry in response to climate change.

Assessment of GDGTs as paleotemperature proxies in a series of lacustrine sediments from southwestern Greenland

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The proven utility of glycerol dialkyl glycerol tetraethers (GDGTs) in the reconstruction of marine paleotemperatures has prompted assessment of the applicability of these proxies in lacustrine environments. This study of lake systems in southwestern Greenland near Kangerlussuaq seeks to examine the veracity of GDGTs as temperature proxies in these settings in concert with assessment of the effects of environmental variables on their distributions. GDGT distributions have been examined in sediments from a series of 5 lakes (informally named EVV Upper, EVV Lower, Teardrop, Potentilla, and South Twin) in a narrow valley, overlying a structural shear zone, extending from the Russell Glacier to the Søndre Strømfjord. The lakes are characterized by varied water chemistry (e.g. pH, $[SO_4^{2-}]$), a range of depths (4 – 8 m) and areas (0.19 – 3.17 ha), and different distances (2 - 7 km) from the edge of the ice sheet. The close proximity of the lakes within a single valley suggests that their temperature history and likely sources of GDGTs, both autochthonous and allochthonous, should be similar. None of the samples contained sufficient isoprenoid GDGTs to allow use of TEX_{86} (Schouten et al., 2002), whereas all samples contained significant abundances of branched GDGTs enabling application of other established GDGT-based proxies for temperature reconstruction. Temperatures recorded by surface sediments (using the calibration of Pearson et al., 2011) ranged from 7.4°C at Upper Lake (closest to the ice sheet) to 15.2°C at South Twin (furthest from the ice sheet), with the other 3 lakes yielding temperatures within this range. The proximity to the ice sheet appears to exert greater influence on the lake GDGT-based temperatures than other environmental parameters. Down-core GDGT records, obtained from Upper Lake and Lower Lake at 2 cm intervals, follow similar depth trends. Both sequences exhibit inter-sample temperature fluctuations of ~3°C (ranges 7.2 – 12.5 °C and 8.8 – 12.3°C, respectively) and Upper Lake also shows a progressive (7.4°C to ~10°C at 18cm) temperature increase with core depth. Elucidation of sources of GDGTs and sediment ages will benefit from ongoing analysis of soil samples collected from surrounding areas, down-core analysis of alkenones, and radiocarbon dating of sediment cores. These complementary data will help resolve the paleoclimate history recorded by GDGTs in these Greenland lake sediments thereby furthering knowledge of past climate changes in this critical region and advancing understanding of environmental controls on this molecular proxy.

Cyanobacterial EPS as a Matrix for Apatite Precipitation

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Phosphorites are marine sedimentary formations rich in the phosphorus-bearing mineral apatite: $Ca_5(PO_4)_3(F,Cl,OH)$. The mechanisms involved in marine precipitation and subsequent concentration of apatite are not fully understood, but some ancient and modern phosphorites show evidence of an association between phosphorite and microbes. Today, most phosphorites are forming under upwelling zones in oxygen minimum zones hosting extensive microbial mats. The role of microbes in the formation of marine phosphorites, long suspected, has yet to be elucidated and the mechanism(s) by which microbes may influence apatite precipitation is an active area of research. One possible mechanism may involve the polymeric nature of some organic substances: It is well-known that biogenic bone and tooth apatite nucleate and develop in close relationship with collagen, a polymeric macromolecular structure. Similarly, extracellular polymeric substances (EPS) have been shown to influence the precipitation of calcite by providing nucleation sites. As with calcite, microbial metabolism may be important for apatite precipitation in nature, but here we begin to explore only the influence of the organic matrix.

To explore the role of microbial EPS in the precipitation of apatite, we subjected EPS from *Crocosphaera watsonii 003,* a cyanobacteria that produces prolific EPS, to duplicate experimental conditions conducive to apatite precipitation. To slow ion diffusion sufficiently to preclude instantaneous precipitation, the EPS was placed within a plug of gelatin through which apatite constituent cations and anions diffused toward each other. EPS and non-EPS-containing gelatin was harvested after one and two weeks, and analyzed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. EPS fresh from culture and not subjected to experimental conditions was analyzed as a control. Calcium associated with the control EPS was detected, providing a possible mechanism for enhanced nucleation. Apatite precipitation within the gelatin plug was largely confined to well-defined precipitation bands, yet EPS outside of these bands also showed extensive apatite precipitation, further supporting the premise that microbial EPS can influence apatite precipitation.

Seasonal Occurrences and Production of Odorous Algal Metabolites (MIB and Geosmin) in Eagle Creek Reservoir, Central Indiana

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Cyanobacteria (blue-green algae) cause a multitude of water-quality concerns, including the potential to produce toxins and taste-and-odor (T&O) compounds. Algal metabolites (toxins and taste-and-odor compounds) may cause significant economic and public health concerns, and are of particular interest in lakes, reservoirs, and rivers that are used for drinking-water supply, recreation, or aquaculture. Many cyanobacteria produce intracellular and extracellular metabolites, such as biotoxins (microcystin and cylindrospermopsin) and T&O compounds (*e.g.*, 2-methylisoborneol (MIB), trans-1,10-dimethyl-trans-9-decalol (geosmin)) that impact water supplies in reservoirs, rivers, canals, and within water treatment plants. Geosmin and MIB have extremely low odor thresholds to humans and can be detected by consumers at concentrations as low as 5–10 ng/L (or ppt, part per trillion). Aesthetics are the primary criteria that determine consumer confidence in the safety of a water supply for water industries. These metabolites, particularly in dissolved (extracellular) forms, have been shown to be resistant to conventional water treatment. The presence of odorous metabolites in the finished water can be a source of numerous complaints by consumers. However, T&O compounds found in water have no known effects on human health.

Central Indiana water supply reservoirs have been experiencing T&O issues since at least 2002. Long term patterns show that taste-and-odor episodes are highly variable in frequency, intensity and duration between years and amongst the same reservoir. Occurrences of T&O episodes in central Indiana reservoirs are very often associated with the presence of blue-green algae. In Eagle Creek Reservoir, T&O events have been increasing in intensity, in duration and are becoming more frequent since 2007. First detections of MIB and/or geosmin in the raw water of the reservoir most often appear during the months of April and May while a spring bloom of Oscillatorialean Cyanobacteria (*Pseudanabaena* and *Planktothrix*) is growing. Production of these T&O compounds is also often associated with production of the cyanotoxin, Microcystin.

Assessment of GDGTs as paleotemperature proxies in a series of lacustrine sediments from southwestern Greenland

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The proven utility of glycerol dialkyl glycerol tetraethers (GDGTs) in the reconstruction of marine paleotemperatures has prompted assessment of the applicability of these proxies in lacustrine environments. This study of lake systems in southwestern Greenland near Kangerlussuaq seeks to examine the veracity of GDGTs as temperature proxies in these settings in concert with assessment of the effects of environmental variables on their distributions. GDGT distributions have been examined in sediments from a series of 5 lakes (informally named EVV Upper, EVV Lower, Teardrop, Potentilla, and South Twin) in a narrow valley, overlying a structural shear zone, extending from the Russell Glacier to the Søndre Strømfjord. The lakes are characterized by varied water chemistry (e.g. pH, $[SO_4^{2-}]$), a range of depths (4 – 8 m) and areas (0.19 – 3.17 ha), and different distances (2 - 7 km) from the edge of the ice sheet. The close proximity of the lakes within a single valley suggests that their temperature history and likely sources of GDGTs, both autochthonous and allochthonous, should be similar. None of the samples contained sufficient isoprenoid GDGTs to allow use of TEX_{86} (Schouten et al., 2002), whereas all samples contained significant abundances of branched GDGTs enabling application of other established GDGT-based proxies for temperature reconstruction. Temperatures recorded by surface sediments (using the calibration of Pearson et al., 2011) ranged from 7.4°C at Upper Lake (closest to the ice sheet) to 15.2°C at South Twin (furthest from the ice sheet), with the other 3 lakes yielding temperatures within this range. The proximity to the ice sheet appears to exert greater influence on the lake GDGT-based temperatures than other environmental parameters. Down-core GDGT records, obtained from Upper Lake and Lower Lake at 2 cm intervals, follow similar depth trends. Both sequences exhibit inter-sample temperature fluctuations of ~3°C (ranges 7.2 – 12.5 °C and 8.8 – 12.3°C, respectively) and Upper Lake also shows a progressive (7.4°C to ~10°C at 18cm) temperature increase with core depth. Elucidation of sources of GDGTs and sediment ages will benefit from ongoing analysis of soil samples collected from surrounding areas, down-core analysis of alkenones, and radiocarbon dating of sediment cores. These complementary data will help resolve the paleoclimate history recorded by GDGTs in these Greenland lake sediments thereby furthering knowledge of past climate changes in this critical region and advancing understanding of environmental controls on this molecular proxy.

Evaluating Plant-derived Terpenoids as Paleovegetation Proxies with Paleogene megafloras and Plant Biomarkers from the Bighorn Basin, USA

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Plant terpenoids (defense compounds synthesized from the 5-carbon building block isoprene) have a long history of use as geochemical plant biomarkers, and potentially can be used to reconstruct changes in the abundances of major land plant groups in rocks and sediments that do not preserve plant megafossils or pollen. Pentacyclic triterpenoids are synthesized almost exclusively by angiosperms whereas conifers produce the tricyclic diterpenoids. Many previous studies have focused on the use of di- to triterpenoid ratios to reconstruct floral changes in the geologic past, however few studies have compared terpenoid-based paleoflora proxies to pollen or megafossils. Prior reconstructions also did not take into account differences in biomarker production between plant functional types, such as deciduous and evergreen plants, which can be quite large.

To investigate the use of terpenoids as paleoflora proxies, we examined sediments from the Bighorn Basin (Wyoming, USA) where ancient megafloras have been studied in detail. We analyzed di- and triterpenoid abundances as well as plant leaf waxes (*n*-alkanes) and other biomarkers in a total of 75 samples from 15 stratigraphic horizons from the late Paleocene (62 Ma) to early Eocene (52.5 Ma). By comparing terpenoid ratios with abundances estimated from plant megafossils, we can evaluate the utility of terpenoids as paleovegetation proxies.

In nearly all samples, angiosperm triterpenoids are significantly lower in abundance than conifer diterpenoids. This contrasts with leaf fossil data that indicate paleofloras were dominated by angiosperms in both abundance and diversity. Traditional use of terpenoid paleovegetation proxies would therefore significantly overestimate the abundance of conifers, even when accounting for plant production differences. To determine if this overestimate is related to the loss of angiosperm triterpenoids (rather than enhanced production of diterpenoids in the geologic past), we compared angiosperm triterpenoids to the *n*-alkane leaf waxes, which are produced primarily by angiosperms. After accounting for concentration differences between these two biomarker groups in modern plants, it is apparent that triterpenoid amounts are still significantly lower than expected in nearly all of our samples. We suggest a loss of triterpenoids might be related to enhanced diagenesis of triterpenoids in oxidizing terrestrial sediments. In order to reconstruct paleovegetation we propose a new method that employs a ratio of diterpenoids (conifers) to *n*-alkanes (angiosperms) and accounts for biomarker biomass abundance differences. Using this approach, we estimate paleovegetation communities similar to those predicted from megafossils. Although this new biomarker-based paleovegetation proxy works for sites within the Bighorn Basin, we stress this approach will need to be evaluated for other depositional environments using pollen or megafossil data.

Natural Organic Matter Characterization to Better Understand Uranium Mobility in Aquifer Systems

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A major factor in bioremediation of uranium (U) is long term sustainability. The solubility of U is influenced by the form of natural organic matter (NOM) in aquifer systems. At the Department of Energy's Integrated Field Research Challenge (IFRC) site in Rifle, Colorado bioreduced soil zones that are high in NOM are enriched in U, suggesting that NOM sequesters U in subsurface aquifers. However, other studies assessing the role of NOM on U solubility have shown that sediments readily release U when in contact with aqueous phase humic and/or fulvic acids. In order to address how NOM influences U solubility, samples were collected from ten key hydrologic locations at the Rifle field site including a seep/spring, a shallow subsurface aquifer, and the Colorado River. Samples within the aquifer include multilevel wells, wells within bioreduced zones, and background wells. Dissolved organic matter (DOM) was extracted using solid phase extraction columns with recoveries between 65-80%. Recovered DOM was analyzed in duplicate using Fourier transform ion cyclotron mass spetrometry with electrospray ionization (ESI FT-ICR-MS) at the Environmental Molecular Sciences Laboratory. The bulk compositions of the samples were compared and showed variations between the hydrologic sources. Colorado River DOM had a greater percent carbon heteroatoms (CHO) whereas groundwater and seep samples were dominated by sulfur heteroatoms (CHS/CHOS) reflecting the relative mixing of these hydrologic sources with atmospheric oxygen. Data analysis is currently underway to determine which chemical structures (lignins, lipids, proteins, hydrocarbons, etc.) dominate the samples and how these signatures change as a result of microbial processing. Ongoing studies include the injection of extracted DOM to Rifle groundwater and sediment microcosms to monitor changes in U through time. These studies will help elucidate how differing NOM sources and their molecular composition may influence solubility of U through the use of the ultra high resolution mass specrtometry analytical method FT-ICR-MS with ESI.

