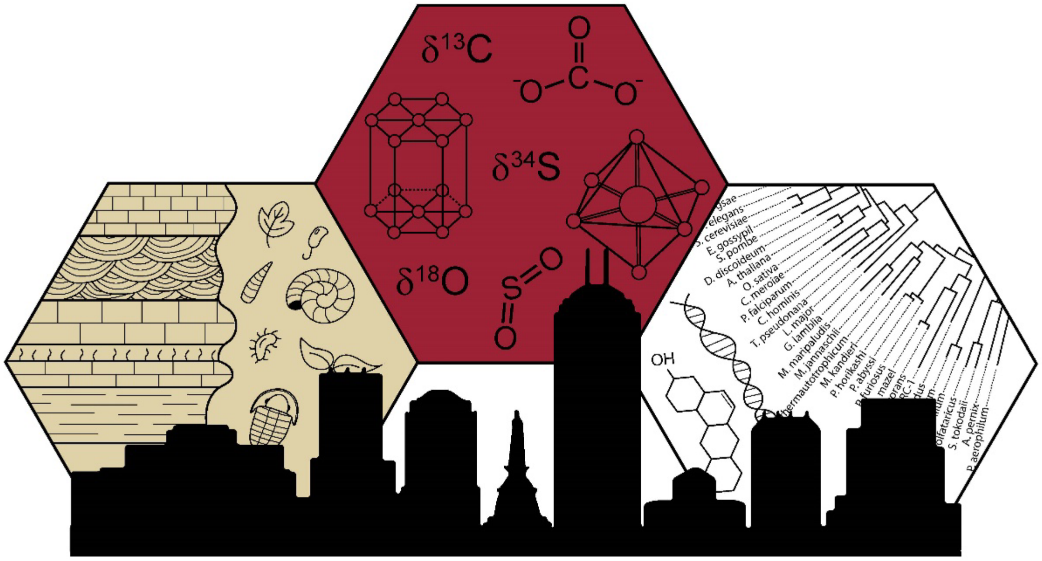

MIDWEST GEOBIOLOGY 2021
Indiana University Purdue University - Indianapolis

2021 Midwest Geobiology Symposium

September 25, 2021 – Indianapolis, Indiana

Hosted by: Indiana University Purdue University Indianapolis (IUPUI)

Planning team: Dr. Greg Druschel, Dr. Bill Gilhooly, John Shukle, Brooke Vander Pas, Lynn Thomas, Natalie Nichols, Spencer Strout

With generous support from:

The Agouron Foundation, IUPUI Earth Science Dept., IUPUI School of Science, IUPUI Office of the Vice Chancellor for Research, and the IUPUI Conference fund.

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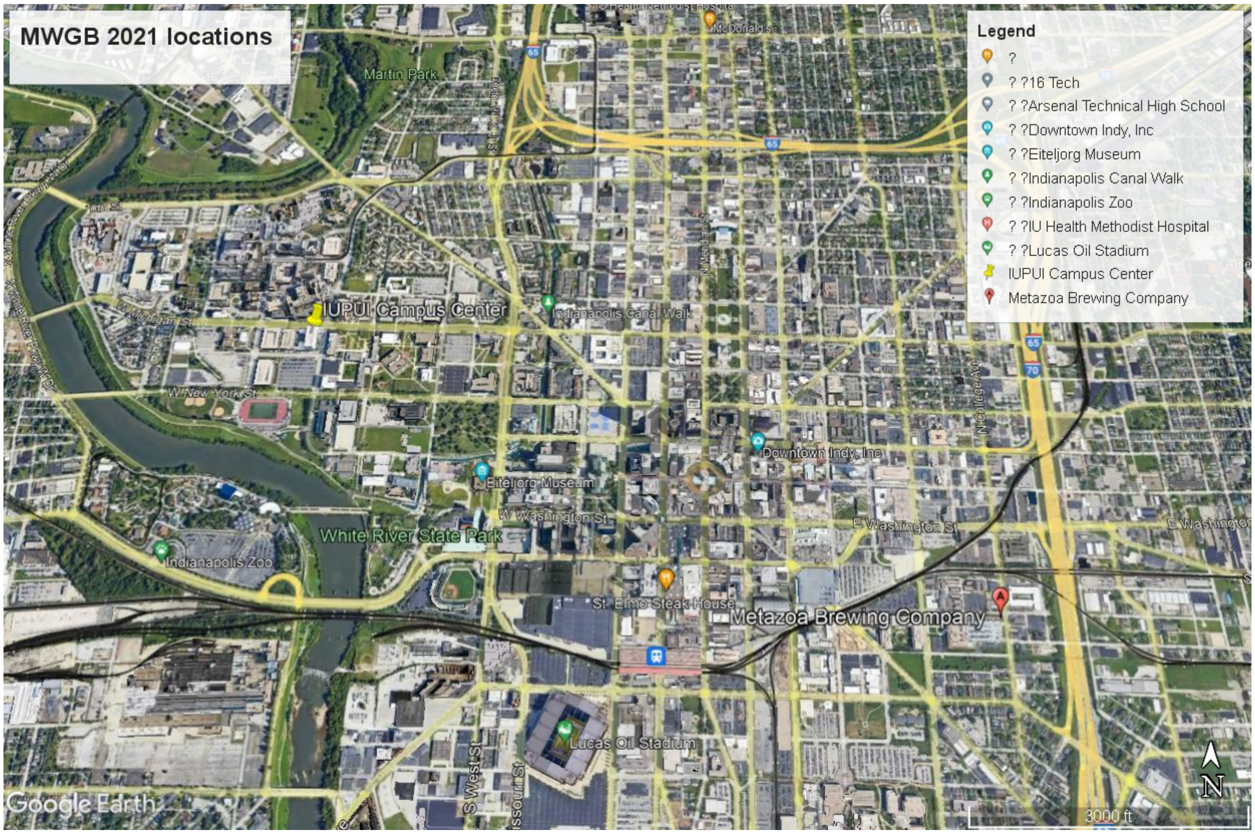
Midwest Geobiology Symposium 2021 Program

Friday, September 24, 2021 – 6:00 p.m. to 9:00 p.m. - Icebreaker event at Metazoa Brewing, 140 South College Ave, Indianapolis, IN (https://www.metazoabrewing.com/). 2021 Indiana Brewery of the Year! Parking available at brewery and streets nearby.

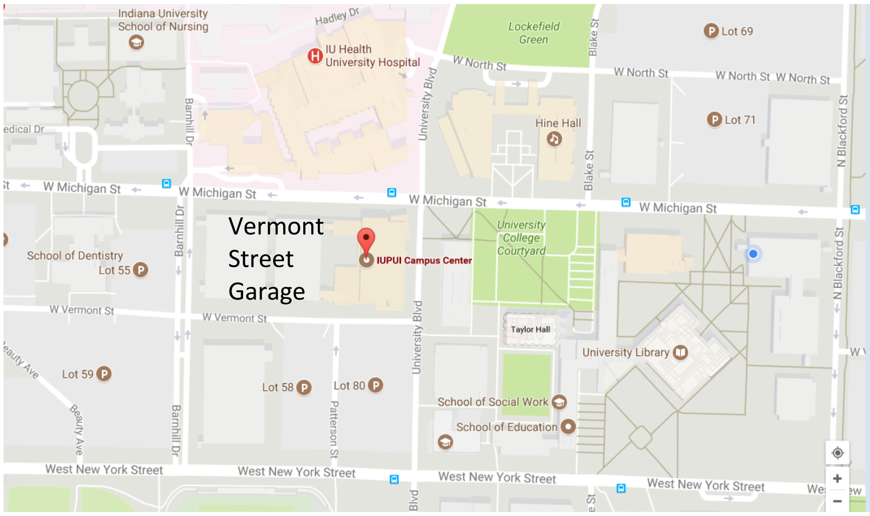


OLD GOLD BARBECUE

BBQ (selection of Beef Brisket, Pulled Por, Pork Ribs, Turkey, and Vegetarian Sausages, with Mac n Cheese and Street Corn) from resident food truck and smoker at Metazoa Old Gold Barbeque.

Drink tickets for free beers/non-alcoholic beverages available from your organizing team!

Saturday, September 25, 2021, IUPUI Campus Center – 420 University Boulevard. Parking available at Vermont Street Garage (attached to Campus Center Building), take a ticket on way in, grab a validated ticket from us at registration desk!



We will be located on the 4th floor of the Campus Center, easiest way is to take the escalators all the way up – Registration will be at the top of Escalators – pick up your badge at the table!

The Oral sessions will be held in room 450 B&C, the poster session will be held next door in room 450 A. Coffee and lunch will be served in the space outside these rooms and the outdoor terrace on the 4th floor (weather permitting)

Health and Safety Protocols:

The 2021 Midwest Geobiology Symposium hosted by Indiana University Purdue University Indianapolis submitted a full Covid19 Safety plan, reviewed and approved by a panel of health and safety experts (We are affiliated on campus with IU Health, a leading research hospital and medical research system, including some top people that have been key resources in the fight against Covd-19).

We will observe the following to ensure maximum safety of the attendees and the population of students, staff, and faculty at IUPUI:

- We will ask all attendees to be fully vaccinated in order to attend (exceptions made for religious and health reasons per Indiana State Law),
- If exempted, require proof of a negative covid test within 48 hours of attendance,
- Masks will be required during the event,
- Sanitation stations will be arranged with campus services,
- Extended times for entry and dismissal to maintain physical distancing will be observed,
- A provided lunch and coffee breaks will be arranged for physically distanced consumption outside (or in the case of inclement weather, spaced as possible in the campus center)
- Room capacities for Campus Center 450 A, B, and C are within limits for spacing of our expected gathering, with a calculated excess of 50% (i.e. campus center A&B have a max capacity of 210 people per covid restrictions on distancing, we expect 75).

We are confident that our space, protocols, and the responsibility of our attendees will allow us to host a successful, minimal risk, minimal stress, event where we all stay healthy in body and mind, and have a positive and productive exchange of scientific ideas!

MIDWEST GEOBIOLOGY 2021
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Oral Session I – 450 BC

9:00: Welcoming Remarks: Greg Druschel, Bill Gilhooly

9:10: Roger Bryant, University of Chicago - Seeing Past Sulfate Reduction In The Bulk-Carbonate Sulfur Isotope Record

9:30: Kaert Paiste, Washington University in St. Louis - New insights to the sulfur isotope record of the Paleoproterozoic Francevillian succession of Gabon

9:50: R. Seth Wood, Washington University in St. Louis - S heterogeneities in barite, aragonite, & pyrite record geochemical evolution of cold seeps

10:10: Raisa Islam, Iowa State University - Identifying the intermediate sulfur species in sedimentary pyrite formation under anoxic & ferruginous conditions

10:30: Coffee Break

Oral Session II – 450 BC

10:50: Mohammed Hashim, Western Michigan University - An Experimental Investigation of Iodine Incorporation into Dolomite: Implications for the Iodine Redox Proxy

11:10: Alexi Schnur, Michigan State University - Insights from shipboard radiotracer experiments into the role of reactive oxygen speices on iodine speciation transformations at the Bermuda Atlantic Time Series

11:30: Matt Smart, Indiana University Purdue University Indianapolis - A multi-proxy analysis of Devonian lacustrine systems: insights into geochemical cycling and potential global implications

11:50: Kelsey Doiron, Indiana University Bloomington - Sedimentary Biomarkers, including Botryococcenes, from Ia M'He, a Maar Lake in the Central Highlands of Vietnam

Lunch (provided) – 12:10 – 1:30 –Terrace at top of escalators & outdoor terrace (weather permitting)

Oral Session III – 450 BC

1:30: Leah Trutschel, University of Cincinnati - Determining drivers of microbial metabolism in a high pH serpentinizing system-Ney Springs

1:50: Xiaolong Liang, Washington University in St. Louis – Correlated single-cel growth during carbon source switching

2:10: Lynn Thomas, Indiana University Purdue University Indianapolis - Good Enough, Fast Enough: A Method to Identify Harmful Algae Blooms Using Water-Only Drone Imagery

2:30: Yizhi Sheng, Miami University - Lignin-enhanced reduction of structual Fe(III) in smectite: Dual roles of lignin as electron shuttle and donor

2:50: Coffee Break

3:00- Keynote: Prof. Bruce Fouke (Director Roy J. Carver Biotechnology Center, Professor of Geology, Health Innovation Professor, Carle Illinois College of Medicine, Faculty Member Carl R. Woese Institute for Genomic Biology, Affiliate Professor of Evolution, Ecology and Behavior), University of Illinois.

