



Midwest Geobiology Symposium 2018  
October 6, 2018  
Northwestern University  
Evanston, IL



Northwestern  
University



AGOURON  
INSTITUTE



**Welcome** to Northwestern University and the seventh annual Midwest Geobiology Symposium. This event provides a unique opportunity for graduate students and post-doctoral scholars to share ongoing research within the local geobiology community. The focus of this event is to give these emerging scholars a platform at which to discuss science, and to build networking and communication skills with peers and established members of the field. This regional symposium is an annual event that has been ongoing since inception at University of Washington in St. Louis in 2012. At this year's symposium we have approximately 95 participants from 20 institutions, presenting a diverse array of research spanning many areas of geobiology. We thank the Agouron Institute, NAISE, the Northwestern Nemmer's Prize in Earth Sciences, and Northwestern University for providing generous support for this meeting.

Sincerely,

The Midwest Geobiology 2018 Organizing Committee

Magdalena Osburn (Northwestern University)  
Theodore Flynn (Argonne National Laboratory)  
Caitlin Casar (Northwestern University)  
Jamie McFarlin (Northwestern University)

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# SCHEDULE

FRIDAY, 5 OCTOBER 2018

6:30 pm - 9:30 pm Welcome reception at the Celtic Knot

SATURDAY, 6 OCTOBER 2018

8:00 am - 9:00 am Arrival at Northwestern McCormick Center and Breakfast

9:00 am - 9:10 am Opening remarks

9:10 am - 10:30 am Oral session 1

10:30 am - 10:50 am Coffee break

10:50 am - 12:30 pm Oral session 1, continued

12:30 pm - 1:40 pm Lunch

1:40 pm - 3:00 pm Oral session 2

3:00 pm - 3:20 pm Coffee break

3:20 pm - 4:00 pm Oral session 2, continued

4:00 pm - 4:45 pm Keynote speaker

4:45 pm - 7:30 pm Poster session with snacks and bar service

7:45 pm Optional gathering at Bat17

# SPEAKERS

## ORAL SESSION 1

- 9:10 am - 9:30 am      **Justin Podowski**, University of Chicago  
Compositional and metabolic differences in nitrifying communities across the Laurentian Great Lakes
- 9:30 am - 9:50 am      **Kathryn Hobart**, University of Minnesota  
Understanding Microbial Contributions to Pyrrhotite Oxidation at Circumneutral pH
- 9:50 am - 10:10 am    **Caitlin Casar**, Northwestern University  
Mineral-hosted biofilm communities within the continental deep subsurface
- 10:10 am - 10:30 am    **Samuel Miller**, University of Chicago  
Novel Metaproteomic Approaches Applied to Arctic Soils Reveal Niche Partitioning of Microbial Biogeochemical Functions and Systematic Variations with Vegetation Type
- 10:50 am - 11:10 am    **Scott Beeler**, Washington University in St. Louis  
Interpreting the meaning of extreme isotopic enrichments in modern microbialites and implications for the rock record
- 11:30 am - 11:50 am    **Roger Bryant**, Washington University in St. Louis  
Local Environmental Controls on Marine Sedimentary Pyrite Sulfur Isotope Ratios
- 12:10 pm - 12:30 pm    **Derek Smith**, Washington University in St. Louis  
Changes in Bacterial Growth Rate Lead to Hydrogen Isotope Fractionation

## ORAL SESSION 2

- 1:40 pm - 2:00 pm      **Daniel Jones**, University of Minnesota  
Mercury methylation and methylating communities in sulfate-impacted freshwater ecosystems
- 2:00 pm - 2:20 pm      **Clayton Johnson**, University of Notre Dame  
Developing and utilizing a novel cadmium-specific fluorescent probe technique to test the component additivity approach to surface complexation modeling
- 2:20 pm - 2:40          **Stephan Hlohowskyj**, Central Michigan University  
Molecular geochemistry of molybdenum-organic matter interactions in black shales
- 2:40 pm - 3:00 pm      **Mary Sabuda**, University of Minnesota  
Biogeochemical transformations of selenium by common saprotrophic soil fungi
- 3:20 pm - 3:40 pm      **Jocelyn Richardson**, Washington University in St. Louis  
The source of sulfate in biogenic calcite: insights from  $\mu$ -XRF imaging, XANES spectroscopy and isotope studies of ancient and extant brachiopods
- 3:40 pm - 4:00 pm      **Stephanie Olson**, University of Chicago  
Ediacaran oxygen oases and the emergence of bilaterian burrowing

## KEYNOTE SPEAKER

- 4:00 pm - 4:45 pm      **Francis Albarède**, Ecole Normale Supérieure de Lyon  
Transition metals, their isotopes, and biology

# KEYNOTE SPEAKER

4:00 pm - 4:45 pm

## **TRANSITION METALS, THEIR ISOTOPES AND BIOLOGY**

Francis Albarède  
Ecole Normale Supérieure de Lyon

The natural variations of stable isotopes of transition elements in biological material offer a novel perspective on metal functionalities and pathways in the cells of unicellular and multicellular organisms. Three transition elements have found critical roles in biological processes, Cu, Zn, and Fe. Their cellular homeostasis is rather well understood, although some critical links are still missing. For the microbiologists, tasks of different nature are calling for geochemist's attention. First, a huge analytical investment is needed to describe the extent of isotopic variability in different cell components and organelles. Second, predicting the isotope fractionation caused by the different cellular components using theoretical (*ab initio*) methods is a task best handled by theoretical chemists and biochemists. Third, testing the isotopic expression of the genes involved in metal homeostasis (e.g., importer, oxidoreductases, storage) requires a close interaction between molecular biologists and geochemists. Fourth, quantitative and robust models of homeostasis should be put together in order to demonstrate that our understanding of the processes account for the observations. Fifth, it is hoped that interaction between cells and their environment can be traced by specific biomarkers. On each part, decisive progress has been achieved over the last decade, but what is now known as 'Isotope Metallomics' is still in infancy. The purpose of this talk is to review these principles and to provide some applications to biology and medicine.

# POSTERS

**Jake Bailey**, University of Minnesota

Carbonate dissolution by sulfur-oxidizing bacteria in marine cold seep settings

**Evelyn Becerra**, Indiana University- Purdue University Indianapolis

A High Resolution Study of Nutrient and Redox Cycling in the Kope Formation of the Late Ordovician

**Jake Callaghan**, University of Minnesota Duluth

New spin on methylotrophy in a freshwater sediment: Novel archaeal phylum implicated in methyl compound degradation

**Howard Chase**, Indiana University Purdue University Indianapolis

Spatial and Temporal Variations of Water Quality in a Eutrophic Freshwater Lake and Their Correlation to Seasonal Algal Blooms

**Sarah Denny**, Indiana University Purdue University Indianapolis

Phosphorus Uptake in Constructed Wetlands for Possible Nutrient Loading Mitigation

**Fotios Fouskas**, Indiana University Purdue University Indianapolis

Sulfurization pathways in modern euxinic lakes: Exploring the key constraints for organo-sulfur and pyrite formation

**Gwendolyn Gallagher**, University of Chicago

Physiology and Protein-Level Proteorhodopsin Expression Patterns in *Vibrio campbellii* CAIM 519

**Alyssa Henke**, Indiana University Purdue University Indianapolis

Using Reactive Iron Distribution to Characterize Redox Conditions in the late-Holocene record of Martin Lake, USA

**Jennifer Houghton**, Washington University in St. Louis

Evaluating proxies of microbial carbon and sulfur cycling in methane seep sediments

**Ioanna Koltsidou**, Indiana University Purdue University Indianapolis

Assessment of Microbial Community Composition in Eagle Creek Reservoir using 16S Next Generation Sequencing and qPCR

**Robert Kupper**, Washington University in St. Louis

Assessment of Microbial Community Composition in Eagle Creek Reservoir using 16S Next Generation Sequencing and qPCR

**Martin Kurek**, Indiana University Purdue University Indianapolis  
Rates and Products of Fe(II) Oxidation in Trioctahedral Smectites

**Maisie Lenards**, University of Minnesota  
Metagenomic analysis of a novel potential mercury-methylating population from a hypereutrophic, sulfidic lake

**Barbara MacGregor**, University of Minnesota  
Sequencing read distribution in bacterial genomes with and without GC skew

**Jamie McFarlin**, Northwestern University  
A new global synthesis of sedimentary leaf wax isotopes: expanding to include the Arctic

**D'Arcy Meyer-Dombard**, University of Illinois at Chicago  
The deep biosphere in the jungle: following carbon in serpentinizing springs in a tropical surface biome

**Senthil Murugapiran**, University of Minnesota  
Exploring the “microbial dark matter” through large-scale genomics

**Edward O'Loughlin**, Argonne National Laboratory  
Effects of Fe(III) inputs on the rate of methanogenesis in wetland sediment microcosms

**Jaelyn Oliver**, Central Michigan University  
Reconstructing methane-supplemented foodwebs using carbon isotope analysis of aquatic invertebrate remains in North American lake sediments

**Elizabeth Olson**, Northern Illinois University  
Isotopic disequilibrium in Prosopis tree cellulose as an indicator of water stress and hydroclimate variability

**Lindsay Putman**, Michigan State University  
Assessing Microbial Community Assembly in a Serpentinization-Influenced Aquifer over Time

**Kathryn Rico**, University of Michigan  
Sediment trace metal contents do not reflect porewater chemistry in a low-oxygen Precambrian analogue

**Annette Rowe**, University of Cincinnati  
Microbes, Minerals and Electrodes at the Sanford Underground Research Facility (SURF): Electrochemistry 4000 ft below the surface

**Cody Sheik**, Large Lakes Observatory  
Microbial contributions to the sediment N and C isotopic record

**John Shukle**, Indiana University Purdue University Indianapolis  
Phosphorous speciation and mobility in Missisquoi Bay mesocosms under extended conditions of reduction, oxidation, and fluctuating oxidation-reduction

**Benjamin Tiger**, Washington University in St. Louis  
Preliminary biogeochemical characterization of sediments from Lake Sibinacocha, Peruvian Andes

**Gabriel Vargas**, University of Chicago  
Illuminating environmental and molecular controls on aerobic anoxygenic phototrophy

**R. Seth Wood**, Washington University in St. Louis  
Formation and Stabilization of Biogenic Vaterite

**Ming Wu**, Washington University in St. Louis  
Mixed sources of n-alkanes in the late Ediacaran in the East European platform constrained by Primary Compound-specific hydrogen isotopic composition

**Allie Wyman**, University of Illinois  
Salinity information from lipid biomarker isotope ratios in a central tropical Pacific lake sediment record

**Ziming Yang**, Oakland University  
The Influence of Earth Abundant Minerals in Deep Ocean Hydrothermal Organic Transformations

**Qiang Yu**, University of Notre Dame  
Adsorption of selenite onto *bacillus subtilis*: the overlooked role of cell envelope sulfhydryl sites in the microbial conversion of Se(IV)