Secondary Ionization Mass Spectrometry (SIMS) Applications in Geobiology

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Secondary ionization mass spectrometry (SIMS) allows for high spatial resolution (μm-scale) *in situ* analysis of elemental and/or isotopic compositions in a variety of solid-phase samples. A new Cameca ims 7f-geo SIMS instrument is being installed at Washington University this fall (Nov 2013). This instrument has been optimized for high-sensitivity and high-precision, allowing for the rapid analysis of a variety of stable isotope and trace element proxies of geobiological interest. Here we highlight some SIMS applications in modern and ancient environments, including using sulfur isotopic variability ($\delta^{34}S$) to understand: (1) the spatial organization and ecological structure in modern microbial mats; (2) the impact of syndepositional reworking and diagenetic alteration on $\delta^{13}C_{carb}/\delta^{18}O_{carb}/\delta^{34}S_{CAS}$ in Ordovician carbonates from Anticosti Island, Quebec; and (3) how multiple stages of sulfidization impact $\delta^{34}S$ and $\Delta^{33}S$ signatures in Archean pyritic shales.

Modern Microbial Mats

The sulfur isotopic compositions of aqueous and sedimentary sulfate and sulfide species provide insights into modern microbial ecology. These observations can provide constraints on the occurrence and environmental importance of particular microbial metabolisms. However, interpretations of isotopic data are frequently non-unique and additional information is necessary to reconstruct the breadth of sulfur cycling metabolic activity. Here we document spatial variability in stable isotopic composition of aqueous sulfide ($\delta^{34}S$) measured by SIMS at a spatial resolution of ~1-50 um, and linked together to construct 2D isotopic datasets that document vertical isotope gradients as well as lateral heterogeneity on a scale comparable to traditional mesoscale analyses. These data can be paired with molecular and microscopic characterization of sulfur-cycling organisms to gain insight into the spatial distribution of different microbial metabolisms and to link changes in these to variations in the isotopic composition of the ambient H_2S pool. This understanding allows us to refine our understanding of the environmental controls on microbial metabolic activity and how the signatures of this activity can be encoded in sediments and preserved over geologic time.

Ordovician Carbonate Strata

The proliferation of carbonate-associated sulfate (CAS) isotope analyses in recent years has revolutionized our understanding of marine sulfur cycling over Earth history. In marine carbonate rocks, $\delta^{34}S_{CAS}$ is often thought to be a faithful recorder of marine sulfate $\delta^{34}S_{SO4}$. However, as the chemostratigraphic record becomes better resolved in time and space, reports of coeval but discordant $\delta^{34}S_{CAS}$ values are becoming increasingly common. These differences could arise in part from (a) water column stratification or physiographic separations between separate ocean basins; (b) syndepositional processes that decouple the relationship between $\delta^{34}S_{SO4}$ and $\delta^{34}S_{CAS}$ during deposition or prior to lithification; or (c) diagenetic alteration of the $\delta^{34}S_{CAS}$ signal following deposition. To help disentangle these processes, we present a microanalytical approach to analyze $\delta^{34}S_{CAS}$ by SIMS with a precision of ~1‰. With a spatial resolution as low as ~ 5 μm, it is possible to analyze suites of primary and diagenetic phases, including individual carbonate grains, muds, and cements. Preliminary results indicate that $\delta^{34}S_{CAS}$ can vary by as much as 10‰ between phases in a single sample. This scale of analysis allows for a rigorous evaluation of the susceptibility of $\delta^{34}S_{CAS}$ to syndepositional and diagenetic alteration, especially when coupled with parallel SIMS analysis of $\delta^{13}C_{carb}/\delta^{18}O_{carb}$ and diagnostic trace element abundances.

Archean Pyritic Shales

Sulfur isotope data have been used to provide significant insights into Archean biogeochemical cycling. Small fractionations in $\delta^{34}S$ have been used to argue for low sulfate concentrations in the Archean ocean and large, mass-independent ($\Delta^{33}S$, $\Delta^{36}S$) signatures in Archean age strata are one of the most robust indicators for anoxic atmospheric (and oceanic) conditions at this time. These interpretations often rest on data collected from bulk samples (cm- to m-scale) and here we investigate the additional information that can be gained about the operation of the Archean sulfur cycle by analyzing isotopic compositions on much finer spatial scales using SIMS to generate relatively non-destructive sulfur isotope ratio data at high spatial resolution (~1-10μm). While SIMS analysis of $\delta^{34}S$ variability is not, in itself, new, here we conduct numerous (50 - 500) analyses in a regularly spaced framework over a length scale of just a few mm. This allows for the identification of significant isotopic trends that are not possible to observe using conventional techniques or even by relatively cursory surveys at higher spatial resolution. Specifically, by analyzing samples in a regular grid framework, we can meaningfully link the data from successive measurements, allowing for the identification of 'long-range' (e.g., mm-scale) trends. We demonstrate the power of our approach by examining spatially coherent sulfide isotope variability in pyritic Archean black shales, which are characterized by multiple successive episodes of sulfidization, each of which can possess their own unique $\delta^{34}S$ and $\Delta^{33}S/\Delta^{36}S$ values. The isotopic variability within a particular generation of sulfide preserves information about the physical/biological processes associated with their formation, whereas the isotopic differences between success generations of sulfide precipitation record a picture of environmental change during deposition, early (soft-sedimentary) diagenesis, and late-stage (post-lithification) diagenesis.

We hope that this new SIMS instrument will be of interest to the Midwestern Geobiology community and look forward to discussing collaborations at the symposium.

Pearl in the mud: Genome assembly and binning of a *Thiomargarita*-like bacterium and associated epibionts from an environmental metagenome

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Geobiology and Metagenomics

As the study of microbes and their impact on their surrounding environment grows, it is ever more important to understand the machinery that drives the metabolism and development of these organisms. As it is now much more cost-effective to sequence bacterial genomes, environmental metagenomic assembly is a very attractive option for obtaining the genetic blueprints of bacterial physiology. Bailey et al. (2011) [1] reported on an apparent dimorphic life cycle in attached *Thiomargarita*-like bacteria, including *Thiomargarita nelsonii*. As one of the world's largest bacteria, the ecophysiology of *Thiomargarita*-like bacteria pose a particularly interesting quandary, as neither their developmental biology, their gigantism, nor their metabolic activity is well understood. In order to investigate the genetic basis for these modes, we used a single cell MDA amplification approach on *T. nelsonii buds* (Figure 1) released from stalks attached to the shell of a gastropod, which was collected at the Hydrate Ridge methane seep off of the coast of Oregon. Next-generation sequencing (Illumina 1.8) produced a metagenomic product consisting of short reads (100 bp) representing both *T. nelsonii* and attached epibiont bacteria. These reads were assembled into contigs using both Iterative De Bruijn Graph Assemblers with Uneven Depth (IDBA-UD) and MetaVelvet, binned using the tetranucleotide frequency of the resultant contigs, and re-assembled using a more stringent OLC assembler (cap3). We show here a complete denitrification pathway, previously unseen in large, vacuolated, sulfur-oxidizing bacteria, and the genes necessary for accumulation of phosphorous in the form of polyphospate, thought to be an important contribution to the phosphorous cycling. Continued work will include a comprehensive study of the assembled genome and associated metagenome with the goal of better understanding the ecophysiology of the substrate-attached *Thiomargarita* and the epibiont community associated with them, alongside a comparative study of the metabolic pathways that *Thiomargarita* and similarly equipped gammaproteobacteria employ.

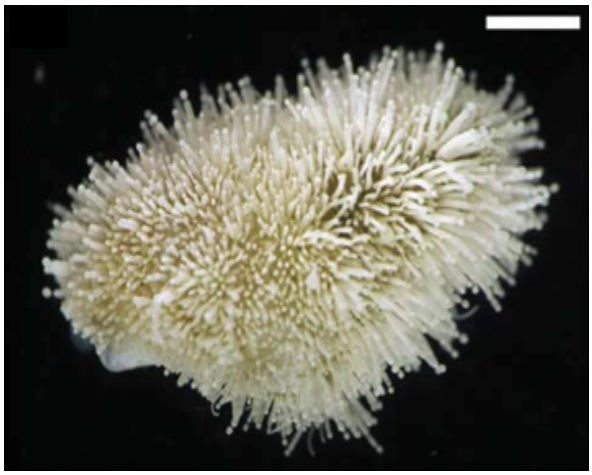

Figure 1: The microbial community present on the shells of the gastropod *Provanna laevis*, recovered from the Costa Rica margin and the Hydrate Ridge. The elongated, immobile form of *T. nelsonii* forms a fur-like coat. Scale bars represent ~1 mm.

[1] Bailey JV, Salman V, Rouse GW, Schulz-Vogt HN, Levin LA, Orphan VJ. (2011). *Dimorphism in methane seep-dwelling ecotypes of the largest known bacteria*. **The ISME Journal** 5: 1926-1935.

Modeling Bacterial Metal Toxicity using a Surface Complexation Approach

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In this study, the detailed understanding of the metal binding reactions on bacterial cell envelopes was used to create an advanced biotic ligand model based on mechanistic adsorption reactions of the surface complexation model (SCM) and used to relate metal toxicity to the speciation and concentration of the metal adsorbed to the bacterial surface. Batch measurements of Cd toxicity to *Bacillus subtilis* was used to validate and calibrate this approach. Bacterial growth was measured by optical density (O.D.) in the presence of a constant Cd concentration of 1 or 2 ppm. EDTA was added to control the bacterial adsorption of Cd, using EDTA:Cd molar ratios of 0, 0.25, 0.5, 1 and 2. Cd induced growth inhibition was measured as a growth factor which was calculated as the experimental O.D. divided by the O.D. of the corresponding Cd-free control at each time point. In all cases, a minimal growth medium was used to limit variables, allowing the precise calculation of aqueous and surface speciation of Cd for each experimental condition. These calculations used previously determined site-specific binding constants, acidity constants and site concentrations for the *B. subtilis* cell envelope functional groups. Cd toxicity increased with decreasing EDTA concentrations. A strong correlation between the total concentration of adsorbed Cd and the calculated growth factor was observed, with a dramatic increase in the growth factor when adsorption was less than 0.31 μM/g. Results suggest biotic ligand models that incorporate more sophisticated models of the metal binding environment on cell walls, such as the SCM, are more flexible and accurate than current bioavailability models. Therefore, advanced bacterial biotic ligand models that include mechanistically-sound metal binding reactions enhance our ability to predict metal bioavailability in complex geologic systems.

The preferential reduction of elemental sulfur by metal-reducing bacteria under alkaline conditions

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Geochemical modeling suggests that under alkaline conditions, the direct microbial reduction of ferric iron (Fe^{III}) ceases to be energetically favorable. Under these conditions metal-reducing bacteria must utilize alternative electron acceptors to survive. These models also show that the reduction of elemental sulfur (S^0) provides more energy with increasing pH. Under these conditions, S^0 is produced by the reaction of ferric minerals with dissolved sulfide provided by sulfate-reducing bacteria. Results from bioreactor experiments conducted at a pH of 9 show that *Shewanella oneidensis* strain MR-1 can enzymatically reduce S^0 but not goethite ($Fe^{III}OOH$). The HS^- produced by the reduction of S^0 reduces goethite abiotically. In alkaline environments where direct enzymatic reduction of Fe^{III} is not favorable the reduction of Fe^{III} may proceed via this indirect route. In the absence of geological deposits of S^0, which are rare in the terrestrial subsurface, metal-reducing bacteria such as *Shewanella* may require active sulfate reduction (and the reaction of sulfide with ferric minerals) to provide S^0 for respiration. These results provide valuable insight into redox-active biogeochemical cycling processes within subsurface environments that receive injections of supercritical CO_2 and the dependence of its subsequent mineralization on the activity of metal- and sulfate-reducing microorganisms.

Microbial Fe(III) oxide reduction potential in Chocolate Pots hot springs, Yellowstone National Park

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Previous research into microbial Fe(III) reduction in Yellowstone National Park has focused on high temperature, low pH environments where microbial communities are able to utilize soluble Fe(III) as an electron acceptor for respiration. Much less attention has been paid to Fe(III)-reducing microbial communities in lower temperature, circumneutral pH environments, where solid phase Fe(III) oxides are the dominant forms of ferric iron. This study explored the potential for microbial reduction of Fe(III) in the warm (ca. 40-50°C), circumneutral pH (ca. 6.0-6.5) Chocolate Pots hot springs (CP) in Yellowstone National Park. Endogenous microbial communities were able to reduce native CP Fe(III) oxides, as documented by most probable number (MPN) enumerations and ongoing enrichment culture studies. Enrichment cultures have demonstrated sustained Fe(III) reduction tied to acetate and lactate or H_2 oxidation. These cultures have also exhibited growth through reduction of synthetic amorphous Fe(III) oxides and oxidation of either acetate or lactate alone. The extent to which bacterial sulfate reduction contributes to Fe(III) reduction was explored by eliminating sulfate from the culture media, and inhibiting sulfate reduction with molybdate. Results indicate that bacterial sulfate reduction does not contribute extensively to Fe(III) reduction. Genomic DNA was extracted from the enrichment cultures for 16S rRNA gene pyrosequencing. The results showed that dominant bacterial sequences were closely related to the well known Fe(III) reducer *Geobacter metallireducens*. Additional taxa included relatives of *Desulfohalobium* and *Thermodesulfovibrio*, although their involvement in Fe(III) reduction remains unclear at this time. Future studies will include metagenomic analysis of existing enrichments, as well as materials from newly collected sediment cores and in vitro Fe(III) reduction experiments. Together these studies will provide the first detailed insight into the reductive side of the iron redox cycle in Chocolate Pots hot springs, setting the stage for future studies of coupled iron reduction and oxidation and the influence of these processes on the stable iron isotope composition of fluids and solids in this neutral pH geothermal environment.