Poster Session – 450 A

3:30 – 6:00 p.m.

MIDWEST GEOBIOLOGY 2021
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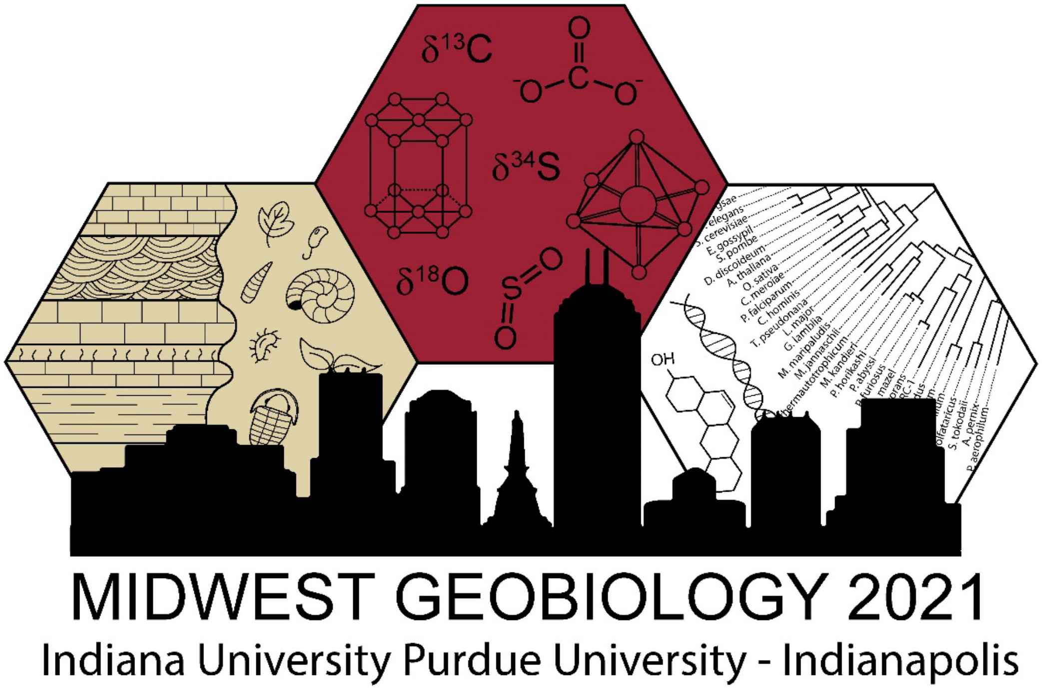
Abstracts

(in alphabetical order)



Archaeal Biomarker Records in Marine Sediments Impacted by Methane Transport: Insights from Peru Margin

SAJJAD AKAM[1,2]*, HUSSAIN ABDULLA[2], RICHARD COFFIN[2], YI GE ZHANG[3]

[1] Geological and Atmospheric Science, Iowa State University, (*correspondence: sajjad@iastate.edu)
[2]Physical & Env. Science, Texas A&M-Corpus Christi
[3]Dept. Of Oceanography, Texas A&M University

The transport of methane from deep sediments towards the seafloor is widespread in ocean margins and has important biogeochemical implications for the deep ocean [1]. A significant portion (>80%) of methane entering the shallow sediments from below at present are anaerobically oxidized by microbially-driven anaerobic oxidation of methane (AOM), which mainly involves a microbial consortium of anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria. Isoprenoid Glycerol dialkyl glycerol tetraethers (GDGTs) derived from core lipid membranes of ANMEs are often well preserved in sediment records. Methane Index (MI) is an organic geochemical proxy for methane seepage intensity which weighs in the relative proportion of GDGTs (GDGT-1,-2, and -3) preferentially synthesized by ANMEs with that of non-methane-related biomarker contribution from planktonic and benthic sources (Crenarchaeols) [2].

This study analyzed the GDGT composition of sedimentary core lipids from IODP Site 1230 (Peru Margin) using two silica columns and a high-resolution and accurate mass Orbitrap Fusion Mass Spectrometer. Our results report novel GDGT isomers with concentration peaking at the Sulfate-Methane Transition Zones (SMTZ) with highest AOM activity around 8 mbsf. Further, these isomers were almost absent above and below the SMTZ. Our observations suggest that these characteristic isomers of GDGT compounds preserved at the SMTZ depth are sourced from ANMEs. Identification of these novel isomers has important implications in refining the MI and additional GDGT based palaeoceanographic proxies like TEX86.

1. *Akam et al. (2020), Frontiers in Marine Science 7, 206.*
2. *Y. G. Zhang et al. (2011), Earth and Planetary Science Letters 307, 525-534.*

The Phylogeny and Purpose of a Duplicate Copy of the Squalene-Hopene Cyclase Gene

ROWAN BEHNKE[1], ALEX BRADLEY[2], MELANIE SUESS[3]

[1]rowanbehnke@wustl.edu
[2]Washington University CB1169 1 Brookings Dr. St. Louis, MO 63130 abradley@wustl.edu
[3]msuess@wustl.edu

Hopanoids, a group of isoprenoid lipids produced by certain bacteria, are common biomarkers that are informative about past life and climate. However, several mysteries remain regarding their purpose and production *in vivo*. One of these mysteries is why certain strains of bacteria possess two copies of a gene, *sqhC*, whose product, the enzyme squalene-hopene cyclase, is instrumental in the production of hopanoids. One copy, *sqhC1*, is on the chromosome, and the other, *sqhC2*, is on a plasmid. It is unusual for bacteria to have two copies of a gene due to the added energetic cost of replicating the second copy. Therefore, we posit that there is some evolutionary advantage to this second copy of *sqhC*. Additionally, every *sqhC2*-containing strain examined so far also has a gene for a TetR-family transcriptional repressor immediately upstream of *sqhC2* which may regulate *sqhC2* expression. Starting from Pearson's (2007) list of genera whose strains may have two copies of *sqhC*, three phylogenetic trees were constructed based on (a) the nucleotide sequences of *sqhC* (1 and 2) regardless of the strains' *sqhC2* possession, (b) the nucleotide sequences of *sqhC2* in strains which possess *sqhC2*, and (c) the nucleotide sequences of the upstream *tetR* in strains which possess *sqhC2*. On tree (a), the *sqhC2* sequences form several clusters, indication that they may be at least partly orthologous. Trees (b) and (c) are similar, with a weighted RF of 3.7645 (compared to 21.9959 for two random trees with the same number of leaves), indicating that *sqhC2* and *tetR* may have co-evolved, which supports the idea that this TetR protein regulates *sqhC2*. Further experiments are in progress to compare the lipid product profiles of the enzymes encoded by *sqhC1* and *sqhC2*, and to determine via electrophoretic mobility shift assay whether the TetR protein truly binds to the promoter of the downstream *sqhC2*.

[1]Pearson, Page, Jorgenson, Fischer & Higgins (2007), *Environmental Microbiology* 9, 2175-2188.

The influence of iron on anoxygenic photosynthesis within a ferruginous, meromictic lake

KALEIGH BLOCK*[1], NICHOLAS LAMBRECHT[2] & ELIZABETH SWANNER[1]

[1]Department of Geological and Atmospheric Sciences, Iowa State University, 253 Science I, Ames, IA 50011, USA
[2]Abbott, Structural Heart, 5050 Nathan Lane N, Plymouth, MN 55442, USA
(*correspondance: kblock@iastate.edu)

Brownie Lake (BL), located in Minneapolis, MN, is meromictic, meaning it is comprised of permanentley stratified layers which do not overturn seasonally. Ferruginous meromictic lakes exemplify an abundance of iron (Fe) within the water column, most notably dissolved ferrous iron which accumulates within the anoxic bottom waters.[1] Oceans on ancient Earth (during the Precambrian, >540 million years ago) were once ferruginous before the Great Oxidation Event occurred.[2] During this period of time, photoferrotrophs (organisms which utilize Fe(II), light, and inorganic carbon for anoxygenic photosynthesis) contributed to approximatley 10% of primary productivity on the early Earth (before the rise of oxygenic photosynthetic microbes, i.e. cyanobacteria).[2]

The chemocline of BL encompasses low oxygen, light and Fe levels and the presence of a deep chlorophyll maximum. These unique conditions permit the proliferation of photoferrotrophic microbes, and therefore, BL is an excellent anlog for an early Earth ferruginous ocean. Furthermore, these physicochemical conditions within BL provide the optimal environment to answer the question – do low oxygen and light levels and the presence of iron within the chemocline of BL either promote or inhibit primary productivity done by photoferrotrophs?

To answer this question, preliminary 16S rRNA sequence and metagenomic datasets have been analyzed and reveal that photoferrotrophic organisms are indeed present within the chemocline of BL, and have the gene (*cyc2*) necessary for putative Fe(II) oxidation. Additionally, *in situ* stable carbon isotope bottle experiments have been conducted to quantify carbon fixation rates across a gradient of iron conentrations. The results from these experiments will allow us to determine if photoferrotrophs are contributing to carbon fixation via anoxygenic photosynthesis.

[1] Lambrecht et al. (2020), *Geobiology* 18, 54-69.
[2] Lambrecht et al. (2021), *Fronteirs in microbiology* 12, 695

Seeing Past Sulfate Reduction In The Bulk-Carbonate Sulfur Isotope Record

ROGER N. BRYANT*, CLARA L. BLÄTTLER

Department of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave, Chicago, IL 60637, USA
(*correspondence: rnbryant@uchicago.edu)

Our knowledge of the history of Earth's surface oxidation state owes much to measurements of the sulfur isotope composition ($\delta^{34}S$) of sulfur-bearing phases in marine sedimentary rocks. Rock-derived sulfate-$\delta^{34}S$ values are thought to approximate seawater sulfate-$\delta^{34}S$, which when coupled with sulfide-$\delta^{34}S$ values allow for semi-quantitative assessment of seawater sulfate concentration. However, the most ubiquitous and temporally continuous archive of sulfate-$\delta^{34}S$, bulk-rock carbonate-associated sulfate (CAS), is prone to overprinting during early diagenesis. Most commonly, microbial sulfate reduction in sedimentary pore waters coupled with recrystallization of primary carbonate minerals results in CAS-$\delta^{34}S$ that is more positive than seawater sulfate-$\delta^{34}S$. Without a way to verify if bulk-rock CAS-$\delta^{34}S$ bears the imprint of sulfate reduction, the archive becomes a poor recorder of seawater sulfate-$\delta^{34}S$. We offer up calcium isotopes as a solution. When carbonate recrystallization occurs in close contact with seawater, both bulk-rock CAS and calcium resemble seawater isotopically; when recrystallization occurs in more restricted pore waters, bulk-rock CAS gets more positive and calcium isotopes remain more negative. The resulting negative correlation allows calcium isotopes to be used to pinpoint samples whose bulk-rock CAS-$\delta^{34}S$ values have been overprinted by sulfate reduction. This tool has the potential to improve our record of seawater sulfate-$\delta^{34}S$ and our understanding of Earth's surface oxidation dynamics throughout geologic history.