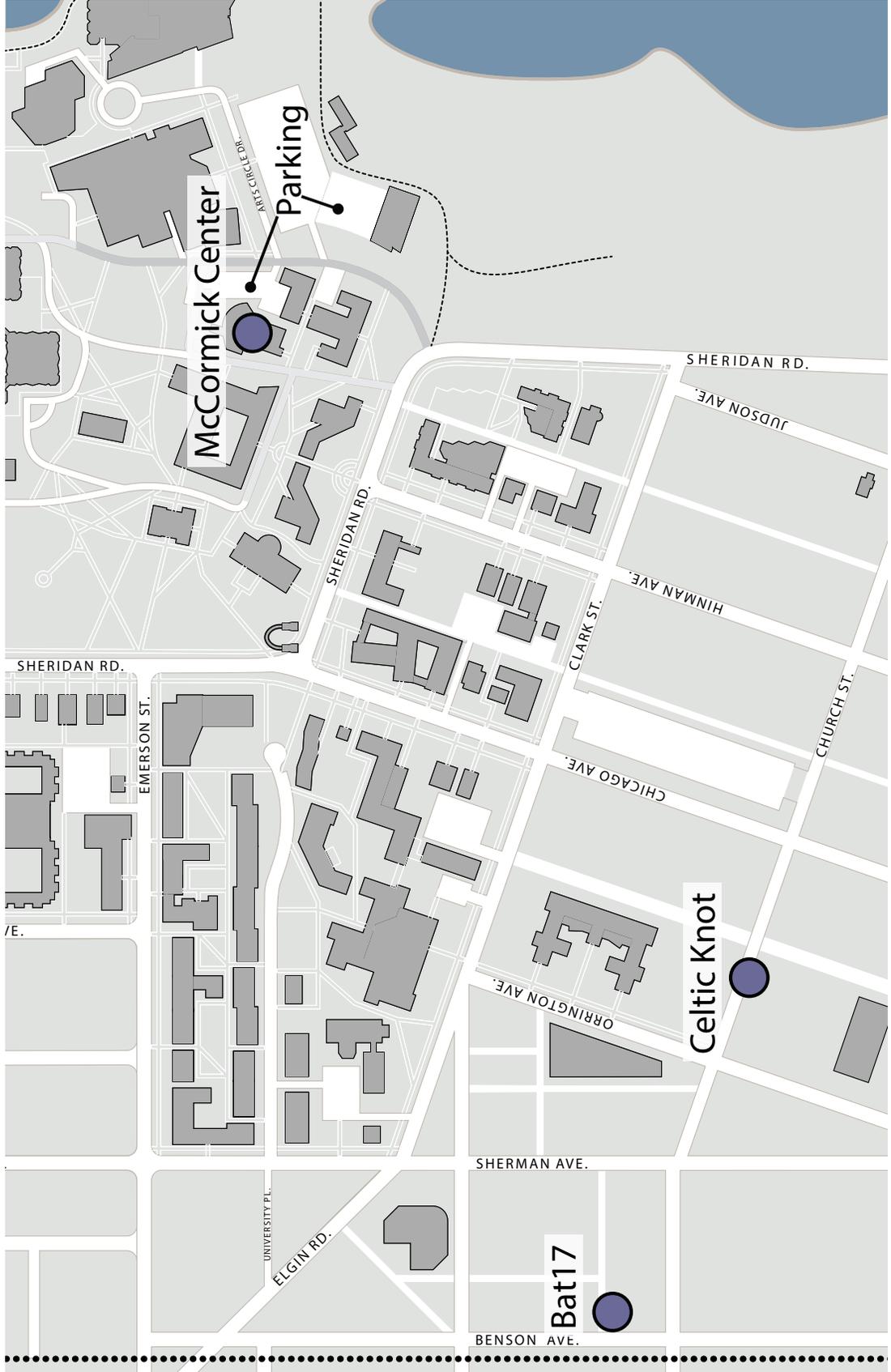
# PARTICIPANTS

<b>First Name</b>	<b>Last Name</b>	<b>Institution</b>
Francis	Albaréde	Ecole Normale Supérieure de Lyon
Nouf	Aldossari	University of Minnesota
Jake	Bailey	University of Minnesota
Evelyn	Becerra	Indiana University Purdue University Indianapolis
Patricia A.	Beddows	Northwestern University
Scott	Beeler	Washington University at St. Louis
Sarah	Ben Maamar	Northwestern University
Clara	Blättler	University of Chicago
Alex	Bradley	Washington University at St. Louis
Roger	Bryant	Washington University at St. Louis
Jake	Callaghan	University of Minnesota Duluth
Caitlin	Casar	Northwestern University
Howard	Chase	Indiana University Purdue University Indianapolis
Luoth	Chou	University of Illinois at Chicago
Chris H.	Crosby	Oakton Community College
Sarah	Denny	Indiana University Purdue University Indianapolis
Greg	Druschel	Indiana University Purdue University Indianapolis
Jeremy	Fein	University of Notre Dame
David	Fike	Washington University at St. Louis
Theodore	Flynn	Argonne National Laboratory
Fotios	Fouskas	Indiana University Purdue University Indianapolis
Gwendolyn	Gallagher	University of Chicago
Bill	Gilhooly	Indiana University Purdue University Indianapolis
Trinity	Hamilton	University of Minnesota
Leanne	Hancock	Michigan State University
Dalton	Hardisty	Michigan State University
Benjamin	Harrison	Central Michigan University
Jeff	Havig	University of Minnesota
Alyssa	Henke	Indiana University Purdue University Indianapolis
Stephan	Hlohowskyj	Central Michigan University
Kathryn	Hobart	University of Minnesota
Jennifer	Houghton	Washington University at St. Louis
Jack	Hutchings	Washington University at St. Louis
Andy	Jacobson	Northwestern University
Clayton	Johnson	University of Notre Dame
Daniel	Jones	University of Minnesota

<b>First Name</b>	<b>Last Name</b>	<b>Institution</b>
Ioanna	Koltsidou	Indiana University Purdue University Indianapolis
Bronwen	Konecky	Washington University at St. Louis
Joshua	Kuether	University of Minnesota
Robert	Kupper	Washington University at St. Louis
Martin	Kurek	Indiana University Purdue University Indianapolis
Sohyun	Lee	Northwestern University
Maisie	Lenards	University of Minnesota
Barbara	MacGregor	University of Minnesota
Andy	Masterson	Northwestern University
D'Arcy	Meyer-Dombard	University of Illinois at Chicago
Samuel	Miller	University of Chicago
Senthil	Murugapiran	University of Minnesota
Adam	Nuccio	Northern Illinois University
Connor	O'Loughlin	Downers Grove South High School
Edward	O'Loughlin	Argonne National Laboratory
Jaclyn	Oliver	Central Michigan University
Stephanie	Olson	University of Chicago
Elizabeth	Olson	Northern Illinois University
Maggie	Osburn	Northwestern University
Joseph	Pasterski	University of Illinois at Chicago
Justin	Podowski	University of Chicago
Lindsay	Putman	Michigan State University
Jocelyn	Richardson	Washington University at St. Louis
Kathryn	Rico	University of Michigan
Megan	Rohrsen	Central Michigan University
Annette	Rowe	University of Cincinnati
Fabrizio	Sabba	Northwestern University
Mary	Sabuda	University of Minnesota
Jarunetr	Sae-lim	Washington University at St. Louis
Sarah	Schroeder	University of Minnesota
Matt	Selensky	Northwestern University
Cody	Sheik	University of Minnesota Duluth
John	Shukle	Indiana University Purdue University Indianapolis
Derek	Smith	Case Western Reserve University
Hammy	Sorkin	Washington University at St. Louis
Melanie	Suess	Washington University at St. Louis
Wesley	Swingley	Northern Illinois University
Benjamin	Tiger	Washington University at St. Louis

<b>First Name</b>	<b>Last Name</b>	<b>Institution</b>
Howard	Truong	Northwestern University
Brooke	Vander Pas	Indiana University Purdue University Indianapolis
Gabriel	Vargas	University of Chicago
Yubo	Wang	Northwestern University
George	Wells	Northwestern University
R. Seth	Wood	Washington University at St. Louis
Ming	Wu	Washington University at St. Louis
Allie	Wyman	University of Illinois
Ziming	Yang	Oakland University
Qiang	Yu	University of Notre Dame

# NORTHWESTERN UNIVERSITY CAMPUS MAP



# ABSTRACTS

IN ALPHABETICAL ORDER BY PRESENTING AUTHOR

## CARBONATE DISSOLUTION BY SULFUR- OXIDIZING BACTERIA IN MARINE COLD SEEP SETTINGS

Dalton Leprich, Beverly Flood, Elizabeth Ricci, Peter Schroedl, **Jake Bailey**

Dept. Of Earth Sciences, University of Minnesota., Minneapolis, MN  
55455, USA

We observed an affinity for the colonization of carbonate rocks by sulfide-oxidizing bacteria at marine methane seeps. These bacteria commonly co-occur with etch pits that suggest active dissolution. Aerobic sulfide oxidation is an acid-producing reaction that has the potential to dissolve carbonate minerals. We investigated carbonate dissolution in the laboratory using bioreactors that contain sulfur-oxidizing bacteria growing on calcium carbonate rock chips. The bioreactors were inoculated with *Celeribacter baekdonensis* LH4, and run under continuous flow conditions for 21 days. The pH, alkalinity, [Ca<sup>2+</sup>], and OD were monitored daily. Aragonite coupons were aseptically sampled and weighed over three weeks to determine the rate of dissolution. The biotic and abiotic dissolution rates were  $\sim 1774 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{a}^{-1}$  and  $\sim 358 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{a}^{-1}$ , respectively. Select coupons were transferred to a flow-cell at the end of the experiment. Laser-scanning confocal microscopy revealed steep pH gradients within the biofilms. Our results show that *C. baekdonensis* LH4 biofilms are actively dissolving aragonite coupons by producing acidic microenvironments, even under well-buffered conditions. These results support the hypothesis that sulfide-oxidizing bacteria in marine seafloor settings can increase the rate of carbonate dissolution by decreasing the pH within the biofilm, and in the process, flux carbon from the carbonate rock reservoir to the ocean and atmospheric carbon reservoirs.

## A HIGH RESOLUTION STUDY OF NUTRIENT AND REDOX CYCLING IN THE KOPE FORMATION OF THE LATE ORDOVICIAN

**Becerra, E.S.**<sup>1</sup>, Gilhooly, W.P.<sup>1</sup>, Dattilo, B.F.<sup>2</sup>, Orazi, D.L.  
<sup>1</sup>Indiana University-Purdue University Indianapolis, <sup>2</sup>Purdue  
University Fort Wayne

The Ordovician (485-444 Mya) was a period of evolutionary and climatic change; it began with The Great Ordovician Biodiversification Event (GOBE), which caused a rapid increase in diversity and dramatic changes in paleoecology, and ended with the Hirnantian Glaciation which is thought to have caused the first major mass extinction of the Paleozoic resulting in the loss of  $\sim 85\%$  of marine species. Though several studies document long time-scale changes in geochemistry, there is currently a lack of high resolution geochemical data that can elicit different interpretations concerning the Ordovician biosphere. The Kope formation within the Cincinnati contains a series of interbedded mudstone and fossiliferous limestone beds deposited within a shallow epeiric sea. Its well established C-isotope, lithologic, and biostratigraphic records allow for a controlled environment to study smaller scale nutrient cycles not previously recorded. Preliminary N-isotope analysis of a high-resolution section of the Kope formation shows what appears to be an overall positive excursion as well as smaller scale cycles based on lithology suggesting broader scale studies overlook these small time-step cycles. In this study, high resolution bulk N-isotopes and redox proxies will be used on a core section above and below existing N-isotope data to determine nutrient and redox cycles not previously recorded for this basin leading into the end Ordovician mass extinction.

## INTERPRETING THE MEANING OF EXTREME ISOTOPIC ENRICHMENTS IN MODERN MICROBIALITES AND IMPLICATIONS FOR THE ROCK RECORD

Scott R. Beeler<sup>1</sup>, Fernando J. Gomez<sup>2</sup>, Alexander S. Bradley<sup>1</sup>

<sup>1</sup>Dept. of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, USA, <sup>2</sup>Laboratoria de Análisis de Cuencas, CICTERRA-CONICET, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba, Argentina

Microbialites are among the earliest and longest lasting records of life on Earth. Analyzing the stable isotopic composition of carbonate minerals that comprise microbialites is a commonly used tool to understand the environmental conditions associated with their formation. However, the isotopic signatures associated with different processes may be non-unique and determining which process is responsible for an isotopic signature can be difficult. Investigating the processes that generate isotopic signatures in microbialites in modern environments can improve our ability to interpret similar signatures in the rock record. We analyzed the processes driving the isotopic evolution of lake waters from the modern microbialite forming environment of Laguna Negra, Argentina in order to better understand extreme enrichments in <sup>13</sup>C and <sup>18</sup>O previously described in microbialites and associated non-microbial carbonates from the lake. Modern lake waters showed isotopic enrichments comparable to those preserved in carbonates that can be explained through a combination of evaporation, degassing, and carbonate precipitation. Together these results suggest that the isotopic enrichments in microbialites record information regarding the environmental conditions of the lake waters in which they formed. However, despite being associated with microbially generated minerals isotopic enrichments can have an abiotic origin.

## LOCAL ENVIRONMENTAL CONTROLS ON MARINE SEDIMENTARY PYRITE SULFUR ISOTOPE RATIOS

Roger N. Bryant<sup>1</sup>, Clive Jones<sup>1</sup>, Itay Halevy<sup>2</sup>, Virgil Pasquier<sup>2</sup>, William M. Berelson<sup>3</sup>, Alex L. Sessions<sup>4</sup>, David A. Fike<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO, USA, <sup>2</sup>Department of Earth & Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel, <sup>3</sup>Department of Earth Sciences, University of Southern California, Los Angeles, CA, USA, <sup>4</sup>Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

Controls on the sulfur isotope ( $\delta^{34}\text{S}$ ) composition of sedimentary pyrite are poorly understood and changes in bulk  $\delta^{34}\text{S}$  values can be attributed to multiple biological and/or environmental causes. To address this, we performed grain-specific S isotope analyses on pyrites extracted from modern marine sediments, using Secondary Ion Mass Spectrometry (SIMS). For a site in NW Mediterranean, bulk  $\delta^{34}\text{S}_{\text{pyr}}$  in interglacials is low and invariant and high and variable for glacials. We show that samples from interglacials feature a narrow inter-grain distribution in  $\delta^{34}\text{S}_{\text{pyr}}$ , generally close to  $-45\%$ , whereas samples from glacials feature a large inter-grain range, from  $\sim -50$  to  $\sim 110\%$ . A sample from Santa Barbara Basin also features a large inter-grain range in  $\delta^{34}\text{S}_{\text{pyr}}$  from  $-42\%$  to  $29\%$ , but a high average  $\delta^{34}\text{S}_{\text{pyr}}$  value of  $\sim 24\%$ . For each sample, little to no intra-grain  $\delta^{34}\text{S}$  variation was detected in grains large enough for multiple analyses. Our results suggest that, (i) the biological fractionation ( $\epsilon_{\text{bio}}$ ) from microbial sulfate reduction (MSR) was invariant, both between sites and over time at the Mediterranean site, (ii) rapid sedimentation can induce closed-system pore water evolution, resulting in more <sup>34</sup>S-enriched bulk pyrite, and (iii) the shapes of inter-grain  $\delta^{34}\text{S}_{\text{pyr}}$  distributions in closed systems reflect the relative rates of MSR and pyrite formation. These distributions can thus be used to infer sedimentation patterns and iron availability and reactivity.

