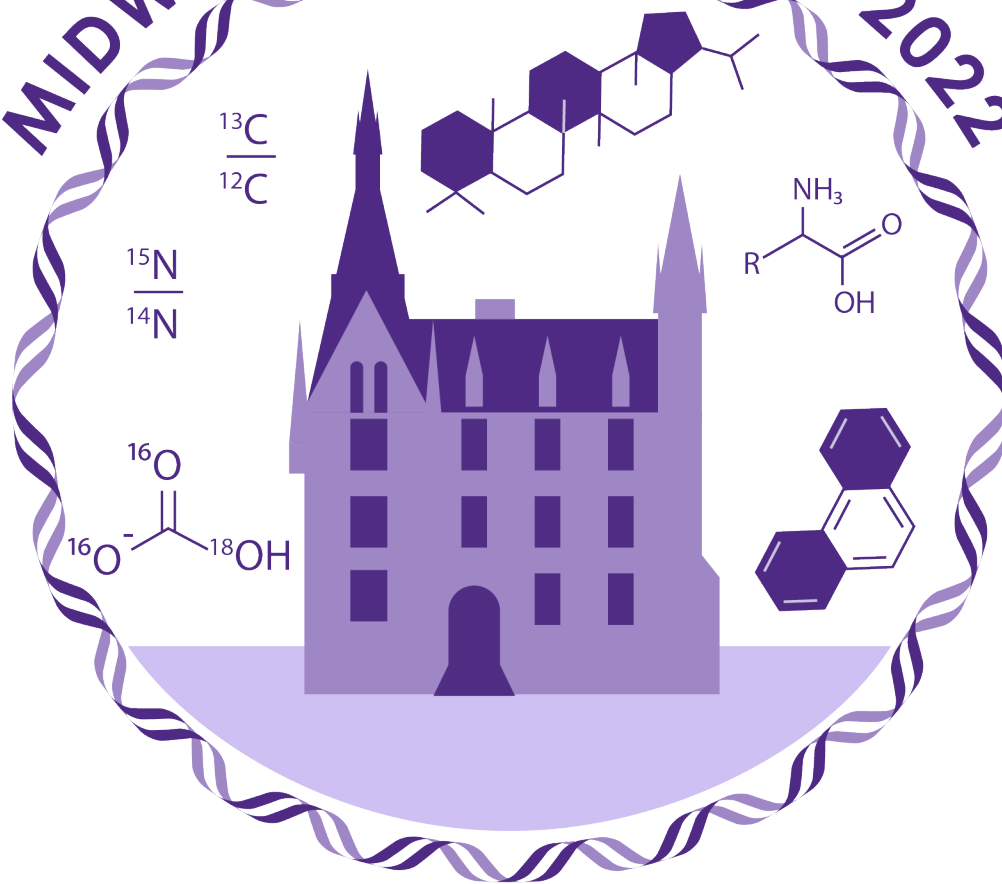


# MIDWEST GEOBIOLOGY 2022



NORTHWESTERN UNIVERSITY  
EVANSTON, IL

## Midwest Geobiology Symposium 2022 Program Booklet

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Northwestern University  
Evanston, IL  
October 1, 2022

**Northwestern**

WEINBERG COLLEGE OF ARTS & SCIENCES

Department of  
Earth and Planetary Sciences

AGOURON  
INSTITUTE





## **covid-19 precautions** at Midwest Geobiology 2022

Following Northwestern University's covid [masking policy on campus](https://www.northwestern.edu/coronavirus-covid-19-updates/university-status/guidelines/facemasks.html)<sup>1</sup>, masks are not required, but are recommended for attendees. We strongly suggest wearing masks during the Oral and Poster sessions. Weather permitting, outdoor spaces for lunch and planned breaks can be available for attendees to foster social distancing. Masks and hand sanitizer will be made available for attendees during the day of the Symposium.

<sup>1</sup> <https://www.northwestern.edu/coronavirus-covid-19-updates/university-status/guidelines/facemasks.html>

**Welcome to Northwestern University**, where we have the pleasure of hosting the **10<sup>th</sup> annual Midwest Geobiology Symposium!** This meeting draws talented researchers from around the Midwest to present their latest work on a diverse range of topics pertinent to geobiology. The event's focus is to provide emerging scholars – undergraduate students, graduate students, and post-doctoral researchers – with a space to share their science and build community with each other and leaders in the field of geobiology. This event began at Washington University in St. Louis in 2012 and has met every year other than 2020 due to the coronavirus pandemic. This year, over 100 people representing 27 institutions are attending the Symposium.

We sincerely thank the Augoron Institute and the Earth and Planetary Sciences Department at Northwestern University for their generous support to facilitate this meeting.

Sincerely,

The Midwest Geobiology 2022 Organizing Committee

Matthew Selensky, Floyd Nichols, Jackson Watkins, Mia Tuccillo, and  
Magdalena Osburn

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# Schedule of Events

## **Friday, September 30, 2022**

6:00pm-9:00pm                      Welcome reception at The Peckish Pig  
623 W Howard St, Evanston, IL 60202

## **Saturday, October 1, 2022**

8:00am-9:00am	Breakfast	EPS atrium
9:00am-9:10am	Opening Remarks	LR3
9:10am-10:00am	Oral Session I	LR3
10:00am-10:30am	Coffee Break	EPS atrium
10:30am-11:20am	Oral Session II	LR3
11:20am-12:45pm	Poster Session I	EPS atrium
12:45pm-1:45pm	Lunch	EPS atrium
1:45pm-2:30pm	Oral Session III	LR3
2:30pm-3:00pm	Coffee Break	EPS atrium
3:00pm-3:50pm	Oral Session IV	LR3
3:50pm-6:00pm	Poster Session II	EPS atrium

## Oral Presenters

### **Oral Session I** - 9:10am-10:00am

9:10am - **Judy Malas**, University of Illinois Chicago  
Microbial Gene Expression at Titan-like High Pressures

9:27am - **M Joseph Pasterski**, University of Illinois Chicago  
Multimodal Analysis of Indigenous Organic Molecular Biosignatures in a Geologic Sample: ToF-SIMS, GC-MS, SEM-EDS and Machine Learning

9:45am - **Amanda Patsis**, University of Minnesota-Twin Cities  
Metagenomic Analyses Support the Importance of Organosulfur Degradation in the Deep Biosphere

### **Oral Session II** – 10:30am-11:20am

10:30am - **Nicole Fiore**, University of Nebraska-Lincoln  
Calcium carbonate as a sole inorganic carbon source for methanogenesis at alkaline pH

10:47am - **Maria D Hernandez Limon**, University of Chicago  
Towards Understanding the Microbial Response to Changing Winters in the Laurentian Great Lakes

11:05am - **Taylor Price**, University of Minnesota-Twin Cities  
Microbial diversity differs across alpine streams in a glaciated mountain range of Northwestern WY, United States

### **Oral Session III** – 1:45pm-2:30pm

01:45pm - **Leah Trutschel**, University of Cincinnati  
Chemolithotrophy at pH 12: A look at a serpentinizing system microbial community and its use of sulfur

02:00pm - **Keyi Cheng**, Michigan State University

Iodine Speciation in the Redox-stratified Baltic Sea and Implications for I/Ca paleoredox interpretations

02:15pm - **R. Seth Wood**, Washington University in St. Louis

Modeling the Geochemical Behavior of Methane Seeps & Inferring Paleo-seep Conditions from Microscale Textural and  $\delta^{34}\text{S}$  Heterogeneities in Seep Barite

### **Oral Session IV** – 3:00pm-3:50pm

03:00pm - **Sajjad Akam**, Iowa State University

A case for methane-derived authigenic carbonates as a globally relevant marine carbonate factory

03:17pm - **Lauren Bryan**, Hope College

Selective Preservation of Structural Carbohydrates During Peat Formation

03:35pm - **Jack Hutchings**, Washington University in St. Louis

Optimization of the Picarro L2140-i Cavity Ring Down Spectrometer for Routine Measurement of Triple Oxygen Isotope Ratios in Meteoric Waters



# Poster Presenters

## **Poster Session I** – 11:20am-12:45pm

**Roger Bryant**, University of Chicago

A Local Origin for Carbonate Carbon and Sulfur Isotopic Trends after the GOE

**Janet Burke**, Michigan State University

Eastern Tropical Pacific Oxygen Deficient Zones During the Miocene Climatic Optimum

**Ashika Capirala**, Purdue University

Earth's Geophysical Evolution and the Role of the Marine Biosphere in Surface Oxygenation

**Kelsey Doiron**, Indiana University-Bloomington

Preliminary Assessment of Organic Geochemistry in Sediments from the Transkei Basin (IODP Site U1581)

**Alexandra Grajales**, Iowa State University

Changes in atmospheric composition during the Phanerozoic recorded in fossilized plants

**Christopher Greidanus**, University of Chicago

Protein diagenesis during experimental silicification of cyanobacteria

**Presley Hernandez**, Hunter College

Distributions of Leaf Wax n-Alkanes in Modern Palm (*Areaceae*) Species

**Michaela Hostetler**, The Ohio State University

Proxies of Ancient Life through Magnetotactic Bacteria

**Jonathan Jernigan**, Purdue University

Marine Habitability and Productivity on High-Obliquity and High-Eccentricity Planets

**Benjamin Johnson**, Iowa State University

Where did life survive during the Cryogenian Snowball Earth? Comparison of cryoconites and sedimentary geochemistry ocean redox and refugia

**William Kane** and **Cimmy Nakum**, University of Illinois Chicago

When There's 'Surface' in Your 'Subsurface' Biosphere: Cellulose Degrading Bacteria from 'Extreme' Environments

**Kaitlin Koshurba**, University of Michigan

Braunite synthesis after simulated low temperature diagenesis of Mn-oxides with reduced manganese

**Alessandro Mauceri**, Washington University in St. Louis

Hydroclimate and Vegetation Changes in Eastern Amazonia since the Mid-Holocene Recorded by Biomarkers in Lacustrine Sediments

**Emily Millman**, Washington University in St. Louis

Selective Adsorption of Amino Acids on Montmorillonite

**Dana Mineart**, Iowa State University

Constraining Continental Emergence: Proterozoic Ocean Crust as a Record Of Seawater Isotopes

**Lily Momper** and **Morgan Petrovich**, Exponent, Inc.

Scientific Careers at Exponent

**Alexi Schnur**, Michigan State University

Mass balance constraints on euphotic iodine speciation from GEOTRACES meridional and zonal Pacific transects

**Matthew Selensky**, Northwestern University

Microbial Biogeography of the Eastern Yucatán Carbonate Aquifer

**Madison Smith**, Hope College

Temperature sensitivity of nitrogen mineralization in peat from a southwestern Michigan Bog

**Lynn Thomas**, Indiana University Purdue University Indianapolis  
Optical Characteristics of Chrysotile, an Unhealthy Contaminant in Talcum Powder

**Zoe Vincent**, Northwestern University  
Microbes to Meta: Mapping Food Chain Dynamics of Mammoth Cave using Stable Isotopes

**Amy Vodopyanov**, Michigan State University  
Investigation of Denitrification Processes in Shallow Groundwater near Grand Traverse Bay, Michigan

**Jacob Waldbauer**, University of Chicago  
Nitrogen tracking reveals active protein biosynthesis in the surface ocean

**Jin-Sang Yu**, University of Cincinnati  
Quantifying the physiological changes in NADH in *S. oneidensis* in response to extracellular electron uptake

## **Poster Session II** – 3:50pm-6:00pm

**Thais Altenberg-Vaz**, University of Wisconsin-Madison  
Organic Carbon Metabolism and Dissolved Oxygen Dynamics in Sandy Riverbed Sediments

**Evan Collins**, University of Pittsburgh  
Hydrothermal Inputs Drive Dynamic Shifts in Microbial Communities in Lakes Magadi and Nasikie Engida, Kenya

**Sam Duncanson**, Iowa State University  
Evaluating terrestrial nitrogen cycling from modern tills

**Abby Hsaio**, Northwestern University  
Ammonia After Dark: Constraining Microbial Aerobic Ammonia Oxidation in Mammoth Cave Sediments

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

Evaluating the impact of changing sedimentary environments on individual pyrite  $\delta^{34}\text{S}$

**Mingxi Hu**, Washington University in St. Louis

Lateral and secular variability in  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  from the Late Ordovician GICE interval

**Tara Kalia**, University of Chicago

Sulfur-based signatures of chemosymbiosis in modern *Lucinidae*

**Sarah Khoury**, University of Illinois Chicago

Microplastic - Soil Separation Methods

**Tamara McConnell** and **Mia Riddley**, Iowa State University

Biological and Geochemical Controls on Iron Deposition in an Intermittent Stream

**Natalie Nichols**, Indiana University Purdue University Indianapolis

Redox Induced Cycling of Fe and P Near the Sediment Water Interface

**Zoey Papka**, University of Chicago

Wide-spread salinity tolerance across diverse *Synechococcus* strains

**Kathryn Rico**, Arizona State University

Resolving the fate of trace metals during microbial remineralization of phytoplankton biomass in precursor banded iron formation sediments

**Imelda Romero**, Michigan State University

Iodine Cycling in Hydrothermal Fluids and Plumes from the East Pacific Rise, 9° N

**Nilou Sarvian**, Northwestern University

Constraining the Shuram  $\delta^{13}\text{C}$  Excursion with the  $\delta^{44}/^{40}\text{Ca}$  –  $\delta^{88}/^{86}\text{Sr}$  multi-proxy

**Hailey Sauer**, University of Minnesota-Twin Cities

Impacts of Terrestrial Organic Matter on Methanogenic Archaea in Pelagic and Littoral Sediments

**Zackry Stevenson**, Iowa State University

Insights of 2,4-D degradation by Fe(II)-oxidizing bacteria and Fe(III)-reducing bacteria

**Mia Thompson**, Northwestern University

Microbes from Mars Analog Hypersaline Lakes

**Evangeline Unger-Harquail**, Colgate University

Evaluation of the diatom species *Fragilariopsis kerguelensis* as a Paleotemperature Proxy on the Sabrina Coast

**Brooke Vander Pas**, Indiana University Purdue University Indianapolis

Landscape evolution during the Middle Devonian: Evidence from an Old Red Sandstone lacustrine sequence

**Alice Zhou**, University of Michigan

Silica inhibits biological iron oxidation and mineral evolution in an Archean ocean analog