Assessing the Impact of Diagenesis on Foraminiferal I/Ca Ratios Using Adjacent Miocene Assemblages

JANET BURKE[1] AND DALTON HARDISTY[1]

[1]Department of Earth and Environmental Sciences, Michigan State University, East Lansing, MI, 48824

The foraminiferal iodine-to-calcium (I/Ca) proxy employs the iodine content of foraminiferal tests to track hypoxia in ancient oceans. I/Ca works because onlt the oxidized iodine species, iodate, cab be incorporated into foraminiferal calcite. However, interpretations of I/Ca data rely on the assumption that iodate depletion caused by hypoxia is the primary driver low iodine concentrations in foraminiferal tests. Another process that could impact the I/Ca ratios of foraminiferal fossils is post-depositional dissolution and recrystallization. Such diagenetic considerations are important because recrystallization of foraminiferal tests in corrosive pore fluids could result in a false OMZ signal, as porewaters—like oxygen-poor waters of a severe ODZ—are depleted in iodate. Currently, the susceptibility of the foraminiferal I/Ca proxy to diagenetic offsets has not been directly tested. Here, we present preliminary data from a comparative analysis of two adjacent assemblages of mid-Miocene planktonic foraminiferal fossils from the Eastern Tropical Pacific (IODP 321-U1337 and 321-U1338). These localities contain similar species compositions but differ significantly in the preservation quality of the foraminiferal tests. We used SEM imaging to directly compare the level of dissolution and diagenetic recrystallization on the specimens from each locality and compared measurements of foraminiferal I/Ca from each sample. Our findings indicate that although the preservation state of samples from U1337 is inferior to those from U1338, the I/Ca signal detected in both samples is consistent.

Electrochemical detection of microbiological activities in benthic sediments

JOSHUA DAVIS[1], JOHN SENKO[2],CHELSEA MONTY-BROMER[3]

[1][jad195@uakron.edu-302 Buchtel Common
Akron, OH 44325]
[2][senko@uakron.edu-302 Buchtel Common
Akron, OH 44325]
[3][c.montybromer@csuohio.edu-2121 Euclid Ave., FH 104
Cleveland, Ohio 44115-2214]

Microbial reductive dissolution of Fe(III) phases in benthic sediments can influence the solubility of phosphate, and consequently the potential for harmful algal blooms (HAB) that arise due to the enhanced availability of that nutrient. The aim of our work is to use an electrochemical approach, spefically zero resistance ammetry (ZRA) to monitor microbial activity. Zero resistance ammetry is a electrochemical method of measuring galvanic current flow and features a split-cell configuration that utilizes two working electrodes (referred to as WE1 and WE2) deployed in sediments with contrasting redox or terminal electron accepting regimes. Using ZRA we monitored the electrochemical signatures of microbialogical Fe(III) reduction. The split-cell configuration of our ZRA system allows us to manipulate conditions of both chambers and mimic contrasting aerobic and anaerobic condtions in sediments. For our experiments, we featured two sets of chambers with the WE1 and WE2 side conditioned to be oxic and anoxic, respectively. We also had one of the set of chambers act as the sterile control, to differentiate between biological and abiotic processes. For the live set of chambers, we detected a negative electrical current, which was indicative of microbial activity, as the WE1 side of the chamber served as the cathode, while the WE2 side served as the anode. Fe^{2+} concentration increased in the WE2 side, indicating that the microbes present in the sediment are reducing ferric iron into ferrous iron. At the same time we saw a decrease in the concentration of phosphate, which helps reinforce the idea of the microbial activity influencing the solubility of the internalized phosphate. This is in comparison to the dead set of chambers, in which there was zero current, little to no increase in Fe^{2+} concentrations and no decrease in the phosphate concentrations. Analysis of 16S rRNA gene sequences from organisms associated with the sediments indicated numerous Fe(III) reducing taxa, including *Desulfuromonadales*. Based on our results, we plan to deploy field ZRA in sediments to monitor real-time sediment-associated microbiological processes that could control phosphate solubility.

Sedimentary Biomarkers, including Botryococcenes, from Ia M'He, a Maar Lake in the Central Highlands of Vietnam

KELSEY E. DOIRON[1] LORA STEVENS[2] SIMON C. BRASSELL[3]

[1] Indiana University, Bloomington; kedoiron@iu.edu
[2] California State University Long Beach; lora.stevens@csulb
[3] Indiana University, Bloomington; simon@iu.edu

The climate of the Central Highlands of Vietnam is influenced by dynamic interactions between Asian monsoonal circulation and the position of the Intertropical Convergence Zone (ITCZ), augmented by El Niño events and the frequency & intensity of tropical storms. Lake sediments from this part of southeast Asia afford an opportunity to decipher paleoclimatic records that reflect the evolution and temporal history of the region's climate. Lake Ia M'He, Vietnam (14°11'N, 107°52'E) is a shallow lake with a low sediment accum-ulation rate that yielded a core extending back beyond the Last Glacial Maximum (LGM), based on ^{14}C dating. Biogeochemical signatures in these sediments record temporal variations in algal productivity and terrestrial vegetation reflecting changes in the lake environment associated with the transition from glacial to interglacial climate. *n*-Alkanes maximize at C_{27} in glacial samples, succeeded by a prominence of C_{33} or C_{35} homologs prior to the LGM. The dominance of n-C_{35} in some core intervals is unprecedented, likely reflecting a discrete biological source. Aliphatic hydrocarbon distributions include $C_{34:2}$ botryococcene and two related $C_{34:3}$ monocyclic alkenes. Temporal variations in these compounds likely reflect changes in strains of their source alga, *Botryococcus braunii*, or the lake climate. C/N ratios record shifts in the sources of sedimentary organic matter before and after the LGM, that coincide with the appearance of diatoms and a negative shift in d^2H values for *n*-alkyl lipids indicative of changes in terrestrial vegetation, or precipitation, or both.

Predictive Weathering and Secondary Mineral Formation of Hadean Mafic and Ultramafic Rocks

ANDREW GUERTIN[1] AND JEFFREY CATALANO*[2]

[1]Department of Earth & Planetary Sciences, Washington University in Saint Louis, St. Louis, MO, USA [andrewguertin@wustl.edu]
[21]Department of Earth & Planetary Sciences, Washington University in Saint Louis, St. Louis, MO, USA [catalano@wustl.edu]

Mineral surface adsorption may have played a key role in the synthesis of biomolecules related to the origin of life. This study uses geochemical modeling to predict mineral weathering products on early Earth environments. New solubility constants were estimated for a series of smectite minerals to increase the accuracy of the model. These new constants, when compared against previous research, appear to have a minor effect on which minerals formed. Several initial rock compositions are considered, ranging in silica content from mafic to ultramafic. Weathering of komatiite primarily formed saponite and serpentines at low water-rock ratios. Basalt weathering produced significant saponite as the only smectite, but also formed significant quartz, and Fe-oxide minerals. Carbonate minerals formed consistently in high abundance under high water-rock ratios. Rather than montmorillonite, the subject of much origin of life adsorption research, saponite and serpentines appear to be the most abundant clay minerals formed in early Earth environments. These minerals, predicted to be abundant, are more likely to have played a role in the origin of life.

An Experimental Investigation of Iodine Incorporation into Dolomite: Implications for the Iodine Redox Proxy

MOHAMMED S. HASHIM[1], JANET E. BURKE[2], DALTON S. HARDISTY[2], AND STEPHEN E. KACZMAREK[1]

[1]Department of Geological and Environmental Sciences, Western Michgian University, Kalamazoo, MI 49008
[2]Department of Earth and Environmental Sciences, Michigan State University, East Lansing, MI, 48824

The emergence, evolution, and extinction of life on Earth are closely linked to the redox state of the oceans, which has dramatically varied through Earth history. Numerous redox-sensitive proxies are used to study the oceanic redox state over geologic time, one of which is I/(Ca+Mg) in carbonates. The iodine proxy assumes that only IO_3^- – the oxidized form of iodine – is incorporated into carbonate minerals, whereas I^- – the reduced form – is excluded, making it possible to track O_2 availability in ancient oceans. This assumption has been experimentally tested in calcite but not in dolomite, despite dolomite being the host mineral for much of the ancient iodine record. Here we use high temperature (170 - 200 °C) dolomitization experiments to explore the factors that control iodine incorporation into dolomite.

Our experimental results yield two major observations: (i) experiments where iodine-containing aragonite sediments are dolomitized in iodine-free solutions yield dolomite with I/(Ca+Mg) values that decrease to zero with reaction time, (ii) experiments conducted in solutions containing KI produce dolomite with no iodine, whereas those conducted in KIO_3 solutions produce dolomite containing I/(Ca+Mg) the amount of which broadly correlates with solution [IO_3].

These results have several implications. First, they validate the assumption that the occurrence of iodine in ancient dolomites indicates formation under oxic conditions, which represents the basis for the iodine proxy. Second, zero or low I/(Ca+Mg) values in ancient rocks may reflect anoxic water columns or dolomitization in anoxic pore fluids. Third, the strong correlation between dolomite I/(Ca+Mg) and solution [KIO_3] suggests that deriving an iodine partition coefficient for dolomite is attainable, though the wide ranges of I/(Ca+Mg) values observed for each solution [KIO_3] renders this task complex and urges further work.

Reproducibility of Witherite ($BaCO_3$) Biomorphs

MAGGIE A. HINKSTON[1] AND LINDA C. KAH[2]

[1]Washington University in St. Louis, hinkston.m@wustl.edu]
[2]University of Tennessee, Knoxville, [lckah@utk.edu]

A pertinent problem in the exploration of biogenicity in the geological record is the methodology in which we differentiate fossilized structures from crystallized materials. It has been shown in crystallization experiments that chemical processes can create crystalline structures that resemble biotic structures, meaning the morphology is not necessarily the best indicator of past life. Current literature has shown that there are a wide range of crystal morphologies, but little information is known regarding the conditions of formation and the range of shapes that form at each set of conditions [1].

My goal in this project was to explore a variety of initial conditions and their reproducibility in witherite (BaCO3) biomorphs. Biomorphs were made in a silica solution, and pH was varied with the addition of a 0.1 M solution of either sodium hydroxide (NaOH) or hydrochloric acid (HCl). Biomorph formation was initiated with the addition of barium chloride (BaCl2), whose molarity ranged from 1-100mM. The solution was left to equilibrate with the atmosphere, allowing for the dissipation of carbonate (CO3) into the solution. These solutions were left at three different temperature points: 20C, 40C, and 60C. Through these experiments, it was found that biomorphs formed across a range of pHs and a variety of barium chloride molarities; that biomorph shape was reproducible; and that there was an apparent correlation between the set of initial conditions and the range of shapes formed.