Halomonas sulfidaeris-dominated Microbial Communities Inhabit 1.8 km-deep Subsurface Cambrian Sandstone Reservoirs

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An indigenous low-diversity microbial community, dominated by the γ-Proteobacteria *Halomonas sulfidaeris*, inhabits warm saline formation pore water in the Cambrian Mt. Simon Sandstone of the Illinois Basin, North American Midcontinent (1.8 km-5872 ft. burial depth, 50^{o} C, pH 8, 181 bars pressure). These highly porous and permeable quartz arenite sandstones are directly analogous to reservoirs around the world targeted for large-scale hydrocarbon extraction, as well as subsurface gas and carbon storage. A new downhole low-contamination subsurface sampling probe was used to collect *in situ* formation water samples for microbial environmental metagenomic analyses. Metabolic pathway reconstruction, constrained by the geology, geochemistry and present-day environmental conditions of the Mt. Simon Sandstone, implies that the native microbes utilize iron and nitrogen metabolisms and extensively recycle indigenous nutrients and substrates. The presence of aromatic compound metabolic pathways suggests this microbial community can readily adapt to and survive subsurface hydrocarbon migration.

Enriched Pyrite $\delta^{34}S$ Signals in Modern Tropical Deltaic Muds

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The biogeochemical cycling of sulfur is one of the primary processes that regulate the Earth's surface redox conditions. In this study, we examine the abundance and sulfur isotopic composition ($\delta^{34}S$) of pyrite through a series of cores collected from different water depths from the Gulf of Papua, Papua New Guinea. Physically undisturbed cores from deep water (depths up to 50 m) show relatively smooth $\delta^{34}Spyr$ profiles with small scatter between adjacent samples within a core. In these cores, $\delta^{34}Spyr$ gets gradually enriched from ~ -32‰ in the upper section to ~ -25‰ in the lower section. On the other hand, the $\delta^{34}Spyr$ profiles in cores from shallow water depths (8 – 18 m) present larger scatter (up to 35‰) and unusually enriched $\delta^{34}Spyr$ values (up to +36‰) are observed. These disparate results can be understood by combining a Rayleigh distillation model to explain elevated $\delta^{34}S$ values under closed-system conditions, together with the impact of episodic reworking of sediments, which enhances the stratigraphic variability of sulfide isotopic signals. Such different $\delta^{34}S_{pyr}$ patterns (both in their mean values and the degree of variability) between shallow water and deep water depositional environments, if preserved in the geologic record, could result in disparate interpretations. Understanding how modern depositional and diagenetic environments impact sulfur cycling processes gives us new insights when interpreting ancient sulfur isotope records.

Passive sampling of dissolved methane through the water column in a Greenlandic lake: understanding lacustrine methane dynamics at half-meter scales

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Arctic lakes are key participants in the global carbon cycle, releasing methane in a warming climate and contributing to a positive feedback to climate change. In order to produce detailed methane budgets and understand the implications of warming on methane production and consumption pathways, high-resolution profiles that can reveal methane behavior within the water column need to be obtained. Single-day sampling using disruptive techniques has the potential to result in biases. In order to obtain high-resolution, undisturbed profiles of methane concentration and isotopic composition, this study evaluates a passive-sampling method over a multi-day equilibration period. One small lake (<1 km^2) was selected for this study, which is part of an ongoing study of seven lakes located along a narrow valley stretching between Russells Glacier and Søndre Strømfjord in southwestern Greenland. Commercially available, polyethylene, passive-diffusion bags (PDB's) were deployed in July 2013 for five days at 0.5-meter depth intervals. PDB samples were compared to samples collected with a submersible, electric pump taken immediately before PBD deployment. Preliminary CH_4 concentrations and carbon isotopes were obtained in a field laboratory using a Los Gatos Research Methane Carbon Isotope Analyzer (LGR MCIA). PDB sampling and pump sampling resulted in statistically similar concentrations (R^2=0.89), ranging from 0.85 to 135 uM from PDB and 0.74 to 143 uM from pump sampling. In anoxic waters of the lake, where concentrations were high enough to yield robust isotopic results on the LGR MCIA, $\delta^{13}C$ were also similar between the two methods, yielding -73‰ from PDB and -74‰ from pump sampling. Further investigation will produce results for a second lake and methane carbon and hydrogen isotopic composition for both lakes. Preliminary field results for this passive sampling method are promising. We envision the use of this technique in future studies of dissolved methane and expect that it will provide a more finely resolved vertical profile, allowing for a more complete understanding of lacustrine methane production, oxidation, and emission.

The Effects of Road Salt Deicers on Redox Stratification and Salinization of Eutrophic Lakes in Southwest MI, USA

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Eutrophication in lakes can be caused by agricultural and residential runoff, due to an excess of nutrients, particularly phosphorus and nitrogen. Previous studies suggest that seasonal applications of the road salt deicers result in the increase of chloride concentrations which may impact lake aquatic ecosystems and geochemistry. The goal of this study is to examine the effects that road salt deicers have on the geochemistry of Woods and Wintergreen Lake, two kettle lakes located in Southwest MI, USA. Woods Lake is located in urban Kalamazoo, MI it has a surface area of ~ 9.7 ha and a max depth ~ 14m. Wintergreen Lake is located in rural Hickory Corners, MI, has a surface area of ~16.4 ha and a max depth of ~ 7.9 m. Water column samples were collected during May, June, September, November, and December at 1 m intervals, using a van Dorn sampler. The water samples were filtered with two samples from each depth acidified and two un-acidified, and analyzed colorimetrically for Fe^{2+}, Mn^{2+}, total alkalinity, ΣNH_4^+, and ΣPO_4^{3-}, by IC for anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}, F^-, PO_4^{3-}), and by ICP-OES for major ions and trace metals (Ca, Mg, K, Na, Co, Cd, Zn, Ni, Al). Using an YSI 650MDS/600QS probe, pH, temperature, dissolved oxygen, and conductivity were measured in situ at 0.5 m intervals. Nutrient and redox-sensitive species profiles demonstrate that both Woods and Wintergreen Lake are eutrophic, in agreement with results reported in prior studies. In Woods Lake, DO drops from >100% sat in the epilimnion to < 2% in the hypolimnion. In fall, as DO decreases, dissolved Fe^{2+}, Mn^{2+}, ΣNH_4^+, and ΣPO_4^{3-} increase below 8 to 12 m depth, reaching ~230, ~50, ~950, and ~65 μM, respectively. Conductivity increases from 475 μS/cm at the surface to >1000 μS/cm which suggests salinity is contributed from road salt inputs. DO similarly decreases from >100% sat at the surface to ~4% in the bottom waters of Wintergreen Lake during the summer. In contrast, in fall, it is ~86% at 6 m. In summer, dissolved Mn^{2+} and ΣNH_4^+ are present at Wintergreen Lake, but smaller concentrations (16 and ~25μM, respectively, at 5 m) compared to Woods Lake. Conductivity is much lower than at Woods Lake, increasing slightly from ~237 μS/cm in the epilimnion to ~392 μS/cm at 6 m. Continued sampling will be used to assess seasonal changes in lake stratification and to determine whether these two lakes are dimictic.

Physical and geochemical controls on cave dripwater microbial diversity

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Dripwater entering a karst environment, like a cave, can introduce material produced from water-rock reactions or directly from the surface as a function of the hydrological connectivity and water budget of the epikarst system. Dripwater can also serve as a significant reservoir for microbial communities that can impact organic carbon cycling, carbonate geochemistry, and other processes, although the microbial diversity and geochemical controls on that diversity for most karst systems are poorly constrained. To evaluate the potential relationship between dripwater chemistry and microbial community composition, 10 dripwater samples were collected at 6 sites within the Cascade Cave system, Kentucky. Sites were separated from each other by 20 m to more than 100 m. From each site, drip rate was measured, field geochemical data were collected (e.g., pH, temperature, conductivity), and filtered water subsamples were taken for measurements of total organic carbon (TOC), and cations and anions. Nucleic acids were extracted from Sterivex filters after filtering 230-500 mL of water, and the V1-V3 region of the 16S rRNA gene was used for tag-encoded GS FLX+ pyrosequencing. Proteobacteria accounted for 62%-71% of the phylum-level abundance for all dripwaters, including representatives of *Alpha-*, *Delta-*, *Beta-*, and *Gammaproteobacteria*. Additional significant representation at the phylum-level by the putative Candidate Division OP3 (7-31% of recovered reads) was observed in all samples. *Flavobacteria* showed the greatest range in abundance, from 0.8-14.4%. An unweighted pair group method with arithmetic mean (UPGMA) cluster analysis based on class-level abundances revealed that sample diversity varied by no more than ~20%, suggesting that the microbial communities may originate from the same or similar sources (e.g., surface forest soil). The relationships among drip rate, geochemistry, and class-level relative abundances from the UPGMA analysis were verified using canonical correspondence analysis (CCA). Almost 80% of the variability could be explained by two axes of the final CCA (P-value = 0.0009) obtained for any stepwise iteration of geochemistry and diveristy. CCA axis 1 (P-value = 0.007) positively correlated to TOC and negatively correlated to sulfate concentration, whereas CCA axis 2 (P-value = 0.002) correlated to drip rate. Notable associations between presence/absence of taxonomic groups and geochemical variables were observed. For instance, the slowest dripping site had the highest relative abundance of Candidate Division OP3 pyrosequences, and that site also positively correlated to high TOC and low sulfate. Sites with faster drip rates positively correlated to alkalinity, bicarbonate concentration, and pH, but did not strongly (and significantly) correlate to calcium concentration. Two sites that were separated by several tens of meters from each other had similar drip rates, TOC and nitrate concentrations and contained similar phylum-level diversity, including similar relative abundances of Chloroflexi, Bacteroidetes, Actinobacteria, OP3, and Proteobacteria. Previous studies of dripwaters from other caves using culture-dependent and –independent methods suggest that Actinobacteria and gram-positive bacteria comprise the majority of the communities, and that differences in community composition were due to environemtnal conditions in the cave. The cave environment most likely affects the extent to which dripwater microbes may inoculate and colonize other surfaces, but the preliminary results from this study not only reveal a greater bacterial diversity in dripwater than previously known, but also demonstrate that drip rate and dripwater geochemistry play a significant role in community composition. Consequently, understanding the physicochemical controls on microbial community composition in dripwaters and particularly seasonal effects that influence drip rates can help to evaluate the role of microbes in speleothem formation, as well as other processes in the karst environment.

Characterization of microbial populations across geochemical and lithological boundaries in urban lake sediments under environmental change in Minneapolis-St. Paul

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The characterization of microbial communities within urban lake sediments may offer a promising method to observe changes in lake geochemistry due to human impact. By mapping the abundances and diversity of microorganisms through the uppermost meter of sediment in three distinctive Minneapolis-St. Paul lakes (Brownie Lake and Twin Lake, both meromictic, and oligomictic Lake McCarrons) using 16S rRNA characterization, our aim was to observe changes in microbial populations across steep geochemical and lithological gradients.

Lake McCarrons underwent a process of eutrophication and a shift to bottom water anoxia beginning around 1910 due mostly to agricultural run-off. This shift greatly increased the preservation potential of seasonal sedimentation and finely laminated varve accumulation. The onset of meromixis in Brownie Lake in ~1915 is abrupt and has been attributed to a sudden drop in water level. Twin Lake is perennially meromictic due to the topography of the watershed. The three lakes were sampled by collecting freeze cores in July, 2012 (McCarrons, Brownie) and February, 2013 (Twin) at the deepest locations beneath anoxic to hypoxic bottom waters. The cores were then subsampled with high resolution techniques at places of interest: within individual lamina, across mass flow deposits, and near the onset of laminae preservation (beginning of oxygen-depleted bottom waters). Terminal Restriction Fragment Length Polymorphism (T-RFLP) allows for comparison of the microbial assemblages throughout the sediment columns of each lake and from lake to lake, with a focus on the horizons mentioned previously. The microbial assemblages present in specific horizons are often introduced via sedimentation and are partially derived from community composition at the time of deposition. Preliminary work has demonstrated distinct bacterial communities across lithological boundaries, suggesting community differences are preserved over 100-year time scales.

This study examines variability in microbial community assemblages through time and space within these lake sediments. Changes seen in the ecology of the communities are related to changes in chemical and physical parameters, namely, shifts in lithology and sediment accumulation via the onset of meromixis. Freeze coring exceptionally allows super-high resolution subsampling techniques to identify differences across geochemical gradients and between individual seasonal laminae within each lake and from lake to lake.