## NEW SPIN ON METHYLOTROPHY IN A FRESHWATER SEDIMENT: NOVEL ARCHAEOAL PHYLUM IMPLICATED IN METHYL COMPOUND DEGRADATION

Jake Callaghan<sup>1</sup>, Cody Sheik<sup>1</sup>

<sup>1</sup>University of Minnesota Duluth, Duluth MN

Subsurface ecosystems are one of the least explored habitats on Earth, but we do know they host a broad diversity of microorganisms and a significant amount of Earth's surface biomass. While organic rich marine sediments have been well studied, freshwater systems remain largely under sampled. Using Lake Superior sediments, we sought to understand the biogeochemical roles of microorganisms in a low carbon, freshwater setting. Using a shotgun sequencing approach, we identified a near-complete archaeal metagenome assembled genome, *Ca. Sedimenti methylvorans*, belonging to the TACK super phylum. Phylogenetic reconstruction supports the placement of the genome in a new phylum, *Candidatus* Superiorarchaeaota, basal to the Thaumarchaeaota. Genome coverage indicates the *Ca. S. methylvorans* is present throughout the core but increases with depth below 9 cm, which corresponds with the sulfate methane transition zone. Metabolic reconstruction revealed a bacterial style methylotrophy which has not been described in Archaea, and it may be coupled to dissimilatory nitrate reduction. Carbon fixation appears to occur via a modified reductive pentose phosphate pathway using a deeply branching Ribulose Bisphosphate Carboxylase/Oxygenase (RuBisCO) that phylogenetically clusters with type III-a methanogenic archaea. Ability to utilize polysulfides was also identified. Together, we have identified a novel biogeochemically important microorganism that has the potential to couple carbon, nitrogen and nitrogen and sulfur cycles.

## MINERAL-HOSTED BIOFILM COMMUNITIES WITHIN THE CONTINENTAL DEEP SUBSURFACE

C. P. Casar<sup>1</sup>, M. R. Osburn<sup>1</sup>, T. M. Flynn<sup>2</sup>, A. L. Masterson<sup>1</sup>, B. R. Kruger<sup>3</sup>

<sup>1</sup>Northwestern University (Evanston, IL), <sup>2</sup>Argonne National Laboratory (Argonne, IL), <sup>3</sup>Desert Research Institute (Las Vegas, NV)

Minerals are likely an important energy source for biofilm-forming members of the deep continental biosphere in which other substrates are limited. However, the microbial ecology and constituent microbe-mineral interactions in these environments are not yet well understood due to sampling challenges. We investigated the utilization of minerals as lithotrophic energy sources by biofilm communities inhabiting fluid-filled fractures in the Deep Mine Microbial Observatory (DeMMO), South Dakota. Fracture fluids continuously flowed through *in situ* colonization reactors filled with an array rocks and minerals as attachment surfaces. These experiments were installed at depths of 244, 610 and 1,478 m for 2-8 months. 16s rRNA gene sequencing and scanning electron microscopy revealed diverse microbial communities and a variety of biogenic precipitates. Experiments with rocks and minerals enriched for dramatically different communities from fluids and from experiments with inert substrates. These results suggest that members of the biofilms may be using minerals as both a surface for attachment and a metabolic energy source. Specifically, manganese oxide appears to be a favorable substrate for members of the family Desulfobulbaceae and class Thermodesulfobibrionia. Further, our results provide insight into the lifestyles of candidate taxa; i.e. consistent with observations from other studies, members of candidate phylum Omnitrophica tend toward a planktonic lifestyle at DeMMO.

## SPATIAL AND TEMPORAL VARIATIONS OF WATER QUALITY IN A EUTROPHIC FRESHWATER LAKE AND THEIR CORRELATION TO SEASONAL ALGAL BLOOMS

Howard, Chase S.<sup>1\*</sup>, Ogashawara, Igor<sup>1</sup>, Koltsiduo, Ioanna<sup>2</sup>, Druschel, Gregory K.<sup>1\*\*</sup>

<sup>1</sup>Department of Earth Sciences, Indiana University Purdue University Indianapolis, Indianapolis, IN, USA, howardch@iupui.edu\*; gdrusche@iupui.edu (\*\*corresponding author), <sup>2</sup>Department of Biology, Indiana University Purdue University Indianapolis

Eagle Creek Reservoir (ECR) is a eutrophic freshwater lake located in central Indiana that experiences seasonal algal blooms producing taste and odor compounds (T&O), chiefly 2-methylisobornel (MIB) and geosmin. The reservoir supplies ~80% of Indianapolis' drinking water and serves as an important recreational area. Water samples were collected between April and September 2018 from fourteen different locations across the reservoir to examine the spatial and temporal distribution of water quality, nutrient levels, and microorganisms. Samples were collected at 0.5m depth, Phycocyanin/Chlorophyll data was collected simultaneously using remote sensing equipment, and additional subsamples were prepared for genomic and taste & odor compound analysis. Initial sample analyses have shown that significant changes exist through both time and space, at multiple scales, for measures including soluble reactive phosphorus, total phosphorus, total dissolved phosphorus, MIB and geosmin concentrations, and Phycocyanin/Chlorophyll concentrations. Triplicate samples for single locations showed a maximum of 10-15% variation, with more significant variability spatially. The most significant changes were observable north to south along the long axis of ECR, but also with pronounced changes for close (<1,000 ft.) sampling points. These initial observations support the hypothesis that certain areas within the reservoir serve as initial hotspots of activity and that ECR is a fairly dynamic system that operates differently between the north and south basins.

## PHOSPHORUS UPTAKE IN CONSTRUCTED WETLANDS FOR POSSIBLE NUTRIENT LOADING MITIGATION

<sup>1</sup>Denny, Sarah E., <sup>2</sup>Brinkman, Jacob, and <sup>1</sup>Druschel, Gregory K.

<sup>1</sup>Indiana University Purdue University Indianapolis Department of Earth Science, Indianapolis, IN, <sup>2</sup>Eagle Creek Park, City of Indianapolis, Indy Parks.

Phosphorus loading to freshwater lakes and reservoirs can result in impaired water quality, including formation of harmful and nuisance algal blooms. Eagle Creek Reservoir (ECR), a significant source of drinking water for Indianapolis, has a long history of algal blooms due to excess nutrient input. Floating wetlands have been installed as both an educational resource for people to learn about nutrient cycling, and as a pilot study to investigate their impact on reservoir water quality. Sampling hydrophytes for total phosphorus using XRF to measure phosphorus cycling and uptake in constructed floating wetlands will allow us to determine the approximate mass of P sequestered in plant material to mitigate impacts of nutrient loading on ECR water quality.

To understanding the effectiveness of constructed wetlands on up-taking and cycling phosphorus, sampling plant matter bi-weekly, drying biomass in an oven for approximately 5-6 days, grinding the dried material into powder with a ball mill, pressing the powder into pellets with a hydraulic press, and lastly using X-Ray Fluorescence to measure phosphorus content. Standards were also developed to calibrate the XRF for plant matter, a series dilution with my ground plant matter and silicon dioxide. Results indicate significant P uptake in grasses over the course of the season, but placing sufficient numbers of floating wetlands in the reservoir to impact P loading may be impractical as a mitigation strategy.

## SULFURIZATION PATHWAYS IN MODERN EUXINIC LAKES: EXPLORING THE KEY CONSTRAINTS FOR ORGANO-SULFUR AND PYRITE FORMATION

Fotios Fouskas<sup>1\*</sup>, William P. Gilhooly III<sup>1</sup>, Molly D. O'Beirne<sup>2</sup>, Josef P. Werne<sup>2</sup>, Alice Bosco-Santos<sup>1,3</sup>, Martin Kurek<sup>1</sup>, Gregory K. Druschel<sup>1</sup>

<sup>1</sup>Earth Sciences, Indiana University-Purdue University Indianapolis, Indianapolis, IN, USA; \*ffouskas@iu.edu, wgilhool@iupui.edu, markurek@iu.edu, gdrusche@iupui.edu, <sup>2</sup>Geology & Environmental Science, University of Pittsburgh, Pittsburgh, PA, USA; mdobeirne@pitt.edu, jwerne@pitt.edu, <sup>3</sup>Geology and Natural Resources, University of Campinas, Campinas, São Paulo, Brazil; alicebosco@gmail.com

Modern euxinic lakes are ideal settings for studying the two competitive sulfurization pathways that lead to pyrite and organo-S compounds (OSCs) formation by means of S isotopes. Mahoney Lake, Canada and Green Lake, NY, contain productive communities of purple S bacteria and sulfate-reducers. The variability in the levels of  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{S}$  and organic matter (OM) between the two lakes can help elucidate factors that influence these sulfurization reactions. Within the Mahoney Lake sediments, the  $\delta^{34}\text{S}$  of pyrite and total organic sulfur (TOS) decrease with depth, supporting no diagenetic effects. The isotope offset between pyrite and TOS also changes downcore from  $\sim 15\%$  down to nearly zero. In contrast, the corresponding  $\delta^{34}\text{S}$  values within the surface sediments of Green Lake increase downcore with a relatively constant offset. We suggest thus that the hyper-euxinic environment of Mahoney Lake has changed through time including changes in the Fe availability, the nature of OM and therefore, the relative kinetic rates between pyrite and OSCs formation. Kinetic modeling will evaluate the dominating pathway by varying  $\text{C}_{\text{org}}$ ,  $\text{H}_2\text{S}$ ,  $\text{S}_8$ , and Fe. Initial results show that only significant levels of labile  $\text{C}_{\text{org}}$  can trigger OM sulfurization rates in levels similar to those of pyritization which could support a zero isotopic offset between pyrite and TOS. FT-ICR-MS analysis of DOM in Mahoney water column revealed abundant OSCs suggesting that rapid sulfurization of OM can occur syngenetically.

## PHYSIOLOGY AND PROTEIN-LEVEL PROTEORHODOPSIN EXPRESSION PATTERNS IN *VIBRIO CAMPBELLII* CAIM 519

Gwendolyn Gallagher<sup>1</sup>, Jacob Waldbauer<sup>1</sup>  
<sup>1</sup>Department of the Geophysical Sciences, University of Chicago

Proteorhodopsin, a light activated proton pump, has garnered attention for its apparent prevalence in a wide variety of both environments and taxa [1]. PR, a form of anoxygenic phototrophy, generates a proton gradient that microbes can potentially use for ATP synthesis, flagellar movement, or nutrient transport, but its physiological role in marine microbes and its contribution to the overall energy budget of marine microbial communities is not yet clear. Previously, environmental PR abundance has been estimated using metagenomics [2,3] and retinal concentrations [4], but not yet using proteomics.

Here we quantify protein-level PR expression using mass spectrometry-based proteomics. We developed new techniques for extracting PR, a hydrophobic integral protein, and quantified it using in vitro isotopic peptide labeling. Growth of *Vibrio campbellii* CAIM 519, a PR-containing microbe, was monitored under a range of carbon, nitrogen, and light conditions, including single carbon sources and varying concentrations of Marine Broth. The purpose of this work was to identify the expression patterns of PR in an environmentally relevant microbe in order to determine if and to what extent PR is used as a survival mechanism to generate energy under starvation stress.

[1] Rusch, D. B. et al. (2007) PLoS Biol. 5, 0398–0431 [2] Sabehi, G. et al (2005) PLoS Biol. 3. [3] Venter, J. C. et al. (2004) Science 304, 66–74. [4] Gómez-Consarnau, L. et al. (2017) bioRxiv 231167. doi:10.1101/231167

## USING REACTIVE IRON DISTRIBUTION TO CHARACTERIZE REDOX CONDITIONS IN THE LATE-HOLOCENE RECORD OF MARTIN LAKE, USA

Alyssa Henke<sup>1</sup>, William Gilhooly III<sup>2</sup>, Broxton Bird<sup>3</sup>  
<sup>1,2,3</sup> Department of Earth Sciences, Indiana University Purdue University Indianapolis

Iron geochemistry, specifically Fe-based proxies, have widely been used as the key approach to assess local oxygen conditions in ancient marine environments; to our knowledge these Fe-based proxies have not been applied to lacustrine water columns. Like marine basins, lakes experience fluctuations in oxygen availability, which is why we propose the implementation in Fe-based proxies in lacustrine environments, such as our study site, Martin Lake. Martin Lake is a kettle lake in LaGrange County, Indiana. Despite its hydraulically open conditions, Martin Lake remains seasonally stratified from April through November, which causes bottom water anoxia from March through December. A regional 2100 year-long precipitation reconstruction has already been created, from a multi-proxy study of Martin Lake. New research focusing on geochemical proxies, will help bridge the gap between the climate and its effect on the geochemical processes within the lake. I hypothesize Martin Lake became oxic during time periods of low water levels and anoxic when water levels were higher. Times of increased precipitation will show up in the record as an enrichment in the  $\delta^{13}\text{C}$  and an increase in anoxia, due to stable bottom water and prolonged seasonal thermal stratification, caused by the overall increase in depth. During extreme drought periods, the shallow water will allow for complete mixing and should remain oxic.

