

# 2014 Northeastern Geobiology Symposium



Yale

O. C. MARSH  
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# Northeastern Geobiology Symposium 2014

March 29th, 2014  
Yale University, New Haven, CT



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## Schedule

The oral presentations will be held in the Kline Geology Lab room 123, poster presentations and meals will be spread out between the main auditorium of the building and room 102.

**9:20 am**

Light Breakfast

**10:00 am**

Oral Presentation Session 1

**12:00 pm**

Lunch

**12:30 pm**

Poster Session 1

**1:40 pm**

Oral Presentation Session 2

**3:20 pm**

Coffee Break

**3:00 pm**

Oral Presentation Session 3

**4:40 pm**

Coffee and Poster Session 2

**6:00 pm**

Dinner

**6:30 pm**

Poster Session 3

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## Oral Presentation Schedule

### Oral Presentation Session 1

#### 10:00am - 10:20am

Stratigraphic expression of Earth's deepest  $\delta^{13}\text{C}$  excursion in the Wonoka Formation of South Australia

*Jon M Husson\**, Adam C Maloof, Blair Schoene, Christine Y Chen, John A Higgins

#### 10:20am-10:40am

A metabolically versatile cyanobacterium and the low-oxygen Proterozoic world

*Trinity L Hamilton\**, Judith Klatt, Laurence Bird, Katherine H Freeman, Dirk de Beer, Jennifer L Macalady

#### 10:40am-11:00am

Chemostratigraphy of the Cryogenian Taishir Formation, Zavkhan basin of Mongolia

*Uyanga Bold\**, Francis Macdonald, Daniel Schrag, David Johnson

#### 11:00am-11:20am

Redox stability and mineralogy of biogenic iron oxides from Calumet Mine, Quebec, Canada

*Sarina Cotroneo\**, L FZ Guimaraes, E Duchesne, D Fortin

#### 11:20am-10:40am

Marine trace-metal drawdown during the Cenomanian-Turonian Oceanic Anoxic Event and implications for global redox and biological perturbation

*Jeremy Owens\**, Christopher T Reinhard, Megan Rohrssen, Gordon D Love, Timothy W Lyons

#### 11:40am-12:00pm

Assessing the distribution of carotenoids through time using tandem mass spectrometry

*Katherine L French\**, D Rocher, J E Zumberge, R E Summons

### Oral Presentation Session 2

#### 1:40pm-2:00pm

A major, trace element and pyrite multiple sulfur isotope record from the Neoproterozoic of Svalbard; Seawater sulfate limitation associated with low-latitude glaciations?

*Marcus Kunzmann\**, Galen P Halverson, Boswell A Wing, Clint Scott, William G Minarik

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**2:00pm-2:20pm**

Early Cambrian biostratigraphy in the Zavkhan basin in western Mongolia

*Emily F Smith\*, Francis A Macdonald, Tanya N Petach, Uyanga Bold*

**2:40pm-3:00pm**

Extreme environmental changes accompanying the Marinoan deglaciation: multiple O and S isotope evidence from NW Canada

*Peter Crockford\*, Benjamin R Cowie, Thi Hao Bui, André Pellerin, Ichiko Sugiyama, Justin Hayes, Paul F Hoffman, Francis Macdonald, Galen P Halverson, David T Johnston, Boswell A Wing*

**3:00pm-3:20pm**

Protracted development of the mixed layer: Implications for substrate evolution and exceptional preservation in early Paleozoic marine shelfal environments

*Lidya G Tarhan\*, Mary L Droser*

**Oral Presentation Session 3**

**4:40pm-5:00pm**

Multiple Equilibria of pO<sub>2</sub>

*Thomas Laakso\*, Daniel Schrag*

**5:00pm-5:20pm**

Metagenomics, single cell genomics, and steady-state free energy flux provide insight into the biogeochemical cycling of deep, meteoric water

*Cara Magnabosco\*, Kathleen Ryan, Maggie Lau, Greg Slater, Esta van Heerden, Barbara Serwood-Lollar, Tullis Onstott*

**5:20pm-5:40pm**

Sulfur isotope fractionation during reduction of sulfate by *Desulfovibrio fructosovorans*

*David T Wang\*, Shuhei Ono, Tanja Bosak*

**5:40pm-6:00pm**

Contrasting the population structure of macroscopic benthic communities across the Precambrian-Cambrian boundary

*Simon Darroch*

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## Stratigraphic expression of Earth's deepest $\delta^{13}\text{C}$ excursion in the Wonoka Formation of South Australia