## Attendees

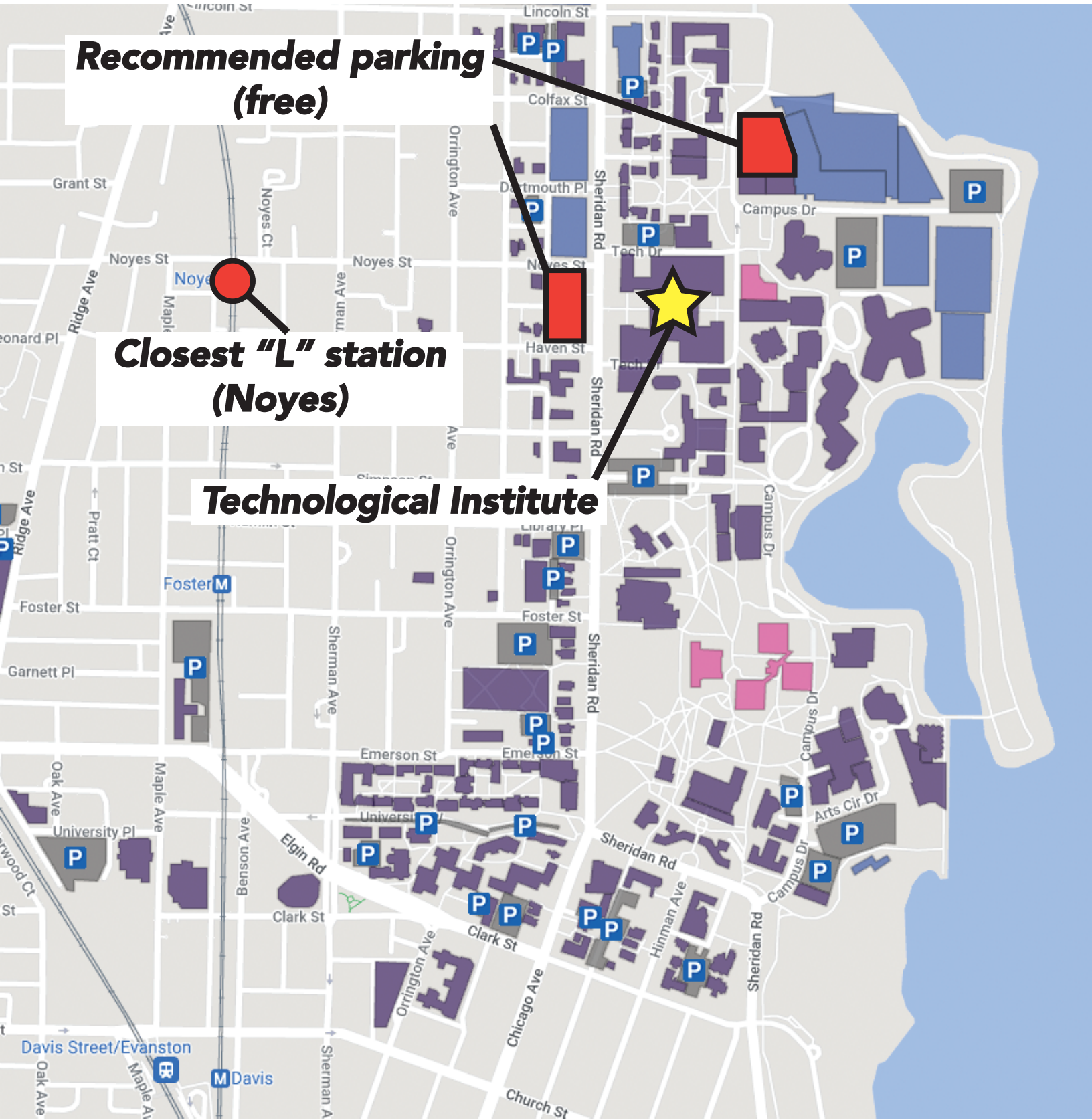
Sajjad	Akan	Iowa State University
Thais	Altenberg-Vaz	University of Wisconsin-Madison
Anna	Bennett	NREL (formerly University of Minnesota-Twin Cities)
Simon	Brassell	Indiana University-Bloomington
Lauren	Bryan	Hope College
Roger	Bryant	University of Chicago
Janet	Burke	Michigan State University
Ashika	Capirala	Purdue University
Anthony	Chappaz	Central Michigan University
Keyi	Cheng	Michigan State University
Maureen	Coleman	University of Chicago
Evan	Collins	University of Pittsburgh
Laura	Congote	Indiana State University
Chris	Crosby	Oakton Community College
Kelsey	Doiron	Indiana University-Bloomington
Sam	Duncanson	Iowa State University
Gregory	Druschel	Indiana University Purdue University Indianapolis
Kirsten	Fentzke	Michigan State University
David	Fike	Washington University in St. Louis
Nicole	Fiore	University of Nebraska-Lincoln
Jean-François	Gaillard	Northwestern University
Bill	Gilhooly	Indiana University-Purdue University Indianapolis
Alexandra	Grajales	Iowa State University
Christopher	Greidanus	University of Chicago
Trinity	Hamilton	University of Minnesota-Twin Cities
Presley	Hernandez	Hunter College
Maria	Hernandez Limon	University of Chicago
Maggie	Hinkston	Washington University in St. Louis
Michaela	Hostetler	The Ohio State University
Jennifer	Houghton	Washington University in St. Louis
Cecilia	Howard	University of Michigan
Allison	Howes	Queen's University
Abby	Hsiao	Northwestern University
Mingxi	Hu	Washington University in St. Louis
Jack	Hutchings	Washington University in St. Louis
Moses	Jatta	Indiana University-Purdue University Indianapolis

Jonathan	Jernigan	Purdue University
Benjamin	Johnson	Iowa State University
Tara	Kalia	University of Chicago
William	Kane	University of Illinois Chicago
Preston	Kemeny	University of Chicago
Sarah	Khoury	University of Illinois Chicago
Ben	Klein	University of Michigan
Kaitlin	Koshurba	University of Michigan
Lauren	Bergeron	University of Chicago
Wil	Leavitt	Dartmouth College
Judy	Malas	University of Illinois Chicago
Andrew	Masterson	Northwestern University
Alessandro	Mauceri	Washington University in St. Louis
D'Arcy	Meyer-Dombard	University of Illinois Chicago
Tamara	McConnell	Iowa State University
Chiza	Mwinde	University of Chicago
Mia	Riddley	Iowa State University
Michael	Philben	Hope College
Emily	Millman	Washington University in St. Louis
Dana	Mineart	Iowa State University
Lily	Momper	Exponent, Inc.
Cimmy	Nakum	University of Illinois Chicago
Bailey	Nash	Northwestern University
Nhi	Nguyen	University of Illinois Chicago
Natalie	Nichols	Indiana University-Purdue University Indianapolis
Floyd	Nichols	Northwestern University
Maggie	Osburn	Northwestern University
Zoey	Papka	University of Chicago
M. Joseph	Pasterski	University of Illinois Chicago
Amanda	Pastis	University of Minnesota-Twin Cities
Morgan	Petrovich	Exponent, Inc.
Kathryn	Preibisch	Iowa State University
Marcelo	Prianti	Central Michigan University
Taylor	Price	University of Minnesota-Twin Cities
Trinity	Pryor	University of Michigan
Kathryn	Rico	Arizona State University
Imelda	Romero	Michigan State University
Leanne	Rossi	University of Michigan
Taylor	Rosso	University of Nebraska-Lincoln

Nilou	Sarvian	Northwestern University
Hailey	Sauer	University of Minnesota-Twin Cities
Alexi	Schnur	Michigan State University
Matthew	Selensky	Northwestern University
Meera	Shah	Northwestern University
Madison	Smith	Hope College
Rebecca	Sponenburg	Northwestern University
Bradley	Stevenson	Northwestern University
Zackry	Stevenson	Iowa State University
Melanie	Suess	Washington University in St. Louis
Elizabeth	Swanner	Iowa State University
Wesley	Swingley	Northern Illinois University
Benjamin	Teerlinck	University of Minnesota-Twin Cities
Lynn	Thomas	Indiana University-Purdue University Indianapolis
Mia	Thompson	Northwestern University
Jordan	Todes	University of Chicago
Leah	Trutschel	University of Cincinnati
Mia	Tuccillo	Northwestern University
Evangeline	Unger-Harquail	Colgate University
Brooke	Vander Pas	Indiana University-Purdue University Indianapolis
Diana	Velazquez	University of Michigan
Zoe	Vincent	Northwestern University
Amy	Vodopyanov	Michigan State University
Jacob	Waldbauer	University of Chicago
Anna	Waldeck	Northwestern University
Zi'Onay	Walker	University of Chicago
Chuyan	Wan	Northwestern University
Jackson	Watkins	Northwestern University
R. Seth	Wood	Washington University in St. Louis
Sara	Yen	Northwestern University
Jin-Sang	Yu	University of Cincinnati
Alice	Zhou	University of Michigan



# Northwestern University Campus map



## **Abstracts**

Alphabetized by first author

## **A Case for methane-derived authigenic carbonates as a globally relevant marine carbonate factory**

SAJJAD A AKAM<sup>1\*</sup>, ELIZABETH D SWANNER<sup>1</sup>, WEI-LI HONG<sup>2</sup>, JÖRN PECKMANN<sup>3</sup>

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<sup>2</sup> Department of Geological Sciences, Stockholm  
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<sup>3</sup> Institute for Geology, Center for Earth System Research  
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Hamburg, Germany

Marine sediments impacted by methane transport from deep sediments towards seafloor are often characterized by the presence of methane-derived authigenic carbonates (MDAC). Microbially driven anaerobic oxidation of methane in shallow sediments and methanogenesis coupled with marine silicate weathering in deeper sediments generate alkalinity resulting in carbonate authigenesis. MDAC formation is integral to methane-driven carbon cycling in marine sediments, but their relative significance to the global marine carbon cycle is not well understood.

Here we provide a synthesis and perspective to highlight MDAC from a global marine carbon biogeochemistry viewpoint. MDAC precipitation is a result and archive of carbon-sulfur (C-S) coupling in the shallow sulfatic zone and carbon-silica (C-Si) coupling in deeper methanogenic sediments. Quantification of the global MDAC reservoir from a bottom-up carbon flux model suggests a carbon burial of 2 Tmol C yr<sup>-1</sup> (range 1 — 4 Tmol C yr<sup>-1</sup>) in the modern ocean and is the third-largest carbon burial mechanism in marine sediments. This carbon pool is comparable to 14% (9–17%) of the organic carbon, 10% (6–12%) of the carbonate carbon burial in the continental margins at present, and a higher fraction during the past oceanic anoxic events. MDAC formation is also an important sink for benthic alkalinity in methane-laden sediments and, thereby, a potential contributor to bottom water acidification. Our understanding of the impact of MDAC on global biogeochemical cycles has evolved over the past five decades from what was traditionally considered a passive carbon sequestration mechanism in a seep-oasis setting to what is now considered a dynamic carbonate factory, operational since Precambrian, influencing deep sediments to the bottom water column.

## **Organic Carbon Metabolism and Dissolved Oxygen Dynamics in Sandy Riverbed Sediments**

ALTENBERG-VAZ, THAIS<sup>1</sup>; PASSI-SIMHAN, MANASI<sup>2</sup>;  
CARTWRIGHT, MARISSA<sup>3</sup>; GINDER-VOGEL, MATT<sup>4</sup>;  
RODEN, ERIC<sup>5</sup>

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1215 W. Dayton St. Madison, WI 53706

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<sup>5</sup>[[eroden@geology.wisc.edu](mailto:eroden@geology.wisc.edu)]

Understanding how particulate organic matter (POM) infiltrates and degrades in porous stream and riverbed sediments is important for quantifying and predicting biogeochemical processes in the hyporheic zone. This study aimed to quantify POM degradation and transport processes in the uppermost layer of sandy sediments of the Wisconsin River near Spring Green, WI. Concentrations of POM (ca. 0.3-0.4% dry weight) decreased with depth in sediment cores, indicating a source of POM input at the sediment surface. Laboratory incubation experiments showed that rates of organic carbon metabolism in surface sediment (0-2 cm) were ca. 2 fold higher than bulk sediment from the upper 20 cm of the riverbed. Column experiments were conducted with bulk riverbed sediment to examine the relationship between advective fluid flow, dissolved oxygen (DO) concentration, and dissolved organic and inorganic carbon (DOC and DIC) dynamics. Dissolved oxygen sensors (optodes, Pyroscience) were placed along a 15 cm column filled with riverbed sediment, and artificial river water (ARW) was pumped through the column at different flow rates. By stepping down the flow rate from 2, 1, 0.5, 0.25, to 0.125 mL/min, stopping flow, and stepping back up to 2 mL/min, we were able to demonstrate a dynamic equilibrium between DO consumption and replenishment from the ARW that was dependent on flow rate and distance from the column inlet. Outlet concentrations of DOC and DIC were measured at each flow rate. Concentrations of DOC, an intermediate in POM metabolism, remained constant with changing flow rate, except when anoxic conditions arose after cessation of flow when they increased 2-4 fold. In contrast, DIC, an end-product of POM metabolism, showed an increasing trend with decreasing flow rate, reflecting a shift in the balance between release and advective transport through the column. The results of this study will be useful for the development of transport-reaction models of organic matter metabolism in near-surface permeable stream and riverbed sediments.

## Selective Preservation of Structural Carbohydrates During Peat Formation

LAUREN BRYAN<sup>1</sup>, MICHAEL PHILBEN<sup>1</sup>

<sup>1</sup>Departments of Chemistry, Geological and Environmental Sciences, Hope College, Holland, MI, 49423

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Previous studies show the structural carbohydrate “sphagnum” plays a role in slowing the degradation of *Sphagnum* moss, resulting in carbon sequestration in peatlands. Sphagnum is composed of a galacturonic acid and rhamnose backbone. It is currently unclear whether sphagnum persists beyond early-litter degradation and plays into long-term preservation of peatland organic matter. This study analyzed hydrolyzable neutral sugars, using rhamnose as a proxy for sphagnum content, and tracked concentration of rhamnose within moss before and after decomposition, and at different depth intervals within peat cores from southwest Michigan. An increase in relative abundance of rhamnose over moss decomposition was indicated, but little change occurred in rhamnose concentrations in peat cores compared to depth, implying that the degradation of sphagnum occurs at roughly the same rate of other sugars over long periods of time. However, an increase in glucose concentration occurred with depth, alongside decreasing xylose and arabinose abundances, indicating cellulose may be selectively preserved. Our results indicate that sphagnum plays a greater role in the short-term preservation of *Sphagnum* mosses and sequestration of carbon, but this effect is not as prominent over long-term peat accumulation.