Kinetics of complex sulfur oxidation and disproportionation by *Thiomicrospira thermophila*

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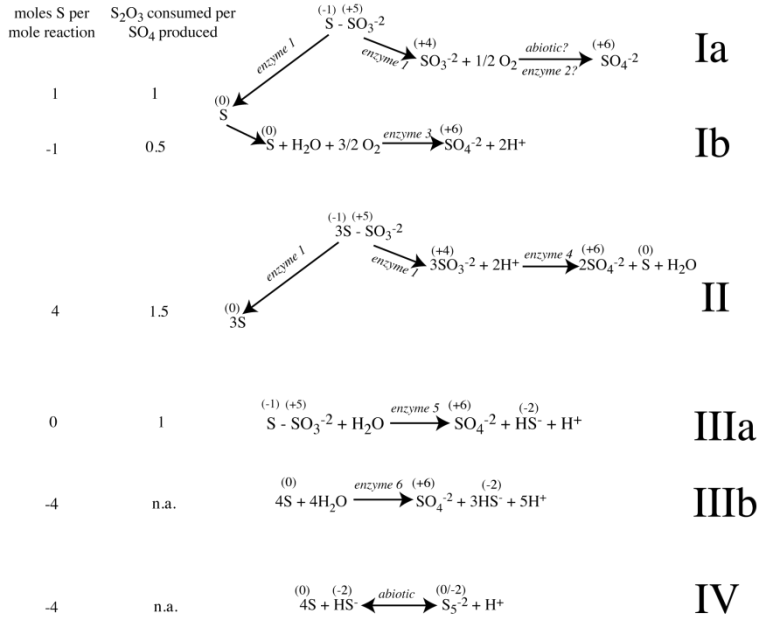
Near-seafloor hydrothermal environments such as diffuse flow venting or subsurface mixing are characterized by rapidly changing conditions and steep chemical and thermal gradients. Microorganisms living in these environments can take advantage of these changes by switching among metabolic pathways rather than specializing. We present reaction stoichiometry and rates for *T. thermophila* grown in a closed system both at ambient and elevated pressure (50 bar) that demonstrate substantial metabolic flexibility, shifting between up to 5 different sulfur cycling reactions over a 24 hour period. Based on the stoichiometry between S_2O_3 consumed and SO_4 produced, several different reactions occur:



Partial oxidation of thiosulfate, described in path Ia, is a combination of an enzymatic and abiotic reaction that give a S_2O_3:SO_4 ratio of 1 and an accumulation of 1 mole of elemental sulfur per mole of reaction. However, we rarely measure ratios of 1, but rather closer to the 0.5 ratio expected for full oxidation of thiosulfate. Path Ib results in no accumulation of elemental sulfur and the microbially mediated oxidation of sulfur has a 6 e^- transfer. Ratios between 0.5 and 0.7 are measured until O_2 becomes limiting, at which point the reaction stoichiometry shifts to a S_2O_3:SO_4 ratio of 1.5. Path II (disproportionation) describes this process with a total of 8 electrons transferred. However, the net gain of elemental sulfur is 4 moles per mole of reaction, and at most only 0.2 moles per mole of reaction is measured. Reactions that consume elemental sulfur in the absence of available O_2 include paths IIIa and IIIb (disproportionation) and IV. The ability to catalyze disproportionation of thiosulfate has not previously been demonstrated for *Thiomicrospira* strains. The presence of μmolal concentrations of HS^- has been confirmed during the time series only when observed S_2O_3:SO_4 stoichiometry predicts disproportionation. Production of HS^- in the presence of elemental S results in abiotic conversion to polysulfides (path IV), keeping the sulfide concentrations low in solution. When HS^- was scavanged from solution by silver wire, preventing further microbially mediated reactions, the stoichiometry is quantitatively that of disproportionation.

The transition from oxidation to disproportionation appears to be triggered by a depletion in dissolved oxygen and the rate of reaction is a second order function of S_2O_3 and O_2 concentrations. Growth was tested at conditions spanning their pH tolerance (5.0 – 8.0) using a citrate buffer (pH 5.0), unbuffered media (initial pH 7.0), and Tris buffer (pH 8.0). The highest reaction rates are observed at pH 8.0 with rates decreasing as a function of pH. The lowest rate occurs at pH 5.0 and exhibits pseudo-first order behavior over a 24 hour period, likely due to a long lag and very slow growth. Repeat injections after the culture is acclimated to the experimental conditions result in very high pseudo-first order rates due to rapid consumption of all available thiosulfate prior to oxygen depletion. Results from high-pressure closed system experiments (at 50 bar, buffered at pH 5.0) exhibit comparable reaction rates to the corresponding ambient pressure condition.

The specific growth rates are highest at high pH (~1 hr^{-1} at pH 8.0) and decrease as a function of pH. In the unbuffered experiments, specific growth rate decreases as pH decreases, with max specific growth rate identical to the corresponding buffered experiment. Growth at 50 bar in citrate buffer (pH 5.0) occurs at comparable rates as those at ambient pressure. Future work will address the effect of dissolved O_2 on sulfur disproportionation using continuous culturing of *T. thermophila* at deep-sea pressure conditions (>200 bar).

Archaeal and bacterial diversity in acidic to circumneutral hot springs in the Philippines

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The microbial diversity was investigated in sediments of six acidic to circumneutral hot springs (Temperature: 60-92^{o}C, pH 3.72-6.58) in the Philippines using an integrated approach that included geochemistry and 16S rRNA gene pyrosequencing. Both bacterial and archaeal abundances were lower in high-temperature springs than in moderate-temperature ones. Overall, the archaeal community consisted of sequence reads that exhibited a high similarity (nucleotide identity >92%) to phyla *Crenarchaeota*, *Euryarchaeota*, and unclassified *Archaea*. The bacterial community was composed of sequence reads moderately related (nucleotide identity >90%) to 17 phyla, with *Aquificae* and *Firmicutes* being dominant. These phylogenetic groups were correlated with environmental conditions such as temperature, dissolved sulfate and calcium concentrations in spring water, and sediment properties including total nitrogen, pyrite, and elemental sulfur. Based on the phylogenetic inference, sulfur metabolisms appear to be key physiological functions in these hot springs. *Sulfobacillus* (within phylum *Firmicutes*) along with members within *Sulfolobales* were abundant in two high-temperature springs (>76^{o}C), and they were hypothesized to play an important role in regulating the sulfur-cycling under high temperature conditions. The results of this study improve our understanding of microbial diversity and community composition in acidic to circumneutral terrestrial hot springs and their relationships with geochemical conditions.

Evaluating the Effects of Sediment Reworking on the Sulfur Isotopic Composition of Aqueous and Mineral Sulfides

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The sulfur isotopic compositions of sulfide minerals preserved in the rock record are widely used in reconstructions of past ocean and atmospheric chemistry. However, little is known about the effects that syndepositional reworking can have on these compositions. Sediments from recent tropical deltaic environments with evidence of storm-induced or tidal reworking have pyrites whose $\delta^{34}S$ values are higher and more variable than typically found in more quiescent deeper water environments (Aller et al., 2010). Pyrites in these sediments are occasionally more enriched in ^{34}S than coeval sulfate, which requires unusual distillation of aqueous sulfate/sulfide given the generally large isotopic fractionation associated with sulfate reduction in the modern ocean. A similar discovery of pyrites more enriched in ^{34}S than coeval sulfate (preserved as carbonate-associated sulfate) in the rock record (e.g., Ries et al., 2009) has led to reconstructions of ancient sulfur cycling that are very different from the modern (characterized by low (< 1mM) sulfate and negligible isotopic fractionation during sulfate reduction). However, it is possible that these ancient records also could be impacted by sedimentary reworking similar to that observed in the modern, with a corresponding increase in $\delta^{34}S_{pyr}$ and possibly a concomitant decrease in $\delta^{34}S_{SO4}$. Specifically, we hypothesize that reworking-associated sulfide reoxidation is capable of significantly enriching aqueous and mineral sulfide phases in ^{34}S, while the newly oxidized sulfide results in a ^{34}S-depletion of the local sulfate pool (Fry et al., 1988; Kaplan and Rittenberg, 1964). Although modelling (Aller et al., 2010) supports this hypothesis, laboratory experiments have yet to demonstrate that reworking is a viable process to enrich aqueous and mineral sulfides in ^{34}S (and correspondingly deplete ^{34}S in sulfate) in sediments. Here, we report porewater [H_2S], and [SO_4^{2-}] data from an ongoing controlled laboratory experiment focused on evaluating the effects of repeated oxidative reworking on sediment columns established from sediments collected in Florida Bay. In parallel, we are investigating the corresponding evolution that arises in the $\delta^{34}S$ composition of aqueous and mineral sulfides, as well as porewater sulfate. Our results may have significant implications for the environmental interpretation of existing and future $\delta^{34}S_{pyr}$ data, as many sediments preserved in the rock record originate in high-energy settings akin to the tropical deltaic environments in which ^{34}S-enriched sulfide has been observed in recent sediments.

References:

Aller, R.C., Madrid, V., Chistoservdov, A., Aller, J.Y., and Heilbrun, C. (2010). Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: Implications for oceanic isotope cycles and the sedimentary record. *Geochimica et Cosmochimica Acta*, 74, 4671-4692.

Fry, B., Ruf, W., Gest, H., and Hayes, J.M. (1988). Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chemical Geology: Isotope Geoscience Section*, *73*(3), 205-210.

Kaplan, I.R., and Rittenberg, S.C. (1964). Microbiological fractionation of sulphur isotopes. *Journal of General Microbiology*, *34*(2), 195-212.

Ries, J.B., Fike, D.A., Pratt, L.M., Lyons, T.W., and Grotzinger, J.P. (2009). Superheavy pyrite ($\delta^{34}S_{pyr}$> $\delta^{34}S_{CAS}$) in the terminal Proterozoic Nama Group, southern Namibia: A consequence of low seawater sulfate at the dawn of animal life. *Geology*, *37*(8), 743-746.

Insights into microbial phosphorus cycling through metatranscriptomic analysis of hypoxic marine sediments

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Polyphosphate (poly-P) metabolism by benthic microbial communities represents a dynamic component in the global phosphorus (P) cycle. By synthesizing and later hydrolyzing these P reserves, polyphosphate-accumulating organisms can affect P availability and potentially alter the saturation state of sedimentary pore waters with respect to phosphate minerals. In particular, marine polyphosphate-accumulating bacteria such as the sulfur-oxidizing genera *Thiomargarita* and *Beggiatoa* have been implicated in phosphogenesis at modern upwelling zones and in the formation of ancient phosphorite deposits. However, phosphogenesis may involve more than large sulfur bacteria: sediment microbial communities are diverse, and likely contain numerous poly-P metabolizing taxa. Therefore, we used incubation experiments of sediment-hosted microbial communities followed by comparative metatranscriptomics to identify important polyphosphate metabolizing organisms in different aquatic environments and compare their activity under distinct environmental conditions.

We collected and incubated sediments from three locations: (i) marine cold-seep sediments near Barbados that contain abundant sulfur-oxidizing bacteria, including Thiomargarita-like organisms; (ii) sulfidic marine sediments from Santa Barbara Basin (SBB) with no microscope-observable sulfur bacteria; and (iii) freshwater sediments from Spring Lake, MN, a eutrophic lake with seasonally anoxic bottom waters. In all incubations, P was consumed under oxygenated conditions and liberated under anoxic conditions, with and without sulfide and acetate additions. Incubation sediments were preserved for RNA extraction, and metatranscriptome libraries were generated from Barbados and SBB experiments. Preliminary results from Barbados indicate that sulfur oxidizing and organoheterotrophic bacteria are likely important poly-P metabolizers at this site. Only certain gamma- and epsilonproteobacteria were expressing poly-P kinases and exopolyP-ases, even though rRNA and rpoB transcripts show that active microbial populations also included representatives of the Methanosarcinales, Bacteroidetes, and Deltaproteobacteria. Comparative analyses of lacustrine and marine sediments holds promise for gaining a better understanding of the microbial communities and processes responsible for biogeochemical P cycling in these distinctive regimes.

Geochemical dynamics in Yellowstone Springs: Sulfur chemistry changes at seconds-scale temporal resolution

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Sulfur speciation can drastically change through a variety of redox reactions, by changing the oxidation state of the element (between S^{-2} to S^{+6}). It participates in oxidation, reduction and disproportionation reactions, polymerization (S-S bonding), and aggregation which leads to (nano)-particulate elemental sulfur ($S_{8(nano)}$). Elemental sulfur additionally can go through a series of nucleophlic and hydrolysis reactions to yield dissolved intermediates, most importantly via the reaction

$$S_8 + H_2S = S_x^{2-} + 2\ H^+ \qquad (1)$$

to form polysulfides (S_x^{2-}, with the most prevalent forms being S_4^{2-} and S_5^{2-}; Kamyshny, 2009). Polysulfides then are reactive in acidic solutions to go through a series of chain elongation reactions, eventually reforming elemental sulfur and sulfide (reverse of reaction 1) but here the elemental sulfur is as a dissolved S8 ring ($S8_{(aq)}$). In the presence of oxygen polysulfides forms species such as thiosulfate ($S_2O_3^{2-}$), which further disproportionate to sulfite (SO_3^{2-}) and elemental sulfur (S8(aq)) in acidic solutions. These reactions are hypothesized to affect the availability of dissolved sulfur forms that may be more bioavailable for microorganisms than bulk elemental sulfur, providing insight on their specific metabolisms (Boyd and Druschel, 2013).

Recent field observations in Yellowstone National Park hydrothermal system have investigated the dynamics of sulfur speciation and concentration as a function of time were investigated by in-situ, ex-situ, and grab sample cyclic voltammetry analyses in selected hot springs of Yellowstone National Park. Hydrogen sulfide levels were observed to change by orders of magnitude over seconds (Figure 1), and Fourier transforms of the data reveal no periodicity over the course of hours. Chaotic gas delivery of H2S(g) affects H2S(aq) and reactions controlling intermediate sulfur chemistry and potentially puts new chemical stresses on possible microbial metabolisms

Boyd and Druschel (2013) *Appl. Environ. Microbiol.* **79**(6) 2061-2068

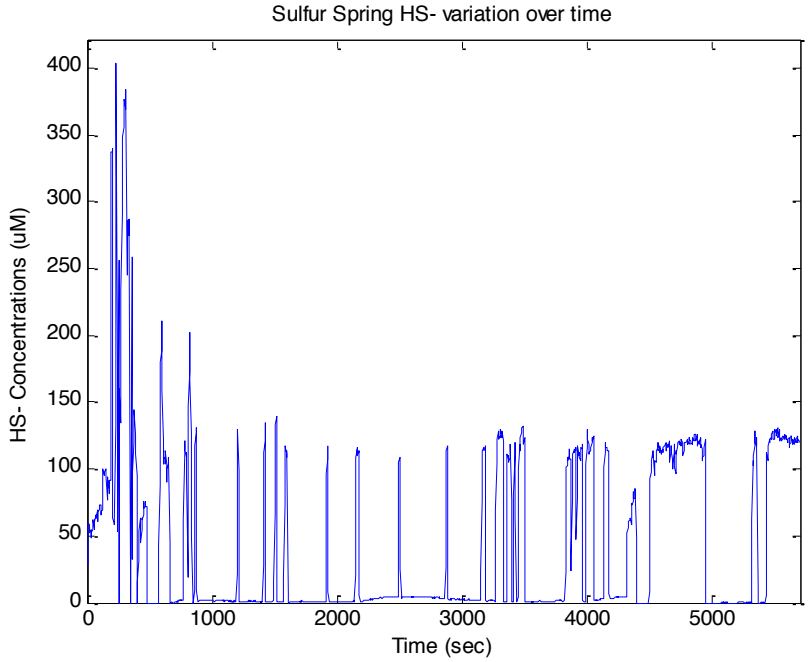

Figure 1: Sulfide variation over time in Sulfur Spring Geyser waters

Using leaf wax biomarkers to constrain land-use changes associated with Mississippian settlements

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The Mississippian culture was a mound-building Native American pre-Columbian culture prevalent throughout the midwestern and southeastern United States. Among the most spectacular archaeological remains of this culture is the settlement at Cahokia Mounds, Illinois, which was inhabited from approximately 700 – 1400 CE, with a population that may have exceeded 20,000. The reasons for the decline of the settlement remain controversial, but hypotheses include changes in land use or environment [1].