REFERENCES

Garcia-Ruiz, Hyde, Carnerup, Christy, Van Kranendonk, and Welham (2003) *Science* 302: 1194-1197.
Kellermeier, Cölfen, Garcia-Ruiz (2012) *European Journal of Inorganic Chemistry* 2012: 5123-5144.
Rouillard, Garcia-Ruiz, Gong, van Zuilen, (2018) *Geobiology* 2018: 279-296.
Schopf (1993) *Science* 260: 640-646.

Storm Pulse Controls on Fluvial Organic Carbon Transport in A Midwestern Agricultural Watershed

Tingyu Hou[1], Timothy R. Filley *[2], and Neal E. Blair [3]

[1] Department of Earth & Atmospheric Sciences and the Center for the Environment, Purdue University, West Lafayette, IN, USA. (hou56@purdue.edu)
[2] Department of Geography and Environmental Sustainability, University of Oklahoma, Norman, OK, USA. (*correspondence: filley@purdue.edu)
[3] Departments of Civil and Environmental Engineering, and Earth and Planetary Sciences, Northwestern University, Evanston, IL, USA (n-blair@northwestern.edu)

Transport of organic carbon (OC) within fluvial systems plays a major role in connectivity between terrestrial and aquatic compartments of the global carbon cycle and the exchange of atmospheric CO_2 with inland waters. Storm events are the primary mechanisms of net terrestrial OC export through fluvial networks within agricultural landscapes of the Midwest United States, such as the Clear Creek Watershed (CCW) of eastern Iowa, where land use and hydrologic management over the last 150 years have dramatically altered for both surface and subsurface flow pathways compared to the pre-settlement landscapes.

High-resolution monitoring of DOC and POC concentration and $\delta^{13}C$ values obtained during six storm events across two hydrological years in the CCW landscape, including in-stream, subsurface tile drains, shallow groundwater, paired with soil water-extractable OC, were used to investigate the export mechanisms, landscape connectivity, and biogeochemical signature of fluvial OC as it passes from the upper to lower reaches of the CCW. Our results demonstrated a greater dominance of POC vs. DOC during high-flow periods (i.e., storm period) where POC accounted for 54-94% of total fluvial OC export during individual events. The relationships between DOC concentration and discharge as well as $\delta^{13}C_{DOC}$ values of storm and baseflow conditions of events under dry and wet antecedent conditions, suggested that increased hydrological connectivity is driving a more pronounced exchange of OC between hillslope and groundwater due to seasonally-wet conditions. There are few examples of such high-resolution storm event sampling to explore the dynamics of fluvial OC, but such efforts provide important clues into the dynamics of OC sourcing and transformation in inland water systems.

Impact of depositional facies on marine sedimentary pyrite textures and sulfur isotopes: a case study of the Early-Mid Pleistocene transition from the Valle di Manche section (Crotone Basin, Southern Italy)

J. Houghton, D. Fike[1]

[1]Earth and Planetary Sciences, Washington University in St. Louis; jhoughton@wustl.edu, dfike@wustl.edu

Interpretations of the bulk $\delta^{34}S$ in sedimentary pyrite tend to be relatively robust in deep marine environments with low/steady sedimentation rates. However, in more commonly preserved shallow environments, regional or local processes may overprint such signals by modulating the delivery of sediments and organic matter that fuels microbial activity within sediments. We have constructed the bulk (cm-scale) $\delta^{34}S_{pyr}$ record from the Valle di Manche section in the Crotone Basin, Southern Italy, preserving the stratal stacking patterns of two continuous transgressive-regressive cycles from the Mid Pleistocene. To evaluate the history of sedimentary pyrite formation hidden within the bulk $\delta^{34}S_{pyr}$ signal, we have analyzed the $\delta^{34}S_{pyr}$ of individual pyrite grains on the micron-scale using secondary ion mass spectrometry (SIMS) to characterize the distribution of values responsible for the observed bulk $\delta^{34}S_{pyr}$ in samples throughout the section. All samples analyzed, regardless of bulk $\delta^{34}S_{pyr}$ (ranging from -44 to +7‰) and depositional setting (outer to inner shelf) contain a significant population of ^{34}S-depleted pyrite (<-40‰) with minima from -55 to -50‰, suggesting that maximum (i.e., near-equilibrium) microbial fractionation (□~70‰) is ubiquitous and that preservation of syndepositional pyrite occurs even in very shallow sediments or when post-burial pyrite formation skews the bulk $\delta^{34}S_{pyr}$ value.

Sedimentology, Stratigraphy, and Carbonate Chemostratigraphy of Lower Devonian to Lower Mississippian Strata in Northern WY, United States

*MINGXI HU[1,2], PAUL M. MYROW[1], DAVID A. FIKE[2], MERCEDES DI PASQUO[3], MICHAŁ ZATOŃ[4]

[1]Department of Geology, Colorado College, Colorado Springs, CO 80903 USA; (*correspondence: h.mingxi@wustl.edu); pmyrow@coloradocollege.edu
[2]Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA; dfike@wustl.edu
[3]Laboratory of Palynostratigraphy and Paleobotany, CONICET-ER-UADER, Diamante CP, Entre Ríos, Argentina; medipa@cicyttp.org.ar
[4]Institute of Earth Sciences, University of Silesia in Katowice, Będzińska 60, 41-200 Sosnowiec, Poland;

This study presents a detailed sedimentological and chemostratigraphic analysis of Lower Devonian to Lower Mississippian strata in northern Wyoming, U.S., deposited during the transition from Devonian greenhouse to the Carboniferous–Permian icehouse condition. The Lower Devonian Beartooth Butte Formation represents the infill of incised valleys that vary dramatically in thickness and lithology, and include coarse continental lower parts and upper estuarine facies. The timing of erosion and infill of the studied channels varied from Emsian to Lochkovian–Pragian stages. The overlying Givetian Maywood Formation records another period of valley incision and deposition. All of these paleochannels preceded the Antler Orogeny, suggesting eustasy as a possible driving mechanism. Both formations record similar brackish fluvio-lacustrine environments with a distinctive faunal assemblage of microconchids, plant fossils, and microspores. These faunas lived in salinity-stressed ecological niches and tracked marine incursions into these successively cut channels during lowstand conditions, over a span of ~ 30 m.y of the Early to Middle Devonian. This remarkable and repeated paleogeographic and paleoecological pattern is a unique feature of the geologic history of this part of Laurentia. The Frasnian Jefferson Formation was deposited in a shallow carbonate shelf and records a significant $\delta^{13}C$ negative excursion (~ -6‰). This excursion correlates globally to the *punctata* event, a record of the Alamo Impact. The unconformably overlying Mississippian Madison Limestone contains two positive $\delta^{13}C$ excursions (up to ~ 7.5‰) that correlate to the Kinderhookian–Osagean TICE event. These isotope data provide for both regional and global correlation of northern Rocky Mountain strata and events for the middle–late Paleozoic transition interval.

Identifying the intermediate sulfur species in sedimentary pyrite formation under anoxic & ferruginous conditions

RAISA ISLAM[1*], ELIZABETH D. SWANNER[1]

[1] Department of Geological and Atmospheric Sciences, Iowa State University, 253 Science I, Ames, IA 50011, USA
(*correspondence: rislam@iastate.edu, eswanner@iastate.edu)

Pyrite (FeS_2) is the most thermodynamically stable iron-sulfide mineral in anoxic and sulfidic terrigenous sediments, making it the most abundant iron-sulfide on the Earth's surface.[1] The burial of iron minerals as pyrite is a sink for the removal of up to 35% sulfur from the modern marine system, and is a major driver of the terrestrial and oceanic sulfur cycle.[2] The abundance of pyrite in organic-rich shales serves as a constraint in the quality of petroleum extracted by 'souring' the oil, thereby having major implications for global petroleum reserves.

Sedimentary pyrite formation initiates via microbial sulfate reduction to form sulfide (S^{2-}), which is buried with iron minerals, whereby sulfide is oxidized to the S^{1-} in pyrite. The sulfur intermediates involved in this transformation of sulfate, and the precursor minerals present during early sedimentary diagenesis are poorly understood, and constrained mainly from experiments rather than natural systems. Previous lab experiments show that pyrite forms when FeS reacts with elemental sulfur (S^0) or polysulfides, or through the sulfidation process of Fe(III)(oxyhydr)oxides. These pathways, including possible sulfur intermediates, have not been validated via detection and quantification in anoxic sediments.

To detect the sulfur intermediates and constrain the possible mechanism(s) of sedimentary pyrite formation, we studied authigenic water column particulates and diagenetic sediments from merromictic and ferrugnious Brownie Lake in Minneapolis, MN, where bottom waters exceed 1000µM in dissolved iron and maximum sulfate concentrations throughout the water column range between 80-100µM. We use a combination of Mössbauer spectroscopy and synchrotron-based bulk and microscale X-Ray Absorption Spectroscopy on anoxic samples to identify the Fe and S phases, which point towards the presence of a metastable iron monosulfide mineral, as well as sulfite, thiosulfate and elemental sulfur, which are key intermedaites in the sedimentary sulfur cycle.

[1] Rickard D. and Luther G. (2007) *Chemical Reviews* 107, 515-562; [2] Tostevin R., Turchyn A. V., Farquhar J., Johnston D. T., Eldridge D. L., Bishop J. K. B. and McIlvin M. (2014) *Earth Planet. Sci. Lett.* 396, 14–21

Microplastics: Abundance and Effect on Microbial Life in Landfills, Wetlands, and Grassland.

SARAH KHOURY [1], D'ARCY MEYER-DOMBARD [2], JEAN BOGNER [3], JUDY MALAS, GRACIE-ANNE FISCHER

[1] skhour5@uic.edu
[2] drmd@uic.edu
[3] jbogner@uic.edu

Microplastics (MPs) and microfibers (MFs) have been an increasing problem in many environments due to a global surge in anthropogenic activity and waste. While the impact of MPs is largely studied in marine environments and larger marine organisms, little is known about how MPs affect microbial communities in soil and freshwater sediments as well as their abundance in these environments. As the release of MPs continues to become a larger problem, our team has decided to look into the abundance of MPs in landfills, grasslands, and wetlands using a density based separation unit, as well as the impact MPs have on microbial communities over time by simulating the conditions in the aforementioned environments. Initial analysis of community structure in the simulated landfill experiments showed a shift in microbial populations; however, identifying the main microbes affected requires further experimentation. We are in the early phases of testing the column density separation unit, which will be used to determine retrieval error for the multitude of testing environments. The preliminary results have suggested multiple separation media to be used in complex organic soils such as landfills.