## MOLECULAR GEOCHEMISTRY OF MOLYBDENUM-ORGANIC MATTER INTERACTIONS IN BLACK SHALES

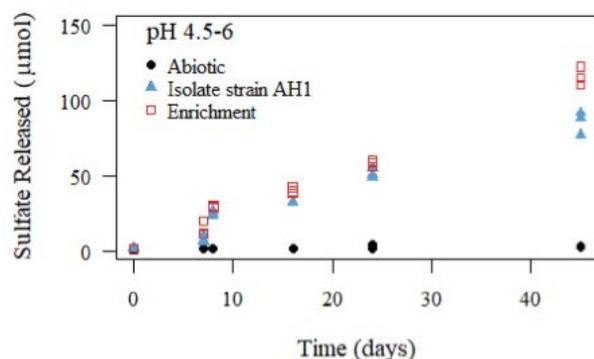
Stephan R. Hlohowskyj<sup>1</sup>, Omid H. Ardakani<sup>2</sup>, Anthony Chappaz<sup>1</sup>  
<sup>1</sup>Dept. of Earth and Atmospheric Sciences, Central Michigan University, MI, USA, Stephan.rh@cmich.edu, <sup>2</sup>Natural Resources Canada, Geological Survey of Canada, Calgary, AB, Canada

Molybdenum (Mo) has been used as a paleo-redox proxy to identify sedimentary environments deposited under sulfidic conditions (*i.e.* euxinia). Initial research into Mo geochemistry led the geochemical community to conclude that in sulfidic systems, Mo was generally dominated by iron sulfide mineral interactions which contributed the main burial pathway of Mo into sediments. More recently experimental approaches have shown Mo to strongly interact with organic matter demonstrating an increasingly important pathway for Mo in both oxic and anoxic settings. Here, we examined the organic rich black shales of the Late Devonian Bakken formation to explore the molecular geochemistry (*e.g.*, *in situ* chemical speciation) of Mo in relation to organic matter at m resolution. Our preliminary results confirm that Mo is often found in association with organic matter phases, and that low temperature (100-200 °C) hydrothermal alteration can modify the original Mo speciation. These new insights have important implications for the interpretation of the Mo paleo proxy records and emphasize the need for including molecular geochemical analysis to improve our understanding of how redox conditions fluctuated in ancient systems.

## UNDERSTANDING MICROBIAL CONTRIBUTIONS TO PYRRHOTITE OXIDATION AT CIRCUMNEUTRAL pH

Kathryn K. Hobart<sup>1,2</sup>, Daniel S. Jones<sup>1,3</sup>, Joshua M. Feinberg<sup>1,2</sup>  
<sup>1</sup>Dept. of Earth Sciences, University of Minnesota, Minneapolis MN;  
<sup>2</sup>Institute for Rock Magnetism, Dept. of Earth Sciences, University of Minnesota, Minneapolis MN; <sup>3</sup>BioTechnology Institute, University of Minnesota, Saint Paul MN

The dissolution of sulfide minerals, particularly pyrite and pyrrhotite, results in the production of acidic water high in concentrations of dissolved metals and sulfate. Microorganisms accelerate dissolution of sulfide minerals in acidic systems, but less is known about their impact at near-neutral pH. Pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ,  $0 \leq x \leq 0.125$ ) is the second-most-abundant iron sulfide in the earth's crust, and dissolves 10-100 times faster than pyrite under equivalent conditions. Understanding its dissolution is critical to maintaining water quality standards in regions with active and historical mining. Microbial isolates and communities substantially accelerate pyrrhotite dissolution under circumneutral conditions as compared to abiotic controls. Six strains of sulfur-oxidizing bacteria isolated from waste rock piles and humidity cells and an enrichment community containing iron- and sulfur-oxidizers were used in batch experiments with a starting pH of 4.5 and 6 where pyrrhotite was the only available electron donor. Measurements of aqueous sulfate, aqueous iron (II), and bulk magnetic susceptibility were used to measure the dissolution of pyrrhotite and accumulation of secondary iron phases. The presence of surface-attached bacteria appears to alter the formation or adhesion of passivation layers on the pyrrhotite grain surface. The figure below shows sulfate release versus time for an abiotic control (●), a sulfur-oxidizing isolate (▲), and an enrichment (□) at starting pH 4.5.



## EVALUATING PROXIES OF MICROBIAL CARBON AND SULFUR CYCLING IN METHANE SEEP SEDIMENTS

J. Houghton<sup>1</sup>, P. Willis<sup>2</sup>, D. Yang<sup>3</sup>, K. Dawson<sup>4</sup>, V. Orphan<sup>5</sup>, D. Fike<sup>1</sup>  
<sup>1</sup>Washington University, St. Louis, MO; <sup>2</sup>Westminster Christian Academy, St. Louis, MO; <sup>3</sup>Francis Howell High School, St. Louis, MO; <sup>4</sup>Rutgers University, New Brunswick, NJ; <sup>5</sup>California Institute of Technology, Pasadena, CA

The effect of environmental conditions on microbial activity is complex and can lead to non-unique or apparently inconsistent chemical records. Here, we evaluate several sedimentary proxies with corresponding porewater chemistry from active methane seeps in Santa Monica Basin (water depth ~820 m). Porewater profiles in the top 10 cm are consistent with high fluxes of biogenic methane supporting elevated activity of anaerobic methane oxidation consortia that lead to [DIC] 10x higher than seawater with  $\delta^{13}\text{C}_{\text{DIC}} < -50\text{‰}$ , and corresponding complete consumption of seawater  $\text{SO}_4$ . Sediment  $\delta^{13}\text{C}_{\text{TOC}}$  is relatively invariant ( $-25\text{‰}$ ), with relatively constant [TOC] of 4-6 wt% and C:N ratios of 8-9, consistent with a typical marine source and little evidence for methanotrophy. In situ  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  ranges from  $\sim 0$  to  $+20\text{‰}$ , consistent with Rayleigh distillation, fast rates of sulfate reduction (unlimited carbon supply) and a low apparent biological fractionation of  $\sim 20\text{‰}$ . In contrast,  $\delta^{34}\text{S}_{\text{CRS}}$  is variable but much for negative, typically from  $-30$  to  $-10\text{‰}$ . Values of  $\delta^{34}\text{S}_{\text{org}}$  are closer to present day  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  but closely track the depth pattern of CRS with an offset  $\sim +20\text{‰}$ . Sediment proxies suggest open system sulfur cycling at relatively slow sulfate reduction rates with a relatively high apparent biological fractionation of  $\sim 45\text{‰}$ . These inconsistencies could be explained by Fe limitation, resulting in near instantaneous capture of  $\text{H}_2\text{S}$  as pyrite but continued growth and equilibration of  $\text{S}_{\text{org}}$  after burial.

## DEVELOPING AND UTILIZING A NOVEL CADMIUM-SPECIFIC FLUORESCENT PROBE TECHNIQUE TO TEST THE COMPONENT ADDITIVITY APPROACH TO SURFACE COMPLEXATION MODELING

Clayton R. Johnson<sup>1</sup>, Joshua D. Shrout<sup>1</sup>, Jeremy B. Fein<sup>1</sup>  
<sup>1</sup>University of Notre Dame, Notre Dame, IN 46556, USA

The component additivity (CA) approach to surface complexation modeling (SCM) is a method commonly used to predict the extent of metal adsorption in multi-sorbent systems containing bacteria. Quantitative tests of the CA approach are rare because it is difficult to quantify bacterial metal adsorption, and thus determine metal distribution, in multi-sorbent systems. In order to test the CA approach, we develop a novel fluorescent probe technique which allows us to quantify the concentration of Cd that is adsorbed to a bacterial population in fully hydrated samples. We conduct an extensive suite of control tests that verify that our treatment does not affect the extent of Cd sorption, that the measured fluorescence response can be correlated to the concentration of Cd that is adsorbed to a bacterial cell population, and that the technique can be used to quantify Cd distribution in simple multi-sorbent samples. This study uses our technique to quantify bacterial Cd adsorption and Cd distribution in mixed bacteria-mineral samples. We compare measured Cd distributions to CA predictions in order to test the CA approach. Our findings show that the CA predictions generally agree, within uncertainties, with the measured Cd distributions in all systems studied. Our results demonstrate that the Cd-fluorescent probe technique is a suitable, and relatively simple, option for quantitatively testing CA surface complexation models.

## MERCURY METHYLATION AND METHYLATING COMMUNITIES IN SULFATE- IMPACTED FRESHWATER ECOSYSTEMS

Daniel S. Jones<sup>1,2</sup>, Nathan W. Johnson<sup>3</sup>, Carl P.J. Mitchell<sup>4</sup>, Gabriel M. Walker<sup>2</sup>, Jill K. Coleman Wasik<sup>5</sup>, Maisie Lenards<sup>2</sup>, Edward B. Swain<sup>6</sup>,  
Jake V. Bailey<sup>2</sup>

<sup>1</sup>University of Minnesota, BioTechnology Institute, St. Paul, MN,  
<sup>2</sup>Dept. of Earth Sciences, University of Minnesota, Minneapolis, MN,  
USA, <sup>3</sup>Dept. of Civil Engineering, University of Minnesota Duluth,  
Duluth, MN, USA, <sup>4</sup>Department of Physical and Environmental  
Sciences, University of Toronto – Scarborough, Toronto, Ontario,  
Canada, <sup>5</sup>Department of Plant and Earth Science, University of  
Wisconsin River Falls, River Falls, WI, USA, <sup>6</sup>Minnesota Pollution  
Control Agency, St Paul, MN

Methylmercury (MeHg) is a bioaccumulative neurotoxin that is produced by certain sulfate reducers and other anaerobic microorganisms. We are using an integrative geochemical and molecular approach to study the relationship between microbial community composition and methylation potential in sulfate-impacted freshwater sediments on Minnesota's Iron Range. First, we performed a detailed characterization of methylating communities in two sulfate-impacted lakes using metagenomics, rRNA methods, and *hgcA* sequencing. Then, we extended our results to a larger number of samples by combining methylation rate measurements with *hgcAB* sequencing across a sulfate gradient in experimental wetland sediment mesocosms.

Methylation rates and MeHg accumulation were not clearly related to sulfate concentration or sulfide accumulation in either the lakes or the sulfate-amended mesocosm sediments. In the lakes, *hgcA* gene sequencing and metagenomics showed that methylating communities differ among the sites, and that the most abundant methylating organisms were from taxa not previously associated with MeHg production or *hgcAB* genes. We will describe metabolic capabilities of these novel potential methylators based on genome reconstruction from metagenomic datasets, including improved binning and genome recovery of the most abundant *hgcAB*<sup>+</sup> populations by combining long-read PacBio sequencing with short-read Illumina datasets. In the sulfate-amended mesocosm sediments, methylmercury production rates varied over two orders of magnitude across the experiment but did not show a clear relationship with the level of sulfate amendment. In general, differences among microbial communities trended with the sulfate gradient. We will describe the composition of methylating communities based on *hgcAB* amplicon sequencing from across the experiment, and relate *hgcAB* libraries to rates of mercury methylation and sulfate amendment. Our results show that previously unrecognized methylating populations are abundant and may be important for MeHg production, and expand our knowledge of the clades and environmental factors that affect MeHg production in sulfate-impacted freshwater ecosystems.

## ASSESSMENT OF MICROBIAL COMMUNITY COMPOSITION IN EAGLE CREEK RESERVOIR USING 16S NEXT GENERATION SEQUENCING AND qPCR

Ioanna Koltsidou<sup>1</sup>, Christine J. Picard<sup>1</sup>, Gregory K. Druschel<sup>2</sup>  
<sup>1</sup>Department of Biology, Indiana University Purdue University, Indianapolis, IN, USA, <sup>2</sup>Department of Earth Sciences, Indiana University-Purdue University, Indianapolis, IN, USA

The presence of taste and odor (T&O) compounds, especially the odorous bacterial metabolites 2-methylisoborneol and geosmin (trans-1,10 dimethyl-trans-9-decalol), is a global problem impacting freshwater quality. Eagle Creek Reservoir in Central Indiana supplies approximately 80% of Indianapolis' drinking water and experiences odor problems frequently. In order to get critical insights into the origins of odor episodes, 16S rRNA genomic sequencing, has been used in conjunction with measurements of MIB and geosmin concentrations. Samples were collected at various locations of ECR from May to August of 2017 and filtered through a Sterivex filter unit. DNA was extracted using the DNeasy PowerWater Sterivex kit by Qiagen and 12 representative samples were selected for 16S sequencing and OTU clustering analysis was performed using the CLC Genomic Workbench software. MIB and geosmin concentrations from GC-MS analysis were provided by the Citizens Energy Group lab. Clustering analysis of the 16S rRNA gene revealed that the relative abundance of cyanobacteria in samples followed the pattern of MIB and geosmin fluctuation, ranging from 5% at low concentrations up to 83% at high concentrations. Actinobacterial relative abundance was significantly lower than cyanobacteria in every sample, ranging from 3% up to 14%. Additionally, these analyses indicated *synechococcus* and *pseudanabaena* as the dominant cyanobacterial genera. Future work aims to utilize these results to develop environment-specific qPCR primers to target geosmin production as a tool in predicting and preventing taste and odor episodes.