We attempt to better understand the context of environmental and land-use changes near the Cahokia settlement over the past two millenia by examination of environmental records from lake sediments. Several sediment cores were taken from Horseshoe Lake (Madison County, IL), about a mile away from the Cahokia site. We detected abundant leaf wax lipids throughout the core. In conjunction with pollen analysis, leaf waxes have the ability to preserve information about the history of vegetation in the area surrounding the lake. In particular, we aim to address two questions: i) can we place age constraints on the onset and disappearance of extensive maize agriculture in the area surrounding Horseshoe Lake? ii) can we identify any significant changes in paleohydrology in this region over the course of the last two millenia?

To address agricultural changes, we take advantage of the fact that unlike most plants native to the Mississippi valley, maize uses C4 carbon fixation, which typically results in an enrichment of ^{13}C in its biomass relative to other vegetation. By examining the ^{13}C content of leaf waxes through the sediment core, we may be able to detect shifts coincident with the onset and decline of agricultural land use by the Cahokian settlement. Leaf waxes also contain paleohydrological infomration, manifested in their deuterium to hydrogen (D/H) ratio, which derives from that of environmental water [2]. Observations of excursions in leaf wax D/H could be indicative of hydrological stress, such as associated with a drought.

Our intial investigation reveals abundant leaf waxes present throughout a core sampled in the summer of 2011. Further study will involve detailed measurement of the strucutres and isotopic compositions of leaf waxes in the 2011 and 2012 cores from Horseshoe Lake, as well as future investigation into cores collected in summer 2013 from Horseshoe Lake (Alexander County) and Grassy Lake (IL).

Methods

Samples were collected from Horseshoe Lake (Madison County) in summers of 2011 and 2012. The 2011 core was treated with hydrochloric acid to remove carbonates. Selected samples were chosen as an initial screen for the viability of this study. Organic molecules were extracted from the sediment layers using a mixture of organic solvents (methanol/dichlormethane 7/3) in a microwave-assisted reaction system. Elemental sulfur was removed via precipitation as copper sulfide, then total lipid extracts were separated by polarity using silica gel chromatography. Structures were identified via GCMS (Agilent 7890 coupled to an Aglient 5975C), and isotopic compositions of individual compounds were measured via separation on a Thermo TraceGC coupled to a Delta V Advantage isotope ratio monitoring mass spectormeter via a GC Isolink and Conflo IV interface.

[1] Lopinot, N.H. Woods, W.I. (1993) Wood Overexploitation and the Collapse of Cahokia. *in* Scarry, C.M. *Foraging and Farming in the Eastern Woodlands*, pp 206-231. University Press of Florida. Gainesville. [2] Sachse, D. and 16 others (2012) Molecular Paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annual Reviews of Earth and Planetary Sciences* 40: 221-249.

Visualizing the early diagenesis of bone

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The process of bone fossilization is thought to result from the chemical alteration and incorporation of fluorine and/or chlorine and carbonate ions into the calcium phosphate mineral comprising the main inorganic phase of bone, (hydroxy)apatite (HAP). Bone fossilization has almost exclusively been evaluated in terms of mineral alteration and ion substitution based on mineral solubilities of homogenous fluorinated and/or carbonated phases. However, while the fossil record is replete with vertebrate remains, thermodynamic modeling of mineral stabilities under variable geochemical conditions encountered in different depositional environments reveals that most depositional solutions are undersaturated with respect to HAP. To begin to address the limited knowledge of HAP ion substitution timing, the impact of increasing diagenesis on ion substitution and HAP crystal stability, and the changes to and loss of collagen during fossilization, we tested the hypothesis that structural and chemical transformations during early stages of burial, from days to years, are initiated by changes in oxidation state during burial that alter bond lengths between available substituting ions in the crystal lattice. We assessed crystallinity and ion bonding changes within the mineral lattice, and geochemical constraints that influence HAP lattice disruption, crystallinity, and ion substitution under conditions observed in modern wetland environments by using a series of mesocosm experiments and a longer-term field study involving modern alligator bones. Experimental bones were examined using infrared spectroscopy and electron microprobe analyses. Initial results suggested that changes in HAP chemistry and structure happened quickly. After a week of burial under biotic (i.e. colonized with native microbes from sediment and water) and abiotic (i.e. bone in dialysis tubing to prevent direct microbial colonization) treatment conditions, an increase in mean HAP crystal length, from 41.5 nm in fresh bone to 44.0 nm in both treatments, was measured. Under biotic conditions alone, the carbonate:phosphate (C:P) ratio increased as a consequence of decreased phosphate concentration. In contrast, the abiotic treatments did not exhibit measurable changes to C:P. The $_{v1v3}PO_4$ vibrational band indicated an increase in peak asymmetry for the biotic treatment, which potentially was due to protonation of the PO_4^{3-} ion to form HPO_4^{2-}. After three years of burial in natural wetland sediments and examination of bone using electron microprobe analyses, Na concentration decreased, from 0.76 wt. % in fresh bone to 0.60 wt. % in the buried bone, Fe was enriched from 0.0 wt. % in fresh bone to 0.76 wt. % in buried bone, and F was enriched from 0.07 wt. % in fresh bone to 0.29 wt. % in buried bone. The incorporation of Fe appeared to be largely accommodated at Ca sites within the HAP lattice. From the buried bone after three years, structural changes were evident based on alteration of the crystallinity, which was more crystalline than fresh, unaltered bone, but not completely recrystallized compared to Late Cretaceous fossil bones. These results suggest that changes occur not only to the organic component of bone (i.e. collagen) immediately following burial, a process long invoked as necessary for fossilization, but also to the HAP, mineralized phase. Bone diagenesis proceeds more rapidly than previously thought after burial, and these early substitutions and alterations to the mineral phase are potentially pivotal for long-term preservation of bone over geologic time.

Microbial Transformation of Hydraulic Fracturing Chemical Additives

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Hydraulic fracturing introduces millions of gallons of water and thousands of gallons of chemicals to the subsurface to facilitate recovery of oil and natural gas. In Pennsylvania and Ohio, approximately 15% of injected fluids return to the surface while the rest presumably remains within deep subsurface rock formations. The fate of unrecovered fluid is currently poorly constrained. Specifically, little is known of the potential attenuation of organic chemical additives used in hydraulic fracturing in the natural environment. The purpose of this research is to begin to quantify the rates and extents of organic additive degradation by representative microorganisms. The first research step was to develop a synthetic hydraulic fracturing fluid based on industry formulas that could be used for bench-scale experiments. The synthetic fracturing fluid was found to be both physically and chemically similar to mixtures used by industry. Fluid biodegradation potential was measured by monitoring the consumption of dissolved organic carbon (DOC) by wastewater sludge bacteria. About 90% DOC loss occurred within 15 days across a range of concentrations. However, 5-10% of added DOC remained in solution after this time, suggesting that some organic chemicals used in hydraulic fracturing are initially resistant to microbial transformation and may persist in the environment. Studies currently underway will identify specific organic compounds that are degradable or recalcitrant by wastewater and subsurface bacteria. This data will be used to estimate the potential risk of chemical additives in shallow aquifers.

Bacterial and fungi contribution to N2O production in soils under different tillage managements

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Abstract

Nitrous oxide (N_2O) is an atmospheric constituent implicated in the accelerated greenhouse effect and stratospheric ozone depletion. Since the agricultural sector is the largest source of N_2O (60-65% of total anthropogenic emission), there is a need to investigate the impact of different management practices on N_2O production in agricultural soils. During the last several decades, no-till (NT) farming has been widely promoted as a best management practice to sequester soil carbon, maintain soil fertility and protect soil health. However, comparison of N_2O emission under NT and conventional plow till (PT) has yielded mixed and variable results, underscoring our limited understanding of the factors controlling denitrification in NT soils. A study was conducted to investigate the N_2O production potential of soils under long-term NT (10 to 48 years) compared to PT. By conduction selective inhibition assays (using streptomycin, cycloheximide, captan, and bronopol), the relative contribution of fungi and bacteria to the denitrification process was determined in the different soil types. Results of this study will shed light on some of the controversial questions surrounding N_2O production in NT systems.

Enzymatic constraints on the global sulfur cycle

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By coupling quantitative geochemical models with enzyme and whole cell observations stand to gain access to the archives of environmental histories encoded in the geological S isotope record. The sedimentary sulfur isotope record is initiated and driven by the central biochemical machinery of microbial sulfate reducers (MSRs), performing dissimilatory sulfate reduction coupled to organic matter oxidation. Our present understanding of MSR sulfur isotope fractionation stems from a series of robust cellular-scale (*in vivo*) studies [1-3]. Still, biogeochemical models of the S cycle lack fundamental constraints on the fractionations associated with enzymatic S transformations within the MSR pathway, rendering our best models semi-quantitative. Inspired by the early carbon isotope work on RuBisCO [5, 6] and the influence those studies hold on our understanding of the global carbon cycle [7], both past and present, we extend our recent open-system *in vivo* [5] and preliminary pure-enzyme (*in vitro*) experimental work. This study is part of a broader on-going effort to precisely calibrate the multiple S-isotope effects associated with whole-cell sulfate and intracellular sulfite reduction, each underpinned by the MSR enzyme dissimilatory sulfite reductase (Dsr) [c.f., Johnston et al., and Bertran et al., *Goldschmidt, 2013*].

To provide fundamental boundary conditions for the network fractionation models by MSR [2, 8, 9], we performed *in vitro* closed-bottle sulfite reduction experiments. From these experiments we measure isotopic composition of the product sulfane-S moieties in reduction products trithonate and thiosulfate, relative to the sulfonate-S of those same compounds, in parallel with the residual and initial sulfite compositions. Form here we apply a modified Rayleigh model to calculate the enzyme-specific isotope fractionation factors for DsrAB ($^{33}a_{DsrAB}$, $^{34}a_{DsrAB}$). We repeat this procedure over a range of experimental conditions including temperature, pH, and DsrAB host species. To address the latter we work with purified fractions of DsrAB from the model Bacterial or Archaeal sulfate reducers *Desulfovibrio vulgaris* Hildenborough and *Archaeoglobus fulgidus*, respectively. Isotope and mass balance is conserved in all individual experimental volumes allowing us to directly calculate fractionation factors. Interestingly, the major isotope fractionation factors ($^{34}a_{DsrAB}$) we most often observe are significantly smaller than predicted those from equilibrium estimates [2, 10], but readily fit with indirect estimates from a seminal study by Jørgensen [11].

Through coupled biochemical and physiological observations of MSR, we are better able to constrain the fractionations that dominate the global biogeochemical S cycle. As a result we gain insight into the environmental controls on the directionality and extent of sulfur isotope fractionation in multiple sulfur isotope space. This work will ultimately allow for a more thorough interpretation of modern and ancient multiple sulfur isotope records.

[1] *Harrison & Thode (1958), Trans. Faraday Soc., **54**, 84–92. [2] Johnston et al. (2007) GCA **71**, 3929–3947. [3] Leavitt et al. (2013)* PNAS. *2013 110 (28). [4] Leavitt et al. 2013 Goldschmidt. [5] Park & Epstein (1960) GCA **21**, 110–126. [6] Farquhar et al. (1982) Aus. J. Plant Physio.* **9**, 121-137. [7] Berner (2001) *GCA* **65**, 685–694. [8] Rees (1973) *GCA* **37**, 1141-1162. [9] Bradley *et al*. (2011) *Geobiology* 9, 446-457. [10] Guo, unpub. [11] Jørgensen (1979) *GCA* **43**, 363-374.

Genome-enabled transcriptomics reveals the organic carbon and sulfur metabolisms of *Methylophaga* sp. in deep-sea hydrothermal vent plumes

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Deep-sea hydrothermal systems are important sources of carbon and reduced sulfur to the deep-ocean. While the biotic and abiotic cycling of inorganic carbon and sulfur has been well documented in deep-sea hydrothermal environments, the cycling of organic carbon and sulfur has received less attention, especially organic sulfur metabolism. Geochemical modeling has predicted that the organic carbon and sulfur-based metabolisms may be prevalent with deep-sea hydrothermal vent microbial communities; however, microbial organic carbon and sulfur metabolisms in deep-sea hydrothermal environments are still unknown. Here, we present metagenomic, metatranscriptomic, and geochemical insights into the microbial metabolisms of organic carbon and sulfur in deep-sea hydrothermal plumes of the Mid-Cayman Rise (Caribbean). Applying a random shotgun sequencing and *de novo* assembly approach, we reconstructed a near-completed genome of *Methylophaga* sp. from hydrothermal plumes at Mid-Cayman Rise. A total of 3.2 Mb *Methylophaga* sp. genome recovered from 11 contigs contains a single copy of 16S rRNA gene with 99% similarity to *Methylophaga aminisulfidivorans*, a restricted facultatively methylotrophic and sulfur oxidizing marine bacterium. The annotation indicates that this deep-sea hydrothermal *Methylophaga* genome contains two distinct methanol dehydrogenase coding genes. Together with genes encoding methylamine dehydrogenase, formaldehyde dehydrogenase and formate dehydrogenase in this genome, a completed metabolism pathway for methanol/methylamine utilization was identified. Metatranscriptomics showed that these methanol/methylamine metabolisms related genes have much higher expression in the plumes than in the background. Interestingly, a cluster of gene encoding flavin-containing monooxygenase (FMO) was found in both genome and transcriptome of this hydrothermal *Methylophaga* group. This FMO has been previously confirmed to be capable of oxidizing many nitrogen- and sulfur-containing compounds, such as trimethylamine, dimethylsulfide, and dimethyl sulfoxide. Given the wide distribution of *Methylophaga* in the deep-sea hydrothermal environments, our data indicated that this population is one of important microorganisms involving in the vent-driven organic carbon and sulfur metabolisms, which might play an important yet overlooked role in the deep-sea carbon, sulfur and nitrogen cycles. In addition, this *Methylophaga* sp. has a novel cluster of genes involved in siderophore production and uptake that are expressed in the plume, indicating this *Methylophaga* group also participates in hydrothermal iron cycling.