## A Local Origin for Carbonate Carbon and Sulfur Isotopic Trends after the GOE

ROGER BRYANT<sup>1\*</sup>, JOCELYN RICHARDSON<sup>2</sup>, TONY PRAVE<sup>3</sup>, AIVO LEPLAND<sup>4</sup>, TARA KALIA<sup>1</sup>, JORDAN TODES<sup>1</sup>, CLARA BLÄTTLER<sup>1</sup>

<sup>1</sup>Department of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave, Chicago, IL 60637, USA; \*correspondence: rnbryant@uchicago.edu

<sup>2</sup>SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, CA 94025, USA; jocelynr@slac.stanford.edu

<sup>3</sup>School of Earth & Enviro Sciences, Irvine Building, University of St Andrews, St Andrews, KY16 9AJ, UK; ap13@st-andrews.ac.uk

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During and following the Great Oxidation Event (GOE), the concentration of marine sulfate is thought to have fluctuated widely, reaching ~10 mM around 2.0 Ga before undergoing a hypothesized decline. Here, we present carbonate  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$  and  $\delta^{44/40}\text{Ca}$  data integrated with facies analyses for rocks from the Onega Basin in Russia to assess the effects of depositional environment and early marine diagenesis on those geochemical indices. The two key units are the ca. 2.3-2.0 Ga Lomagundi-Jatuli-bearing carbonate rocks of the Tulomozero Formation and the gradationally overlying organic-carbon-rich shales of the Zaonega Formation. Over their transitional interval,  $\delta^{34}\text{S}$  values increase whereas  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{44/40}\text{Ca}$  values become more negative. Synchrotron methods show that the dominant form of sulfur also changed concomitantly, shifting from more mineralized sulfate and CAS to variable mixtures of sulfide, organic sulfur, and dolomite CAS. Those changes map directly onto the facies change from shallow-marine evaporitic/nearshore settings to deeper-marine (below storm wave base) slope settings. The  $\delta^{44/40}\text{Ca}$  data indicate that the geochemical and isotopic compositional changes correspond to changes in the local diagenetic environment as shown by a shift from more seawater-buffered (open system) to more sediment-buffered (closed system) carbonate precipitation. Therefore, despite  $\delta^{34}\text{S}$  trends that closely match previously reported data, we find no evidence for an increase in the  $\delta^{34}\text{S}$  value of marine sulfate and a decrease in sulfate concentration at ca. 2.0 Ga. More work deconvolving the effects of diagenesis on carbonate  $\delta^{34}\text{S}$  is required to accurately reconstruct the Paleoproterozoic sulfur cycle.

# Eastern Tropical Pacific Oxygen Deficient Zones During the Miocene Climatic Optimum

JANET BURKE\*, KEYI CHENG, DALTON HARDISTY

Michigan State University, Department of Earth and Environmental Sciences, 288 Farm Lane, East Lansing, Michigan

\*correspondence: burkej25@msu.edu

Changes to the spatial extent and intensity of marine oxygen deficient zones (ODZs) are expected to accompany future changes to the global climate. Studying the dynamics of potential oxygen deficient zones over past intervals of increased atmospheric carbon dioxide can provide important context and constraints for anticipating future patterns. The foraminiferal iodine-to-calcium (I/Ca) proxy is a geochemical tool for tracking ODZs in ancient oceans. I/Ca works because the oxidized iodine species, iodate, is exclusively incorporated into foraminiferal calcite, and it facilitates reconstruction of both benthic and pelagic redox states from the fossil tests of foraminifera. Here, we present work applying the I/Ca proxy to study paleo-ODZ dynamics in the Eastern Tropical Pacific (IODP 321-1338 and 1337, ODP 202-1237) over a geologically recent greenhouse climate interval, the Miocene Climatic Optimum (MCO, ~14.5-17ma). The MCO is characterized by a global average temperature increase of up to 3°C, elevated atmospheric CO<sub>2</sub> levels, expansions in organic carbon burial, and evidence for intensification of regional ODZs. Our results show a range of I/Ca values which encompass the levels indicative of hypoxic conditions at the two localities, with varying patterns throughout the interval. Specifically, the samples from 321-1337 and 321-1338, located near the equator, show consistent evidence for depleted oxygen, while site 202-1237 shows more variation, generally above the I/Ca threshold indicative of ambient hypoxia. In order to better explore these regional results from a global perspective, we will analyze them alongside cGENIE model reconstructions of marine iodate and oxygen distributions for the region during the mid-Miocene.

# Earth's Geophysical Evolution and the Role of the Marine Biosphere in Surface Oxygenation

ASHIKA CAPIRALA\*<sup>1</sup>, STEPHANIE OLSON<sup>1</sup>, CAMILLA LIU<sup>2</sup>

<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Purdue University  
(\*correspondence: acapiral@purdue.edu)

<sup>2</sup>Department of the Geophysical Sciences, University of Chicago

Oxygen is crucial for complex life on Earth, but our understanding of the mechanism of Earth's oxygenation remains incomplete. In particular, the reasons for the 500 Myr lag between the evolution of oxygenic photosynthesis and the first major rise of atmospheric O<sub>2</sub> during the Great Oxygenation Event—and the nature of marine biogeochemical feedbacks during this time—remain uncertain [1].

Parallel to changes in biogeochemical cycling and chemistry of the ocean-atmosphere system during the Precambrian, Earth also experienced changes in its orbit and continental configuration, possibly influencing biotic mechanisms of O<sub>2</sub> accumulation. A slowing of Earth's rotation rate through time may have significantly altered ocean circulation patterns and thus nutrient availability to the marine biosphere [2]. Accompanying changes in diurnal illumination may have also affected rates of O<sub>2</sub> production in benthic microbial mats, likely an important source of photosynthetic O<sub>2</sub> on early Earth [3, 4]. However, the interplay between geophysical changes, global biogeochemistry, and marine productivity is unresolved on global scales.

We use a sophisticated Earth system model (cGENIE) to explore the impact of changing rotation rate and continental distribution on marine productivity and resolve the overall contribution to marine oxygenation. Our results show that increasing daylength enhances marine O<sub>2</sub> production, and this effect is additionally controlled by the spatial pattern of upwelling and illuminated seafloor defined by continents. We will discuss how these effects may have factored into the timeline of Earth's oxygenation, as well as possible constraints on habitability for complex life posed by rotation rate and continentality through time.

[1] Lyons, T. W. et al. (2014) *Nature*, 506(7488): 307–15.

[2] Olson, S. L. et al. (2020), *ApJ*, 895(1): 19.

[3] Klatt, J. M. et al. (2021) *Nat. Geosci.*, 14(8): 564–70.

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# Iodine Speciation in the Redox-stratified Baltic Sea and Implications for I/Ca paleoredox interpretations

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Iodine is a redox-sensitive element in the ocean. In the modern ocean, the distribution of the major species of iodine, iodate (IO<sub>3</sub><sup>-</sup>) and iodide (I<sup>-</sup>), is thought to be related to local or regional seawater redox conditions. Due to this relationship, the I/Ca in ancient carbonates has been widely used to interpret redox variations of local seawater during the geologic past. However, despite the thermodynamic calculations which predict that iodine oxidation/reduction are sensitive to ambient dissolved O<sub>2</sub>, the relationship between O<sub>2</sub> and iodate accumulation is not well understood. To provide constraints on the conditions of IO<sub>3</sub><sup>-</sup> accumulation in modern marine low oxygen settings—and hence to better reconstruct paleoredox using the I/Ca proxy—we sampled and analyzed iodine speciation (IO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, dissolved organic iodine, and total iodine) in seawater collected from a transect through the redox- and salinity-stratified Gotland Basin in the restricted Baltic Sea.

We observe relative IO<sub>3</sub><sup>-</sup> depletion and high I<sup>-</sup> in the Baltic seawater samples across the whole depth profile, including the fully oxygenated surface layer. Comparing to the previous observation of iodine speciation in the same area, we hypothesize that the major source of IO<sub>3</sub><sup>-</sup> into the Baltic Sea is from the well-oxygenated North Sea during episodic Major Baltic Inflows (MBI). Our observed iodine-O<sub>2</sub> decoupling in the Baltic Sea surface waters may then be caused by rapid IO<sub>3</sub><sup>-</sup> reduction and sluggish I<sup>-</sup> oxidation across the oxycline during the long stagnant period between MBIs. These data may help explain factors beyond local redox that contribute to iodine distributions in open ocean ODZs. Our results also hint that sedimentary records of ancient iodate accumulation may require long-lasting oxidizing conditions on regional or even ocean basin-wide scales.

# Hydrothermal Inputs Drive Dynamic Shifts in Microbial Communities in Lakes Magadi and Nasikie Engida, Kenya

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The Methane Index (MI) is an organic geochemical proxy that uses isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs) as a proxy for methane cycling. The MI has historically been used to discern methanotrophy, and is based on the observation that GDGTs 1, 2, and 3 have a larger contribution from methane cyclers than Crenarchaeol, which is produced by mesophilic archaea.<sup>1</sup> Here, we report results from a core spanning 700 ka in Lake Magadi, Kenya showing a switch between high and low MI values intermittently in the core. These intermittent switches are coincidental with interspersed tuffaceous silt deposits; when tuffaceous silts are present, the MI switches “off” (MI < 0.2) and when these silts are absent from the core, we see a switching “on” of the MI (MI > 0.4). Samples taken from a recent core (spanning ~2.2 ka) at neighboring Nasikie Engida had MI values greater than 0.8, indicating that the MI is currently “on” in this system. Bulk organic matter is enriched in <sup>13</sup>C in Magadi during “MI-off” periods, with values ~-18‰ in the upper part of the core and -22 to -25‰ in the lower portion. These δ<sup>13</sup>C measurements are similar to δ<sup>13</sup>C values of biphytanes measured by Pearson et al (2004) in bicarbonate-rich hydrothermal waters similar to Nasikie and Magadi.<sup>2</sup> In contrast, in sediments deposited when the MI is “on” showed δ<sup>13</sup>C values in the range of -28 to -30‰ in both Nasikie and Magadi, which is consistent with methanogens rather than methanotrophs. Thus, the likely source of these high MI values is methanogenic archaea rather than methanotrophs in both Nasikie Engida and Magadi. Our results show that hydrothermal inputs of bicarbonate rich waters into Lakes Magadi and Nasikie Engida cause a shift in the dominant archaeal communities, alternating between two alternative stable states.

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## Generalized Additive Models (GAMs) as tools for identifying the onset of ecological change in high-altitude lakes

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Diatom paleoecology often results in large and complex data sets that need to be dissected in several ways to understand the history of ecosystem change. One of the strongest tools to do this is Generalized Additive Models (GAMs). In this study, GAMs were used to identify the onset of ecological change in two high-elevation lakes in the Sierra Nevada, California. Our results suggest that traditional statistical approaches such as Stratigraphically Constrained Cluster Analysis (CONISS) and Principal Component Analysis (PCA) yield information regarding diatom species succession in the ecosystem and how this relates to environmental change, while the GAMs reveal critical ecosystem shifts. Additionally, we were able to discern differential ecosystem response in these lakes. In this case, the deeper lake showed an earlier response to warming with respect to the shallower lake analysed. The ecological changes identified in the lakes are related to changes in nutrient cycling as a response to increasing temperatures and a more stable thermocline. The 70-year lag identified between the lakes is hypothesized to be a function of lake depth, and hence, depth of the thermocline. A deeper thermocline is more stable and more sensitive to increasing temperatures. Our approach yielded valuable information for understanding lake dynamics in the Sierra Nevada.

## Preliminary Assessment of Organic Geochemistry in Sediments from the Transkei Basin (IODP Site U1581)

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A series of organic-rich sedimentary sequences that span the Paleocene through the Campanian was recovered from the Transkei Basin during IODP Expedition 392. Preliminary analyses of their organic geochemistry reveals suites of biomarkers that reflect diverse contributions of organic matter from both marine and terrestrial sources. Samples from both the Paleocene and Campanian contain series of C<sub>37</sub> to C<sub>40</sub> diunsaturated alkenones, including the earliest record of C<sub>38</sub> alkadien-2-ones and C<sub>39</sub> alkadien-3-ones. Samples from the Campanian (~72.5 Ma) reveal an abundance of C<sub>28</sub> steradienes and steryl ethers that are potentially indicative of upwelling conditions. Polyaromatic hydrocarbons within the sequence include compounds that suggest inputs of OM derived from angiosperms and paleofires. Dominant hopanoids in the samples include ββ-homohopane, hop-17(21)-ene, and 29-norhop-17(21)-ene, accompanied by fernenes, a C<sub>35</sub> hopanoid thiophene and also dammarenes in Paleocene samples. These initial results provide evidence that biomarker profiling will facilitate determination of the sources of OM from the Late Cretaceous to the Paleocene in the Transkei Basin and paleoenvironmental conditions of deposition.

## Evaluating terrestrial nitrogen cycling from modern tills

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Despite being an essential element for life and a major component of the atmosphere, many aspects of nitrogen (N) cycling throughout Earth history remain poorly understood. This includes the flux of nitrogen between modern reservoirs and terrestrial environments. Typically, N entering surface environments is assumed to be sourced from the atmosphere [1]; however, recent studies have identified rock-hosted continental N reservoir could be a significant source [2, 3].

To assess the role of the continental reservoir in nitrogen cycling, we measured N concentrations and stable isotopic signatures in modern glacially derived sediment (tills) from across Canada. The geochemical composition of tills reflects upper continental crust composition because (1) ice sheets grind and transport sediment from large areas of continental crust, and (2) the lack of chemical weathering during till formation and deposition. These factors can provide robust records of soluble element concentrations, including N [4]. Seventy till samples spanning eight Canadian provinces were measured for [N] concentrations and <sup>15</sup>N using an Isotope Ratio Mass Spectrometer (IRMS) in the Earth System Evolution Lab (EaSEL) at Iowa State University. Initial measurements show average  $\delta^{15}\text{N}$  and N concentrations of 5.75‰ and 249 ppm, with values ranging from 0.40 to 13.40‰, and from 84 to 747 ppm, respectively. Next steps include mineralogical analyses and till provenance identification to constrain the role of bedrock in N concentrations and isotopic signatures. Doing so will allow for potential comparisons to see how the continental N reservoir has changed through time, and further how rock bound N might cycle through the biosphere.

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## Calcium carbonate as a sole inorganic carbon source for methanogenesis at alkaline pH

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Most of the carbon on Earth (ca. 80%) is sequestered in the form of sedimentary carbonates [1]. Under alkaline conditions, carbonate minerals are often considered metastable and inaccessible for microbial metabolism. Here, we demonstrate the use of calcium carbonate as a sole inorganic carbon source for hydrogenotrophic methanogenesis over a range of alkaline pH conditions. Saline, alkaline wetland soil served as an initial inoculum in minimal medium (100% argon headspace, pH 8.3) yielding an anaerobic enrichment culture that was continuously maintained on hydrogen and calcium carbonate. In subsequent experiments, the enriched consortium was cultured under five alkaline pH conditions (from 7.6 to 8.5) in sealed serum bottles amended with 10 mmol L<sup>-1</sup> of synthetic calcium carbonate and ca. 12 mmol L<sup>-1</sup> of hydrogen gas. Parallel reactors were initiated to serve as negative controls and were either uninoculated or killed. Over the experimental incubation, headspace methane increased in all live cultures with a simultaneous decrease in headspace H<sub>2</sub>. These changes were of greater magnitude as pH approached neutral, but could be standardized against cell density. An increase in dissolved calcium was measured in reactors inoculated with live cultures, with no change in pH. This result demonstrates microbially mediated mineral dissolution rather than abiotic pH mediated dissolution. Shotgun metagenomic sequencing confirmed the presence of a methanogen (a novel *Methanobacterium* sp.) alongside five other bacterial community members. Genomic data confirm the *Methanobacterium* sp. has a complete pathway for hydrogenotrophic methanogenesis and possesses a carbonic anhydrase to facilitate the conversion of bicarbonate to carbon dioxide for use in methanogenesis and biomass production. These results affirm the potential for carbonate mineral deposits to sustain past or present methanogens (or other lithoautotrophs), even at alkaline pH, supplying a viable inorganic carbon source either on Earth or another carbonate-bearing planet or moon.