Correlated single-cell growth during carbon source switching

XIAOLONG LIANG[1], MELANIE SUESS[1], CLIVE JONES[1], DAVID A. FIKE[1], ALEXANDER S. BRADLEY[1]*

[1]Department of Earth and Planetary Sciences, Washington University, Saint Louis, Missouri 63130, USA
[liang.x@wustl.edu; msuess@gmail.com; clivejones@wustl.edu; dfike@levee.wustl.edu]
(*correspondence: abradley@eps.wustl.edu)

Bacteria constantly encounter fluctuations in natural environments, and bacterial fitness and cellular resource allocation are dependent on the rate of cell growth. Increasing evidence suggests that single-cell heterogeneity at gene expression level and cellular growth rate within isogenic bacterial populations may enable the bacterial population bet-hedging strategies to exploit new conditions. However, it remains unclear how single-cell growth rate is determined under dynamic environmental conditions, and microbial uptake of organic carbon in fluctuating environments is a lack of understanding. Fundamental trade-offs between cell growth and physiological adaptation may exist in shifting environments in which high growth rate boosts population size and makes cells sensitive to fluctuations. Here we report the correlated cell growth of Methylobacterium extorquens during carbon substrate switching, observed when a growing culture was abruptly shifted from a one-carbon compound, methanol, to a preferred carbon source, succinate, or from succinate to methanol. Secondary ion mass spectrometry (SIMS) analysis revealed a large variation in the growth rate of individual cells via assimilation of substrates. The single-cell growth rate before carbon source shift mostly correlated negatively to the growth rate on the new carbon substrate, but the correlation became positive when the growth rate was lower than a specific limit which phenomenon was more obvious in transition from methanol to succinate. Bacterial cells need to repress pathways of the depleted metabolites and initiate different metabolic pathways to feed on the new substrates when switching to new resources. Our results indicate that lower growth rate facilitates cell adaptation in new substrate while appropriate growth rate is needed for bacterial fitness.

Influence of an invasive, geophagous insect on the aggregate dynamics of a native soil

GORDON R. MACLEOD[1], TIMOTHY R. FILLEY[2], DOUGLAS S. RICHMOND[3]

[1] gmacleo@purdue.edu
[2] filley@purdue.edu
[3] drichmond@purdue.edu

Macrofauna can support or drastically alter the biophysical state and function of soil. Many soil-dwelling invertebrates can affect soil stability by facilitating or hindering the soil aggregation process, changing the availability of plant and soil organic matter (SOM) for aggregate incorporation, and shifting the predominant mechanisms by which carbon and nitrogen are incorporated into soil aggregates. The current study examines soils affected by soil-dwelling larvae of the invasive Japanese beetle *Popillia Japonica* Newman (JB) in a Northern Indiana silt-clay-loam. We hypothesize that larval root-herbivory will inhibit the natural mechanisms of root input-driven, large soil aggregate formation, and consequently impede formation of intra aggregates. However, JB will promote a different pathway for the creation of large soil aggregates by mixing digested root tissue and mineral soil through formation of frass, but with the absence of large intra-aggregate decaying root fragments. Present findings show a proportional increase of larger soil size fractions (2mm – 4.75mm) in the rhizosphere of infested soil after 1½ life-cycles of the beetle, but a decrease in the smaller soil size fractions (212µm – 1mm). These results may indicate an overall destabilization of soil structure over time in the stratum of highest JB larval activity, which in turn has the potential to expose a greater portion of soil carbon and nitrogen to mineralization processes and loss.

Predicting Biomarkers for Astrobiology using Laboratory Adaptation

JUDY MALAS[1], DANIEL C. RUSSO[2], FABIEN KENIG[3], D'ARCY R. MEYER-DOMBARD[4]

[1,2,3,4] University of Illinois at Chicago, Department of Earth and Environmental Sciences
[1] jmalas2@uic.edu
[2] drusso@uic.edu
[3] fkenig@uic.edu
[4] drmd@uic.edu

The discovery of ocean worlds in our solar system has reignited the interest in astrobiology. Icy ocean world Titan, for example, is an excellent model for astrobiological exploration because its abundant surface organics and global subsurface aqueous ocean both provide potential support for microbial life. Models suggest potentially habitable environments on Titan are cold (-15-10°C) and under high hydrostatic pressures (~150 MPa at the bottom of the lithosphere, up to ~750MPa at the core-ocean interface) [1]. Our work seeks to determine the potential biomolecules produced if Titan is inhabited by conducting laboratory adaption of microorganisms to Titan-like pressure and temperature conditions using a novel very-high pressure culturing chamber (VHPCC). Preliminary results show that multiple organisms tested in our lab are able to withstand pressures of >750 MPa for short periods of time (15 minutes), after training during incremental pressure steps. Incremental time increases have also been conducted, and model organisms are able to withstand high pressures for up-to 24 hours. We predict changes in the genome, lipidome, transcriptome, and proteome after demonstrating that growth is happening *in situ* in the VHPCC. These changes will inform the search for life by enabling us to understand the molecular machinery might allow organisms to grow in alien oceans, including that of Titan.

[1] Vance, S.D., et al. (2018). *Journal of Geophysical Research: Planets*

Mid-late Holocene hydroclimate and vegetation changes in Lago Caranã, Brazil: preliminary insights from plant wax biomarkers

Alessandro A. Mauceri[1]*, Bronwen L. Konecky[1],
Jack A. Hutchings[1], S. Yoshi Maezumi[2]

[1]Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO, USA (*correspondence: a.a.mauceri@wustl.edu)
[2]Department of Ecosystem and Landscape Dynamics, University of Amsterdam, Amsterdam, North Holland, Netherlands

The isotopic and structural composition of plant wax derived biomarkers from lacustrine sedimentary archives can reveal details about past shifts in hydrology and ecology. Utilizing such biomarkers for paleoclimate reconstruction may be useful in South America, where records from the Holocene are lacking—especially from Amazonia. They also have the potential to decode both climate and vegetation shifts, including changes in forest composition and structure driven by humans, who have been present in lowland Amazonia for over 13,000 years (Roosevelt, 2013). Here, we present preliminary data on the hydrogen isotopic composition (δD) and relative *n*-alkane distributions of plant waxes from Lago Caranã, northeast Brazil. Our initial interpretations aim to characterize climate and vegetation changes over the past ~5,600 years. The *n*-alkane chain length distribution suggests mixed aquatic and terrestrial plant wax sources throughout the entire record, with a transition beginning around ~1,700 cal yr BP that indicates a progressive increase in the contribution from terrestrial plants, and a shift at ~300–500 cal yr BP suggesting increased grass inputs. Detailed pollen and charcoal stratigraphy (Maezumi et al., 2018) suggests that these shifts broadly coincide with changes in the abundance of edible trees, palms, and herbs in the region, largely driven by pre-Columbian human activities. The δD of C_{31} *n*-alkanes shows an overall shift from D-enriched to D-depleted waxes, suggesting a general shift from drier to wetter conditions since ~4,350 cal yr BP—a transition also seen in other regional hydroclimate records, including the decadally-resolved Paraíso Cave speleothem $\delta^{18}O$ record (Wang et al., 2017). This study is an important first step for potentially disentangling human and climate driven ecological changes recorded in Lago Caranã.

The Dynamics of Fe Redox Transformations in Banded Iron Formation and Implications for Cave Formation

Melissa K Mulford[1,2*], Anela Mukherjee[2], John M
Senko[1,2,3], Hazel A Barton[1,2,3]

[1]Integrated Bioscience, University of Akron, Akron, OH, USA (*correspondance: mkm118@uakron.edu)
[2]Department of Biology, University of Akron, Akron, OH, USA
[3]Department of Geosciences, University of Akron, Akron, OH, USA

In the Carajás region of Brazil, banded iron formation (BIF) and its cap rock of canga, which is composed of BIF fragments in a goethite matrix, are highly resistant to erosion and are poorly soluble. Despite this, over 3,000 caves (referred to as iron formation caves; IFCs) have formed at their interface. Our previous research has shown that microbial communities from IFCs include bacterial species capable of Fe(III) reduction and the community is capable of extensive Fe(III) reduction. We hypothesize that microbial Fe(III) reduction transforms the insoluble Fe(III)-oxides into soluble Fe(II), which is then mobilized out of the system, allowing caves and voids to form. Our previous research has focused primarily on the reductive dissolution of canga rather than BIF. Here we tested the ability of cave-associated microorganisms to reduce Fe(III)-oxides in three different types of BIF. BIF-Fe(III) was less reducible than canga-Fe(III), but still extensively reduced, with average total Fe(II) concentrations of 5-10 mmol/L. To better understand the dynamics of Fe(II) oxidation in these systems, we added O_2 to incubations after maximum Fe(III) reduction. Upon O_2 addition, <10% of the total Fe(II) was oxidized, despite repeated addition of air to the headspace. We also evaluated the microbial communities in incubations after Fe(III) reduction and addition of O_2. Notable shifts towards *Clostridia* and *Bacilli* dominated batch incubations under Fe(III) reducing conditions. Aerated incubations had lower abundances of *Bacilli* and higher abundances of *Betaproteobacteria* and *Gammaproteobacteria* than the anoxic treatments. These community changes may have implications in the cave formation process and may indicate the effects of O_2 availability on the communities. Our results indicate BIF-Fe(III) is susceptible to reduction, but the biogenic Fe(II) is resistant to oxidation, which may be due to the formation of Fe(II)-Si complexes. The prevention of Fe(II) oxidation in these cave environments may allow Fe(II), which, unlike Fe(III), is soluble at circumneutral pH, to stay in solution and be washed away, allowing voids and eventually caves to form.

Biosignatures in Mars Analog Hypersaline Enviornments

FLOYD L. NICHOLS[1], MAGDALENA R. OSBURN[1], ANDREW L. MASTERSON[1], ALEXANDRA PONTEFRACT[2]

[1]Department of Earth and Planetary Sciences, Northwestern Univeristy, Evanston, IL, USA [Correspondence: floydnichols2025@u.northwestern.edu]

[2]Department of Biology, Georgetown University, Washington DC, USA

Evidence for modern and ancient hypersaline lakes and oceans have been identified across the solar system and thus study of terrestrial analogues can help inform potential characteristic geochemical and isotopic signatures of astrobiological targets. Here, we evaluate the organic biosignature production and preservation in four alkaline Mg and SO_4-dominated hypersaline lakes, a Na and HCO_3-dominated hypersaline lake, and a freshwater spring in the Fraser Plateau of British Columbia, Canada.

Due to the robust nature of lipids and their ability to persist on geologic time scales, we focus our analysis on fatty acids, determining which biosignatures are found in modern brines and which are incorporated into surface sediments. Additionally, we use organic carbon isotopes to provide information on source and productivity. In all targeted lakes, the predominant biosignatures found in the brines and sediment suggest microbial primary productivity. This is shown in the lipid composition which shows primarily short chain (saturated and unsaturated) fatty acids (carbon chain length < 23) generally associated with microorganisms. Additionally, the C/N ratios primarily fall below ten, which further indicates aquatic and microbial origin. The fatty acid composition of sediments is more diverse than that of brines and appears to integrate lipids derived from terrestrial plants. In addition, sites with higher sulfate concentrations sediments contained higher percentages of TOC, potentially suggesting preferential organic matter preservation within these systems. Our preliminary results imply that hypersaline Mg and SO_4-dominated environments trap and preserve biosignatures of both aquatic life and surrounding vegetation. Previous studies on acidic Mg-SO_4 dominated hypersaline systems have shown little microbial acitivty and preservation, thus, our study also impies that the alkaline nature of these hypersaline lakes serve as better astrobiological targets than their acidic counterparts.