Investigation on mechanism for dolomite precipitation in Deep Springs Lake, California

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The formation of dolomite has two aspects: failure to precipitate dolomite experimentally at Earth surface temperature conditions due to kinetically inhibition; and the lack of modern analogues to explain the abundance in the geological record. Modern dolomite is observed to form in hypersaline and alkaline marine environments. Such modern dolomite precipitation is commonly attributed to microbial mediation. It was reported that there are primary dolomite precipitation in Deep Springs Lake in California, a hypersaline playa. (Jones, 1961) The biomass in the lake is dominated by micro-organisms of *Halorhabdus* (the major archaea), and *Halobacteroides halobius*. *Halorubrum* and *Halorhodospira halophila* are also detected in the biomass. The micro-organisms live between sediment mud and top sulfate salt layer. *Halorhabdus* causes red color of the surface the lake. In order to understand the roles of microbes in mediating dolomite precipitation, we use the biomass collected from Deep Springs Lake in California in dolomite precipitation systems.

The experimental results prove that disordered dolomite can be synthesized at low temperature using the biomass collected from Deep Springs Lake. Based on the glycosyl composition analysis of the biomass, about ten monosaccharides were detected with glucose, ribose and xylose as the most abundant. These bacterially derived extracellular polymeric substances (EPS) might play a crucial role in dolomite precipitation. It is proposed that polysaccharides can be strongly adsorbed on Ca-Mg carbonate surfaces through hydrogen bonding, and weaken the chemical bonding between Mg and water molecules, which can enhance Mg incorporation into carbonate, therefore contribute to the growth of disordered dolomite.
XRD patterns of synthesized HMC (high-magnesium calcite) and disordered dolomite demonstrate that there is a positive relationship between biomass concentration and mole percent of $MgCO_3$ in the precipitates. No dolomite precipitates in solutions without biomass. The Mg^{2+}/Ca^{2+} ratio from initial solution and temperature also have strong effects on synthesized dolomite based on our experiments. EDS results demonstrate Mg:Ca ratio of precipitates could be as high as 45% under room temperature and 60% under 40°C. SEM images indicate synthesized HMC and dolomite grew on the surface of calcite seed crystals. TEM images reveal that synthesized dolomites are nano-crystals with similar crystallographic orientations.

Biogeochemistry of Stinking Springs, UT: Inorganic carbon dynamics and constraints on nutrient fluxes in a warm, salty, sulfidic spring

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Saline microbial mats are among the most phylogenetically and metabolically diverse ecosystems found on Earth; however, we lack a detailed understanding of the controls on genetic and metabolic diversity. Culturing and maintaining mats in lab experiments is difficult making field observations a primary method to study these systems. Modeling of nutrient fluxes within and through mats requires assumptions about the local hydrology that are often difficult to justify. Here, we discuss downstream changes in geochemistry at Stinking Springs, Utah to constrain hydrologic inputs and outputs to a mat system. Stinking Springs, is a warm (40°C), salty (30 ppt), sulfidic (0.5 mM) and bicarbonate-rich (7.8 mM) spring that hosts several morphologically distinct microbial growth structures including layered mats in areas of laminar sheet flow and streamers and floating mats in the faster moving portion of the stream channel. Over a ~80m downstream transect, dissolved inorganic carbon [DIC] decreases from 7.8mM to 4.5mM. This large drop in [DIC] can be explained by the rapid outgassing of CO_2 to the atmosphere. Predicted downstream trends in [DIC] and $\delta^{13}C_{DIC}$ using a Rayleigh distillation model closely match those of the observed trends. The Rayleigh model assumes no carbon inputs to the stream and only one output mechanism (here, degassing). The best-fit fractionation factor of CO_2 degassing from HCO_3^- was 0.9937.

The fit of the [DIC] and $\delta^{13}C_{DIC}$ data to a purely physical model was unexpected given the microbial abundance and apparent growth occurring throughout the Stinking Springs system. These results suggest that DIC cycling by the mats leaves only a very small imprint on the overall spring-water DIC signature—a result that indicates life's biosignatures may be hidden by overwhelming physical processes. The Rayleigh model's close agreement with *in situ* measurements implies that the *sole source* of hydrologic inputs and therefore dissolved nutrient sources to Stinking Springs is the stream that feeds it. Therefore, nutrient fluxes to the mats can be quantified by measurement of water flow rate and nutrient concentration upstream and downstream of the mats. This constraint on dissolved nutrient source allows a great simplification of biogeochemical modeling within the mat system. This constraint can be added to future models of biogeochemical cycling within the mat layers to help elucidate the relationship between taxonomy, metabolism, and geochemistry.

Microorganisms cultured from highly alkaline serpentinizing springs in the Philippines

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Serpentinization is a subsurface chemical process involving the hydration of ultramafic rocks, the products of which may serve as metabolites for microorganisms such as bacteria and archaea. Gases like hydrogen and methane are abundant in these fluids, while inorganic carbon, nitrogen, and election acceptors are depleted. As the fluids come into contact with oxygen near or at the surface, microbial communities may shift in abundances or preferred metabolisms to reflect the changing chemistry. Our study of serpentinizing and hydrothermal fluids in the Zambales and Palawan regions of the Philippines includes a suite of geochemical analyses that define metabolic potentials, and also targeted culturing efforts based on assumed and verified geochemistry. Here we present a profile of metabolic options in the subsurface of our study sites, and examples of successful culturing of microorganisms from these sites.

Growth media designed to target heterotrophy and sulfate and iron reduction were used for culturing. Variables included sulfate and iron reduction both with and without organic carbon input, as well as incubation of all media with aerobic and anaerobic headspaces. These particular metabolic processes have been calculated to yield energy in these environments. Concentrated spike solutions were prepared prior to arrival at field sites, and appropriate volumes of spring fluid were then used to inoculate the spike media solutions. After transferal to fresh media, positive growth was exhibited by many of the samples from all field locations from temperatures ranging from 28 – 48 °C. Five samples showed successful growth on complex organic media. Organic media which included sugars resulted in two samples showing growth, while positive growth was exhibited by four samples with organic acids. Six samples displayed heterotrophic sulfate reduction, and three samples displayed autotrophic sulfate reduction. Out of the seven field sites, four were conducive to growth of heterotrophic iron reduction, and five contained organisms capable of autotrophic iron reduction. Temperature and pH ranges were also examined for samples that showed abundant growth. Geochemical data will be coupled with culturing data for each location in order to better support proposed metabolic activities, and will then be compared with previously studied microbial communities from other serpentinizing systems.

Thermodynamic modeling of metal-bacteria interactions:

Hg adsorption and Fe(II) oxidation studies

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Bacteria are ubiquitous in soils and near-surface and surface aqueous environments. Their cell walls contain a range of types of organic acid functional groups that bind metals from solution and thereby affect the speciation, distribution, and fate of metals in bacteria-bearing geologic systems. Surface complexation modeling (SCM) provides a flexible thermodynamic-based approach to predicting the fate of metals in these systems, and the modeling approach has been successful in accounting for metal adsorption in a range of simple systems. In my studies, I test the ability of surface complexation modeling to account for metal speciation and bioavailability in more complex systems. I have studied the relationship between Hg adsorption and precipitation on bacterial cell walls, testing whether surface complexation modeling can account for Hg distributions as a function of saturation state with respect to Hg precipitates. In addition, I am using surface complexation modeling to quantify Fe(II) adsorption onto bacteria with the objective being to construct quantitative SCM-based kinetics models of Fe(II) oxidation rates by iron oxidizing bacteria.

The primary objective for the Hg experiments is to quantify the extent of adsorption in under- and super- saturated conditions onto non-metabolizing cells of *Bacillus subtilis* in both chloride-free and chloride-bearing systems with respect to solid phase $Hg(OH)_2$. Experiments were conducted aerobically for two hours to achieve equilibrium with total Hg molalities ranging from 10^{-5} to 10^{-2} M and pH held constant at 4.5 or 7; Bacterial wet mass was held at 5 g/L for the entirety of the experiment, and constant ionic strength was achieved using 0.1M $NaClO_4$. Samples were taken after the equilibration period and the extent of Hg removal from solution was determined by ICP-OES analysis. The extent of removal was compared to predicted Hg adsorption in order to determine if bacteria caused enhanced $Hg(OH)_2$ precipitation under any of the saturation states studied. Biotic systems exhibited enhanced Hg(II) removal relative to the abiotic controls in undersaturated conditions, and the extent of removal agreed well with the extent of Hg(II) adsorption that was predicted to occur onto cell wall functional groups with the use of SCM. Furthermore, there was no evidence for enhanced removal due to precipitation in bulk solutions that were undersaturated with respect to the solid phase. However, under the highest Hg concentrations studied in both the chloride-bearing and chloride-free systems, the bacteria inhibit mineral formation, maintaining high concentrations of Hg in solution, likely due to the presence of bacterial exudates and extracellular polymeric substances that bind with Hg.

The underlying hypothesis for my Fe(II) oxidation studies is that the controlling step in Fe(II) oxidation is the adsorption of Fe(II) onto the bacterial cell wall functional groups, a necessary step to make Fe(II) bioavailable to the bacteria for oxidation. To quantify this step, Fe(II) sorption experiments were conducted anaerobically in hydrogen/nitrogen atmosphere and the extent of Fe(II) adsorption was determined using graphite furnace atomic adsorption analysis. Experiments were conducted with the common soil species *Bacillus subtilis* as well as with the iron oxidizing bacteria *Leptothrix cholodnii* in order to determine if Fe(II) binding varies between species. Both bacterial strains exhibited similar sorption edges suggesting comparable surface properties. In the next stage of research, Fe(II) oxidation rates by *L. cholodnii* will be measured while varying the extent of Fe(II) bound onto the cell walls, and we will determine if a relationship exists between the concentration and/or speciation of Fe(II) on the bacterial cell walls and the measured Fe(II) oxidation rates. If these tests are successful, the resulting relationship can be used to quantitatively model Fe(II) oxidation rates in more complex geologic systems that contain competing metals, Fe-binding ligands, and Fe-binding mineral surfaces.

Oxygenation of the Ediacaran Ocean:

A Study of Sulfur Isotope Profiles and Iron Speciation

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Sediments from the Ediacaran Period (635 – 542 Ma) record both the first animal fossils and what appears to be the second major rise of atmospheric oxygen in Earth history. Multiple studies have used different proxies to assess the extent of this rise in oxygenation both spatially and in terms of relative concentration of oxygen to present day values. Two of the most powerful proxies for these types of studies have been iron speciation and sulfur isotopes. Iron speciation studies work to distinguish if the iron in the sediments is present mostly in a reduced or oxidized form. Iron speciation is useful for studying oxygenation since iron will generally precipitate in an oxidized form in an oxic environment and in a reduced form in an anoxic environment. Sulfur isotope work generally looks at sulfur isotopes of sulfate in the form of carbonate associated sulfate (CAS) and pyrite sulfur. Sulfur isotopes from CAS are thought to record the isotopic composition of sulfate in the water column at the time of deposition. On the other hand sulfur isotopes from pyrite are thought to record the isotopic composition of hydrogen sulfide produced by sulfate reducing bacteria (SRBs), which is later precipitated as pyrite. This proxy can be useful to assess the level of fractionation between seawater sulfate and pyrite produced by the SRBs as the SRBs, in a non-sulfate limited environment, will preferentially take up lighter sulfur.

Here we present results of both iron speciation work and sulfur isotope work from Ediacaran age sediments in the Wernecke Mountains of Northwest Canada. The results from the iron speciation work appear to indicate a trend toward more oxic waters upsection. The sulfur isotope results appear to indicate a trend from high fractionation to low fractionation upsection. This appears at first glance to be incongruous, since higher oxygen content in the water column should lead to higher concentrations of sulfate in the water as well. However, SRBs can only survive in anoxic conditions. We propose that the oxygenation of the water column forced SRBs into the sediments at the bottom of the ocean. Here they became sulfate limited as there should have been little communication between the water column and the lower sediments without vertically burrowing animals, which do not generally appear in the rock record until the Cambrian.

Coupled Processes in the Biogeochemical Dynamics of Fe, S, and C under Sulfate- and Iron-Reducing Conditions

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The mobility of contaminants, the availability of C and nutrients, and the geochemical character of groundwater in subsurface environments is closely tied to the biogeochemical cycling of the major elements, particularly the redox cycling of C, Fe, and S. Because these cycles occur concurrently and interdependently, predicting each element's transformations requires a fundamental understanding of the highly coupled biotic and abiotic processes that drive the biogeochemical cycling of C, Fe, and S in subsurface environments.