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## Changes in atmospheric composition during the Phanerozoic recorded in fossilized plants

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Atmospheric changes have been a key component for the development of the Earth's history. How the abundance of its major components, N<sub>2</sub> and CO<sub>2</sub>, has changed through time has greatly affected the evolution of life on Earth. There are relatively few direct samples of the ancient atmosphere, and thus far we have relied on proxies to estimate N<sub>2</sub> and CO<sub>2</sub> levels. A potential proxy is fossil plant material from the Phanerozoic. Plant evolution during the Paleozoic likely is influenced by and may record changes in atmospheric CO<sub>2</sub> and N<sub>2</sub> levels. From production of numerous proteins, biologic compounds, to the general growth in all living species, nitrogen and carbon dioxide are key elements for the Earth's biomass development. Fossil plants are record keepers for the atmosphere, by recording the atmospheric composition within their fossilized cells. By studying nitrogen and carbon isotopic ratios in fossilized plants, it is possible to obtain information of the N<sub>2</sub> and CO<sub>2</sub> composition on land and in the atmosphere before fossilization, allowing a direct look into the atmospheric makeup throughout the geologic record. The objective of this research is to characterize the nitrogen, carbon, and sulfur isotopes of fossilized plants from the Phanerozoic Eon to provide information on atmospheric composition fluctuations and nutrient sources over time. Preliminary data has been collected from 19 samples, ranging from 350 Ma to 10 Ma, retrieved from the University of Iowa Collections. Three types of plant material were collected and isotopically analyzed: roots, stems, and leaves. The results indicate that the measurements of C and N is feasible from fossilized plants and that atmospheric fluctuation trends can be constructed over time. The data suggests that the average  $\delta^{15}\text{N}$  value of plant material may have changed over this time while  $\delta^{13}\text{C}$  shows no discernible trend through time. More data is being collected to create a detailed analysis of atmospheric levels through geologic time, but one potential interpretation is that atmospheric N<sub>2</sub> has varied over time. The results from this research will give new data on our atmosphere's composition from the past, to compare with existing proxies and provide context for future climate and land use changes.

## Protein diagenesis during experimental silicification of cyanobacteria

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All organisms contribute in one way or another to the fossil record; most famously, many animals leave exquisite body fossils of their mineralized tissues, from which a wealth of paleobiological information can be gleaned. On the other hand, microbes do not often leave behind many informative body fossils. For such taxa, molecular fossils, cellular biochemical constituents preserved (but also chemically altered by diagenesis) in a range of geologic archives can be our best set of clues to the biological past.

In the last two decades many discoveries have been made using ancient DNA and lipids. Less commonly used are proteins which can persist in the environment for much longer than DNA and contain gene sequence information. However, the diagenesis of proteins is not well understood.

In order to better use proteins as a molecular fossil we are exploring the diagenesis of microbial proteins under controlled laboratory conditions using proteomic mass spectrometry. In this experiment *Anabaena variabilis* ATCC 29413 was subjected to silicification under a range of temperatures and concentrations of silica. Proteins extracted from these various experimental treatments were analyzed by Orbitrap mass spectrometry, with the goal of identifying molecular transformations to proteins characteristic of mineralizing fossilization. The resulting diagenetic patterns will help expand the use of ancient proteins as molecular fossils.

## Distributions of Leaf Wax *n*-Alkanes in Modern Palm (*Arecaceae*) Species

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Leaf wax *n*-alkanes preserved in lake sediments provide information about past terrestrial ecosystems and environments. However, a better understanding of *n*-alkane production among modern plants is needed in order to contextualize sedimentary *n*-alkane records [1]. Specifically, measuring the abundance and chain length distribution of *n*-alkanes among modern plants can contextualize downcore changes in sedimentary *n*-alkane chain length distributions, which can potentially characterize temporal changes in plant communities in ancient environments. Palms (*Arecaceae*) are an important component of ecosystems in tropical locations, such as the Amazon Rainforest. However, existing global plant surveys of *n*-alkane chain length distributions have previously excluded palms, making it difficult to reliably interpret sedimentary *n*-alkane records from tropical locations with an abundance of palms. Here, we present *n*-alkane chain length distributions of 15 different palm species from around the world, collected from individual plants grown at the Fairchild Tropical Botanic Garden in Coral Gables, Florida. We find that different palm species exhibit extensive heterogeneity in *n*-alkane yields and dominant chain lengths. Additionally, we examined intraspecies variability by analyzing individual leaflets from three different *Mauritia flexuosa* trees. Leaflets from two of the three specimens had nearly-identical *n*-alkane chain length distributions and similar yields. The third specimen exhibited vastly different *n*-alkane yields, chain length distribution, and dominant chain length when compared with the other two specimens. We are currently evaluating the variables that may explain the heterogeneities observed, including differences in age, origin, environment, sex, and sampling height, among others. Our *n*-alkane data, generated from 15 unique palm species, will help support the interpretations of future studies generating *n*-alkane-based paleoenvironmental records from the tropics.

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## Towards Understanding the Microbial Response to Changing Winters in the Laurentian Great Lakes

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The Laurentian Great Lakes are among the fastest warming lakes in the world. Declining ice cover has been well documented, but other winter season changes are poorly understood due to the challenges of *in situ* winter sampling. In particular, little is known about the dynamics and function of microbial communities in winter and their response to warming. Here we leverage our ongoing timeseries of microbial community structure, collected each spring after ice-off and in late summer, to investigate how winter conditions affect microbial composition and abundance in subsequent seasons. We define the winter season as the period from Dec 1<sup>st</sup> to May 1<sup>st</sup> and within this period calculate summary parameters like median ice, length of ice cover, and mean water temperature. We find that winter parameters, primarily median ice are associated with changes in community structure. In the spring, median ice explains some of the community structure variation seen at the lake level. In the summer, median ice explains some of the community structure variation at specific depths. Our results suggest that microbial composition, and potentially function, is sensitive to winter conditions, and more observations throughout the winter season are urgently needed.

## Proxies of Ancient Life through Magnetotactic Bacteria

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Magnetotactic bacteria (MTB) have been considered as possible proxies of ancient life due to their ability to synthesize magnetite with distinct characteristics through biologically controlled mineralization. These microbes lyse when they die and release magnetosome crystals into the environment, creating what are referred to as magnetofossils, which have been recovered from soils, freshwater and deep-sea sediments, and perhaps even Mars. As MTB are controlled by various environmental chemistry and mineralogy conditions, these organisms provide windows to Earth's present and past chemical and biological systems, as well as perhaps other planetary conditions. The discoveries of putative magnetofossils in Martian samples, such as the 1996 ALH84001 meteorite, has led to controversy as to whether they indicate life on Mars or are created through abiotic processes. Skeptics believe that some "fossils" result from human error during sample preparation and analysis, or that traces of possible life, such as organic molecules or carbon globules, were formed through nonbiological processes, but the evidence of magnetite continues to prove strong evidence, even for skeptics. If magnetite is found in a chain formation, similar to that which forms in the magnetosome, then it would be evident of past magnetotactic bacteria. While controversial, magnetofossils are possible proxies of ancient life and can be identified through the distinct characteristics of the various biogenic magnetite crystals.

## Evaluating the impact of changing sedimentary environments on individual pyrite $\delta^{34}\text{S}$

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Bulk  $\delta^{34}\text{S}$  composition of sedimentary pyrite is a function of two major variables: (1) ambient  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ , affected by changes in microbial fractionation and/or distillation within porewaters, and (2) sulfide preservation as pyrite, occurring potentially intermittently over time in marine sediments (modulated by iron availability). In more commonly preserved shallow environments, regional or local processes may promote more complex patterns in microbial cycling within sediments (e.g., due to anaerobic oxidation of methane (AOM)), possibly leading to multiple intervals of early diagenetic pyrite precipitation. In addition, physical sediment mixing or pulsed sedimentation (e.g., in deltaic settings or associated with turbidites) are likely to affect the oxidation of sulfide or the availability of reduced iron to produce diagenetic pyrite. Such complex processes may overprint the bulk  $\delta^{34}\text{S}_{\text{pyr}}$  signal, yet the history of pyrite formation within sediments can be evaluated through a combination of petrographic and isotopic analysis of individual pyrite grains on the micron-scale using secondary ion mass spectrometry (SIMS).

Samples from the Valle di Manche section in the Crotona Basin, Southern Italy, preserving the stratal stacking patterns of two continuous transgressive-regressive cycles from the Mid Pleistocene, were used to evaluate the effect of depositional environment on  $\delta^{34}\text{S}$  of texturally distinct population(s) of individual pyrite grains. All samples analyzed from the Valle di Manche section, regardless of bulk  $\delta^{34}\text{S}_{\text{pyr}}$  (ranging from -44 to +7‰) and depositional setting (outer to inner shelf) contain a significant population of  $^{34}\text{S}$ -depleted pyrite (<-40‰), suggesting that maximum (i.e., near-equilibrium) microbial fractionation ( $\epsilon \sim 70‰$ ) is ubiquitous. In addition, a detailed SEM/SIMS approach confirms pyrite can retain the record of changes in saturation state of pyrite over the course of sediment burial that bulk  $\delta^{34}\text{S}_{\text{pyr}}$  cannot resolve. In all cases where bulk  $\delta^{34}\text{S}_{\text{pyr}}$  is >-20‰, a large portion of individual pyrite grains within the sample is enriched in  $^{34}\text{S}$  (from -15‰ up to +80‰ or higher), always exhibiting euhedral or massive/infilling textures consistent with slow growth over long timescales. By linking these micron-scale observations in textures and  $\delta^{34}\text{S}_{\text{pyr}}$  with stratigraphic changes on the cm to meter scale, patterns in the history of changing depositional environment begin to emerge.

# Ammonia After Dark: Constraining Microbial Aerobic Ammonia Oxidation in Mammoth Cave Sediments

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Aerobic ammonia oxidation is a key process in the nitrogen cycle and a common energy source for microbes, including in nutrient-limited cave ecosystems. High nitrate concentrations in cave sediments were historically, yet controversially, attributed to bat populations, but ammonia oxidizing bacteria and archaea may be an additional contributing source [1]. Mammoth Cave is the longest mapped cave system in the world, and the variation in its overlying geology enables the study of microbial ammonia oxidation across a wide range of subsurface conditions [2]. Mammoth Cave sediments can exhibit unusually high concentrations of nitrate within and beyond areas of modern and historical bat colonization, yet nitrogen cycling via microbes has not been explored since the characterization of *Nitrobacter* in 1977 [3]. Thus, the role of microbial ammonia oxidation in nitrate accumulation here is unconfirmed. Here we present our ongoing cultivation-dependent work to characterize aerobic ammonia oxidizing microbes from Mammoth Cave to understand their metabolic processes and contributions to the cave's nitrogen cycle. Hundreds of samples were taken encompassing variations in elevation, water source, aridity, access, and animal use. Of these, 20 were selected to inoculate solid and liquid media within hours of collection. Over 80 distinct microbes have since been isolated on autotrophic ammonia agar plates. Morphological observations and 16S rRNA gene sequencing are being used to identify isolates, and the *amoA* functional gene and genomes of novel taxa are being sequenced to characterize the functional capabilities of cave taxa. These data will be compared to 16S rRNA gene surveys to identify the distribution of isolated clades and to metagenomic datasets to capture their functional diversity. We anticipate forthcoming cultivation experiments will be informed by this genomic data and geochemical assays monitoring microbial growth under simulated environmental conditions. Our findings will reveal the drivers of microbial ammonia oxidation in the nitrogen cycle across low-nutrient cave ecosystems.

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# Lateral and secular variability in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ from the Late Ordovician GICE interval

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$\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  are two important stable isotope proxies used to study secular variations in regional to global carbon and sulfur biogeochemical cycles. In practice, however, their utility is often compromised by diagenesis and local depositional controls, which are commonly considered as “noise” and thus ignored. For geochemical excursions of relatively small magnitudes, such “noise” may become dominant and lead to false interpretations of the geochemical signals. This study presents preliminary results of lateral isotopic variability seen on multiple stratigraphic levels of the late Ordovician Guttenberg  $\delta^{13}\text{C}$  excursion (GICE) interval near House Springs, MO, an outcrop well-constrained by radiometric dating. Bulk carbonate samples were collected from stratigraphic heights that cover pre-GICE baseline, rising phase of the GICE, GICE plateau, and post-GICE strata. Carbonate-associated sulfate (CAS) and CRS extractions were performed on replicates of these samples to yield  $\delta^{34}\text{S}_{\text{CAS}}$  and  $\delta^{34}\text{S}_{\text{pyrite}}$ , respectively, and  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}_{\text{org}}$ , and TOC are measured repeatedly from the replicates. Variation up to 1‰ in  $\delta^{13}\text{C}$  is observed from a single stratigraphic level and accounts for almost half of the recorded GICE magnitude. Overall,  $\delta^{34}\text{S}_{\text{CAS}}$  values show relatively consistent values (avg.  $\sim +28$ – $32$ ‰) both laterally and vertically (secularly), in contrast to the large variations seen in  $\delta^{34}\text{S}_{\text{pyrite}}$  in both dimensions (avg.  $\sim 10$ ‰ laterally and  $>20$ ‰ vertically). We propose a component-mixing control on  $\delta^{13}\text{C}$  variation that is determined by the amount of bioclasts, micrite, and diagenetic components. The consistency of  $\delta^{34}\text{S}_{\text{CAS}}$  may reflect the original seawater sulfate values modified by lithological component mixing including diagenetic carbonates, whereas elevated values and variability in  $\delta^{34}\text{S}_{\text{pyrite}}$  may be associated with increasing closed-system distillation and oxidative reworking during microbial sulfate reduction, especially in the shallower facies.  $\delta^{34}\text{S}_{\text{pyrite}}$  data shows a positive excursion that closely follows the  $\delta^{13}\text{C}$  excursion and relative sea level changes. The secular pattern seen in  $\delta^{34}\text{S}_{\text{CAS}}$  and  $\delta^{34}\text{S}_{\text{pyrite}}$  is comparable to those recorded from HICE intervals in Anticosti Island, Canada, indicating similar mechanisms resulted from local depositional environments.