New insights to the sulfur isotope record of the Paleoproterozoic Francevillian succession of Gabon

K. PAISTE[1, 2*], D. A. FIKE[1], K. KIRSIMÄE[2], R. S. WOOD[1], K. BAKAKAS MAYIKA[3], M. MOUSSAVOU[3], A. R. PRAVE[3], A. LEPLAND[2, 5]

[1] Washington University in St Louis, St Louis, 63130 Missouri, USA (*correspondence: kaert@wustl.edu)

[2] University of Tartu, 50411 Tartu, Estonia

[3] Universite des Sciences et Techniques de Masuku, 943 Franceville, Gabon

[4] St Andrews University, KY169AL St Andrews, Scotland

[5] Geological Survey of Norway, 7491 Trondheim, Norway

The early Paleoproterozoic encompasses the postulated ~2.3 – 2.0 Ga Lomagundi-Jatuli Event (LJE), a large-scale positive carbonate C-isotope ($\delta^{13}C_{carb}$) excursion believed to reflect transient oxygenation of otherwise poorly ventilated Paleoproterozoic oceans. The archetypal LJE-bearing Paleoproterozoic Francevillian succession of Gabon is typified by a sequence of LJE-bearing shallow-water carbonates, followed by black shales that preserve unusually positive pyrite sulfur ($\delta^{34}S >$ +20‰) isotopic compositions. The ^{34}S-enriched pyrites in the Francevillian FB – FC interval of the reference lithostratigraphic column have been explained by global deoxygenation that led to decreasing seawater sulfate concentrations [1]. However, the influence of sedimentary and diagenetic processes on the Francevillian S-isotope profile have not been thoroughly evaluated.

Here we reevaluate the meaning of the S isotope record in the upper part of the Francevillian succession by combining classical geological and novel geochemical approaches to investigate two LST12 (139 m) and Doumé (76 m) cores from the stratigraphic FB – FD interval. We demonstrate that the pyrite S isotope record is facies dependent, i.e., lower pyrite $\delta^{34}S$ (typically <5‰, down to -13‰) values associate with deep-water facies, while pyrite $\delta^{34}S$ (>5‰, up to 46‰) become higher in the shallow-water facies. Additionally, the presence of multiple pyrite textures, e.g., minute euhedral and large zoned pyrites, indicate that the ^{34}S enriched pyrites more likely reflect pore-water conditions rather than changes in the seawater sulfate pool. These results are inconsistent with the canonical view of early Paleoproterozoic environmental change and demonstrate that basin-specific conditions strongly influenced the Francevillian S-isotope record.

[1] Ossa-Ossa et al. (2018), EPSL 486, 70–83.

Microbial Sulfate Reduction in the Western Interior Seaway: Examinging the Link between Relative Sea Level Change and the Local S-isotope Record

Luca Podrecca[1], Matthew Hurtgen[1], Andrew Masterson[1], Jordan todes[2], and Bradley Sageman[1]

[1]Dept. of Earth & Planetary Sciences, Northwestern University, Evanston IL 60208
[2]Dept. of Geophysical Sciences, University of Chicago, Chicago IL 60637

The sulfur (S) isotope composition of marine rocks, archived within reservoirs of sedimentary pyrite and gypsum/anhydrite, plays a prominent role in reconstructing the oxygenation history of Earth's surface. This proxy is based on the premise that variability in the S-isotope ($\delta^{34}S$) record is broadly a function of marine sulfate concentrations [SO42-]. However, recent studies invigorate an older hypothesis: that the local $\delta^{34}S$ record might be heavily influenced by local environmental conditions (i.e., sedimentation rate).

In this study, we measure $\delta^{34}S_{py}$ at two sites from the mid-Cretaceous Western Interior Basin (WIB) of North America. The broad and shallow geometry of the WIB provides sedimentary records especially sensitive to changes in relative sea level (RSL) and is complemented by an extremely well-constrained geologic time scale. Together, these features prop up the WIB as an excellent study area for understanding the influence that evolving environmental forces might have on a sedimentary geochemical reservoir.

Our current δ^{34}Spy dataset indicates a strong positive relationship between the $\delta^{34}S$ record and sedimentation rate associated with RSL (> 30‰ change between RSL highs and lows at the most proximal site) at our near-paleoshore site. This suggests that high RSL, associated with a decrease in local sedimentation rates, allows microbial sulfate reduction and attendant S-isotope fractionation to progress unimpeded. Alternatively, as RSL drops, enhanced transport of sediments from the continent increases local sedimentation rates, interfering with the connection between pore waters and the overlying seawater sulfate reservoir, resulting in progressively heavier δ^{34}Spy values. This trend becomes muddied basinward, as changes in sedimentation rates between RSL highs and lows diminish. We now seek to test other local changes in depositional environment (total organic carbon (TOC) content, weight percent pyrite, and changes in reactive iron availability) to establish the modulation of the δ^{34}Spy record further from the influence of a migrating shoreline.

Reconstructing the History of Anoxia and Climate Change in Laguna Encantada in Chetumal, Q.R., Mexico

Giannina Ramirez*[1], Brooke Vander Pas[2], Alexander Correa Metrio[3], Kathy Licht[4], Alice Bosco Santos[5], Josef Werne[6], William P. Gilhooly III*[7]

[1]Dept. of Earth Sciences, IUPUI [*correspondence: gramire@iu.edu]
[2]Dept. of Earth Sciences, IUPUI [vanderpb@iu.edu]
[3] Depto. de Dinámica Terrestre Superficial, Universidad Nacional Autónoma de México [acorrea@geologia.unam.mx]
[4]Dept. of Earth Sciences, IUPUI [klicht@iupui]
[5]Dept. of Earth and Environmental Sciences, Ben-Gurion University of the Negev [alicebosco@gmail.com]
[6]Dept. of Geology and Environmental Science, University of Pittsburgh [jwerne@pitt.edu]
[7]Dept. of Earth Sciences, IUPUI [*correspondence: wgilhool@iupui.edu]

Lakes are sensitive to changes in temperature and oxygen. Dissolved oxygen is less soluble in warmer water, so anoxia (lack of oxygen) is expected to become more widespread as surface temperatures rise in response to increased anthropogenic carbon dioxide. Anoxia can damage aquatic ecosystems and decrease water quality. In a warming world where anoxia can become more common, reconstructions of climate and anoxic conditions from biogeochemical alterations of lake sediment can provide important information about how climate change can impact society in the coming century. Tropical lakes like Laguna Encantada tend to be less prone to mixing and are located in remote areas, making the pristine lakes ideal for studying anoxia. In addition, tropical lakes are drastically understudied compared to temperate zones or boreal lakes. Based on lithology, 3 distinct units were identified from the bottom to the top of the core. Laminations of carbonates and organic matter at the bottom of the core (Unit 1) transition (Unit 2) into massive bedding from rapid deposition (Unit 3). The C/S ratios indicate initial marine influence in Unit 1 that transitioned (Unit 2) into freshwater in Unit 3. Iron and aluminum concentrations are similar, suggesting iron is controlled by detrital input. Reactive iron extractions are ongoing; these data are expected to provide constraints on past oxygen conditions. Future isotope values could also correlate with Mayan settlement history in the Yucatan. This research can give insight into future conditions as climate change continues and implications on the consequences on freshwater systems and agriculture.

Role of Flavins in Extracellular Electron Uptake in *Shewanella oneidensis* MR-1

JOSHUA D. SACKETT[1], AND ANNETTE R. ROWE[1,*]

[1]Department of Biological Sciences, University of Cincinnati, Cincinnati, Ohio, USA 45221
*Correspondence: annette.rowe@uc.edu

Shewanella oneidensis MR-1 is a model organism used in electrochemical and bioremediation studies due to its diverse respiratory capabilities, including dissimilatory metal reduction. Although typically studied for its capacity to deposit electrons from respiration onto solid-phase minerals and electrodes under anaerobic conditions, MR-1 is also capable of obtaining electrons from electrodes when a suitable electron acceptor is present. Rowe et al. [1] demonstrated that MR-1 is capable of oxidizing a solid-phase, poised cathode as a source of electrons for aerobic respiration; however, evidence suggests that extracellular electron uptake (EEU) is not exclusively a reversal of the canonical Mtr respiration pathway [2]. Furthermore, the role of electron shuttles, such as flavins, in extracellular electron deposition is fiercely debated but has not yet been considered in the context of EEU. Xu and colleagues [3] have shown that endogenous flavins increase the rate of electron deposition, primarily when bound to outer membrane cytochromes. To evaluate the role of flavin mononucleotide (FMN) in EEU, we performed bioelectrochemical measurements on MR-1 biofilms in response to incremental FMN additions. Chronoamperometric measurements showed no increase in current production in response to FMN addition. Cyclic voltammograms showed an increase in the magnitude of the catalytic wave, an increase in onset potentials, and an increase in midpoint potentials following FMN addition. These observations suggest 1) FMN does not enhance EEU, and 2) the electron uptake feature of MR-1 has a different redox potential than that of FMN. Although additional studies are needed, these data suggest that EEU in MR-1 is not mediated by flavins. Further bioelectrochemical investigations, such as differential pulse voltammetry, a high-sensitivity method used to evaluate the redox potentials of electron uptake features, will aid in disentangling the role of flavins in EEU.

[1] Rowe et al. 2018. mBio 9:e02203-17. https://doi.org/10.1128/mBio.02203-17.
[2] Rowe et al. 2021. Comms Bio 4, 957. https://doi.org/10.1038/s42003-021-02454-x.

Investigation of hydroclimate shifts around 1000 CE in the high Peruvian Andes

JARUNETR (NADIA) SAE-LIM[1]*, BRONWEN KONECKY [1], JACK HUTCHINGS [1], ISLA CASTAÑEDA[2], MATHIAS VUILLE [3], NEAL MICHELUTTI[4], CHRISTOPHER GROOMS[4], AND JOHN SMOL[4]

[1]Washington University in St. Louis, Department of Earth and Planetary Sciences, St. Louis, MO, USA
[2]University of Massachusetts Amherst, Geosciences, Amherst, MA, USA
[3]University at Albany, State University of New York, Department of Atmospheric and Environmental Sciences, Albany, NY, USA
[4]Queen's University, Biology, Kingston, ON, Canada
* correspondence: jsae-lim@wustl.edu

Much of our understanding of hydroclimate in the Central Andes during the Last Millennium comes from the oxygen isotopic composition ($\delta^{18}O$) of speleothems, ice cores, and lake carbonates. These isotope records generally indicate an isotopic depletion during the Little Ice Age (LIA), which is mainly interpreted to reflect increased intensity of the South American Summer Monsoon (SASM). However, the timing and duration of these depletions are regionally variable, making it difficult to interpret remote vs. local hydroclimate and environmental conditions in the highlands during the LIA. Here we present a new 1,800-year plant wax δD record from long-chain *n*-alkanes along with a suite of geochemical data derived from lacustrine sediments of Lake Chacacocha (-13.96, -71.08; 4,860 m asl.), southeastern Peru. We observe a transition to more negative δD_{wax}, more enriched bulk $\delta^{13}C$, lower carbon-to-nitrogen ratio, and lower total carbon after ~1070 CE. Similar isotopic depletion occurs in several other isotopic records from the central Andes at this time, indicating possible regional increase in effective moisture and/or an intensification of the SASM prior to the timing of peak LIA conditions in the Andes. We use change point detection and other statistical techniques to assess the relative timing of these changes and investigate the mechanisms that may have driven water isotopic and climatic shifts in some, though not all, paleoclimate records from the Central Andes at the beginning of the Last Millennium. Our results will help to characterize the roles of climate forcings and variability on localized and regional hydroclimate and highland environments of the Peruvian Andes.