To better understand the effects of specific electron donors on the biogeochemical dynamics of Fe, S, and C under sulfate- and iron-reducing conditions, we created batch systems containing either acetate, lactate, or glucose as electron donors and ferrihydrite and sulfate as electron acceptors. The batch systems were inoculated with the native microbial community present in sediment from the Rifle, CO, IFRC site. Mineral transformations were monitored by XRD and XAFS spectroscopy, and changes in the microbial communities were determined from 16S rRNA-based tag sequence inventories. All electron donors tested promoted ferrihydrite reduction to varying extents: glucose >> lactate > acetate. The rates and extents of sulfate reduction were faster with lactate than with acetate, while glucose did not stimulate sulfate reduction. Surprisingly, the two replicates of the glucose-amended incubations exhibited different rates and extents of Fe^{II} production and glucose fermentation product profiles. The communities in both of the glucose-amended incubations shifted rapidly and remained stable for the rest of the experiment, consistent with the rapid initial reduction of iron with glucose; however, the microbial populations in each replicate were very different. The incubations with acetate and lactate also showed major community shifts over time, but they were different from each other and from the community profiles in glucose amended incubations.

A parallel set of incubations containing lactate as the electron donor and ferrihydrite, goethite, or lepidocrocite in the presence of high (10 mM) or low (0.2 mM) sulfate was also examined. In the presence of low sulfate, Fe^{III} reduction was slow and limited for all of the Fe^{III} oxides. However, the extent of Fe^{III} reduction increased more than 10 times in the presence of high sulfate. In addition, the extent of Fe^{III} reduction was higher in ferrihydrite and lepidocrocite incubations than in goethite incubations. The concurrence of Fe^{III} and sulfate reduction in the high-sulfate incubations, along with the low levels of Fe^{II} production in the low-sulfate incubations, suggests that Fe^{III} oxide reduction in these systems was primarily the result of abiotic reduction of Fe^{III} by sulfide produced by dissimilatory sulfate-reducing bacteria (DSRB) and not via direct reduction by dissimilatory iron-reducing bacteria (DIRB). Distinctly different community profiles were observed for each of the Fe^{III} oxides. These results suggest that when dissimilatory iron reduction is slow and both sulfate and Fe^{III} oxide are available, sulfide produced by DSRB can drive Fe^{III} oxide reduction. However, the rate and extent of the Fe^{III} reduction by sulfide are strongly affected by the specific Fe^{III} oxide.

We also examined the potential coupling of Fe and S redox processes under alkaline conditions, where the reduction of Fe^{III} by DIRB ceases to be energetically favorable; under these conditions, metal reducers must utilize alternate electron acceptors. One possible alternative is elemental sulfur (S^0), which is produced when dissolved sulfide (a product of microbial sulfate reduction) reacts with Fe^{III} phases. Using geochemical modeling, we show that unlike the reduction of ferric minerals, the reduction of S^0 becomes more energetically favorable as pH increases. We observed experimentally that, under alkaline conditions, *Shewanella oneidensis* MR-1 is capable of reducing S^0 to sulfide, which then reacts with ferric minerals to form Fe^{II}. These results suggest that in slightly alkaline environments where both sulfate and Fe^{III} are available, metal-reducing bacteria may survive primarily by respiring the S^0 created by DSRB.

Jarosite formation associated with an Archean gneiss weathering in Southwest Greenland

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The mineral jarosite occurs at the ice-free margin of southwestern Greenland in association with a gossan overlying weathered Archean gneiss. The conditions during jasorite formation (including temperatures of formation, environments of deposition, fluids chemimistry, and fluid/atmospheric interactions) can be reconstructed from stable isotopes of O, H, and S, leading to improve understanding of environmental change during an ice sheet retreat. Furthermore, the mineral Jarosite was discovered by Opportunity rover at Meridiani Planum on Mars but the origin of jarosite on Mars remains unclear. To investigate the origin of this jarosite at Greenland, in our 2012 field campaign, we excavated a soil pit to a depth of 40 cm and collected samples at 5-cm interval. No visible pyrite was found in the nearby outcroppings of gneiss in the field. XRD data show that all samples were composed of anorthite, quartz, albite, jarosite, muscovite, and microcline. Jarosite was the only sulfur-bearing mineral identified by XRD, with abundance of jarosite increasing with depth (up to 8.4 wt. %) in the soil pit. Water-soluble and acid-soluble sulfate were sequentially extracted using 10% NaCl and 2N HCl solutions, respectively. Pyrite was then extracted from insoluble residues using a chromium reduction method. The average abundance of water-soluble sulfate, acid-soluble sulfate, and pyrite were 100 ppm, 70,000 ppm, and 10 ppm, respectively. Value of $\delta^{34}S$ for water-soluble sulfate, acid-soluble sulfate, and pyrite range from -0.7‰ to 3.1‰ (average= 1.5‰), -1.2 to 1.5‰ (average= 0.7‰), and 0.3‰ to 6.7‰ (average= 2.6‰) respectively. Value of $\delta^{34}S$ for all water-soluble sulfate and pyrite, were higher than acid-soluble sulfate. Value of $\delta^{34}S$ for pyrite was higher than all water-soluble sulfate except the surficial sample (0-10 cm depth). Value of $\delta^{34}S$ for water soluble sulfate and acid soluble sulfate did not change with depth while $\delta^{34}S$ values of pyrite increased with depth from 2.4‰ to 6.7 ‰ (10-15 cm) and then dropped to 2.0‰. Preliminary data indicate that the acid-soluble sulfate was dominated by jarosite while the water-soluble sulfate was a mixture of jarosite and other sulfate minerals. Jarosite formation may result from the oxidative weathering of pyrite inferred to originate from localized, stratiform, hydrothermal mineralization. Multiple sulfur isotopes and triple oxygen isotopes for sulfate will be analyzed, which can define the source of sulfur and oxygen in order to further constrain the origin of jarosite. Improved understanding of the formation of jarosite on the ice-free margin of Greenland provides valuable insight into jarosite formation on Mars.

Deciphering Earth History: Mapping the spatial distribution and speciation of sulfur in Ordovician carbonates

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The sulfur cycle can be studied through measurement of secular changes in the isotopic composition of oxidized and reduced forms of this element preserved in carbonates. Sulfate can be preserved within the carbonate mineral matrix (~100 – 10,000 ppm) as carbonate-associated sulfate (CAS), while pyrite and other metal sulfide species often are found finely disseminated throughout. Isotopic measurements of these phases in geological samples help shape our understanding of the redox evolution of Earth's surface over geologic time. As the isotopic record of ancient oceanic conditions becomes better resolved, however, reports of coeval but discordant geochemical/isotopic proxies are becoming increasingly common. Such varied assessments could arise from (i) primary differences in the chemistry of the water column from which these sediments were deposited (LI et al., 2010); (ii) geochemical alteration during physical reworking as sediments are being deposited (ALLER et al., 2010); or (iii) as the result of secondary alteration of geochemical signals after deposition and lithification (MARENCO et al., 2008). As a bulk-rock proxy, these signals can be influenced by the complex histories that ancient sediments often have experienced during and after deposition. Deciphering the multiple origins of sulfate and sulfide within carbonate minerals is critical to extracting meaningful information from these isotope proxies about the depositional and diagenetic environment in which the samples formed.

Here, we use X-ray spectromicroscopy to map the distribution of primary and secondary S-bearing sedimentary phases at the micron-scale in a well-characterized suite of Ordovician-aged (~444 million years ago) carbonate strata from Anticosti Island, Quebec (JONES and FIKE, 2013; JONES et al., 2011). Using this technique we have generated the first maps of sulfate variability at the micron scale on these carbonate samples. These results show differences between major phases (e.g., clasts vs. cement), as well as subtle differences in sulfate concentrations between fossil clades (e.g., crinoids vs. gastropods). Furthermore, we can distinguish the sulfate content of different stages of calcite cement, helping to constrain the diagenetic history and relate specific cements with the chemistry of the waters from which they formed. In conjunction with high-resolution secondary ionization mass spectrometry (SIMS) $\delta^{34}S$ measurements, this work will allow us to distinguish between primary and post-depositional isotopic signatures in different phases, and enhance our ability to use $\delta^{34}S$ isotopic signatures to reconstruct biogeochemical sulfur cycling over Earth history.

Glacial microbial community structure

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Microorganisms are necessary components of geochemical cycles at low temperatures (<100 ºC), as they are capable of mediating metal reduction and oxidation reactions that in turn are coupled to the organisms core metabolism and drive intracellular carbon oxidation or fixation. Much work has focused on understanding microbial mediated geochemical cycling, especially in acid mine drainage environments, whereby dissolution of sulphide minerals releases toxic metals such mercury into the environment. Recent work has identified and implemented microorganisms as potential catalysts for mineral weathering in interstitial waters underlying glaciers, which under a warming climate, could indirectly impact carbon and nutrient cycling in coastal marine ecosystems by the enhanced glacial discharge of weathered minerals. Thus we sought to understand the composition, diversity and seasonal dynamics of microbial communities associated with the Lemon Creek Glacier in southern Alaska. Water with suspended glacial flour was filtered and from three primary locations which also approximate sampling time; a small catchment lake (early season, May), stream feeding the lake from the glacial toe (mid season, July), and the outflow from the glacial toe (late season, August). DNA was extracted and microbial ribosomal genes were sequenced by pyrosequencing. Independent of sampling time Betaproteobacteria were the most abundant class of microorganisms encountered. Many of the Betaproteobacteria encountered have been previously recognized for their ability to cycle metals under micro-oxic and anoxic conditions. Bacteroidetes, known for fermentation metabolisms, were also highly abundant in many of these samples suggesting fermentation by products such as acetate may play an important role in carbon cycling in these environments. Phlyogenetic diversity, a measure of unique taxonomic lineages, corresponded with the time of sampling such that early season lakes and feeder stream were less diverse than late season communities associated with the glacial discharge. While fluctuations in phylogenetic diversity was observed, mid to late season communities were quite stable over time suggesting a diverse interstitial flora exists and is being discharged from the glacier. Beta diversity, a measure of how related the entire community from a single sample is to other samples, showed similar trends to the phylogenetic diversity such that late season communities were stable over time. Mantel tests of significance show that conductivity ($P=0.002$, $r^2= 0.135$), alkalinity ($P=0.038$, $r^2= 0.034$), sodium ($P=0.001$, $r^2= 0.408$), Potassium ($P=0.047$, $r^2= 0.043$) and potassium: sodium ratio ($P=0.001$, $r^2= 0.23$) were significantly correlated with beta diversity patterns. While the correlation coefficient was not strong for many of these geochemical factors, it does suggest that over time, shifts in microbial community structure is driven by the discharge of glacial melt water and the interstitial communities it harbours. Our work suggests that microbial communities in interstitial waters are unique from communities that populate discharge lakes and is likely driven by alterations to the geochemical environment. Furthermore our results corroborate earlier work and suggest that interstitial microbe mineral interactions are likely pervasive and warrants further study as these ecosystems are ephemeral under a warming climate yet extremely important as glacial discharge may alter coastal marine ecosystems.

Redox Chemistry of West Antarctic Peninsula Margin Surface Sediments

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Continental margin sediments are commonly studied using trace metal enrichments as proxies for characterizing their modern redox conditions and tracking past changes in bottom water ventilation and marine primary productivity. Currently little is known about the sedimentary redox history of the continental shelf west of the Antarctic Peninsula. Yet, environmental conditions of the West Antarctic Peninsula have changed rapidly in recent decades in response to global warming. Paleoclimate archives including bulk sediment trace metal enrichments can provide insight into both past and future environmental changes in this climatically sensitive region. Therefore, characterization of redox conditions in surface (modern) sediments is essential for establishing a framework for paleoredox interpretations. In this study we measured concentrations of trace metals (Ag, Cd, Re, and Mo) and productivity proxies (total Ba, organic carbon, and biogenic silica) in surface sediments from the Marguerite Bay, Gerlache Strait, and Bransfield Strait areas. Proxy concentrations suggest that sediments are generally suboxic due to seasonally high export of organic carbon from surface waters. Comparison of West Antarctic Peninsula trace metal enrichments to trace metal and pore water data from continental margins outside the Antarctic region demonstrates that although the West Antarctic Peninsula water column differs from other continental margins (e.g., it lacks a strong oxygen minimum zone), sedimentary redox chemistry is similarly controlled by organic matter decomposition, through slow recycling of highly seasonal export production falling through a cold water column.

MARINE URANIUM ISOTOPE ARCHIVE TIED TO EVOLUTION OF PHOTOSYNTHESIS IN EARTH'S EARLY HISTORY

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We propose that it is possible to use U isotopes to track the earliest emergence of oxygenic photosynthesis. In Earth surface environments, U exist in two valence states, U(IV) and U(VI). In most situations, U(IV) is immobile while U(VI) is mobile (Langmuir, 1978). Oxidative weathering mobilizes U(IV) in continental rocks. Rivers then carry the product U(VI) to the ocean. Ocean U is eventually reduced and buried in marine sediments. Among weathering, transport, and reduction processes, redox cycling are the major processes causing large U isotope fractionation (Weyer et al., 2008; Bopp et al., 2009; Montoya-Pino et al., 2010; Bopp IV et al., 2010; Brennecka et al., 2011a; Brennecka et al., 2011b). Further, high temperature processes induce limited U isotope fractionations (Brennecka, 2011c). Therefore, the U isotope composition in sedimentary rocks is very sensitive to redox state of the atmosphere and the ocean and wide variation of U isotope values indicates an oxidative U cycle.