# Optimization of the Picarro L2140-i Cavity Ring Down Spectrometer for Routine Measurement of Triple Oxygen Isotope Ratios in Meteoric Waters

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The demanding precision of triple oxygen isotope ( $\Delta^{17}\text{O}$ ) measurements in water has restricted its measurement to dual-inlet mass spectrometry until the recent development of infrared-laser analyzers. Laser-based measurements of triple oxygen isotope ratios are now increasingly performed by laboratories seeking to better constrain the source and history of meteoric waters. However, in practice, these measurements are subject to large analytical errors that remain poorly documented in scientific literature and by instrument manufacturers, which can effectively restrict the confident application of  $\Delta^{17}\text{O}$  to settings where variations are relatively large ( $> 25$  per meg). We present our operating method of a Picarro L2140-i cavity ringdown spectrometer during the analysis of rainwaters where confidently resolving daily variations in  $\Delta^{17}\text{O}$  (differences of  $\sim 10$ - $20$  per meg) was desired. Our approach was optimized over  $\sim 3$  years and uses both published best-practices plus additional steps to combat spectral contamination of trace amounts of dissolved organics, which, for  $\Delta^{17}\text{O}$ , emerges as a much more substantial problem than previously documented – even in rainwaters. We resolve the extreme sensitivity of the  $\Delta^{17}\text{O}$  measurement to organics through their removal via Picarro's micro-combustion module, whose performance is evaluated using alcohol-spiked standards. While correction for sample-to-sample memory and instrumental drift significantly improves traditional isotope metrics, these corrections have only marginal impact (0-1 per meg) on  $\Delta^{17}\text{O}$ . Our post-processing scheme uses the analyzer's high-resolution data, which improves  $\delta^2\text{H}$  measurement and allows for much more rich troubleshooting and data-processing compared to the default data output. In addition to competitive performance for traditional isotope metrics, we demonstrate  $\Delta^{17}\text{O}$  performance that is comparable to mass spectrometry (7 per meg error, calculated by averaging 3 analytical replicates) and requires only  $\sim 6.3$  h per sample. We demonstrate the impact of our approach using a rainfall dataset from Uganda and offer recommendations for other efforts that aim to measure meteoric  $\Delta^{17}\text{O}$  via CRDS.

# Marine Habitability and Productivity on High-Obliquity and High-Eccentricity Planets

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Planetary obliquity and orbital eccentricity together modulate climate through their influence on the quantity and spatio-temporal distribution of incoming stellar radiation. The implications for planetary habitability in terms of the stability of liquid water have been thoroughly investigated. However, the effects of the extreme seasonality generated by high obliquity or eccentricity on the survivability of a potential biosphere are not well understood.

We use cGENIE-PlaSim, a 3D marine biogeochemical model coupled to an atmospheric general circulation model [1], to characterize seasonality in the oceans of earth-like planets for various obliquity and eccentricity combinations. We additionally quantify the productivity of the marine biosphere both seasonally and annually. We vary obliquity between 0 and 90 degrees and eccentricity from 0 to 0.4.

We find that marine biospheric productivity increases significantly with obliquity and to a smaller degree with eccentricity for all orbital scenarios. Annual productivity is greatest in scenarios with both high obliquity and high eccentricity. Productivity is driven by seasonal variability in the depth of the mixed layer, which increases with both obliquity and eccentricity. This presentation will discuss the spatiotemporal patterns of marine biospheric productivity on Earth-like exoplanets with high planetary obliquity and eccentricity and implications for habitability.

[1] Holden, Edwards, Fraedrich, et al. (2016), *GMD* 9, 3347-3361

# Where did life survive during the Cryogenian Snowball Earth? comparison of cryoconites and sedimentary geochemistry ocean redox and refugia

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The Cryogenian Snowball Earth glaciations represent some of the most formidable barriers to continued habitability over Earth's history. Extreme cold, high salinity, and potentially ice-covered oceans could have severely limited productivity. Yet, life, and specifically photosynthetic life, survived. How, where, and under what geochemical conditions remain elusive. In this study, we present geochemical measurements of redox-sensitive trace elements, Fe-speciation, and nitrogen and carbon isotope data from syn-Snowball ocean deposits. Specifically, the Ghaub formation from Namibia and the Mineral Fork formation from Utah, USA, record ocean redox conditions during the Marinoan and Sturtian glaciations, respectively. Taken together, these data suggest areas of oxygenated water, with a redox-stratified ocean. Positive nitrogen isotope values and slight enrichments in U, V, and Mo indicate oxic weathering and denitrification, requiring oxygen produced by photosynthesis over the lifetime of each glaciation.

We further compare isotopic data from the Cryogenian to modern measurements from cryoconite holes. Modern holes from Antarctica show evidence for carbon limitation and limited nitrogen cycling. Snowball data, on the other hand, suggest no carbon limitation with combined oxygen dependent and independent nitrogen cycle fluxes. Thus, we suggest that there were areas of open ocean with active photosynthesis, and no carbon limitation during the Snowball glaciations.

# Sulfur-based signatures of chemosymbiosis in modern *Lucinidae*

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Modern lucinid bivalves are hosts to sulfide-oxidizing bacterial symbionts that use energy released by the oxidation of environmental sulfide to fix carbon from carbon dioxide into organic compounds utilized by hosts. The earliest known lucinid bivalves date back to the Silurian: fossil specimens that are anatomically similar to modern lucinids have been found preserved in life positions consistent with their descendants. Despite compelling morphological evidence, there is no geochemical data that can corroborate when these bivalves developed a symbiotic relationship with sulfur-oxidizing bacteria. Previous attempts to fingerprint chemosymbiosis were limited to analyzing the shell organic matrix of seep bivalves. While the shell organic matrix is a powerful tool for studying metabolism in modern bivalves, it may be less useful for studying fossil bivalves due to its labile nature.

Thus, we aimed to identify geochemical signatures that indicate thioautotrophic symbiosis in modern lucinid shells collected from environments with relatively low and high concentrations of hydrogen sulfide. We collected infaunal lucinid bivalves and a non-symbiotic oyster from low-sulfide seagrass beds and high-sulfide mangroves in Guadeloupe and an epifaunal symbiotic bivalve from the Mid-Atlantic Ridge. We measured the spatial distribution, speciation, and abundance of sulfur in modern infaunal lucinids in addition to epifaunal bivalves with and without thioautotrophic symbionts using synchrotron methods. We found that carbonate-associated sulfate (CAS) concentrations in all infaunal lucinid shells were less than CAS concentrations in the shell of the epifaunal bivalve with no symbionts. In addition, CAS sulfur isotope ratios were lower in all the infaunal lucinids in comparison to the epifaunal bivalves with and without thioautotrophic symbionts. These observations indicate that infaunal lucinids with symbionts incorporate hydrogen sulfide-derived sulfate into the carbonate lattice of their shells as a consequence of chemosymbiosis. Therefore, it is possible that hydrogen sulfide-derived sulfate could be a key geochemical indicator of chemosymbiosis in ancestral *Lucinidae*.

## Microplastic - Soil Separation Methods

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Anthropogenic waste is the primary source of plastic in natural environments. In the past decade, there has been an increased interest in the research community in understanding microplastic (MP) distribution and abundance in various environments. A significant focus has been on marine environments with very low organic matter (beaches and water column). Our team has decided to focus on environments with higher concentrations of organic matter, including grasslands, wetlands, and landfills. In this study, we focused on density-based separation methods. Initially, we used an adaptation of Coppock et al., (2017) Sediment-Microplastic Isolation (SMI) Unit, which successfully separated sandier, low organic carbon samples. However, the success did not translate for the organic-rich samples. Instead, we found that samples rich in organic matter separate from MPs better using a density-based centrifugal method. While this method requires more preparation, the percent yields are higher than the SMI unit. Ultimately, both separation methods are effective but must be chosen as appropriate for the sample type. The SMI unit is preferred for samples low in organic carbon, while the centrifugal method is a more fitting choice for samples higher in organic carbon.

## Braunite synthesis after simulated low temperature diagenesis of Mn- oxides with reduced manganese

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The transition metal manganese is a useful paleo-redox proxy because it can exist in a wide range of valence states, and due to its high redox potential, this metal is not generally oxidized in the absence of oxygen or related species. Consequently, concentrations of manganese in the rock record are usually inferred to record manganese oxidation, likely indicating interactions between Mn(II) and oxygen.

Manganese deposits associated with potential Paleoproterozoic and Neoproterozoic global oxygen variations are enriched in the manganese silicate braunite [Mn(II)Mn(III)<sub>6</sub>O<sub>8</sub>(SiO<sub>4</sub>)]. While this mineral's formation process has thus far been relatively unexplored, sedimentary textures suggest that braunite is a diagenetic phase. Unravelling the mineralization of braunite should inform interpretations of the depositional and biogeochemical history of these manganese enrichments, improving paleoenvironmental reconstructions of these intriguing deposits.

We hypothesize that braunite mineralization requires Mn oxide deposition and later diagenetic reactions of oxide precursors with porewater Si and Mn(II). To test this idea, we synthesized precursor Mn(III) and Mn(IV) oxides and aged them at diagenetic temperatures in siliceous solutions with or without Mn(II). We found that precursory Mn oxides, when incubated with reduced manganese and silica, will indeed form braunite, further supporting the use of braunite as a tracer for Mn oxidation. As no braunite was formed in samples lacking Mn(II), our results also demonstrate the importance of reduced manganese, and thus reducing porewaters, during the time of braunite mineralization.

## Microbial Gene Expression at Titan-like High Pressures

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Ocean worlds such as Europa, Enceladus, and Titan are excellent candidates for extraterrestrial life detection because they possess the canonical factors for life as we know it: liquid water, organics, and energy. However, questions remain about life's ability to withstand the "extreme" environmental conditions on Titan. The subsurface ocean on Titan is modeled to be at pressures 150–750 MPa (Vance et al., 2018), while the highest observed growth for a piezophile is 140 MPa (Kusube et al., 2017). We have conducted high pressure incubations to elucidate the mechanisms of survival and potential growth under Titan-relevant pressures in model organism *Shewanella oneidensis*. This organism has been previously shown to survive 1.5 GPa for 15 minutes (Hazael et al., 2014). However, the molecular adaptations for survival and growth capacity at high pressures for this organism are unknown. Transcriptomic analyses for *S. oneidensis* subjected to 150 MPa for 15 minutes and 2 hours have been conducted and results show that cells are still viable and capable of transcribing RNA immediately after depressurization. Previous high pressure incubation studies have shown that pressures above the optimal (supraoptimal) growth conditions affect gene transcription, protein synthesis, motility, cell division, cell morphology, and fatty acid composition, among other responses (*reviews in* Oger and Jebbar, 2010; Macdonald et al., 2021), however, to our knowledge, this study is the highest pressure reported for gene expression at supraoptimal conditions. These results indicate that high-pressure environments in Titan's subsurface may be capable of harbouring life. In addition, understanding how biomolecules will be affected by high pressure conditions in the subsurface, and subsequent depressurization and delivery to the surface is a key piece of biosignature recognition in future life detection missions.

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## Hydroclimate and Vegetation Changes in Eastern Amazonia since the Mid-Holocene Recorded by Biomarkers in Lacustrine Sediments

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Lacustrine sedimentary deposits serve as important archives for molecular paleoclimate reconstructions, owing to their potential for preserving organic matter, and ability to integrate and record basin-wide environmental changes. Specifically, the isotopic and structural composition of plant wax-derived biomarkers from lacustrine sedimentary archives can reveal details about past shifts in hydrology and ecology. Here, we present biomarker-based records of climate and vegetation shifts over the past ~5,600 years from Lago Caraná, Brazil. We compare the  $\delta^{13}\text{C}$  and  $\delta\text{D}$  of leaf waxes to detailed fossil pollen and charcoal data analyzed from the same core to disentangle hydroclimate and vegetation changes. Amazonian freshwater resources depend on precipitation from the South American Summer Monsoon (SASM) and the Intertropical Convergence Zone (ITCZ), and the SASM strongly influences modern precipitation  $\delta\text{D}$  ( $\delta\text{D}_{\text{precip}}$ ). However, unlike several proxy records located elsewhere in the SASM domain, we observe no orbital-scale trend in reconstructed  $\delta\text{D}_{\text{precip}}$ . Instead, we observe pronounced centennial-scale  $\delta\text{D}_{\text{precip}}$  variability after ~2,000 yr BP, potentially coinciding with fluctuations in the mean position of the ITCZ. This suggests regional heterogeneities and distinct responses to orbital forcings across the SASM domain. Local vegetation changes do not have a consistent relationship with the centennial-scale precipitation variability evident from the  $\delta\text{D}_{\text{precip}}$  record. However,  $\delta^{13}\text{C}$  and *n*-alkane chain length distributions, together with fossil pollen and charcoal data, may reflect human-driven changes in land use. We contextualize down-core changes in *n*-alkane chain length distributions with analyses of modern plants whose taxa exist in the Lago Caraná ecosystem today and in the fossil pollen assemblage. Our results demonstrate the utility of adopting a multi-proxy approach for identifying the different mechanisms driving hydroclimate and vegetation changes in eastern Amazonia.



## Biological and Geochemical Controls on Iron Deposition in an Intermittent Stream

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In Clear Creek, which runs through the Iowa State University campus in Ames, Iowa, U.S.A., we have observed several forms of iron mineralization within stagnant pools and slow-moving water. Iron redox cycling is related to the amount of dissolved oxygen, a key indicator of water quality. We are investigating the source of iron to these pools, as either 1) discharge of shallow, reducing groundwater bearing Fe(II) or 2) a sedimentary Fe(III) source that is mobilized after Fe(III) reduction with organic matter present in the pools. Accumulating mineralized Fe(III) can provide reactive surfaces for the absorption and immobilization of inorganic contaminants and can also undergo degradation reactions with organic contaminants. Our observations have cataloged a variety of mineralization patterns that recur within specific pools. One example is iridescent films “schwimmeisen”) skimming the surface of these pools. To study these patterns, sediments taken from Clear Creek are put through a series of chemical extractions to determine the chemical form of Fe. Fe(II) and total Fe concentrations are measured through colorimetric ferrozine assays. The presence of microorganisms near such sediment is being assessed using 16S rRNA amplicon sequencing to determine the variance of Fe-oxidizing and Fe-reducing microorganisms. Researching the source of iron in these pools can lead to a better understanding of their ecological and environmental roles.