Jon M Husson<sup>\*1</sup>, Adam C Maloof<sup>1</sup>, Blair Schoene<sup>1</sup>, Christine Y Chen<sup>1,2</sup>, John A Higgins<sup>1</sup>

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\*Presenter (jon.husson@gmail.com)

The most negative carbon isotope excursion in Earth history is found in carbonate rocks of the Ediacaran Period (635–542 Ma). Known colloquially as the 'Shuram' excursion, workers have long noted its tantalizing, broad concordance with the rise of abundant macro-scale fossils in the rock record. Thus, many interpretations of the Shuram depend upon a dramatically changing redox state of the Ediacaran oceans. More recently, diagenetic models have challenged the various primary models. Here, we present chemo-stratigraphic data ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{44/42}\text{Ca}$  and trace element abundances) from the Ediacaran-aged Wonoka Formation of South Australia that require a syn-depositional age for the extraordinary range of its  $\delta^{13}\text{C}$  values (-12 to +4 permil). Fabric-altering diagenesis, where present, occurs at the sub-meter vertical scale and results in sub-permil offsets in  $\delta^{13}\text{C}$ . In some localities, the Wonoka formation is host to deep (~1 km) paleocanyons, which are partly filled by carbonate clasts sourced from eroded Wonoka canyon-shoulders. By measuring the isotopic values of the clasts, we show that canyon-shoulder carbonates acquired their  $\delta^{13}\text{C}_{carb}$ - $\delta^{18}\text{O}_{carb}$  values before brecciation and redeposition in the paleocanyons, thereby ruling out late stage alteration models and placing interpretations that depend upon the Ediacaran redox state on firmer ground.

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## **A metabolically versatile cyanobacterium and the low-oxygen Proterozoic World**

Trinity L Hamilton<sup>1\*</sup>, Judith Klatt<sup>2</sup>, Laurence Bird<sup>1</sup>, Katherine H Freeman<sup>1</sup>, Dirk de Beer<sup>1</sup>, Jennifer L Macalady<sup>1</sup>

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The delay in the rise of oxygen to present day levels at the end of the Proterozoic represents an important gap in our understanding of ancient biogeochemical cycling. Little Salt Spring, a karst sinkhole in Sarasota County, FL, USA, water has low sulfate concentrations (<5 millimolar) and micromolar concentrations of both oxygen and sulfide in the photic zone, similar to ocean surface conditions expected during long stretches of the Proterozoic. Red microbial pinnacle mats which are rich in 2-methyl bacteriohopanepolyols, an important microbial biomarker, occupy the sediment-water interface in the sunlit upper basin of the sinkhole. We isolated a dominant member of the pinnacle mat, a red cyanobacterium, which is capable of primary productivity by anoxygenic photosynthesis and also produces 2Me-BHPs. *in situ* analyses indicate the isolate is capable of performing anoxygenic photosynthesis in the pinnacle mats. Physiological characterization suggests the isolate is poised to rapidly switch between oxygenic and anoxygenic photosynthetic activity. We discuss the role of this metabolic versatility *in situ* and as a mechanism that could have stabilized the low-oxygen Proterozoic world in the presence of oxygenic phototrophs.



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## Chemostratigraphy of the Cryogenian Taishir Formation, Zavkhan basin of Mongolia

Uyanga Bold\*, Francis Macdonald, Daniel Schrag, David Johnson

Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA 08138

\*Presenter (ubold@fas.harvard.edu)

The Taishir Formation is composed of exceptionally low grade, well-preserved and well-exposed carbonates that are bound by Sturtian and Marinoan glacial deposits. Here we report new mapping, stratigraphic, petrographic, carbon and sulfur isotope, and elemental concentration data. Undolomitized sections record the Taishir anomaly in carbonate carbon across the basin. Carbonate associated sulfur and pyrite sulfur isotopes from the Taishir Formation covary and are extremely enriched. We also mapped out and sampled dolomite fronts in the Taishir Formation to better understand the effect of dolomitization on geochemical proxy records. The carbon isotopic composition of samples from dolomitized sections is as much as 8 ‰ different than undolomitized sections. On smaller scales, we found variable carbon isotope signatures that are texture dependent. Carbon isotopes varied by up to 3 ‰ in partially dolomitized sequences whereas the variability is much less, up to 1 ‰, or almost negligible in completely dolomitized sequences of the Taishir. We propose that this variability is due to replacement and recrystallization from a dolimitizing fluid during the post-Marinoan transgression. These data do not compromise the interpretation of the Taishir anomaly as a primary, basinal, if not global signal, but do help distinguish the effects of dolomitization on these chemostratigraphic records.