Insights from shipboard radiotracer experiments into the role of reactive oxygen speices on iodine speciation transformations at the Bermuda Atlantic Time Series

ALEXI SCHNUR[1], DALTON HARDISTY[1]

[1]293 Farm Ln, East Lansing, MI 48825 [schnural@msu.edu]
[1]293 Farm Ln, East Lansing, MI 48825 [hardist1@msu.edu]

The distribution of iodine in the surface ocean – an important proxy in the construction of Earth's redox evolution - can be attributed to both *in situ* (i.e., iodate (IO_3^-) reduction by bacteria and phytoplankton) and *ex situ* (i.e., vertical mixing) drivers of distribution. Concentration profiles of iodine with depth and over latitude are well known, however, the rates and mechanisms of iodide (I^-) oxidation and IO_3^- formation are yet still uncertain. This uncertainty hinders quantitative applications of carbonate iodine-to-calcium ratios – which track marine IO_3^- distribution – to marine redox conditions. It has been hypothesized that reactive oxygen species (ROS), such as superoxide (O_2^-) or hydrogen peroxide (H_2O_2), may be needed for I^- oxidation to occur at the sea surface, but this has yet to be demonstrated in natural marine waters. To test the role of ROS in iodine redox transformations, shipboard radiotracer incubations under ambient conditions were used as part of the Bermuda Atlantic Time Series (BATS) in the Sargasso Sea in September of 2018. Incubation trials evaluated the effects of biology (filtered/unfiltered), light (light/dark), $MnCl_2$, and the presence and absence of ROS (O_2^-, H_2O_2) on I^- oxidation over time and at euphotic and sub-photic depths. Rates of I^- oxidation were assessed using a $^{129}I^-$ radiotracer (half-life of 15.7 million years) added to all incubations, and $^{129}I/^{127}I$ ratios of individual iodine species (I^-, IO_3^-, and DOI) determined using Neptune high-resolution multi-collector ICP-MS (MC-ICP-MS). Our results show that I^- oxidation did not take place in the presence of ambient concentrations of O_2^- and H_2O_2, but that other redox transformations are induced instead. In addition, current results suggest limited change in iodine redox chemistry associated with *in situ* processes, therefore, *ex situ* processes, such as water mass mixing and diffusion processes, may play a larger role in broader iodine species' distribution in this and similar regions than previously thought.

Defining Earth's Groundwater Microbiome

Jocelyn Brito[1], Maria Berry[2], Matthew Schrenk[2*]

[1]Northeastern Illinois University; J-Brito@neiu.edu
[2]Department of Microbiology & Molecular Genetics,
Michigan State University; berrym35@msu.edu,
schrenkm@msu.edu

Microbiomes, or the aggregate of microorganisms in a specific environment, provide critical functions to varying ecosystems on the planet. As the planet changes rapidly due to both human intervention and natural activities, we face an array of environmental changes, including those which impact our water resources. Most of the groundwater used by human populations today is less than 75 years old, making it prone to disturbance and environmental change. The settings in the continental subsurface which contain this young groundwater are physically and chemically diverse, which consequently impact the composition and function of resident microbial communities. Describing the composite groundwater microbiome has not yet been accomplished in a systematic, comprehensive manner. This raises the question of how many different groundwater microbiomes exist, and the patterns in their diversity and function. Addressing these questions allows us to fill critical knowledge gaps and to incorporate these biogeochemical data into modelling efforts. This project identified existing groundwater microbiome data generated using next generation sequencing approaches in published literature and in publicly available databases. These databases were then queried for taxonomic and functional genetic markers that were characteristic of the different groundwater environments. One challenge that arose in our survey were that different methodological approaches used to collect and analyze groundwater microbial communities, such as different filter sizes, fluid volumes collected, and DNA extraction methods, confounded synthesis. A second challenge was that many groundwater environments had not yet been studied, and aspects of their ecology, such as the temporal dynamics of groundwater ecosystems have not yet been specifically addressed. Through this survey we have documented an emerging picture of multiple distinct groundwater microbiomes that exist in locations such as pristine aquifers, extreme environments, or in areas with anthropogenic influence. This information will be used as a basis to better understand patterns recorded in genetic markers retained within different groundwater microbiomes and use them to trace the influences of potential contamination and environmental change.

Lignin-enhanced reduction of structual Fe(III) in smectite: Dual roles of lignin as electron shuttle and donor

Yizhi Sheng, Hailiang Dong

Department of Geology & Environmental Earth science, Miami University, Oxford, USA, shengy5@miamioh.edu; dongh@miamioh.edu

Lignin is a major component of plant-derived soil organic matter (SOM) in soil and sedimentary environments. Fe-bearing clay minerals are widely distributed in these environments and often co-exist with lignin. While previous studies have reported the electron shuttling and donating roles of certain redox-active SOM in the dissimilatory reduction of structural Fe(III) in Fe-bearing clay minerals, the role of lignin in this process remains unknown. Here we studied this role by incubating an Fe-rich smectite (nontronite NAu-2) with two types of lignin (soluble and insoluble) in the absence and presence of an Fe(III)-reducing bacterium *Shewanella putrefaciens* CN32 under anaerobic condition. Lactate was added in some experiments as an extra electron donor. The results demonstrated that both soluble and insoluble lignins abiotically reduced structural Fe(III) in NAu-2. The reduction extent was proportional to lignin concentration. After abiotic reaction, lignin served as either electron shuttle or electron donor in the presence of CN32: (1) When lactate was present, lignin served as an electron shuttle to enhance the rate of Fe(III) reduction; (2) When lactate was absent, lignin served as an electron donor for Fe(III) reduction. Although the ultimate biotic Fe(III) reduction extents were similar in the presence of either soluble or insoluble lignin, the reduction rates with soluble lignin were higher than those with insoluble lignin, likely owing to their different electron transfer mechanisms. After interaction with NAu-2 and/or CN32, soluble lignin structure largely remained intact, but with some decreases of humic/fulvic acid-like and protein-like compounds, aromatic functional groups (e.g., C-H, C=O, COOH), and aliphatic/aromatic compounds. An increase of semiquinone-like organic radicals was observed after lignin interaction with NAu-2. These chemical changes of lignin were likely coupled with the reduction of structural Fe(III) in nontronite. Upon reduction, the nontronite did not display much dissolution and mineral transformation. The findings of this study provide insights into the role of lignin in promoting mineral-microbe interactions and have significant implications for coupled Fe and C biogeochemical cycles in soil and sedimentary environments.

MULTIPLE FE, MN, AND P MINERAL INTERACTION PATHWAYS AT THE SWI OF A SHALLOW EUTROPHIC LAKE REVEALED BY K-EDGE XANES AND MULTI-ENERGY MAPPING ACROSS EPOXY PRESERVED SEDIMENT PROFILES.

Shukle, John.[1], Richardson, Jocelyn. A.[2], Kurek, Martin. R.[1], Schroth, Andrew.[3], Webb, Samuel. M.[2], and Druschel, Gregory. K.[1]

[1]Dept. of Earth Science, IUPUI
[2]Stanford Synchrotron Radiation Lightsource
[3]Department of Geology, University of Vermont

Phosphorus (P) is often the limiting nutrient governing timing, duration, and severity of harmful algal blooms (HABs). Release of internally loaded P sorbed to iron (Fe) and manganese (Mn) oxyhydroxide minerals is generally the most active form in sediments, and the fate of these minerals responding to redox fluctuations, is intimately linked to the speciation, mobility, and bioavailability of P. We hypothesize frequent redox cycling selects for an increased pool of P bound to amorphous metal oxyhydroxides that are either reduced under water column anoxia by sediment microbes or form by Fe^{2+} oxidation and ripen and recrystallize under oxidizing conditions over time. Sediments from Missisquoi Bay, VT were used in long-term mesocosm experiments (70 days), simulating endmember, and cycled redox conditions at the sediment-water interface (SWI). Bulk chemistry and electrochemistry allowed detailed observations of dissolved species in the water column and pore water. At specific intervals, mesocosm sediment was sampled via miniature freeze core and epoxy embedding, to preserve fine scale preservation across the SWI. Multi-energy μ-X-ray Fluorescence (μ-XRF) mapping was combined with XANES spectroscopy and multivariate analysis to produce detailed maps of in situ chemical and mineral speciation and alteration. Results reveal significant mineralogical differences between endmember redox state sediments (oxic vs. anoxic) and oxic-anoxic cycled sediments. Fe and P K-edge XANES and μ-XRF mapping reveal crystalline Fe oxyhydroxides are concentrated just beneath the SWI under long-term oxidation but are mostly absent under long-term reduction and redox cycling. Under cycling conditions, Fe oxyhydroxides forming, or deposited, at the SWI appear to undergo rapid conversion to amorphous Fe(II)-phosphate before subsequent conversion to strengite-like Fe(III)-phosphate mineral phases. Authigenic vivianite nucleation and growth was observed beneath the SWI in long-term reducing and redox cycled sediments and was closely colocalized with metal-polyphosphates.

A multi-proxy analysis of Devonian lacustrine systems: insights into geochemical cycling and potential global implications

MATTHEW S. SMART[1], JOHN E.A. MARSHALL[2], WILLIAM P. GILHOOLY III[1] ,JESSICA H. WHITESIDE[2], GABRIEL M. FILIPPELLI[1]

[1] Dept. of Earth Sciences, Indiana University-Purdue University Indianapolis, USA smartm@iu.edu

[2] National Oceanography Centre Southampton, University of Southampton, UK

The evolution of land plant root systems occurred stepwise throughout the Devonian, a biological innovation that provided an enhanced pathway for the transfer of terrestrial phosphorus (P) to the marine system via weathering. This enhancement is consistent with paleosol records and has led to fascinating hypotheses about the causes of marine eutrophication and mass extinctions during the Devonian. To gain insights into the transport of P between terrestrial and marine domains, we report here terrestrial P flux, paleoclimate, paleoredox and weathering records from an on-going global study of Mid and Late Devonian lacustrine/near lacustrine sequences that span some of these key intervals. Four of the five sites are temporally proximal to one or more of the Devonian extinction events, including precise correlation with the Kačak extinction event and the two pulses associated with the Frasnian/Famennian mass extinction. Results show evidence of a net loss of P during root development coincident with the appearance of early trees and to Devonian biotic crises. Weathering, climate and redox proxy data for all sites reveal a similar response to external nutrient input and climate variability as seen in extant lacustrine systems. This unexpected similarity leaves questions concerning whether land plants had as great an impact on nutrient cycling within Devonian lacustrine and marine systems as hypothesized and indeed, if the impact of plant colonization may have occurred much earlier than the Mid to Late Devonian.

Strain Variation and Community Interactions Determine the Effects of Hydrogen Peroxide on *Microcystis*

DEREK J. SMITH[1], ROSE M. CORY[1], VINCENT J. DENEF[2], MELISSA B. DUHAIME[2], GEORGE W. KLING[2], KEVIN A. MEYER[1,3], MCKENZIE A. POWERS[1], TIMOTHY W. DAVIS[4], GREGORY J. DICK[1,3*]

[1]Univeristy of Michigan, Department of Earth & Environmental Sciences, Ann Arbor, MI, USA

[2]University of Michigan, Department of Ecology & Evolutionary Biology, Ann Arbor, MI, USA

[3]Univeristy of Michigan, Cooperative Institute for Great Lakes Research, Ann Arbor, MI, USA

[4]Bowling Green State University, Biological Sciences Department, Bowling Green, OH, USA

The cyanobacterium *Microcystis* forms harmful blooms in freshwaters worldwide that threaten human and animal health through the production of microcystins, a class of toxic peptides. Some *Microcystis* strains cannot make microcystins, and the proportion of toxic and nontoxic strains is an important determinant of toxin concentrations in blooms. The factors determining the porpotions of toxic to nontoxic *Microcystis* are not fully understood. Hydrogen peroxide (H_2O_2) was hypothesized to influence *Microcystis* strain proportions. However, the impact of H_2O_2 on toxic vs. nontoxic *Microcystis* is uncertain. Microcystins are thought to shield cells from H_2O_2-induced damage, but *Microcystis* may use catalase and peroxidase enzymes for H_2O_2 detoxification, and community-wide H_2O_2 decomposition may protect *Microcystis* spp.