## When There’s ‘Surface’ in Your ‘Subsurface’ Biosphere: Cellulose Degrading Bacteria from ‘Extreme’ Environments.

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Cellulose could be considered the most important organic molecule on the planet as it’s an end product of most primary production on Earth. Bacterial cellulose degraders are critical to global carbon cycling, utilizing multiple enzymes for complete degradation. To date, the role of cellulose in the terrestrial deep subsurface is largely unexplored as it’s generally assumed to be absent in the subsurface carbon cycle. Surface springs such as serpentinizing or hydrothermal springs have been labeled as potential ‘windows’ into the deep biosphere, but are seldom considered to be a two-way ‘door’. Springs certainly represent a boundary between the subsurface and surface biospheres, but as noted by previous work (Schubotz et al. 2013, 2015; Meyer-Dombard et al., 2019; Meyer-Dombard and Malas, 2022) they are inherently influenced by surface processes that provide exogenous organic carbon and nutrients. Our work presents direct evidence of the influence of the surface biosphere on microbial communities from the subsurface biosphere, in the form of bacterial strains capable of cellulose degradation. Our strains are cultured from ‘extreme’ pH springs sourced from reduced, deep subsurface fluids. Customized growth media were inoculated with spring fluids (pH 2-10), supplemented with cellulose and cellulobiose. Both high and low pH enrichments were dominated by members of the Clostridiales, and pure strains (isolates) of *Micromonospora* were shown capable of cellulose degradation and cellulase production at pH 10. Community similarities in the low pH enrichments suggest that utilization of cellulose in acidic springs may be common to many organisms across the same phyla. If indeed the ability to degrade cellulose in microbial communities is widespread in fluids that originated from the deep subsurface, it may indicate plasticity in strategies of adaptation to surface conditions, and bring into question the role that exogenous organic carbon may play in the carbon cycle of near-subsurface fluids.

## Selective Adsorption of Amino Acids on Montmorillonite

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Concentrating simple organic molecules, such as amino acids, is necessary for prebiotic evolution towards more complex bio-macromolecules on the early Earth. Smectites are 2:1 clay minerals that may have served as selective sorbents for prebiotic molecules because of their high surface area, negative structural charge, and high cation exchange capacity. This study evaluated the adsorption behavior of amino acids to montmorillonite, a well-characterized smectite, at varying pH and fluid compositions. Between pH 5 and 7, amino acids with basic sidechains (L-lysine and L-arginine), which are primarily cationic under these conditions, showed adsorption at least 10 times greater than amino acids that were predominantly zwitterionic or anionic in solution. In the presence of dissolved  $Mg^{2+}$ , adsorption of L-lysine and L-arginine was substantially inhibited. These observations suggest that cation exchange is the dominant adsorption mechanism for amino acids on montmorillonite. X-ray diffraction and infrared spectroscopy indicate that L-lysine enters the smectite interlayer where protonated amino groups have the strongest interactions with the mineral surface, further supporting amino acid adsorption driven primarily through electrostatic interactions. Therefore, smectites on the early Earth may have selectively concentrated cationic amino acids, whereas phyllosilicates without a structural charge, such as serpentine minerals, likely bind amino acids through different mechanisms.

## Constraining Continental Emergence: Proterozoic Ocean Crust as a Record Of Seawater Isotopes

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The timing of continental emergence (CE) above sea level in Earth history is poorly constrained. Estimates range from 3.5 to 0.7 Ga. Constraining CE will lend to a better understanding of how Earth's oceans behaved and the environmental limits for the origin and evolution of life. A tool to further constrain CE is the oxygen isotope composition of seawater (OISW). The OISW reflects the balance of two major fluxes: hydrothermal alteration of ocean crust and continental weathering. If continents are submerged, no weathering occurs, and the OISW will be relatively enriched in  $^{18}O$ , since weathering sequesters  $^{18}O$  relative to  $^{16}O$ . Previous work on Archean crust shows we can use hydrothermally altered oceanic crust as a record of OISW and predict limited emergence at 3.2 Ga<sup>1</sup>. We extend this work to sites between 2.7 to 1.72 Ga: Noranda Caldera Complex<sup>2</sup>, Sturgeon Lake Caldera Complex<sup>3</sup>, and Pecos, NM<sup>4</sup>. The first two sites have been characterized previously, and we have measured new O-isotope data from Pecos. Preliminary  $\delta^{18}O$  data from Pecos range from 2.93‰ to 15.02‰ (V-SMOW), similar to modern crustal settings. We suggest that OISW at 1.7 Ga was therefore similar to today, with significant emergent crust.

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## Redox Induced Cycling of Fe and P Near the Sediment Water Interface

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It is widely accepted that phosphate ( $\text{PO}_4^{3-}$ ) exhibits a high affinity for iron (Fe) and has a closely coupled cycling mechanism strongly influenced by redox transformations between relative soluble ferrous Fe(II) and poorly soluble ferric Fe(III) [2]. Phosphate typically sorbs to Fe (III) (oxyhydr-)oxides, such as ferrihydrite and goethite, and is partitioned in sediment under oxic conditions and desorbed by reductive dissolution of these minerals [1]. Accumulation of aqueous iron and phosphate allows for the possibility of Fe/P precipitates such as strengite and vivianite [2]. Changes in phosphate cycling from sediment to water are important to account for P budgeting in terrestrial aquatic systems, however specific redox-induced pathway intermediates of Fe and P are not well understood. This research aims to use mediated electrochemical reduction and oxidation (MER/MEO) to control rates of electron transfer to and from sediment slurries. Using these MER and MEO techniques coupled with  $\mu$ -XRF energy mapping and XANES analysis, capturing changes in Fe and P intermediate phases during redox changes may provide insight to specific mechanisms of cycling. Characterizing phosphate during these reactions may explain how different forms of iron may limit P mobility and bioavailability and provide a way to better estimate internal loading mechanisms.

[1] Parsons, Rezanezhad, O'Connell & Cappellen (2017), *Biogeosci* 14, 3585-3602

[2] Voegelin, Senn, Kaegi, Hug & Mangold (2013), *Geochimica et Cosmochimica Acta* 117, 216-231

## Wide-spread salinity tolerance across diverse *Synechococcus* strains

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Coastal environments act as transition zones between land, sea, and freshwater ecosystems. As such, they represent diverse, rich ecosystems with high microbial diversity that are essential for industry, recreation, and food. As the climate continues to change, coastal ecosystems are under increasing pressures (e.g., hurricanes, salinity fluctuations, acidification), and understanding the impacts on microbial community structure and function is essential for building predictive models of biogeochemical cycling. Therefore, fluctuations in salinity have the potential to alter nutrient transformations e.g., the carbon cycle, by selecting for different microbial community membership. The Cyanobacteria clade *Synechococcus* is globally widespread and contributes significantly to global primary production. Since its discovery, numerous studies have identified phylogenetically and ecologically diverse lineages. Here, we investigated the phylogenomic distribution and salinity tolerance of 8 *Synechococcus* strains isolated from a singular location – Martha's Vineyard Coastal Observatory -- to understand how salinity changes may alter the distribution of *Synechococcus* subclusters. Phylogenomic analysis showed the *Synechococcus* strains were from all three subclusters (5.1, 5.2, and 5.3). Further, while subclusters 5.1 and 5.3 showed classical salinity evolutionary transitions, subcluster 5.2 had numerous instances of salinity transitions across the subcluster. Supporting this, physiological experiments of the seven cultivars found strains RS9916 (subcluster 5.1) and MV1715 (subcluster 5.3) had a salinity range between 17.9 to 35.56 and 8.9 to 35.56 respectively, while strains from subcluster 5.2 were more likely to grow across a wider range of salinities. For instance, strain MV1006 grew in the salinities 0.45 to 35.56 while strain MV1218c grew in salinities 4.5 to 35.56. This growth from all three subclusters demonstrates variations in the salinity transitions in *Synechococcus*, allowing certain subcluster to inhabit diverse habitats.

# Multimodal Analysis of Indigenous Organic Molecular Biosignatures in a Geologic Sample: ToF-SIMS, GC-MS, SEM-EDS and Machine Learning

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Organic molecular biosignatures (OMBs) detected within samples returned from Mars could provide strong evidence for the existence of extra-terrestrial life [1]. The utility of any OMB depends on its character, which can be: i) indigenous or syngenetic; ii) non-indigenous or incorporated during sub-surface fluid migration; or iii) contaminant. One way to determine OMB character is to determine its spatial distribution within a host rock [2]. Mass Spectrometry (MS) imaging used in conjunction with traditional organic geochemical analysis has been shown to be effective at determining the spatial distribution of OMBs [3].

Here, we use time of flight – secondary ion mass spectrometry (ToF-SIMS), with gas chromatography – mass spectrometry (GC-MS), to detect indigenous sterane molecular ions and fragment ions of isorenieratene derivatives (all excellent OMBs) within the 164-million-year-old Oxford clay. We then perform machine learning (ML) on both ToF-SIMS datasets and secondary electron microscopy – energy dispersive X-ray spectroscopy (SEM – EDS) datasets collected from the same locations to interrogate the geology and organic geochemistry of sample. Custom sample preparation techniques were used for all surface analyses [4].

ToF-SIMS spectra, MS images, and ML models all indicate that the sterane OMBs detected via ToF-SIMS are indigenous to the sample. Further, ToF-SIMS spectra and MS images indicate that steranes are heterogeneously distributed within the sample at the scale of 10's to 100's of  $\mu\text{m}$ . Similar analyses may be critical to determine the provenance of potential OMBs if detected in samples returned from Mars.

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# Metagenomic Analyses Support the Importance of Organosulfur Degradation in the Deep Biosphere

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Sulfur cycling is tightly linked to the cycling of other important elements, including carbon, nitrogen, and iron. Therefore, understanding the scope and mechanisms of biologically mediated sulfur cycling is central to understanding Earth's biogeochemical cycles on a larger scale. The degradation of organic sulfur compounds is known to be an important source of oxidized and reduced sulfur compounds for microorganisms living in low-sulfate freshwater systems. Deep biosphere environments are often nutrient-poor and can have similarly low sulfate concentrations; therefore, we predict organosulfur to also play an important role in such settings. We investigated this hypothesis through shotgun metagenomic sequencing of subsurface fluids from Soudan Underground Iron Mine, MN. Legacy boreholes at this site transect a Neoproterozoic massive hematite iron formation and produce fluids from a fractured rock aquifer 1700 m below the surface. This dataset, along with 46 other deep subsurface metagenomes obtained through the Census of Deep Life, were mined to identify key genes involved in assimilatory and dissimilatory sulfur processes. Genes associated with the degradation and utilization of organic sulfur compounds were also investigated. Our findings indicate that pathways for sulfur assimilation and for dissimilatory sulfur oxidation and reduction are common across the deep subsurface. Additionally, various deep biosphere communities were found to have the genetic potential to mineralize a diverse array of organosulfur compounds, including isethionate, taurine, cysteine, methionine, and dimethyl sulfoxide. These compounds may fuel a cryptic sulfur cycle in low-sulfate deep subsurface settings, with degradation to sulfite providing inorganic sulfur for dissimilatory metabolisms.

## Microbial diversity differs across alpine streams in a glaciated mountain range of Northwestern WY, United States

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Alpine streams harbor diverse cold-adapted microbes [1]. However, warming temperatures and glacier retreat are predicted to impact alpine stream microbial diversity subsequently altering biogeochemical cycles [2,3]. This leads to urgent questions regarding microbial diversity in alpine streams. Recent studies have investigated microbial diversity within alpine watersheds indicating that warming temperatures cause changes to community composition and function [4]. We expanded on previous studies by examining microbial diversity in high elevation alpine streams in Grand Teton National Park (GRTE) in Northwestern, Wyoming which are particularly susceptible to climate change [5]. During the summer of 2018, we measured the physiochemistry of stream water and sampled microbial communities from biofilms across alpine streams in GRTE. We used metabarcoding to target bacteria and archaea (16S rRNA gene) and microbial eukaryotes (18S rRNA gene). Microbial diversity (both 16S and 18S rRNA) was low in biofilms while community composition was significantly different between sites. Stream water temperature was a significant driver of bacterial and archaeal community composition while both temperature and elevation influenced the composition of biofilm eukaryotes. Microbial community composition was more similar in alpine streams (both 16S and 18S rRNA) known to receive high seasonal meltwater from glaciers with high Pfankuch Stability Index values; however, did not significantly correlate with differences in microbial community composition. The most abundant OTUs included Comamonadaceae (16S rRNA) and Chrysophyceae (18S rRNA). Three distinct abundant Chrysophyceae OTUs were recovered suggesting species level differences across sites. Warming temperatures are predicted to increase primary production and alter the abundance of algae with colder thermal limits [2]. Our study supports this prediction as we show warmer alpine streams support dissimilar microbial communities [2].

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## Resolving the fate of trace metals during microbial remineralization of phytoplankton biomass in precursor banded iron formation sediments

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Banded Iron Formations (BIFs) have long been considered a sedimentary record of seawater trace metal composition during the Precambrian. However, recent work has suggested that the trace metal composition of BIFs was derived from phytoplankton biomass, not seawater. In this model, phytoplankton biomass settles from the photic zone to the sediments, where it is then oxidized by heterotrophic microbes, such as dissimilatory Fe(III) reducing (DIR) bacteria, for energy generation. Remineralization of this biomass released the trace metals associated with organic molecules from phytoplankton (*i.e.*, in metalloproteins), allowing these metals to be captured by Fe (oxyhydr)oxides and preserved in BIFs. While there is compelling evidence that the phytoplankton biomass served as a trace metal shuttle to precursor BIF sediments, it is unclear whether the degradation of biomass by DIR bacteria would liberate the biogenic trace metals as the model proposes. This work tests this hypothesis by using anoxic incubations of a model DIR bacterium (*Shewanella oneidensis* MR-1) with phytoplankton biomass as energy and carbon sources and ferrihydrite—a poorly crystalline Fe(III) oxyhydroxide—as electron acceptor. Our results show that while *S. oneidensis* MR-1 can consume some of the carbon substrates found in phytoplankton biomass, there is no evidence that *S. oneidensis* MR-1 degraded metalloproteins and liberated trace metals. In the context of the Precambrian, these data imply that other heterotrophic bacteria may have had a larger role in the liberation of trace metals from dead biomass during early BIF development.

## Iodine Cycling in Hydrothermal Fluids and Plumes from the East Pacific Rise, 9°N

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Iodine is a redox-sensitive element with important contributions to, and even a tracer for, the cycling of oxygen. It includes the atmospheric ozone and dissolved molecular oxygen; however, controls on the sources and mechanisms driving marine iodine variability remain poorly constrained. Hydrothermal vents are a poorly understood mechanism of iodine input that has been demonstrated to be an important control on the distribution of other redox-sensitive elements (e.g., Fe, Mn). Due to the highly reducing conditions, we hypothesize a higher contribution of marine iodine input from the hydrothermal vents and higher concentrations of iodine in the reduced form iodide (I<sup>-</sup>). In this study, we analyzed high-temperature hydrothermal vent fluids (~10-370°) and the overlying plume and seawater samples from the mid-ocean ridge at the East Pacific Rise at 9N. Samples were analyzed using ion chromatography and inductively coupled plasma-mass spectrometry (ICP-MS). Both hydrothermal vent fluids and plumes contained I<sup>-</sup> concentrations higher than in surrounding seawater, which indicates iodine reduction to I<sup>-</sup> in vent fluids and during mixing with bottom waters. However the I<sup>-</sup> concentration does not exceed the total iodine measured in the overlying seawater, suggesting that hydrothermal vents recycle the localized seawater iodine. Because I<sup>-</sup> is long-lived even in oxidizing seawater and the deep ocean is primarily the oxidized iodate, one implication is that hydrothermal vent plumes in the ocean interior may be recognized by I<sup>-</sup> anomalies even at extended distances from their source.