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## Redox stability and mineralogy of biogenic iron oxides from Calumet mine, Quebec, Canada

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Often displaying poorly ordered mineralogical structures, bacteriogenic iron oxides (BIOS) form in close association with bacterial cells, exudates and bacterial exopolysaccharides. In combination with a range of functional groups of the contained organic material, these ferric oxides cell composites have the capacity to sorp heavy metals such as zinc, lead, and copper. Samples were collected from the drainage basin of a Cu-Zn-Pb mine during the summer, and fall of 2012, and spring of 2013 to gain insights on the physiochemical controls of the microbial community and sorption capacity of the BIOS. Microbial reduction of BIOS by *Shewanella putrefaciens* under anaerobic conditions investigated their redox stability. While previous studies have shown variations in mineralogy and microbial communities with season, XRD analysis of Calumet BIOS shows little change in mineralogy. The cycling of metals in the environment is intimately linked to the redox loop carried out by iron-oxidizing and iron reducing bacteria, as well as the sorptive capacity of the BIOS. A thorough understanding of the formation and stability of BIOS is therefore critical to the development of effective bioremediation strategies, and to the broader study of heavy metal cycling in the environment.

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## Marine trace-metal drawdown during the Cenomanian-Turonian Oceanic Anoxic Event and implications for global redox and biological perturbation

Jeremy D Owens<sup>\*1,2</sup>, Christopher T Reinhard<sup>3</sup>, Megan Rohrssen<sup>1,4</sup>, Gordon D Love<sup>1</sup>, Timothy W Lyons<sup>1</sup>

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The global redox state of the oceans during periods of widespread organic-carbon deposition is an essential to understand of Earth's climatic feedbacks. The Cretaceous is renowned for several global organic-carbon burial events marked by coeval positive carbon isotope excursions now widely known as oceanic anoxic events (OAEs). Here we present a high-resolution compiled data set from Demerara Rise spanning the Cenomanian-Turonian (93.9 Ma) or OAE2, which shows a dramatic drawdown of redox-sensitive trace elements. Independently, Demerara Rise is characterized by local euxinia (i.e., anoxic and sulfidic bottom waters) throughout the analysed section. The drawdown of Mo, an effective euxinic tracer, coincides with the onset of OAE2, suggesting a global expansion of reducing and/or euxinic conditions. Significantly, the drawdown of V prior to the OAE, 100 kyr, suggests an expansion of low oxygen but non-euxinic conditions preceding the event. Parallel lipid biomarkers analyses provide compelling evidence for a reorganization of marine microbial ecology during the OAE, with the smallest eukaryotic contributions to total primary production, compared to bacteria, occurring during metal depleted intervals. Mo and V drawdown may have impacted the nitrogen cycle and thus patterns of primary production, and this feedback may have contributed to the termination of the OAE.

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## Assessing the distribution of Carotenoids through time using tandem mass spectrometry

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Two types of tandem mass spectrometry were used to analyze marine rock extracts and oils for fossil green and purple sulfur bacterial C40 carotenoids. These results reveal a new temporal distribution of chlorobactane, paleorenieratane, and okenane in marine samples through geologic time. One interpretation of the revised secular distribution of these compounds is that marine photic zone euxinia (PZE) was more intense and frequent in the geologic past than was previously thought. However, the occurrence of okenane and chlorobactane in marine samples deposited in intervals characterized by atmospheric oxygen levels close to modern levels presents several challenges. For example, the only modern marine okenone or chlorobactene detections have been in sediments of highly restricted coastal water bodies, but these compounds have yet to be detected in larger marine sulfidic environments. In unrestricted, coastal environments turbulent mixing inhibits the development of a sulfidic chemocline stable and shallow enough to promote okenone and/or chlorobactene production in the water column. Therefore, okenane and/or chlorobactane detection in ancient coastal systems likely reflects a high degree of basin restriction, benthic sedimentary sources, or an allocthonous origin. Future research of modern environments and transport pathways of photosynthetic sulfur bacterial carotenoids will better constrain the potential of these additional inputs.