Impacts of community-wide H_2O_2 decomposition were inferred from metagenomics and metatranscriptomics of *Microcystis* blooms in western Lake Erie. Catalase transcripts in *Microcystis* colonies were primarily from non-cyanobacteria, and a minority of the *Microcystis* population had catalases. Therefore, H_2O_2 degradation by other microbes likely protects *Microcystis*. Supporting that H_2O_2 decay is primarily from other organisms, large *Microcystis* colonies, which contained 60% of *Microcystis* 16S amplicons on average, did not impact H_2O_2 decay in Lake Erie water. Photochemistry was a major source of H_2O_2, and there was evidence for H_2O_2 production by cells and particles sized <100 μm. Cultivation of several *Microcystis* strains with an H_2O_2-scavenger suggested that some *Microcystis* benefit from community-wide H_2O_2 decompostion, but the growth of several toxic and nontoxic *Microcystis* strains was not impacted. The data support that community interactions via H_2O_2 production and decay impact *Microcystis* strains differently, but not along a toxic versus nontoxic dichotomy.

Bioremediation of 2,4-D by an iron-oxidizing Green Sulfur Bacterium“*Candidatus* Chlorobium masyuteum”

ZACKRY STEVENSON[1], ELIZABETH D. SWANNER[2]

[1]zackrys@iastate.edu
[2]eswanner@iastate.edu

Iron rich lakes can be hot spots for 2,4-Dichlorophenoxyacetic acid (2,4-D) degradation. 2,4-D is an herbicide that provides selective control for broadleaf weeds; however, the herbicide is highly soluble in water and threatens ecosystem diversity. Ferrugionous meromictic lakes are iron rich and home to anoxygenic phototrophic bacteria that oxidize iron. Abiotic degradation of 2,4-D is enhanced due to an Fe(II)-mineral bound species formed during iron reduction by iron-reducing organisms. An enrichment (BLA1) was taken from meromictic ferrugionous Brownie Lake, Minnesota containing dominant Fe(II)-oxidizing “*Candidatus* Chlorobium masyuteum” and Fe(III)-reducing anaerobe “*Candidatus* Pseudopelobacter ferreus. “*Ca*. C. masyuteum” photoautotrophically grows with Fe(II) utilizing a *cyc*2 gene that encodes for an Fe(II) oxidase. To investigate if Fe(II)-mineral bound species formed from iron oxidation can degrade 2,4-D, the BLA1 enrichment was cultured with various concentrations of 2,4-D +/- iron. 2,4-D degradation was not seen during iron oxidation by *Ca*. C. masyuteum; however, further research is needed to determine the effect different Fe(III) oxyhydroxides have on the formation of mineral bound Fe(II) species and the role *Ca*. P. ferreus can play in 2,4-D degradtion during iron reduction.

Paired Viral-Bacterial Omics and Biogeochemical Mesurements to Investigate Sulfur Cycling in the Water Column of a Seasonally Anoxic Freshwater Lake

PATRICIA Q. TRAN[1]*, SAMANTHA C. BACHAND[1], KATHERINE D. MCMAHON[1], KARTHIK ANANTHARAMAN[1]

(*correspondence: ptran5@wisc.edu)
[1] University of Wisconsin-Madison, 1550 Linden Drive, Madison, WI, USA. 53706

Microbes including bacteria, archea and viruses form complex communities that play critical roles in biogeochemical cycling in anoxic freshwater lakes. With ongoing global change, freshwater lakes in tropical and temperate environments are predicted to be become more stratified and anoxic. Lake Mendota (WI, USA) is a seasonally stratified, anoxic freshwater with low iron and high sulfate concentrations, which gradually becomes rich in hydrogen sulfide (of biotic origin) over the season. Hydrogen sulfide is primarily produced by microbial sulfate respiration and provides ecosystem services, while also being toxic to aquatic organisms. However, little is known about the environmental and biological factors that control this sulfur cycling in anoxic freshwater lakes, and no prior studies have combined it with weekly spatio-temporal change of sulfur biogeochemical cycling over time in a freshwater lake. Here, we collected weekly water column depth-profiles of environmental data including sulfide (H_2S) and sulfate (SO_4^{2-}), as well as 14 viromes, 16 microbial metagenomes, and 16 metatranscriptomes spanning the stratified and mixed portions of the year. We identify and resolve spatio-temporal patterns of microbial and viral diversity and activity, and the roles of microbes and viruses in sulfur metabolism. Overall, our study provides a holistic picture of the microbial, and viral roles in sulfur cycling in seasonally anoxic freshwater lakes.

Determining drivers of microbial metabolism in a high pH serpentinizing system-Ney Springs

Leah Trutschel*[1], Grayson Chadwick[2], Brittany Kruger[3], Jennifer G. Blank[4], Annette Rowe* [1]

[1]Department of Biological Sciences, University of Cincinnati, Cincinnati OH *Correspondence:[Trutsclr@mail.uc.edu], [Annette.Rowe@uc.edu]
[2]Department of Molecular and Cell Biology, University of California, Berkeley CA
[3]Desert Research Institute, Las Vegas, Las Vegas NV
[4]Blue Marble Space Institute of Science, Livermore CA

Ney Springs is a terrestrial serpentinizing spring in northern California with an exceptionally high pH (12.4) and conductivity (38 mS/cm). The spring is geochemically more similar to a marine serpentinizing system, but further geochemical analyses have revealed concentrations of methane (83% volume gas content), sulfide (544 mg/L), and dissolved organic carbon (22 mg/L) that are orders of magnitude above those reported in other characterized serpentinizing systems. Thermodynamic calculations support the potential for anaerobic microbial metabolisms including sulfate reduction, anaerobic methane oxidation, denitrification, and anaerobic sulfide oxidation. Assessment of the microbial community via 16S rRNA taxonomic gene surveys and metagenome sequencing revealed a community largely dominated by poorly characterizered anaerobic fermentative taxa (*Izemoplasmatales* and *Clostridiales*) as well as sulfur-oxidizing taxa frequently associated with alkaline soda lakes (*Desulfobulbales* and *Dethiobacterales*)[1] and the marine Lost City serpentinizing system (*Thiomicrospirales*)[2]. Little evidence is seen for anaerobic methane oxidation and sulfate reduction despite the large theoretical energy abundance for these metabolisms, which begs the question of what unknown physical limitations may prevent microorganisms from using these energy sources. To better understand the physiology and metabolic strategies needed to thrive in this extremely alkaline environment, several microorganisms have been isolated from the spring, including a *Halomonas sp*. and a *Rhodobacteraceae sp*.. These strains are capable of oxidizing thiosulfate to tetrathionate and eventually sulfate, making them the first sulfur-oxidizers to be isolated from a serpentinizing system.

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Characterizing the extraceullar proteome of *Methanosarcina barkeri* in electrotrophic methanogenesis

Linda Vu[1] and Annette Rowe[2]

[1]University of Cincinnati, vula@mail.uc.edu
[2]University of Cincinnati, rowea2@mail.uc.edu

Out of all known life, methanogens are the only organisms capable reducing CO_2 to methane, a natural gas with both significant environmental and financial consequences. Yet fundamental aspects of methanogen biochemistry are poorly understood. *Methanosarcina barkeri,* a genetically tractable model methanogen, can acquire electrons in a hydrogen independent manner from a cathode, through extracellular electron transfer (EET) machinery. However, the mechanisms of EET in *M. barkeri* remain uncharacterized, and a better understanding of the electron uptake in *M. barkeri* could improve the feasibility of engineering methanogen-based technology. Previously, we observed cathodic electron uptake in a *M. barkeri* hydrogenase deletion strain, demonstrating an H_2-independent mechanism for electron acquisition that likely involves direct contact between the cells and the electrode. We predict that surface-level redox proteins other than cytochromes are fundamental to uptake from the electron source during EET. At present, these proteins have been challenging to predict with traditional bioinformatics. Our goal is to identify candidate members of the external electron uptake pathway(s) using proteomic methods that characterize the extracellular proteome and/or identify differentially expressed proteins under EET conditions. This work will present electrochemical data of *M. barkeri* under those EET conditions in preparation for protein extraction and analysis.

S heterogeneities in barite, aragonite, & pyrite record geochemical evolution of cold seeps

R. SETH WOOD[1,*], AIVO LEPLAND[2], JOCELYN RICHARDSON[3], AND DAVID A. FIKE[1]

[1] Department of Earth & Planetary Sciences, Washington University, St. Louis, MO, USA (*correspondence: Woodr@wustl.edu)

[2] Geological Survey of Norway (NGU), Trondheim, Norway

[3] Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, USA

The anaerobic oxidation of methane by sulfate reduction (AOM-SR) produces steep geochemical gradients in active cold seep environments that foster the precipitation of pyrite (FeS_2), barite ($BaSO_4$), and methane-derived authigenic carbonates (MDAC). These minerals preferentially precipitate near the sulfate-methane transition zone (SMTZ) where AOM-SR activity is high and record the $\delta^{34}S$ composition of ambient sulfide (pyrite) and sulfate (barite & carbonate-associated sulfate (CAS) in MDAC). In these environments, SMTZ depth and porewater $\delta^{34}S_{sulfate/sulfide}$ compositions depend on the relative rates of sulfate diffusion and AOM-SR activity, which can also affect mineral saturation state(s). Here, we use a combination of micro X-ray Fluorescence (μ-XRF) mapping, X-ray absorption near edge structure (XANES) spectroscopy, scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) to evaluate the compositional and petrographic variability of MDAC, barite, and pyrite precipitated in active seep environments on the continental shelf of northern Norway. Within cm-scale samples, SIMS $\delta^{34}S_{Py}$ values can range more than 30‰ among framboids, and there appears to be a relationship between framboid diameter, $\delta^{34}S_{Py}$ values, and adjacent MDAC phase (aragonite vs. Mg-calcite). Multimodal distributions of $\delta^{34}S_{Py}$ values suggest pyrite precipitated under multiple discrete environmental regimes. The assessed barite are highly enriched in ^{34}S and the mean SIMS spot $\delta^{34}S_{BaSO4}$ value is 70.3‰, but $\delta^{34}S_{BaSO4}$ values can range more than 40‰ within individual barite aggregates (< 250 μm) and are most variable along growth axes. Similarly, XANES spectra & μ-XRF maps of aragonite reveal systematic fluctuations in CAS concentrations along growth axes and between successive layers, patterns which can be traced over large lateral distances (> 5 mm). We suggest these microscale changes in $\delta^{34}S_{Py,\,BaSO4}$ values and CAS concentrations record the geochemical evolution of microenvironments during mineral precipitation and were likely modulated by variable methane flux. These systematic microscale S heterogeneities can provide novel insight into paleo seep conditions.