With this framework in mind and with the goal of moving forward our understanding of redox conditions on the early Earth, we determined the $\delta^{238/235}$U values (relative to CRM112a) of Steep Rock (ca. 2.9 Ga), and Tumbiana (ca. 2.7 Ga). We compare these new results with published $\delta^{238/235}$U values of recent corals (Stirling et al., 2007; Weyer et al., 2008) and Phanerozoic carbonates (Brennecka et al., 2011b). We found wide variation of $\delta^{238/235}$U in both Steep Rock and Tumbiana carbonate rocks, compared to relatively narrow range of $\delta^{238/235}$U in modern and recent carbonates deposited under stable (oxic or anoxic) redox conditions. These $\delta^{238/235}$U values provide evidence for an early (Mesoarchean) emergence of oxygenic photosynthesis. We link the enhanced $\delta^{238/235}$U variability in these Archean carbonates to more pronounced distillation driven by progressive reduction after oxidative mobilization of continental U. In the Archean, we expect diffuse redox gradients in surface regimes and fluctuations between low oxygen and anoxic conditions—the ideal conditions to amplify isotope effects of a redox sensitive element.

In sum, there is U isotope evidence for the rise of oxygenic photosynthesis well before the GOE, which challenges recent claims for the rise of oxygenesis near the Archean-Proterozoic boundary.

References

Bopp IV C. J., Lundstrom C. C., Johnson T. M., Sanford R. A., Long P. E. and Williams K. H. (2010) Uranium 238U/235U isotope ratios as indicators of reduction: results from an in situ biostimulation experiment at Rifle, Colorado, USA. *Environ. Sci. Technol.*

Bopp C. J., Lundstrom C. C., Johnson T. M. and Glessner J. J. G. (2009) Variations in 238U/235U in uranium ore deposits: Isotopic signatures of the U reduction process? *Geology* **37,** 611.

Brennecka G. A., Wasylenki L. E., Bargar J. R., Weyer S. and Anbar A. D. (2011a) Uranium Isotope Fractionation during Adsorption to Mn-Oxyhydroxides. *Environ. Sci. Technol.*

Brennecka G. A. (2011c) Uranium Isotope Variations in Nature: Mechanisms, Applications, and Implications. Ph.D. thesis, Arizona State University.

Brennecka G. A., Herrmann A. D., Algeo T. J. and Anbar A. D. (2011b) Rapid expansion of oceanic anoxia immediately before the end-Permian mass extinction. *Proceedings of the National Academy of Sciences* **108,** 17631-17634.

Langmuir D. (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* **42,** 547-569.

Montoya-Pino C., Weyer S., Anbar A. D., Pross J., Oschmann W., van de Schootbrugge B. and Arz H. W. (2010) Global enhancement of ocean anoxia during Oceanic Anoxic Event 2: A quantitative approach using U isotopes. *Geology* **38,** 315.

Stirling C. H., Andersen M. B., Potter E. K. and Halliday A. N. (2007) Low-temperature isotopic fractionation of uranium. *Earth Planet. Sci. Lett.* **264,** 208-225.

Weyer S., Anbar A., Gerdes A., Gordon G., Algeo T. and Boyle E. (2008) Natural fractionation of 238U/235U. *Geochim. Cosmochim. Acta* **72,** 345-359.

Elemental Sulfur (So) as a Supplemental Electron Donor for Wastewater Denitrification

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Reduced sulfur compounds such as sulfide (S^{2-}), elemental sulfur (S^o), thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) are available as electron donors for chemolithotrophic bacteria. Since the solubility of S^o in water is extremely low, it is not clear whether microorganisms growing on S^o need to be in direct contact with S^o, or whether a biofilm can develop and be active away from the S^o surface. There is potential for counter-diffusional biofilms to form when S^o serves as an electron donor and an attachment surface, and electron acceptor such as nitrate (NO_3^-) or oxygen diffuses from the bulk into the biofilm, and this behavior would be different from conventional, co-diffusional biofilms.

Due to the increasingly stringent standards for nitrogen and phosphorus, many wastewater treatment plants (WWTPs) have started to implement biological nutrient removal (BNR) processes. This typically requires the addition of a supplemental electron donor, such as methanol, ethanol, acetate, or proprietary organic formulations. Unfortunately, common heterotrophic electron donors are expensive and may have special handling concerns, high biomass yields and a large carbon footprint. Denitrification can also be carried out by autotrophic denitrification using inorganic electron donors. Elemental sulfur (S^o) may provide a more cost-effective and sustainable option. S^o is significantly less expensive, on a per-electron basis, than methanol and ethanol. The low biomass yield with S^o as electron donor minimizes sludge formation. S^o is non-toxic and does not form flammable vapors, making it safer for handling, storage and transportation. In addition, it has "on demand" use without concerns for overdosing.

S^o-based denitrification has been investigated previously for a variety of applications. However, there is little information on S^o-based denitrification in the context of modern BNR systems. Our research focuses on using S^o for BNR applications, specifically tertiary filters and the anoxic compartment of an activated sludge process. In this study, we used packed-bed reactors to study the development of biofilms and their activity as a function of bulk NO_3^- concentrations.

In this study, packed-bed column reactors with S^o granules were used. Recirculation pumps maintained well-mixed conditions within the reactors. The reactors were supplied with synthetic wastewater with 10 mgN/L NO_3^- and inoculated with biomass from previous S^o packed-bed reactor. Influent and effluent samples were analyzed for nitrate, nitrite and sulfate using ion chromatograph. Short-term tests, to determine the denitrification fluxes at different NO_3^- concentrations, were carried out by increasing the influent flow rate to challenge the reactor with higher nitrate loading. Pseudo-steady-state effluent NO_3^- concentrations were measured at different flow rates. Vigorous backwashing was carried out after long-term operation in order to remove biofilm from S^o particles. Removed biomass was collected and added back to the backwashed reactor to perform bioaugmentation tests. Nitrate, nitrite and sulfate concentrations after backwashing were analyzed for reactors with or without added biomass.

During the startup, nitrite accumulation was observed. After 45 days, nitrate and nitrite were fully removed. The maximum nitrate flux was around 0.9 gN/m^2-d. The maximum flux increased as biofilm developed, suggesting that denitrificaton occurred throughout the biofilm, not only on the sulfur surface. The apparent half-saturation constant, K_{app}, was around 0.2 mgN/L to 0.9 mgN/L. Initial slopes of the curves decreased over time potentially due to the increasing diffusional resistance as the biofilm thickness increased. Aggressive backwash was carried out after 140 days. Almost all visible biomass was removed. Recovery of nitrate reduction took about 3-5 days with 6 mgN/L initial NO_3^- effluent concentration. By adding biomass back to the backwashed reactor, it appeared that initial NO_3^- effluent concentration decreased to 4 mgN/L. The recovery time for nitrate removal dropped as well. Nitrite accumulated for both cases. Adding biomass did not improve nitrite reduction. Reactors needed 10-13 days achieve full denitrification for both cases.

Our results suggest that S^o-based denitrification is a promising option for BNR. Biomass accumulated slowly, consistent with the low expected yields for S^o-based denitrification. Initial startup took about 45 days. The increasing maximum fluxes, and decreasing initial slopes of flux vs. bulk NO_3^- concentration, over time suggest biofilm development in reactors. The low K_{app} suggests that low effluent NO_3^- concentrations may be achieved without compromising the high fluxes. Providing bioaugmentation via added S^o-oxidizing biomass could improve nitrate reduction.

Microbial 16S rRNA Gene Clone Libraries from Hydrocarbon Contaminated Sediments

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Contamination from oil spills is a common and widespread environmental problem. It has been shown that microbial degradation of hydrocarbons can effectively reduce contamination in subsurface soil. However, techniques that can be used to observe the presence and progression of biodegradation remain to be evaluated. Magnetic susceptibility (MS) is one geophysical technique that was applied to a subsurface petroleum contaminated site in Bemidji, Minnesota. Spikes in MS readings were found in the zones around the water table. Some microorganisms involved in bioremediation couple hydrocarbon degradation to iron reduction, which may lead to the production of magnetite. We sought to analyze the microbial communities present at these sites through the construction of clone libraries. Several 16S rRNA clone libraries of bacteria and archaea from different depths of contaminated and uncontaminated cores were constructed. Each resulting DNA sequence was analyzed using BLAST and the Ribosomal and Silva sequence databases, and clones were grouped by phyla. In the vadose zone, bacteria similar to *Albidiferax*, an iron reducer, formed the majority of the bacterial community. Below the water table, bacteria similar to the synthrophic *Smithella* and the methanogenic archaeon *Methanoregula* dominated the microbial community. *Desulfosporosinus*, a possible iron reducer, was also prominent beneath the water table. The geophysical technique of measuring magnetic susceptibilities may be a useful tool for indicating microbial biodegradation activities.

Phylogeny and niche partitioning in two serpentinizing fluid seeps

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Serpentinization, the hydrous alteration of ultramafic rock, releases electron donors that can be utilized by chemotrophic microbes dwelling in subsurface ecosystems. The microenvironment created by serpentinization is thought to have given rise to the proton pump mechanism that all organisms utilize to drive cellular processes (Russell et al., 2013). As such, the study of serpentinizing systems is particularly relevant to the fields of astrobiology and origins of life. Surface serpentinizing fluid seeps provide an economical means to access the subsurface biosphere. These seeps have been found in a handful of localities around the world. This study investigates serpentinization-associated communities within the Zambales range ophiolites at Manleluag Spring National Park, the Philippines, and the Tekirova ophiolite complex in Yanartaş, Antalya, Turkey. Source fluids at both sites were characterized by elevated pH and Ca^{2+}:Mg^{2+} ratios typical of serpentinizing fluids. The Manleluag seep originates in a small pool, and large carbonate terraces form downstream of the source. The fluid seep at Yanartaş is much smaller, possibly ephemeral, and actively burning methane and hydrogen. Samples were collected for DNA extraction from the source seeps and several points downstream to determine variations in community compostion and function as a result of surface exposure.

Illumina MySeq platform sequencing of the small-subunit rDNA (using universal primers) revealed multi-scalar niche partitioning with similar inferred metabolic functions at both seeps. The distribution of anaerobic taxa appeared to be dependent on differences in surface mixing at the seeps in Yanartaş and Manleluag. Anaerobic bacterial taxa such as Clostridia and Bacteriodetes were three times more abundant at Manleluag than Yanartaş (35% of total bacterial reads at Manleluag versus 10% at Yanartaş). Anaerobic archaeal taxa were also more abundant at Manleluag; Methanobacteria comprised only 35% of total archaeal reads at Yanartaş, but 90% at Manleluag. Changes in downstream community composition were also more pronounced at Manleluag; the thermophiles Thermales and Hydrogenophilales represent the most abundant taxa downstream (~50%). Hydrogenophiales oxidizes H_2, which may be produced upstream via anaerobic fermentation. At Yanartaş niche partitioning was less evident; downstream communities were mainly composed of Alpha- and Betaproteobacteria (~60%). Rapid surface mixing at the source may have contributed to earlier community stabilization. One major difference between source and downstream communities was pigmentation; 5.5 meters downstream, the previously white biofilm community became orange-red. The pigmentation shift may be attributed to the presence of Rhodobacteraceae, which were only detected from orange-red biofilm communities. Rhodobacteraceae are shown to be the "primary colonizers" of coastal seawater biofilms in the Eastern Mediterranean (Elifantz et al., 2013). Given the proximity of the ocean at Yanartaş, it is possible that these taxa have been transported via aeolian processes.

Despite phylogenetic differences, microbial communities at Manleluag and Yanartaş exhibit similar function. Sequencing data from both localities suggests that favorable metabolic pathways may include methanogenesis, methanotrophy, nitrification, and fermentation; many of these are confirmed by geochemical modeling. Further work is necessary to determine if these metabolisms are actively operating, and whether the methane present at both seeps is biogenic.

Russell, M.J.; Nitschke, W.; Branscomb, E. (2013) The inevitable journey to being. *Phil. Trans. R. Soc. B*. 368(1622): 20120254

Elifantz, H.; Horn, G.; Ayon, M.; Cohen, Y.; Minz, D. (2013) Rhodobacteraceae are the key members of the microbial community of the initial biofilm formed in Eastern Mediterranean coastal seawater. *FEMS Microbiol. Ecol*. 85(2): 348-357

Bacterial cell envelopes using selective site-blocking and potentiometric titrations

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Sulfhydryl binding sites on bacterial cell envelopes play an important role in metal adsorption onto bacterial cells and thus can affect the fate, transport, and bioavailability of metals in a range of geological and engineered settings. In this study, a novel approach was developed to estimate the concentration and acidity constants of sulfhydryl sites within bacterial cell envelopes of *Bacillus licheniformis*, *Bacillus subtilis*, *Bacillus cereus*, *Shewanella oneidensis* and *Pseudomonas fluorescens*. The experiments involved the selective blocking of sulfhydryl sites using a thiol-specific molecule, coupled with total site concentration comparisons of blocked and un-blocked bacterial samples by potentiometric titration measurements to determine sulfhydryl concentrations. All five species studied contained measureable concentrations of sulfhydryl sites, ranging from 16.6±3.3 μmol/g for *Bacillus cereus* to 33.1±7.6 μmol/g for *Shewanella oneidensis*. No significant difference was found between sulfhydryl site concentrations on Gram-positive species relative to those on Gram-negative bacteria in this study. However, the proportion of sulfhydryl sites relative to the total sites on each species was highest for the thermophilic bacterium *Bacillus licheniformis* with 14±3%, and the four mesophilic species exhibited an average of 8±2%. All species contained sulfhydryl sites with a pK_a of ~9.3, but *Bacillus subtilis* and *Pseudomonas flourescens* exhibited significant concentrations of sulfhydryl sites with much lower pK_a values as well. Our results suggest that sulfhydryl sites are present in relatively low concentrations over a wide range of bacterial diversity, but that their concentrations are high enough to control the binding of metals onto bacteria under low metal-loading conditions.