## RATES AND PRODUCTS OF Fe(II) OXIDATION IN TRIOCTAHEDRAL SMECTITES

Robert J. Kupper<sup>1\*</sup>, Jeffrey G. Catalano<sup>1</sup>

<sup>1</sup>Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA. (\*rkupper@wustl.edu)

Trioctahedral Fe(II) smectites form during the anoxic alteration of basalts, are common in the modern subsurface oceanic crust, and likely occur on Mars. Before Earth's oxygenation, these clays would have been exposed on the ocean floor. On modern Earth, however, they rapidly oxidize upon exposure to air. Due to the difficulty in sampling and preserving these clays, their role in the biogeochemical iron cycle remains poorly understood, including their availability as an electron donor to Fe-oxidizing microorganisms.

Fe(II) smectites were synthesized spanning the compositional range observed in altered basalts. Powder XRD confirmed these to be trioctahedral, turbostratic 2:1 phyllosilicates. The oxidation of Fe(II) in these clays was measured during exposure to dissolved O<sub>2</sub> or nitrite, an intermediate produced during denitrification known to abiotically oxidize dissolved Fe(II). Oxidation in air-equilibrated suspensions (PO<sub>2</sub> ≈ 0.2) was incomplete but proceeded more rapidly and to a greater extent in smectites containing more iron. No oxidation was detectable in samples exposed to nitrite (as 5 mM NaNO<sub>2</sub>) compared to oxidant-free controls. Under microaerophilic conditions (PO<sub>2</sub> = 0.02) oxidation proceeded at a slower rate than in air equilibrated samples. XRD patterns of products did not indicate the formation of any new minerals during oxidation

## UNDERSTANDING ORGANIC PHOSPHORUS CYCLING IN REDOX-DYNAMIC EUTROPHIC FRESHWATER SYSTEMS

Kurek, Martin R.<sup>1</sup>, Harir, Mourad<sup>2</sup>, Shulke, John<sup>1</sup>, Leduc, Meagan<sup>3</sup>, Schroth, Andrew<sup>3</sup>, Schmitt-Kopplin, Phillipe<sup>2</sup>, Druschel, Gregory K.<sup>1</sup>

<sup>1</sup>Indiana University Purdue University Indianapolis, Department of Earth Science, makurek@indiana.edu, <sup>2</sup>Helmholtz Zentrum München, Deutsches Forschungszentrum für Gesundheit und Umwelt, schmitt-kopplin@helmholtz-muenchen.de, <sup>3</sup>University of Vermont, Department of Geology

Organic phosphorus represent a significant fraction of phosphorus species in freshwater lakes and are mobilized via changing redox conditions at the sediment-water interface largely by interactions with iron. Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is a powerful analytical technique that can measure molecular masses with remarkable precision, yielding a look at thousands of different molecules in a single sample. This technique has been optimized for characterizing unique organic molecular signatures of dissolved organic matter (DOM). Water and sediment samples were collected from eutrophic Missisquoi Bay in Lake Champlain to assess how biogeochemical redox cycling links to organic phosphorus mobility and bioavailability for cyanobacterial blooms. The focus of this study was to investigate how dissolved organic phosphorus (DOP) is cycled within the water column and seasonally. This was achieved by comparing the molecular signatures of DOP in the mass spectra to the bulk molecular signatures of DOM, which follow a predictable, gaussian distribution. Variations in the heteroatomic distribution between DOM and DOP were seen in the water column, and between different seasons indicating a shift from terrestrial to microbially processed DOM. Quantitative measurements such as chlorophyll a and dissolved oxygen in the water column corresponded to qualitative changes in the molecular diversity of DOP and DOM, driven by biotic and abiotic processes.

## METAGENOMIC ANALYSIS OF A NOVEL POTENTIAL MERCURY-METHYLATING POPULATION FROM A HYPEREUTROPHIC, SULFIDIC LAKE

Maisie Lenards<sup>1</sup>, Jake V. Bailey<sup>1</sup>, Daniel S. Jones<sup>1,2</sup>

<sup>1</sup>University of Minnesota, Dept. of Earth Sciences, Minneapolis, MN, USA, <sup>2</sup>University of Minnesota, BioTechnology Institute, St. Paul, MN

Methylmercury is a bioaccumulative neurotoxin that is produced by certain anaerobic microorganisms. While sulfate-reducing microorganisms are thought to be the primary mercury methylators in most environments, other anaerobes including iron reducers, methanogens, and other organotrophs are also known to methylate mercury. In a recent metagenomic analysis of two sulfate-impacted lakes on Minnesota's Mesabi Iron Range, Jones et al. (*in review*) identified diverse populations with the capability to methylate mercury, many of which represent phyla not previously known to have genes for mercury methylation (*hgcAB*). By combining a short-insert (3-8 Kbp) PacBio library with the existing Illumina HiSeq metagenomes, we improved genome recovery of the most abundant *hgcAB*<sup>+</sup> bins representing one of the lakes. The population represented by this bin, which contains a close relative or member of the "*Aminicenantes*" (formerly Candidate Phylum OP8), was 2-7% of the community in the anoxic sediments and anoxic/microoxic water column. The bin contains respiratory cytochromes, including high-affinity terminal oxygenases and tetrathionate and thiosulfate reductases, indicating that the *Aminicenantes*-like population may reduce or detoxify oxygen and respire some inorganic sulfur compounds. It does not, however, appear to be able to respire sulfate. It has a complete glycolysis pathway and TCA cycle, and encodes diverse fermentation capabilities, an electron bifurcating NADH dehydrogenase/heterodisulfide reductase (*hdrCBA-flxABCD*), and genes for flagella synthesis and chemotaxis. The *Aminicenantes*-like population appears to be an organoheterotroph capable of anaerobic or microaerophilic growth, and makes its living by degrading organic carbon from the algal biomass that is ubiquitous in its hypereutrophic environment. by degrading organic carbon from the algal biomass that is ubiquitous in its hypereutrophic environment.

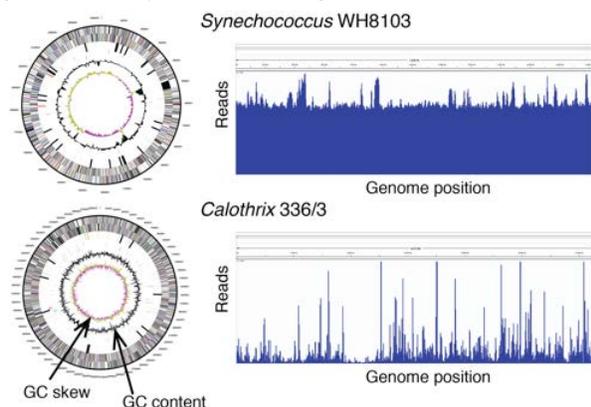
## SEQUENCING READ DISTRIBUTION IN BACTERIAL GENOMES WITH AND WITHOUT GC SKEW

Barbara J. MacGregor<sup>1</sup>, Manuel Kleiner<sup>2</sup>

<sup>1</sup>University of Minnesota, Minneapolis MN, <sup>2</sup>North Carolina State University, Raleigh NC

The large sulfur bacteria (LSB) include species of varied morphology, and some of the largest known bacteria. Possible key events in LSB evolution include loss of canonical genes for septum formation and replication initiation. There are parallels in the Cyanobacteria, with which the LSB appear to have a history of gene exchange. We previously showed that some members of each group lack the GC skew seen in many circular microbial genomes; skew is the preponderance of G over C in the leading strand, with the two origin-to-terminator segments skewed in opposite senses.

Genes near the origin of circular replicons are expected to be at higher copy number in actively dividing cells; given an artifact-free protocol, this could correlate with the distribution of sequencing reads around the chromosome. We have undertaken a look at sequencing read distributions in public cyanobacterial genomes. The first results are intriguing: reads were evenly distributed around the genome of *Synechococcus* WH8103, which exhibits strong skew, but varied over several orders of magnitude for different regions of the unskewed *Calothrix* 336/3 genome. *Calothrix* has numerous annotated transposases, suggesting a genome rearrangement mechanism. But what accounts for the read number differences? If gene copy numbers do differ widely, how are gene expression and chromosomal division regulated? If not, what accounts for the differences? Analysis of additional genomes may shed some light.



## A NEW GLOBAL SYNTHESIS OF SEDIMENTARY LEAF WAX ISOTOPES: EXPANDING TO INCLUDE THE ARCTIC

Jamie M. McFarlin<sup>1</sup>, Yarrow Axford<sup>1</sup>, Andrew Masterson<sup>1</sup>, Magdalena R. Osburn<sup>1</sup>

<sup>1</sup>Northwestern University, Evanston, IL.

The hydrogen isotopic composition ( $\delta^2\text{H}$ ) of plant wax  $\text{C}_{28}$  *n*-alkanoic acids and  $\text{C}_{29}$  *n*-alkanes correlate strongly with the  $\delta^2\text{H}$  values of mean annual precipitation in middle and low latitudes (Sachse et al, 2012). However, systematic examination of the  $\delta^2\text{H}$  values of sedimentary plant waxes in the high latitudes, and compilation of other chain-lengths on a global scale, was heretofore limited. Here, we present new data on the  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  values of sedimentary *n*-alkanes and *n*-alkanoic acids from a modern transect covering northwest to southernmost Greenland in the context of global sedimentary wax data. We show a strong relationship between the  $\delta^2\text{H}$  values of long-chain *n*-alkanes and *n*-alkanoic acids to  $\delta^2\text{H}$  of precipitation, and discuss apparent limitations in using these compounds interchangeably as a paleoclimate proxy. We also present data that cautions against interpreting  $\delta^2\text{H}$  values of mid-chain *n*-alkanes and *n*-alkanoic acids as records of lake water isotopes. We argue that seasonality of plant growth exhibits strong influence on the  $^2\text{H}$  values of plant waxes in the Arctic, with a bias towards utilization of summer water during wax synthesis in Greenland. We argue that apparent fractionation corrections in the Arctic need to consider the season of precipitation utilized during plant growth, but otherwise find that sedimentary long-chain *n*-alkanes serve as a robust proxy for precipitation  $\delta^2\text{H}$  values globally. This finding opens the door to widespread utilization of this proxy in Arctic reconstructions, where records of hydroclimate during past warm periods are urgently needed to contextualize ongoing climate change.

## **THE DEEP BIOSPHERE IN THE JUNGLE: FOLLOWING CARBON IN SERPENTINIZING SPRINGS IN A TROPICAL SURFACE BIOME**

**D'Arcy Meyer-Dombard**<sup>1</sup>, Dawn Cardace<sup>2</sup>, Magdalena Osburn<sup>3</sup>  
<sup>1</sup>University of Illinois, Chicago IL, <sup>2</sup>University of Rhode Island,  
Kingston RI, <sup>3</sup>Northwestern University, Evanston IL

The low DIC and high CH<sub>4</sub> and H<sub>2</sub> gas concentrations of serpentinizing ecosystems have led to interest in H<sub>2</sub> based metabolisms in these subsurface biomes. However, a true subsurface signature can be difficult to identify in surface expressions such as serpentinizing springs. Here, we explore carbon resources in serpentinizing springs in the tropical climate of the Zambales and Palawan ophiolites in the Philippines, with a focus on surface vs. subsurface processes and exogenous vs endogenous C input. Isotopic signatures in fluids, biomass, and carbonates were examined to identify sources and sinks of C, carbonate geochemistry, and the effect of seasonal precipitation. Precipitation affected δ<sup>13</sup>CDIC and δ<sup>13</sup>CDOC, which reflected seasonal gain/loss of atmospheric influence and changes in exogenous DOC input. The primary C source in high flow systems was variable, with DOC contributing to biomass in most springs, and a mix of DIC and carbonates contributing to biomass in select locations. However, primary C resources in low flow systems may depend more on endogenous than exogenous C, even in high precipitation seasons. Carbonate formation occurred as a mixture of recrystallization/recycling of older carbonates and rapid precipitation, with highly δ<sup>13</sup>C and δ<sup>18</sup>O depleted carbonates. Subsurface signatures were most apparent in the driest seasons and lowest flow systems, indicating locations where metabolic processes divorced from surface influences are most likely to be occurring.

## **NOVEL METAPROTEOMIC APPROACHES APPLIED TO ARCTIC SOILS REVEAL NICHE PARTITIONING OF MICROBIAL BIOGEOCHEMICAL FUNCTIONS AND SYSTEMATIC VARIATIONS WITH VEGETATION TYPE**

**Samuel Miller** and Jacob Waldbauer

University of Chicago, Department of the Geophysical  
Sciences

Increasing plant biomass and the spread of large woody shrubs across the Arctic have accompanied warmer temperatures and permafrost thaw. We used novel metaproteomic methods to study the effect of floral type on soil microbial metabolism and biogeochemical cycles. Our computational approach greatly boosts protein identification in environmental samples and associates homologous proteins with metagenome-assembled genomes, enabling determination of the strength of protein expression by different clades.

We applied these methods to tussock, intertussock, and shrub soils collected from the area of Toolik Lake, Alaska. Thousands of different proteins, chiefly bacterial, were identified in the soils. The functional profiles of organic soils cluster by plant type, whereas mineral soils cluster separately regardless of plant type, indicating that a similar set of processes occurs in mineral soils and distinct sets of processes influenced by plant inputs occur in organic soils. Clustering by plant type is due to differences in the abundances of multiple microbial protein functions rather than the presence or absence of a few key functions. When broken down by clade, protein functional profiles shift in the same direction, reflecting consistent changes in the relative abundances of proteins between environments rather than changes in the propensity of clades to express different proteins.