## Constraining the Shuram $\delta^{13}\text{C}$ Excursion with the $\delta^{44/40}\text{Ca}$ – $\delta^{88/86}\text{Sr}$ multi-proxy

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The Shuram Excursion (CIE) in Earth's history. Major questions surround whether the CIE resulted from primary or secondary processes, and whether those processes were local, global, or some combination thereof [1,2]. This research aims to address these questions by employing the novel  $\delta^{44/40}\text{Ca}$ - $\delta^{88/86}\text{Sr}$  multi-proxy, which is sensitive to variable mass-dependent isotope fractionation, fluid buffered early diagenesis, and temporal shifts in the isotopic composition of seawater due to end-member mixing.

Utilizing high-precision TIMS techniques, we apply the multi-proxy to the Shuram CIE recorded in carbonate rocks of the Huqf Supergroup, Oman, which was deposited ~574 – 567 Ma [3]. The mineralogy of these samples varies by unit and includes primary aragonite that has neomorphized to calcite, primary calcite, and very early dolomite. We analyzed 30 samples spanning the Khufai, Shuram, and Buah formations. When examined as  $\delta^{88/86}\text{Sr}$  vs.  $\delta^{44/40}\text{Ca}$ , the data broadly define a negative trend with samples grouping by mineralogy. Calcite samples from the nadir of the CIE display among the lowest  $\delta^{88/86}\text{Sr}$ , as well as the highest  $^{87}\text{Sr}/^{86}\text{Sr}$ . The trend between  $\delta^{44/40}\text{Ca}$  and mineralogy appears to fit a diagenetic model where aragonite transforms to calcite and dolomite in the presence of seawater. However, such a model does not explain the complementary trend in  $\delta^{88/86}\text{Sr}$ . No evidence suggests aragonite could initially incorporate heavier Sr isotopes, nor does a mechanism exist to decrease  $\delta^{88/86}\text{Sr}$  through fluid-buffered alteration as carbonates are well-understood to lose Sr during diagenetic transformation. No evidence supports meteoric alteration of  $\delta^{44/40}\text{Ca}$  values [1]. Carbonates kinetically incorporate lighter Ca and Sr isotopes. Therefore, application of kinetic mass-fractionation laws points to a rapid decrease in seawater  $\delta^{88/86}\text{Sr}$  during the Shuram CIE, which appears superimposed on a longer-term increase in  $\delta^{88/86}\text{Sr}$  up-section. End-Ediacaran seawater likely had high  $\delta^{88/86}\text{Sr}$  [4], whereas continental runoff has low  $\delta^{88/86}\text{Sr}$  [5]. Our initial results raise the possibility that seawater-freshwater mixing was a characteristic of this near shore setting, consistent with observations that the onset of the Shuram CIE coincides with a major marine transgression [6].

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## Impacts of Terrestrial Organic Matter on Methanogenic Archaea in Pelagic and Littoral Sediments

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The impacts of climate change are felt across even the most pristine ecosystems. Unprecedented changes in atmospheric carbon dioxide and nitrogen deposition have resulted in increased terrestrial production and export to aquatic systems as terrestrial organic matter (t-OM). Removal of t-OM from lakes is dominated by microbial processes in anoxic sediments. The decomposition of this complex organic carbon to C1 compounds ultimately leads to methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) emissions. These metabolic byproducts are greenhouse gases (GHGs) that can diffuse out of the water column into the atmosphere resulting in positive feedback loops for GHG emissions, accelerating global warming. The factors driving the rates of GHG emissions in freshwater systems, while biotic in nature, depend on a variety of physicochemical characteristics (e.g., morphometry, residence time, littoral coverage, trophic status, and size) and thus, emissions vary spatially and temporally. In this study we use a microcosm and sequencing (next-gen and qPCR) approach to (i) assess the diversity of methanogenic archaea within the sediments of the Mississippi headwaters system, (ii) quantify sediment CH<sub>4</sub> concentrations, (iii) measure CH<sub>4</sub> emissions, community composition, and function given additional t-OM inputs (5% and 15%), all across a morphometric and hydrologic gradient during the open water season in headwater lakes of the Mississippi River. Preliminary results show an uncoupling of production and methanogenic archaea population size in monthly microcosms. We find that methane concentrations are greatest in pelagic sediments where methanogenic archaea are less abundant. Additionally we see differences in population structure based on methanogenesis pathways wherein littoral sites have larger populations of hydrogenotrophic methanogenic archaea in the orders Methanobacteriales and Methanocellales. We also find that additions of t-OM to both pelagic and littoral sediments lead to an increase in CH<sub>4</sub>; however concentrations do not scale linearly to t-OM quantity added. Collectively, these data suggest that the greater microbial community, rather than the abundance of methanogenic archaea, play an important role in the production of CH<sub>4</sub> in both littoral and pelagic sediments.

## Mass balance constraints on euphotic iodine speciation from GEOTRACES meridional and zonal Pacific transects

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The distribution of iodine species in oxic, euphotic settings follows distinct meridional and offshore trends across ocean basins. While these trends are well known, their driving mechanisms are not well resolved, thus impeding quantitative understanding of iodate (IO<sub>3</sub><sup>-</sup>) accumulation in these areas: a prerequisite for understanding redox and other influences on ancient carbonate-associated iodate proxy records. Euphotic iodide (I<sup>-</sup>) accumulation is generally attributed to variations in *in situ* factors of primary productivity, such as IO<sub>3</sub><sup>-</sup> reduction by bacteria and phytoplankton in surface waters. However, slow reported timescales of I<sup>-</sup> oxidation have implied that *ex situ* conservative mixing processes, such as vertical mixing of IO<sub>3</sub><sup>-</sup> sourced from subphotic waters, may have a larger impact on iodine redox species distribution than previously thought. To quantitatively constrain euphotic iodine speciation trends in the Pacific Ocean basin, we used new and published iodine speciation and trace element data from the GEOTRACES GP16 (2013) and GP15 (2018) cruise transects from Ecuador to Tahiti and Alaska to Tahiti, respectively, for mass balance calculations quantifying the contributions of iodine species from *ex situ* sources of upwelling and vertical diffusion in the Pacific. Together, these data demonstrate iodine variations related to non-redox specific processes—e.g., temperature, nutrients, biologic regimes, and conservative mixing—that offer important insights into the controls on IO<sub>3</sub><sup>-</sup> distribution in modern and ancient marine settings.

## Microbial Biogeography of the Eastern Yucatán Carbonate Aquifer

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The Yucatán carbonate aquifer in southeastern Mexico is one of the largest of its kind in the world and is stratified by meteoric freshwater overlying denser saline groundwater ultimately sourced from the ocean. Cenotes act as direct surface connections into the aquifer, where surface detritus and organic carbon can accumulate at the halocline interface [1]. Previous work (e.g., [2-3]) has examined methane- and sulfur-cycling communities in and downstream of specific cenotes. However, relatively isolated conduits represent the vast majority of the aquifer habitat space [1]. The distribution and abundance of these and other key microbes throughout other habitats in the aquifer water column remains underexplored. In our study, a team of experienced cave divers lead by P. Beddows aseptically sampled water from 11 submerged caves in the Eastern Yucatán Carbonate Aquifer. We extracted the DNA collected from 0.2- $\mu$ m filters and sequenced the V4 region of the 16S rRNA gene for taxonomic analysis. We developed a novel network analysis pipeline (<https://github.com/mselesky/bngal>) to create a pairwise co-occurrence model of microbial niche space. Our network theory-based approach demonstrates the presence of several interconnected subnetworks of co-occurring taxa. The prevalence, abundance, and diversity of these subnetworks, termed “EBCs” after the algorithm used to identify them, can strongly vary by both geographic region and water column zone (freshwater, halocline, saline groundwater). EBCs that are highly prevalent and abundant throughout the platform tend to harbor metabolically flexible and/or uncharacterized taxa, such as uncultured ASVs mapped to the family *Comamonadaceae* and order Campylobacterales. By contrast, other EBCs only proliferate within certain caves or water column zones with distinct geochemistries, tending to harbor similarly distinct guilds of taxa. For example, populations of sulfur-oxidizing bacteria (SOB) colonize the halocline of an open pit cenote and are distinct from other SOB in the aquifer in terms of both phylogeny and co-occurrence patterns with other taxa. Our results shed light on the microbial biogeography of this region of the aquifer to inform future studies of the biogeochemical potential of similar karst aquifer ecosystems.

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## Temperature sensitivity of nitrogen mineralization in peat from a southwestern Michigan Bog

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In this study, we measured inorganic nitrogen (nitrate and ammonium) released from peat cores from Miner Lake bog at two temperatures to analyze the impact of climate warming on the peatland nitrogen cycle. We hypothesized a higher nitrogen release in samples incubated at warmer temperatures. Furthermore, previous research indicates shallow peat decomposes faster than deeper peat. Therefore, we hypothesized faster nitrogen mineralization in shallow samples. We collected peat cores from two locations from Miner Lake Bog in Allegan County, Michigan: a plot in the center of the bog and a sedge meadow site near the edge. Two samples for each depth (0-0.5 meter, 1.5-2 meters) were taken at both sites and homogenized. Microlysimeters, consisting of two-chambered filter towers, were acid washed and 20 g of acid washed sand was added to each upper chamber. 50 g of peat was added onto the sand and was left to equilibrate for four days. Microlysimeters were leached with 80 mL of 0.01M CaCl<sub>2</sub> solution and the concentration of nitrate and ammonium in the leachate were quantified using ion chromatography. Microlysimeters were incubated for two weeks before leaching procedures were repeated. A separate field-based cation-anion exchange analysis was performed through the installation of plant root simulators. In both the lab and field experiments, we found that mineralization was higher in surface peat than in more degraded deep peat layers. Additionally, we consistently found that mineralization was higher at the warmer temperature, indicating that warming will increase the rate of nitrogen cycling in peatlands.



## Insights of 2,4-D degradation by Fe(II)-oxidizing bacteria and Fe(III)-reducing bacteria

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The use of the phenoxy herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) has been steadily increasing in the Midwest in recent years due to its selectivity against broad-leaved weeds and use on genetically modified crops for resistance to 2,4-D. The prevalence of 2,4-D increases the chances of its detection in ground and surface water throughout our aquatic systems, particularly in agriculture-dominated landscapes. Microorganisms are capable of degrading 2,4-D enzymatically under oxygenated conditions. Anaerobic pathways also exist, and iron-reducing bacteria (FeRB) have been hypothesized to augment biological degradation through the production of a mineral bound Fe(II) species adsorbed to Fe(III) oxyhydroxides. To test whether this form of iron can catalyze abiotic degradation of 2,4-D, an enrichment (BLA1) was taken from meromictic ferruginous Brownie Lake, Minnesota. The photosynthetic Fe(II)-oxidizing bacterium (FeOB) "*Candidatus Chlorobium masyuteum*" and the FeRB "*Candidatus Pseudopelobacter ferreus*" produce Fe(II)-adsorbed to Fe(III) oxyhydroxides during alternating iron oxidation and reduction cycles during growth. The BLA1 enrichment was cultured with various concentrations of 2,4-D +/- Fe(II) and light. 2,4-D degradation was not seen during iron oxidation by *Ca. C. masyuteum* or during iron reduction FeRB *Ca. P. ferreus* under any condition. Our results cast doubt on whether iron-based abiotic mechanisms aid in the microbial degradation of 2,4-D in soils and waters.

## Optical Characteristics of Chrysotile, an Unhealthy Contaminant in Talcum Powder

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Asbestos minerals have a long history of use in a wide variety of important products, most notably fire protection. Recent decades have seen recognition of the health hazards associated with fibrous minerals; mesothelioma and other lung disorders have afflicted miners and those who manufacture or work with asbestos-containing products, notably shipyard workers installing asbestos fireproofing. Multiple lawsuits have arisen seeking compensation for those asbestos-related illnesses and deaths, and other suits seek redress for cancers claimed to be caused by asbestos-contaminated consumer products such as talcum powder, which is the subject of suits relating to ovarian cancer in particular. This circumstance drives a need for rapid, reliable, and accessible means of identifying asbestos in talc. Chrysotile is a metamorphic hydrated magnesium sheet silicate with a chemical formula very similar to talc, a usually-platy metamorphic hydrated magnesium silicate. Chrysotile's sheets have slightly mismatched atomic spacing, causing the crystals to roll, carpet-like, into fibers. The two minerals are often found in proximity, and mining and milling yields an impure material. Talc rarely takes fibrous form, however, on-edge talc plates may resemble asbestos mineral fibers. These similarities can make differentiation difficult. Talc's optical properties are well-characterized, chrysotile's less so. This work explores an optical microscopy method for characterizing the optical properties of chrysotile with the goal of determining its range of refractive indices (RI) and dispersion curves, and proposes to investigate the effectiveness of this approach to distinguish chrysotile from talc in various mixtures. Using color filters and a thermal stage to determine RI at three wavelengths establishes the Cauchy curve range for chrysotile. Becke line images in white light and central-stop dispersion staining images provide supporting information about RI and help distinguish talc from chrysotile.

## Microbes from Mars Analog Hypersaline Lakes

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Carbonate and MgSO<sub>4</sub> deposits recording the residues of ancient Martian oceans are of great interest to astrobiology due to their potential to preserve organic biosignatures. Analogous environments on Earth demonstrate that life can exist in these extreme conditions and their study can inform preservation mechanisms. The Cariboo Plateau in British Columbia, Canada is home to hypersaline lakes with unique chemistries, such as the Basque Lakes and Last Chance Lake, that resemble Martian deposits. Thus, these lakes provide natural laboratories for probing the habitability and preservation potential of past Martian environments. Currently, the microbial composition of MgSO<sub>4</sub>-dominated and NaCO<sub>3</sub>-dominated systems are understudied relative to the more abundant NaCl-dominated lakes, and the effects of temperature and salinity on microbial diversity and lipid composition in these systems are essentially unknown. Here, we isolate and identify microbes from the Cariboo Plateau lakes to better understand the microbial community and habitability. Additionally, as nucleic acids are highly labile and not preserved on the necessary billion-year timescales, we further characterize the lipid compositions from microbial isolates as robust potential biosignatures. Ongoing research on the environmental lipid compositions of these lakes has detected non-isoprenoidal ether bound membrane lipids, for which we aim to identify and isolate the source. While final identification and characterization are ongoing, we find a diversity of microbial morphologies of both phototrophic and heterotrophic metabolisms growing at temperatures ranging from 4°C to 30°C in media chemistries resembling the environmental waters. We expect the lipid compositions of these organisms to reflect their respective growth conditions and to be reflected in their biosignature profiles. Our data furthers the understanding of membrane lipid adaptations to multiple environmental stressors in high sulfate environments, ultimately providing further insight into potential biosignatures to target in Martian evaporite deposits.