We found significant niche partitioning between bacterial clades with regard to carbon substrate and nutrient utilization. Separate bacterial groups dominate the degradation of cellulose, hemicellulose, simple sugars and C1 compounds. Amino acid transporters are much more abundant than proteins involved in N<sub>2</sub> fixation and the utilization of urea, polyamines, NH<sub>3</sub>, and NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>. The dominance of amino acid uptake by Rhizobiales may indicate the flow of N between this frequently mutualistic group and plants. Clades are also differentiated by mechanisms of C/nutrient storage, trace element acquisition, motility, and adhesion.

## EXPLORING THE “MICROBIAL DARK MATTER” THROUGH LARGE-SCALE GENOMICS

Senthil K Murugapiran<sup>1</sup>, Jeff R Havig<sup>2</sup>, Trinity L Hamilton<sup>1,3</sup>

<sup>1</sup>Department of Plant & Microbial Biology, College of Biological Sciences, University of Minnesota Twin Cities, MN 55108,

<sup>2</sup>Department of Earth Sciences, Newton Horace Winchell School of Earth Sciences, University of Minnesota Twin Cities, MN 55455, <sup>3</sup>The BioTechnology Institute, University of Minnesota Twin Cities, MN 55108

We use next generation, large-scale ‘omics’ approaches in combination with traditional microbiology, ultra-high resolution geochemical and geological data to understand the functions, interactions of microbes in natural and engineered systems, how they respond and adapt to ‘fringe’ environments -- extreme variations including redox gradients and temperature. Many of the microbes that we study are recalcitrant to laboratory cultivation. Moreover, the complete genome sequences of these microbes are not available in any sequence databases. Due to the paucity of information about these unknown, yet abundant and important microbes, they are sometimes referred to as ‘microbial dark matter’. These microbes offer clues to understand the origin and evolution of life on earth and possibly other planets. We therefore use cultivation-independent methods such as genomics, metagenomics, 16S rRNA analysis to identify and characterize the microbial communities in these fringe environments. Computing facilities provided by the Minnesota Supercomputing Institute (MSI) play a critical role in our bioinformatics pipeline in all stages of data analyses including: quality filtering; assembly; annotation; phylogenomics; methods to accurately estimate the completeness of genomes; metagenomic binning using nucleotide identity and tetranucleotide frequency; customized BLASTP and hmmer searches to predict metabolic capacity; analyzing tandem mass spectrometry metaproteomics data; metatranscriptomics data analysis; submitting metagenomes, isolate genomes, 16S rRNA metadata and sequences to appropriate NCBI sequence databases. Using some of the analyses from our lab research, I will present how a robust, well organized and documented, user-friendly computing environment such as MSI enables our lab to carry out data crunching in a highly reliable, reproducible and replicable manner --- some of the most important characteristics for research in the era of ‘big data’.

## CONSTRUCTING METHANE-SUPPLEMENTED FOODWEBS USING CARBON ISOTOPE ANALYSIS OF AQUATIC INVERTEBRATE REMAINS IN NORTH AMERICAN LAKE SEDIMENTS

Jaclyn Oliver<sup>1</sup>, Jacob J. Meldrum<sup>1</sup>, Benjamin K. Harrison<sup>1</sup>, Maarten van Hardenbroek<sup>2</sup>, Megan Rohrsen<sup>1</sup>

<sup>1</sup>Department of Earth and Atmospheric Sciences, Central Michigan University, Mount Pleasant, MI, 48859, USA., <sup>2</sup>School of Geography, Politics and Sociology, Newcastle University, Newcastle NE1 7RU, UK

Daphnia and Chironomidae consume diverse food sources including algae, terrestrial detritus, and methane-oxidizing bacteria. Daphnia resting egg cases (ephippia) and chironomid larval head capsules are made of chitinous material that retains its carbon isotopic composition after deposition in lake sediments. Because these food sources can have distinctive carbon isotopic compositions, the  $\delta^{13}C$  values of ephippia and head capsules reflect the importance of methane-derived carbon their diet (e.g. Bastviken et al., 2003). We predict that, as has been shown in a European lake (Schilder et al., 2017), methane will be more important in the food webs of Midwestern lakes with abundant nutrients from runoff, whereas methane may be a less important carbon source in waters that are not as eutrophic.

To test our hypothesis, we will collect sediment cores from lakes near Central Michigan University and analyze the carbon isotopic compositions of Daphnia ephippia and chironomid head capsules. In order to see whether there is a clear relationship between methane in the water and in the invertebrates (Schilder et al., 2015), we will also need to measure methane concentrations in lake water, accounting for seasonal variability in methane concentration and ephippium production. With this information we can relate the carbon isotopic compositions of the remains to methane concentrations.

Bastviken, D. et al., (2003) *Ecology*, 84: 969-981.; Schilder, J., et al., (2015) *Limnol. and Oceanogr.*

## EFFECTS OF Fe(III) INPUTS ON THE RATE OF METHANOGENESIS IN WETLAND SEDIMENT MICROCOSMS

Theodore Flynn<sup>1</sup>, Lauren Johnson<sup>1</sup>, Zena Jensvold<sup>1</sup>, Maxim Boyanov<sup>1,2</sup>, Kenneth Kemner<sup>1</sup>, Edward O'Loughlin<sup>1</sup>  
<sup>1</sup>Argonne National Laboratory, Argonne, IL, <sup>2</sup>Affiliation, location,  
<sup>3</sup>Bulgarian Academy of Sciences, Sofia, Bulgaria

Sulfate and Fe(III) have been shown to inhibit methanogenesis in transiently anoxic environments. This has been ascribed primarily to the ability of sulfate and Fe reducers to outcompete methanogens for electron donors. The perceived role of competitive inhibition in limiting methanogenesis, however, is largely based on experiments where methanogenesis was inhibited in microcosms that had Fe(III) or sulfate present at the onset. In dynamic redox environments, the formation of Fe(III) is often controlled by episodic influxes of oxygen into reduced sediments, so the impact of Fe oxide addition on active methanogenic communities is unclear. We conducted experiments using sediment from a freshwater wetland amended with acetate. Shortly after the onset of methanogenesis, we amended each microcosm with either ferrihydrite, lepidocrocite, or goethite. Methanogenesis declined dramatically following the addition of Fe oxide, with greater inhibition of methanogenesis observed with ferrihydrite and lepidocrocite relative to goethite. Unamended microcosms were dominated by Methanomicrobia, a class of methanogenic archaea that comprised 32% of the community during peak methane production. In Fe-amended microcosms these same taxa were initially ~10% of the community prior to the addition of ferric minerals, but Geobacter dominated soon thereafter. Our results suggest that the impact of ferric oxides on methanogenesis is due to more than just thermodynamic limitations or kinetic inhibition.

## ISOTOPIC DISEQUILIBRIUM IN PROSOPIS TREE CELLULOSE AS AN INDICATOR OF WATER STRESS AND HYDROCLIMATE VARIABILITY

Elizabeth Olson, Justin Dodd  
<sup>1</sup>Northern Illinois University, Dekalb, IL

Isotope dendroclimatology has the potential to provide quantitative proxies of past hydroclimate, yet efforts are limited by the variable physiological response of trees to environmental change. *Prosopis* sp. are endemic to the hyper-arid core of the Atacama Desert in northern Chile; where in the absence of precipitation these trees use only groundwater. Tree-rings in stems and branches differ for all three isotopes ( $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ). Branch cellulose values were lower than stem values on average, with a difference of 0.4 ‰ for  $\delta^{18}\text{O}$ , 0.7 ‰ for  $\delta^{13}\text{C}$  and 6.0 ‰ for  $\delta^2\text{H}$ . These differences likely reflect the different proportion of stored versus current photosynthate used during cellulose synthesis in stems and branches. *Prosopis* sp. trees respond to drought stress by shedding biomass (e.g. leaves and branches). This physiological adaptation to extreme aridity provides a mechanism by which the proportion of current photosynthate decreases in response to decreasing water availability (i.e. lowering of the water table). The significant correlation between variations in the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in branches and changes in groundwater depth ( $r = 0.42$ ;  $p < 0.0001$ ) is evidence for the impact of biomass shedding on photosynthate source. This study demonstrates that *Prosopis* sp. branch cellulose are more sensitive to changes in GWD than stem cellulose, which has implications for the use and comparison of different plant tissue types in paleoclimate reconstructions.

## EDIACARAN OXYGEN OASES AND THE EMERGENCE OF BILATERIAN BURROWING

Stephanie Olson<sup>1</sup>, Mary Droser<sup>2</sup>, Timothy Lyons<sup>2</sup>  
<sup>1</sup>University of Chicago, <sup>2</sup>University of California, Riverside

Helminthoidichnites is the most abundant Ediacaran trace fossil. At a glance, Helminthoidichnites appears to be a leaved furrow that traces the horizontal movements of a small bilaterian animal across the seafloor, but it is also frequently preserved in negative relief on the bottom thin, laterally discontinuous beds. This preservation style requires that the animal burrowed beneath the margins of these discontinuous sediments---and was thus among the first in Earth history to penetrate the sediment-water interface, albeit horizontally rather than vertically. Yet the motivation for this energy-intensive behavior is unclear. We probe this enigmatic behavior. We examine the spatial distribution of bed sole Helminthoidichnites in negative relief at Nilpena (Flinders Ranges, South Australia) and we interpret our results in the context of a simple model for benthic oxygen diffusion in sandy sediments influenced by microbial mats, which were ubiquitous in the Ediacaran marine environment. We find that the margins of discontinuous sands likely hosted oxygen levels in significant excess of ambient seawater---potentially enticing the bilaterian responsible for producing the Helminthoidichnites trace to engage in early burrowing behaviors prior to the advent of modern-style burrowing and large-scale mixing of sediments in the Phanerozoic. These results imply an important role for oxygen in the tempo and mode of biological innovation on Earth, including the emergence of burrowing.

## COMPOSITIONAL AND METABOLIC DIFFERENCES IN NITRIFYING COMMUNITIES ACROSS THE LAURENTIAN GREAT LAKES

Justin C Podowski<sup>1</sup>, Sara F Paver<sup>1</sup>, Ryan J Newton<sup>2</sup>, Maureen L Coleman<sup>1</sup>

<sup>1</sup>University of Chicago, Chicago, IL, <sup>2</sup>University of Wisconsin-Milwaukee, Milwaukee, WI

The Laurentian Great Lakes hold 21% of Earth's freshwater, and their shores are home to more than 30 million people. Despite the importance of this ecosystem, the composition and dynamics of microbial communities in the Great Lakes remain poorly characterized. Here we describe genome diversity of water column microorganisms, from our ongoing Great Lakes Microbial Time Series. We find that both abundance and composition of nitrifying communities differ across the Great Lakes, most strikingly between oligotrophic Lake Superior and eutrophic Lake Erie. Ammonia oxidizing archaea appear in the deepest waters of Michigan, Ontario and Superior, but ammonia oxidizing bacteria are also abundant and widespread. Genome reconstruction further sheds light on the novelty of nitrifying microbes in the Laurentian Great Lakes, recovering the dominant nitrite oxidizing taxa in Lake Erie, which are closely related to *Candidatus Nitrotoga*. Analysis of recovered *Nitrosospira* genomes reveals a distinct group that contains the light activated proton pump proteorhodopsin, a first for any ammonia oxidizing organism. Together, these results suggest that rates and controls on nitrification across the Laurentian Great Lakes are likely very different, owing in part to the diverse physiology and metabolism of the different microbes that dominate nitrification across these lakes.

## ASSESSING MICROBIAL COMMUNITY ASSEMBLY IN A SERPENTINIZATION-INFLUENCED AQUIFER OVER TIME

L.I. Putman<sup>1</sup>, M.D. Kubo<sup>2</sup>, W.J. Brazelton<sup>3</sup>, D. Cardace<sup>4</sup>, M.O. Schrenk<sup>1</sup>

<sup>1</sup>Michigan State University, East Lansing, MI 48824, <sup>2</sup>SETI Institute & NASA Ames Research Center, Moffett Field, CA 94305, <sup>3</sup>University of Utah, Salt Lake City, UT 84112, <sup>4</sup>University of Rhode Island, Kingston, RI 02881-0816.

The Coast Range Ophiolite Microbial Observatory (CROMO) is a series of wells drilled into serpentinitized soil and bedrock in Northern California, accessing high pH, moderately saline aquifers. Surface conditions at CROMO are dynamic and are subject to extreme seasonality in precipitation. Due to this, it is expected that substrate availability in the subsurface aquifers fluctuates throughout the year and requires metabolic versatility from the resident microorganisms. This work aims to assess what processes of community assembly are at play in this extreme environment, and what geochemical and physical factors play a role in driving community assembly processes over time. Six years of geochemical and 16S rRNA gene sequence data were compiled for analysis. Preliminary results suggest that community assembly is generally deterministic in this system, indicating that it is driven by environmental conditions. Results also show that assembly processes change over time and seem to be affected by pH, salinity, and redox conditions. Further analysis of this data will inform upon environmental parameters that are driving microbial community assembly and composition over time and in response to changes in the subsurface. Results from this work will elucidate ecological processes resulting in the observed communities within this extreme environment, and also have implications for better understanding microbial community diversity and function in this system.