## Chemolithotrophy at pH 12: A look at a serpentinizing system microbial community and its use of sulfur

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Serpentinizing systems are composed of hyperalkaline fluids (pH>10) and are primarily driven by chemosynthesis rather than photosynthesis at their core. They are regularly marked by the presence of geogenic hydrogen and methane, but local geology can also have a strong influence on the geochemistry of these systems. In the case of Ney Springs, a terrestrial system in Northern California, the ultra-reducing serpentinized fluids pass through ophiolite within the Franciscan Complex to create an environment highly enriched in sulfur species such as sulfate (373 mg/L) and sulfide (516-554 mg/L) much higher than what is seen in other serpentinizing systems [1, 2]. While the microbial community of Ney Springs system appears to mainly be composed of fermenters, previous taxonomic and metagenomic data suggest a strong presence of sulfur-utilizing bacteria as well [1]. In this work we focused on elucidating more of taxonomic composition and metabolic capabilities of the sulfur-utilizing members of this community by performing additional 16S rRNA gene surveys and shotgun metagenomic sequencing on serpentinized fluid sources within the system not previously investigated. Sulfur species (thiosulfate, tetrathionate, sulfate, and sulfide) were monitored over time to check for seasonal patterns and stability while species often less-measured *in situ* such as polysulfide were detected for the first time using HgAu microelectrodes and electrochemical techniques [3]. This geochemical, taxonomic, and metagenomic data was then used to guide growth curve experiments on important sulfur-oxidizing members isolated from the community including a *Thiomicrospira* sp. (chemolithoautotroph) and a *Halomonas* sp. (chemolithoheterotroph), to test for their preferential use of varying sulfur-compounds detected within the system.

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## Evaluation of the diatom species *Fragilariopsis kerguelensis* as a Paleotemperature Proxy on the Sabrina Coast

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*Fragilariopsis kerguelensis* is one of the most common diatoms in the Southern Ocean. Due to its high abundance and observed morphological variability, *F. kerguelensis* is of great interest in paleoenvironmental studies, specifically as a potential paleotemperature proxy. Recent studies have proposed that the morphometric descriptor of rectangularity is directly related to temperature, making it a potential candidate for paleotemperature reconstruction. This study evaluates the feasibility of using *F. kerguelensis* as a paleotemperature proxy on the Sabrina Coast, East Antarctica, an area of high interest due to the significant melting potential of the Totten Glacier System. Analysis of a sediment core was based on samples from 19 depths, covering the entire Holocene. Shape analysis software was used to collect morphometric measurements. In contrast with previous studies, which documented two modal values of rectangularity corresponding to climatic variation, along the Sabrina Coast only a single rectangularity class was observed, with limited downcore variation. A concurrent study analyzed morphometric variation of the diatom from seven sites on the Sabrina Coast shelf and slope, yielding results again inconsistent with existing literature, as the samples demonstrate uniformly low rectangularity across sites and no evidence of two distinct *F. kerguelensis* populations. The lack of variation within the core and across surface sites suggests that rectangularity is not an applicable proxy for paleotemperature in this region and that further research into the link between *F. kerguelensis* variation and bioregionalization in the Southern Ocean is warranted.

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## Landscape evolution during the Middle Devonian: Evidence from an Old Red Sandstone lacustrine sequence

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The Devonian (419-359 Ma) represents a dynamic period in Earth's history with significant biotic, geologic, and climatic events coincident with two major extinction events and numerous marine anoxic events. In addition, this period is characterized by a major expansion of land plants including the evolutionary innovation of advanced root systems and subsequent induction of modern soil formation processes. These processes significantly altered landscapes, enhanced nutrient mobility, and likely influenced water column anoxia. We turned to lake records to better understand landscape stability at the inception of soil formation. Here we present isotopic and geochemical evidence of Mid Devonian lacustrine samples from the Orcadian Basin of the Old Red Sandstone continent. Collected from northern Scotland/Orkney, these samples coincide with the Kačák extinction event and the inception and spread of the progymnosperm Archaeopteris. The Kačák is characterized by widespread marine anoxia and is correlative with evidence of both global eustasy and regional strengthening of orbitally induced monsoonal activity. The Devonian lacustrine sequences have  $\delta^{13}\text{C}_{\text{org}}$  values ranging from -34 to -22‰ that exhibit systematic transitions between positive and negative carbon isotope excursions. Negative carbon isotope excursions correlate with high P, C/N, Sr/Cu, and redox-sensitive elements while positive carbon isotope excursions tend to track increased Rb/Sr coinciding with low Sr/Cu and TOC. This suggests that the lake systems underwent periods of enhanced P flux during wet periods as a result of both increased runoff and elevated P mobilization through stimulated terrestrial plant growth and subsequent shift toward terrestrial organic matter  $\delta^{13}\text{C}_{\text{org}}$  values. Older sediments in the sequence have high amounts of iron. In comparison, younger sediments have a substantial decrease in Fe and P as well as periodicity between Fe, P, and climatic and weathering proxies. This could suggest a heavily weathered unstable landscape followed by a decrease in landscape reworking with periodic nutrient flux, potentially driven by climatically controlled enhanced monsoonal activity.

## Microbes to Meta: Mapping Food Chain Dynamics of Mammoth Cave using Stable Isotopes

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Many cave systems are known to contain abundant microbial biofilms and chemosynthetic microbes in their sediments, yet the role of these organisms in the greater food web has not been explored. To bridge this gap, we focus on Mammoth Cave National Park, KY – the longest mapped cave system on Earth – which offers a diverse array of environmental conditions including natural entrances with active bat populations and regions without historical animal use. We measured bulk carbon and nitrogen stable isotope analysis (SIA) of biofilms, sediments, and macroscopic organisms (crickets, spiders, etc.), then paired them with 16S rRNA microbial gene sequencing, and field measurements to examine food web dynamics across the system. We have found that cave macro-organisms occupy distinct trophic levels based on bulk C and N isotopic enrichment. Microbial biomass is on average 3‰ more <sup>15</sup>N-depleted compared to basal cave fauna, suggesting that microbial communities may act as primary producers within the cave system. The  $\delta^{13}\text{C}$  values of cricket excrement and tree roots (both derived from surface vegetation) are  $\sim -28\text{‰}$  which is <sup>13</sup>C-enriched relative to microbial samples with average values of  $\sim -30\text{‰}$ . These results suggest that select primary consumers feed on in situ microbial biomass rather than detritus from the surface. Forthcoming compound-specific isotope analysis (CSIA) of amino acids will be used to clarify the trophic positions of different organisms and quantify microbial contributions to the subsurface ecosystem. Combined with ongoing biogeochemical and ecological analyses, these results will clarify the roles of microbial communities in subsurface N and C cycling as well as in food webs across other environments.

## Investigation of Denitrification Processes in Shallow Groundwater near Grand Traverse Bay, Michigan

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### Abstract

Human activities impact groundwater quality in a number of ways including through the introduction of pathogens, nutrient loading, organic contaminants, and metals. These activities likely imprint the microbial communities found in groundwater in ways that can be queried using microbiological methods. We used groundwater samples from a shallow aquifer in the Grand Traverse Bay (GTB) region of Michigan's lower peninsula to test this hypothesis. In the GTB potential sources of pollution include agriculture, industry, (waste water treatment plants), and municipal, and point sources of wastewater. Microbial impacts upon the nitrogen cycle (e.g. through denitrification) were used as an initial window into these processes [2], as intake of high nitrate concentrations can have detrimental health effects, and high nitrate is a common proxy for other contaminants [1,3]. Groundwater samples were collected and used to carry out amplicon-based sequencing of the 16S rRNA gene and shotgun metagenomics. In parallel, water was used to obtain microbial isolates on Nitrate Minimal Salts (NMS) and organotrophic (R2A) media. Results of the culture-independent work showed that groundwater red-ox state and pH played important roles in shaping microbial community structure. Analyses of metagenome assembled genomes confirmed the widespread occurrence of denitrification pathways and their enrichment in sites with high nitrogen loads. Finally, cultivation based analyses yielded isolates that coincided with the sequence-based work, particularly on NMS medium. Ongoing work is aimed at document the occurrence of other contaminant signals in the microbial genomes. Taken together, these results show that groundwater microbial communities reflect the predominant contaminant sources at the land surface and may be used to further investigate the presence of some of other human-introduced contaminants.

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## Modeling the Geochemical Behavior of Methane Seeps & Inferring Paleo-seep Conditions from Microscale Textural and $\delta^{34}\text{S}$ Heterogeneities in Seep Barite

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Cold seeps can sustain high rates of anaerobic oxidation of methane by sulfate reduction (AOM-SR) & promote the precipitation of unique authigenic mineral assemblages. As an integral component of the global carbon cycle, there is broad interest in understanding the reactive transport of methane in seep environments. Modern seep conditions - including upwelling rate, methane concentration, and the transport of reactive metals - can be measured directly or calculated from porewater analyses, but relatively little is known about past conditions, especially at a quantitative level. Recently, we've shown high amplitude cyclic changes in the  $\delta^{34}\text{S}$  composition of authigenic seep barite that were interpreted to reflect secular changes in methane flux. In this study, we present a novel geochemical model to characterize the physical and biogeochemical factors that modulate seep behavior and how microscale textural and  $\delta^{34}\text{S}$  heterogeneities in barite may provide insight into past seep conditions. The geochemical model accounts for sediment porosity, sulfate diffusion, advection rate, and both methane and barium concentrations to calculate anaerobic oxidation of methane by sulfate reduction (AOM-SR) activity, the depth of the sulfate-methane transition zone (SMTZ), and both the abundance and  $\delta^{34}\text{S}$  compositions of authigenic barite with depth. Modeling results are compared and validated against empirically measured micro-scale textural and  $\delta^{34}\text{S}_{\text{BaSO}_4}$  heterogeneities in authigenic barite from an array of cold seep environments. Based on secondary ion mass spectrometry (SIMS) analyses and scanning-electron microscope (SEM) imagery, microscale (10-100  $\mu\text{m}$ )  $\delta^{34}\text{S}_{\text{BaSO}_4}$  and textural heterogeneities appear relatively common in seep barite; the range and magnitude of these microscale  $\delta^{34}\text{S}_{\text{BaSO}_4}$  heterogeneities appear consistent with temporal changes in methane and/or barium flux, sediment porosity, or upwelling rate based on geochemical modeling results.

## Quantifying the physiological changes in NADH in *S. oneidensis* in response to extracellular electron uptake

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*Shewanella oneidensis* MR-1 is a Gammaproteobacteria capable of both accepting and donating electrons from solid surfaces, making it an important model organism for studying extracellular electron transfer (EET). Though originally isolated for its capacity to reduce solid minerals in the environment, MR-1 is also capable of the reverse process, taking up electrons from poised potential electrodes. Extracellular electron uptake in *S. oneidensis* has been shown to result in energy conservation (generation of an electrochemical gradient and ATP) and the ability to produce reducing power (i.e., NADH) via reverse electron flow [1]. This NADH generation through extracellular electron uptake is dependent on proton motive force (PMF) [2]. However, the mechanics, and or the environmental conditions under which NADH is generated in response to extracellular electron uptake are still poorly understood. One important challenge is the ability to reliably measure NADH *in vivo* under electron uptake conditions. To address this issue, we are investigating two different NADH fluorescent reporter systems capable of detecting cellular NADH concentrations Using fluorescent reporter systems in MR-1, we will quantify NADH changes in response to extracellular electron uptake by investigating conditions that vary biological electron uptake or current density. This work will help elucidate the relationship between biological current and reverse electron flow, and ultimately help us understand the conditions under which MR-1 exchanges electrons with its environment.

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## Silica inhibits biological iron oxidation and mineral evolution in an Archean ocean analog

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Banded iron formations (BIFs) are one of the best surviving records of the geochemistry of the Archean and early Proterozoic oceans. These iron-rich and siliceous chemical sedimentary rocks precipitated from seawater that was largely anoxic ( $O_2 < 1 \mu\text{M}$ ), ferruginous (0.03-1 mM  $\text{Fe}^{2+}$ ), and enriched in dissolved silica (0.67-2.2 mM)<sup>1,2,3</sup>. The mechanism for the deposition of BIF precursor minerals remains enigmatic, especially prior to the rise of atmospheric oxygen ~2.43-2.22 billion years ago (Ga)<sup>4</sup>.

The activity of anoxygenic photoferrothrophic bacteria, which oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  using light as an energy source, presents a plausible mechanism for the precipitation of partially to fully oxidized Fe phases in anoxic systems. However, previous studies exploring Fe oxidation in ferruginous and high-silica waters have drawbacks with regards to understanding biologically mediated BIF genesis. Few experiments exploring Archean-like systems have included photoferrothrophs, and those that do usually rely on high concentrations of Fe and Si—up to an order of magnitude greater than inferred Archean ocean concentrations—to increase the extent of precipitation<sup>5,6</sup>.

Here I present results from an experiment in which batch cultures of the photoferrothroph *Rhodospseudomonas palustris* TIE-1 were grown under anoxic conditions in defined media representative of the Archean ocean (pH = 7.0, 1.0 mM starting  $\text{Fe}^{2+}$ ), with varying levels of Si (0-1.5 mM). Resulting precipitates were characterized using a combination of wet geochemical methods, scanning electron microscopy, and transmission electron microscopy. Higher concentrations of Si were found to inhibit the extent of Fe oxidation and hinder the transformation of poorly crystalline  $\text{Fe}^{3+}$  (oxyhydr)oxides to more crystalline phases such as lepidocrocite ( $\gamma\text{-Fe}^{3+}\text{O}(\text{OH})$ ). These results suggest that silica could have played an important role in determining the mineral precursors of BIFs by promoting Fe-Si precipitation, stabilizing early-forming Fe phases, and/or inhibiting  $\text{Fe}^{2+}$ -induced mineral transformation.

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## Nitrogen tracking reveals active protein biosynthesis in the surface ocean

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Microbial growth in much of the surface ocean is limited by nitrogen availability, but we know little about the dynamic allocation of this scarce resource among cellular functions in different members of the community. Here we use a novel combination of quantitative isotope-tracking proteomics approaches to assay biosynthetic incorporation of <sup>15</sup>N-labeled nitrogen substrates into the community proteome in the North Pacific subtropical gyre. We find that short term N incorporation is dominated by specific taxa and metabolic functions, revealing a subset of the community proteome that undergoes active biosynthesis. The cyanobacterium *Prochlorococcus* is the most effective competitor for acquisition of ammonium and urea and shifts its proteomic allocation of N over the day/night cycle. Cellular infrastructure functions including protein translation, folding, and turnover comprise the bulk of the biosynthetic N demand for abundant microbial taxa. This proteomic window on in situ competition and allocation of nitrogen reveals substantial variability between taxa in the metabolic basis of N limitation and illuminates the flow of nitrogen in the surface ocean.