## THE SOURCE OF SULFATE IN BIOGENIC CALCITE: INSIGHTS FROM $\mu$ -XRF IMAGING, XANES SPECTROSCOPY AND ISOTOPE STUDIES OF ANCIENT AND EXTANT BRACHIOPODS

Jocelyn A. Richardson<sup>1\*</sup>, Matthew Newville<sup>2</sup>, Anthony Lanzirotti<sup>2</sup>, Samuel M. Webb<sup>3</sup>, Catherine V. Rose<sup>4</sup>, Jeffrey G. Catalano<sup>1</sup> and David A. Fike<sup>1\*</sup>

<sup>1</sup>Department of Earth & Planetary Sciences, Washington University, St. Louis, MO 63130 USA, <sup>2</sup>Consortium for Advanced Radiation Sources University of Chicago Chicago, Illinois, 60637, U.S.A., <sup>3</sup>Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025, USA., <sup>4</sup>School of Geography and Geosciences, University of St. Andrews, Fife KY16 9ST, Scotland

Articulate brachiopods are accepted to be robust archives for geochemical proxies due to their shell structure, comprised of a bi-layered low Mg-calcite. Brachiopods frequently retain high abundances of carbonate-associated sulfate (CAS). This study aims to assess the reliability of CAS in brachiopods by determining the source of inorganic sulfate and role of organic sulfur species within the extant *Terebratalia transversa* and fossil brachiopods by combining  $\mu$ -XRF imaging, XANES spectroscopy, SEM imaging and isotope data. Fossil brachiopods show intra-specimen variability in sulfate abundance, where sulfate varies along the primary shell fabric. XANES spectroscopy indicates that inorganic lattice bound sulfate is the dominant S-species in fossil brachiopods, but low amounts of thiol and sulfoxide are present. *T. transversa* show a greater abundance of, localized, thiol and sulfoxide and esters. Sulfate abundance in *T. transversa* also follows the primary fabric. SEM images indicate that sulfate abundance increases towards the edge of calcite crystals. Bulk rock  $\delta^{34}\text{S}_{\text{CAS}}$  of the samples containing the fossil brachiopods were consistently heavier than time-equivalent brachiopod-only values. In contrast, bulk  $\delta^{34}\text{S}_{\text{CAS}}$  of modern *T. transversa* is 22.4‰, 1‰ heavier than coeval seawater. Although variability exists in CAS in all brachiopods, the variability is muted compared to bulk rock data, and that brachiopods more accurately record seawater sulfate values.

## **SEDIMENT TRACE METAL CONTENTS DO NOT REFLECT POREWATER CHEMISTRY IN A LOW-OXYGEN PRECAMBRIAN ANALOGUE**

**Kathryn I. Rico<sup>1</sup>**, Nathan D. Sheldon<sup>1</sup>

<sup>1</sup>Department of Earth and Environmental Science, University of Michigan, Ann Arbor, MI

Sediment trace metal contents are regularly used to infer water column redox chemistry in the geologic record. Here, redox-sensitive trace metal contents are measured across water column, sediment, and porewater profiles of the Middle Island Sinkhole (MIS). MIS, located 23 m beneath oxic Lake Huron, is a low-oxygen system with microbial mats that utilize various phototrophic and heterotrophic metabolisms. As such, it is a useful system for considering abiotic and biotic controls on trace metal cycling, and has been used as an analogue for shallow shelf biogeochemistry in Proterozoic oceans. Water column profiles show a stark increase in Fe from below detection near the surface to over 100 ppb within the chemocline, whereas Mo and Zn profiles decrease from 538 to 390 ppt, and 81 to 56 ppb, respectively. Although changes in the water column profiles are unidirectional with depth, samples taken across the redoxcline (21–23 m depth) indicate fluctuating trace metal contents. Downcore sediment Fe/Ti ( $9.1 \pm 0.5$  mol/mol) and Zn/Ti ( $25.8 \pm 2.5$  umol/mol) profiles are relatively consistent, whereas sediment Mo/Ti is much more variable ( $40.1 \pm 8.8$  nmol/mol), possibly demonstrating its sensitivity to sulfide and/or the presence of methanogens in the sediments. Inconsistent porewater profiles highlights the need to address spatial and temporal variability when sampling aquatic environments and challenges our understanding of sediment redox proxies in the geologic record.

## **MICROBES, MINERALS AND ELECTRODES AT THE SANFORD UNDERGROUND RESEARCH FACILITY (SURF): ELECTROCHEMISTRY 4000 FT BELOW THE SURFACE**

**Annette Rowe<sup>1</sup>**, Karla Abuyen<sup>2</sup>, Bonita Lam<sup>2</sup>, Brittany Kruger<sup>3</sup>, Caitlin Casar<sup>4</sup>, Magdalena Osburn<sup>3</sup>, Moh El-Naggar<sup>2</sup>, Jan Amend<sup>2</sup>  
<sup>1</sup>University of Cincinnati, Cincinnati, OH, <sup>2</sup>University of Southern California, Los Angeles, CA, <sup>3</sup>Desert Research Institute, Las Vegas, NV, <sup>4</sup>Northwestern University, Evanston, IL

Little is known about the importance of mineral oxidation processes in subsurface environments. This stems, in part from our limited insight into the biochemistry of many of these metabolisms, especially for interactions with solid phases. To this aim, we have been developing electrochemical cultivation techniques, to target enrichment and isolation of microbes capable of oxidative extracellular electron transfer (EET)—transfer of electrons from the exterior of the cell to the interior. Our previous work focused on marine sediments; using an electrode poised at a given redox potential to isolate mineral oxidizing microbes. At the Sanford Underground Research Facility (SURF) in Lead, South Dakota, we have been utilizing similar electrocultivation techniques to understand: 1) the potential for mineral (sulfur) oxidation by subsurface microbes, 2) their selective colonization on mineral vs. electrode surfaces, as well as 3) the community composition of microbes capable of these metabolic interactions. An electrochemical and mineral enrichment scheme was designed and installed into a sulfidic groundwater flow, located at the 4100 ft level of the former gold mine. The communities enriched on electrodes (graphite and indium tin oxide coated glass) and minerals (gypsum, pyrite, and quartz) were compared to the long-term planktonic microbial community observed. Ultimately, these observations will help inform the potential activity of a lithotrophic microbes from a site where these metabolisms have been predicted from the geochemical data.

## BIOGEOCHEMICAL TRANSFORMATIONS OF SELENIUM BY COMMON SAPROTROPHIC SOIL FUNGI

Mary Sabuda<sup>1</sup>, Carla Rosenfeld<sup>2,3</sup>, Joshua Torgeson<sup>1</sup>, Cara Santelli<sup>1,3</sup>  
<sup>1</sup>Department of Earth Sciences, University of Minnesota, Minneapolis, MN, <sup>2</sup>Argonne National Laboratory, Lemont, IL, <sup>3</sup>BioTechnology Institute, University of Minnesota, Saint Paul, MN

Selenium (Se) plays a key role in human and ecosystem health as it is an important trace element for most life yet is an element of increasing environmental concern due to its toxicity in high concentrations. Interestingly, fungi do not require Se for metabolic functions yet some common soil fungi such as *Alternaria alternata* and *Paraconiothyrium sporulosum* are capable of reducing Se from aqueous Se(IV/VI) to solid Se(0) and volatile Se(-II) in an oxic environment. However, little is understood about the chemical and/or genetic mechanism(s) of these mycogenic Se transformations over time. Cultures of these fungi were grown with 0.1 and 0.5 mM selenite (Se(IV)) to track Se remaining in solution, solid-associated Se, and calculate potentially volatilized organic Se over 32 days. Results from this work indicate *Paraconiothyrium* reduces ~0.16  $\mu\text{moles Se/day}$  and *Alternaria* reduces ~0.90  $\mu\text{moles Se/day}$ . Geochemical speciation of aqueous and biomass associated phases shows changes in the proportions of inorganic and organic Se compounds with time. Transmission Electron Microscopy images reveal intracellular Se consists of 50-200 nm electron diffraction amorphous particles in the cytoplasm and aligned along the cell membrane. 25-50 nm Se particles also aggregate into 200 nm clusters along the periphery of the cells in a polymeric substance. Combined, this time-series experiment provides insight for discerning the mechanism(s) behind Se detoxification.

## MICROBIAL CONTRIBUTIONS TO THE SEDIMENT N AND C ISOTOPIC RECORD

Cody S. Sheik<sup>1</sup>

<sup>1</sup>Large Lakes Observatory, University of Minnesota Duluth, Duluth, MN

Earth's large lakes are unique aquatic ecosystems, but we know little of the microbial life driving sedimentary biogeochemical cycles and ultimately the isotopic record. Large lake sediments are biogeochemically active and have oxygen consumption rates akin to pelagic ocean sediments. Thus, large lakes provide biogeochemical contrasts to highly productive freshwater and coastal marine systems. Sediment cores from six stations across the western arm of Lake Superior were sampled. Microbial community structure followed patterns in bulk sediment carbon and nitrogen concentrations. Observed patterns were loosely driven by land proximity. Sediment carbon and nitrogen isotopes correlated significantly with microbial community structure. However,  $^{15}\text{N}$  showed much stronger correlation than  $^{13}\text{C}$ , and became heavier with core depth. Coinciding with the increase in  $^{15}\text{N}$  values, we see evidence of both denitrification and anammox processes in metagenome assembled genomes. Abundance of these genomes also varies with depth suggesting these novel microorganisms are partitioning into specific sediment geochemical zones. Additionally, several genomes are involved in sulphur cycling, suggesting a dual biogeochemical role and cryptic sulfur cycling. Together, the pervasiveness of co-metabolic pathways suggests interpretation of isotopic records may be messier than previously thought.

## PHOSPHOROUS SPECIATION AND MOBILITY IN MISSISQUOI BAY MESOCOSMS UNDER EXTENDED CONDITIONS OF REDUCTION, OXIDATION, AND FLUCTUATING OXIDATION- REDUCTION

John Shulke<sup>1\*</sup>, Martin Kurek<sup>1</sup>, Meagan Leduc<sup>2</sup>, Andrew Schroth<sup>2</sup>,  
Austin Wilkes<sup>2</sup>, Gregory K Druschel<sup>1</sup>

<sup>1</sup> Department of Earth Sciences, Indiana University-Purdue University  
Indianapolis, Indianapolis, IN USA, markurek@indiana.edu

(\*presenting author), <sup>2</sup> Department of Geology, University of Vermont,  
Burlington, VT

Mobility of phosphorus (P) between sediments and water column in many freshwater lakes is a process partially governed by the dynamic interaction of iron and P. Dynamic redox conditions across the sediment-water interface (SWI) have been linked to nutrient mobility and harmful algal blooms in a study site in Missisquoi Bay, a shallow, eutrophic bay located at the northern end of Lake Champlain (Smith et al., 2011). Additionally, mobility and bioavailability of organic P species has been shown to behave differently from inorganic P species (Giles et al., 2015). Defining the timing of the link between redox chemistry changes across the SWI and nutrient mobility is needed to assess how nutrient flux between sediment and water column may be a controlling factor for cyanobacterial blooms.

A series of controlled mesocosm experiments manipulated redox conditions by changing headspace gas supply and light availability. In sediments, mineralogy and P speciation were examined using in-situ voltammetry, XRF, SEDEX extractions, and enzyme hydrolysis of different organic P pools. In water samples, soluble reactive P, total P, enzyme digested P, and metals content at different filter fractions were obtained. Significant flux of P across the SWI to the water column required an initial 1-2-week interval of increasingly reducing conditions. Fluctuating redox conditions likely favor a weakly bound sediment P pool sorbed to precursor iron oxyhydroxides, priming the SWI for increased P mobility.

## CHANGES IN BACTERIAL GROWTH RATE LEAD TO HYDROGEN ISOTOPE FRACTIONATION

Derek A. Smith<sup>1\*</sup>, William Leavitt<sup>2</sup>, Melanie Suess<sup>1</sup>, Alexander  
Bradley<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Washington University  
in St. Louis, <sup>2</sup>Department of Earth Sciences, Dartmouth College,

<sup>3</sup>Department of Biology, Case Western Reserve University

The hydrogen isotopic fractionation of fatty acids in lipid metabolism has been shown to be influenced by salinity, growth phase, and lipid biosynthetic pathway, but all were believed to be secondary to the central metabolism of the organism. This was further complicated when hydrogen isotope values were shown to vary across microbial strain, electron donor, and electron acceptor. Theoretically growth rate could impact the extent of equilibration between the reservoirs of intracellular hydrogen, and the availability of NAD(P)H. Some research even suggested that growth rate might control the production of NAD(P)H. Other research has shown that growth rate may be correlated to hydrogen fractionation of fatty acids in sulfate reducing bacteria and of alkenones in algae. However, inconsistent observations have led others to conclude that growth rate is not a major control of hydrogen isotope fractionation. In order to clarify this issue, we isolated the potential effects of growth rate on fatty acid fractionation by employing continuous culturing techniques for multiple species of bacteria where the only variable altered was growth rate. Our results indicate that there is a large and significant fractionation of hydrogen in fatty acid production directly correlated to growth rate.

## PRELIMINARY BIOGEOCHEMICAL CHARACTERIZATION OF SEDIMENTS FROM LAKE SIBINACOCHA, PERUVIAN ANDES

Benjamin Tiger<sup>1</sup>, Bronwen Konecky<sup>1</sup>, Neil Michelutti<sup>2</sup>, Christopher Grooms<sup>2</sup>, Jack Hutchings<sup>1</sup>, Preston Sowell<sup>3</sup>, John P. Smol<sup>2</sup>  
<sup>1</sup> Department of Earth and Planetary Sciences, Washington University, USA, <sup>2</sup> Paleocological Environmental Assessment and Research Laboratory, Queen's University, Canada, <sup>3</sup> Sibinacocha Watershed Project, USA

High-elevation regions are particularly vulnerable to the physical and ecological consequences of global climate change. The high Andes are at the forefront of these changes due to their sensitivity to fluctuations in glacial mass and energy balance. In this study, we present a preliminary biogeochemical characterization of sediment cores from Lake Sibinacocha, Peru, which sits at ~5,000m asl in a rapidly deglaciating catchment adjacent to the Quelccaya Ice Cap. Due to its remote location and large size, Sibinacocha's sediments have not been well studied to gain a paleoclimatological or paleoenvironmental understanding of the region. Gravity cores spanning ~25 cm and roughly 300 years of sedimentation were taken in 2017 and 2018 from the northern section of the lake close to its glacial source. Initial investigations found that fossil diatoms changed from predominately planktonic to benthic assemblages within the past several centuries. We analyzed the sediment cores for bulk carbon and nitrogen content as well as isotope ratios using EA-IRMS to characterize geochemical changes. We found that bulk carbon, nitrogen, and  $\delta^{13}\text{C}$  are fairly constant until the mid-1800's. Around 1850,  $\delta^{13}\text{C}$  became more negative, and the concentrations of carbon and nitrogen increase, indicating substantial changes in productivity. Additionally, concentrations of sedimentary chlorophyll *a* (including its main diagenetic products) were found to be constant until the mid-1800's when they started to rapidly increase, also possibly indicating an increase in productivity. Our results show marked changes in several proxies from the Laguna Sibinacocha cores over the past ~300 years, indicating the potential for detailed paleoenvironmental reconstructions from this climatically-sensitive region.

## ILLUMINATING ENVIRONMENTAL AND MOLECULAR CONTROLS ON AEROBIC ANOXYGENIC PHOTOTROPHY

Gabriel Vargas, Maureen Coleman  
Department of the Geophysical Sciences, University of Chicago

Aerobic anoxygenic phototrophy (AAP) is a metabolic process found in diverse proteobacteria and widespread across aquatic environments. Unlike classical anoxygenic photosynthetic bacteria, the bacteria that perform AAP are often obligate aerobes and are thought to use this pathway to supplement their primarily heterotrophic metabolism. The environmental and molecular factors that control AAP, however, are poorly understood. Using the model organism *Erythrobacter longus*, we constructed deletion mutants for several genes potentially involved with AAP. Light enhanced the growth of wild-type *E. longus* on acetate or pyruvate minimal medium, but not in rich medium. Furthermore, the light contribution to the growth of *E. longus* was more important under carbon limited conditions. We hypothesized that this advantage could involve the glyoxylate shunt, a pathway which allows cells to conserve two  $\text{CO}_2$  per each acetyl-CoA molecule that enter the TCA cycle. If this hypothesis were true, we predicted that mutants deficient in the glyoxylate shunt would no longer have a growth advantage in the light. Contrary to this prediction, a mutant lacking isocitrate lyase ( $\Delta icl$ ), the first gene in the glyoxylate pathway, maintained a growth advantage in the light, suggesting that the glyoxylate shunt is not solely responsible for the benefit of AAP. In contrast, a strain lacking *bchID*, two genes involved in the biosynthesis of bacteriochlorophyll-*a*, had similar growth in light and dark on pyruvate minimal medium, implying that Bchl-*a* is essential for the light-driven growth phenotype. An important next step is to identify molecular regulators of the AAP process in *E. longus*. Elucidating the molecular mechanisms underlying AAP is essential for understanding the distribution and activity of this metabolism in aquatic ecosystems.

## FORMATION AND STABILIZATION OF BIOGENIC VATERITE

R. Seth Wood<sup>1</sup>, Bryan Chakoumakos<sup>2</sup>, Brenda Pracheil<sup>1</sup>  
<sup>1</sup>Environmental Sciences Division, Oak Ridge National Laboratory (ORNL), <sup>2</sup>Neutron Scattering Division, ORNL

Vaterite is a metastable calcium carbonate polymorph that appears to be a common, if not obligatory, transient phase between amorphous calcium carbonate (ACC) and calcite in supersaturated environments. Yet, due to its instability, vaterite is rarely found in modern environments - let alone the geological record. Instead, vaterite is almost exclusively observed in biogenic structures of certain foraminifera, sea squirts, gastropods, and fish. Comparatively, biogenic vaterite is more stable than its abiotic counterpart, which may be attributable to organic macromolecules that inhibit Ostwald ripening. One of the most notable and semi-common forms of biogenic vaterite is found in otoliths, the accretionary earbones of fish. In some fish, such as lake sturgeon and Chinook salmon, vaterite can precipitate concurrently with aragonite and calcite, yet remain stable in solution for fifty-plus years. Here, we discuss the use of wide-angle neutron diffraction (WAND), x-ray fluorescence (XRF), single-crystal X-ray diffraction (SC-XRD), micro-Raman, and controlled precipitation experiments to elucidate the mineralogical composition of bulk otoliths, the spatial distribution of calcium carbonate polymorphs and trace elements, and the potential biotic and abiotic factors effecting the stabilization of vaterite.

## MIXED SOURCES OF N-ALKANES IN THE LATE EDIACARAN IN THE EAST EUROPEAN PLATFORM CONSTRAINED BY PRIMARY COMPOUND-SPECIFIC HYDROGEN ISOTOPIC COMPOSITION

Ming Wu<sup>1</sup>, David Fike<sup>2</sup>, Alexander Bradley<sup>3</sup>  
<sup>1</sup>Washington University in St. Louis, St. Louis, USA, mingwu@wustl.edu (\*presenting author), <sup>2</sup>Washington University in St. Louis, St. Louis, USA, dfike@levee.wustl.edu, <sup>3</sup>Washington University in St. Louis, St. Louis, USA, abradley@eps.wustl.edu

Several mechanisms have been suggested to explain the inverse isotopic ordering in the  $\delta^{13}\text{C}$  of *n*-alkanes, isoprenoids, and kerogen in Proterozoic hydrocarbons including intensive heterotrophic reworking, preferential preservation of heterotrophic organic carbon and/or a ‘mat-seal’ effect, and major contribution from prokaryotic phytoplankton. Characteristic hydrogen isotopic fractionations associated heterotrophic and autotrophic metabolisms provide a potential tool to constrain sources of hydrocarbons. Previous studies have shown that the hydrocarbons in the late Ediacaran formation in the East European Platform are in low maturity without/with little contamination. So the primary hydrogen isotopic composition of hydrocarbons is probably retained as it is vulnerable to secondary alteration at high temperature. However, the conspicuous UCM makes direct measurement of compound-specific hydrogen isotopes of hydrocarbons impossible. Through molecular sieving and purification of hydrocarbons using HPLC, compound-specific hydrocarbon isotopic composition of pure *n*-alkanes are constrained. The  $\delta\text{D}$  values of *n*-alkanes of all the measured samples show a ‘U’ shape, ranging approximately from -250‰ to -50‰. The short-chain and long-chain *n*-alkanes are more enriched in  $\delta\text{D}$  compared to mid-chain *n*-alkanes with a difference as large as 150‰ in individual samples. So the *n*-alkanes in the Ediacaran samples are mixed sourced which will be discussed during the conference.

## SALINITY INFORMATION FROM LIPID BIOMARKER ISOTOPE RATIOS IN A CENTRAL TROPICAL PACIFIC LAKE SEDIMENT RECORD

D. A. Wyman<sup>1</sup>, J.L. Conroy<sup>1,2</sup>, M. Osburn<sup>3</sup>

<sup>1</sup> Department of Geology University of Illinois Urbana-Champaign,

<sup>2</sup> Department of Plant Biology, University of Illinois Urbana-

Champaign, <sup>3</sup> Department of Earth and Planetary Sciences,

Northwestern University, Chicago

Variability in tropical Pacific Walker Circulation and the nature of the Intertropical Convergence Zone (ITCZ) on centennial timescales over the last millennium remains uncertain given the diverse conclusions of paleohydrologic proxies across the tropical Pacific. Here we use biomarker stable isotope ratios from a lake sediment record taken from a brackish (28 ppt) lake on Kiritimati, in the central tropical Pacific, to reconstruct lake salinity and paleohydrology over the last millennium. Total lipid extracts (TLE) and specific biomarkers were extracted and the  $\delta D$  values were measured at decadal resolution over the last millennium. Preliminary results show lower  $\delta D_{TLE}$  values corresponding with thicker, darker microbial mats and more positive  $\delta D_{TLE}$  corresponding with gypsum rich units. A published transfer function relating salinity to  $\delta D_{TLE}$  indicates this latter period of high  $\delta D_{TLE}$  corresponds to lake water of 4.33-135 ppt. However, this transfer function also suggests modern salinity of 71.2 ppt, 43 ppt higher than measured. Thus, variations in  $\delta D_{TLE}$  likely reflect different microbial communities downcore, rather than the  $\delta D$  of lake water and its relationship with salinity. We plan future research on compound specific  $\delta D$ , paired with inorganic carbonate  $\delta^{18}O$  and detailed isotope-based hydrologic balance modeling, to further define the relationship between biomarker  $\delta D$  and salinity.

## THE INFLUENCE OF EARTH ABUNDANT MINERALS IN DEEP OCEAN HYDROTHERMAL ORGANIC TRANSFORMATIONS

Ziming Yang<sup>1</sup>, Xuan Fu<sup>1</sup>, Yiju Liao<sup>1</sup>, Isaac Thelander<sup>1</sup>

<sup>1</sup> Department of Chemistry, Oakland University, Rochester, MI, USA

Geochemical processes in deep-ocean hydrothermal systems influence the transport and degradation of sedimentary organic matter, the metabolisms of seafloor biosphere, and the deep carbon and nitrogen cycles. Minerals can play a significant role in hydrothermal transformation of deep marine organic compounds, but much still remains unknown about how minerals control the reaction pathways of organic carbon and organic nitrogen. In this study, we developed a laboratory-simulated hydrothermal system and investigated the effects of several Earth-abundant minerals on ketone and amine reactions, respectively, under specific hydrothermal conditions. We found that several iron-containing minerals could significantly increase ketone hydrothermal reactivity through promoted fragmentation or reduction pathway, whereas decomposition of amines were less influenced by the presence of the selected minerals. Based on product distribution analysis, we also provided detailed reaction pathways and plausible mechanisms for the studied organic-mineral hydrothermal interactions. Our results suggest a highly selective role of minerals in organic carbon and nitrogen transformations in deep-ocean hydrothermal environments.

# ADSORPTION OF SELENITE ONTO BACILLUS SUBTILIS: THE OVERLOOKED ROLE OF CELL ENVELOPE SULFHYDRYL SITES IN THE MICROBIAL CONVERSION OF Se(IV)

Qiang Yu<sup>1\*</sup>, Maxim I. Boyanov<sup>2,3</sup>, Jinling Liu<sup>1,4</sup>, Kenneth M. Kemner<sup>3</sup>,  
Jeremy B. Fein<sup>1</sup>

<sup>1</sup>Department of Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, USA (\* presenting author), <sup>2</sup>Bulgarian Academy of Sciences, Institute of Chemical Engineering, Sofia, 1113, Bulgaria, <sup>3</sup>Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, USA, <sup>4</sup>School of Earth Science, China University of Geoscience, Wuhan 430074, China

Microorganisms can reduce, methylate and assimilate Se, controlling the fate and transport of Se in the environment. However, the mechanisms controlling these microbial activities are still poorly understood. In particular, it is unknown how the negatively-charged Se(IV) and Se(VI) oxyanions that dominate the aqueous Se speciation in oxidizing environments bind to negatively-charged microbial cell surfaces in order to become bioavailable.

In this study, the role of sulfhydryl sites in the adsorption was determined by comparing selenite adsorption onto the *Bacillus subtilis* biomass with and without sulfhydryl sites blocked chemically, and the Se speciation on the biomass was analyzed using XANES and EXAFS spectroscopy. Our results show that the adsorption of selenite onto *Bacillus subtilis* bacterial cells is controlled by cell envelope sulfhydryl sites. Once adsorbed onto the bacteria, selenite is reduced, and forms reduced organo-Se compounds (e.g., R1S-Se-SR2). Because sulfhydryl sites are present within cell envelopes of a wide range of bacterial species, sulfhydryl-controlled adsorption of selenite likely represents a general mechanism adopted by bacteria to make selenite bioavailable. Therefore, sulfhydryl binding of selenite likely occurs in a wide range of oxidized Se-bearing environments, and because it is followed by microbial conversion of selenite to other Se species, the process represents a crucial step in the global cycling of Se.