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## **A major, trace element and pyrite multiple sulphur isotope record from the Neoproterozoic of Svalbard: Seawater sulphate limitation associated with low-latitude glaciation?**

Marcus Kunzmann<sup>1,2\*</sup>, Galen P Halverson<sup>1,2</sup>, Boswell A. Wing<sup>1,2</sup>, Clint Scott<sup>3</sup>, William G. Minarik<sup>1</sup>

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The Svalbard archipelago hosts a roughly 7km-thick Neoproterozoic succession that records global perturbations of the biosphere, like the Bitter Springs negative carbon isotope anomaly and the Sturtian and Marinoan glaciations. We analyzed the major element (Fe/Al), trace Element (Mo, U), and pyrite multiple sulfur isotopic composition of organic-rich shales deposited on a broad, thermally subsiding continental shelf between 835 and 615 Ma (Akademikerbreen and Polarisbreen groups). Shales deposited during this interval are not distinguished by enrichment of redox sensitive elements, with the exception of three distinct intervals. Significantly elevated Fe/Al ratios and slight enrichment of U coincide with the ca. 810–800 Ma Bitter Springs isotope anomaly, whereas the pre-Sturtian interval (ca. 750–730 Ma) shows mild enrichments of U and Fe/Al. Shales deposited during the post Marinoan interval contain significant enrichments of Mo, U, and Fe/Al. These results indicate that the basin experienced expanded basinal anoxia during the Bitter Springs anomaly and the prelude and recovery from the Cryogenian glacial epoch.  $\delta^{34}\text{S}$  pyrite values throughout the succession are highly variable and range from -30 to +30‰, akin to published data from other coeval basins. These data suggest varying degrees of open or closed system sulfate reduction. However, multiple sulfur isotopes in shales of the pre-Sturtian and post-Marinoan interval define distinct Rayleigh fractionation trends, which may indicate extreme seawater sulfate limitation associated with Neoproterozoic low latitude glaciations in Svalbard.

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## Early Cambrian biostratigraphy in the Zavkhan basin in Western Mongolia

Emily F Smith, Francis A Macdonald, Tanya N Petach, Uyanga Bold

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\*Presenter (efsmith@fas.harvard.edu)

The Precambrian-Cambrian boundary is one of the most fundamental biological transitions in the geological record, however characterizing the boundary itself and origination rates during the earliest Cambrian has proven to be difficult. The documentation of origination rates depends on the accurate documentation and interpretation of first and last appearances of fossils. The Zavkhan Basin in western Mongolia hosts rich small shelly fossil, archaeocyathid, and trace fossil records within a thick, mixed siliciclastic and carbonate succession, providing an opportunity to more precisely calibrate evolutionary changes in a sequence- and chemo-stratigraphic context. Here we present refined geological mapping, biostratigraphy and carbon isotope chemostratigraphy in the Zavkhan Basin, and present these in the context of a facies model and sequence stratigraphy for the basin. These data highlight the strong taphonomic biases and facies dependence for the preservation of late Ediacaran and early Cambrian fossils, and provide a revised record of the timing and nature of the Cambrian radiation.

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## Extreme environmental changes accompanying the Marinoan deglaciation: Multiple O and S isotope evidence from NW Canada

Peter Crockford<sup>\*1</sup>, Benjamin R Cowie<sup>2</sup>, Thi Hao Bui<sup>1</sup>, André Pellerin<sup>1</sup>, Ichiko Sugiyama<sup>1</sup>, Justin Hayes<sup>4</sup>, Paul F Hoffman<sup>2,3</sup>, Francis Macdonald<sup>2</sup>, Galen P Halverson<sup>1</sup>, David T Johnston<sup>2</sup>, Boswell A Wing<sup>1</sup>

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The Marinoan snowball Earth glaciation ca. 635 Ma punctuates the tumultuous environmental transition from the Cryogenian to Ediacaran period, with some of the most unusual isotopic shifts found in the stratigraphic record [1]. Triple oxygen isotopes of sulfate deposited in the Marinoan aftermath suggest extremely high pCO<sub>2</sub>, supporting a snowball Earth scenario [2]. Here we explore environmental changes accompanying the Marinoan deglaciation, through measurements of multiple oxygen ( $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ) and multiple sulfur isotopes ( $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ ) on barites collected from the top of the Ravensthorpe cap carbonate in northwest Canada. Our oxygen isotope data documents the extreme  $\Delta^{17}\text{O}$  depletion that to date has been recorded in four other paleo-continent [2,3,4,5]. We record  $\Delta^{17}\text{O}$  values as low as -0.75‰ at the base of the barite layer, and values near -0.1 ‰ at the top. Likewise sulfur isotope compositions show large variations, with  $\delta^{34}\text{S}$  values ranging between +27 and +45 ‰ in barite, and between -6 and +33 ‰ from trace pyrite inclusions within the barite. The  $\Delta^{33}\text{S}$  values from both S pools (sulfate and sulfide) vary between -0.037 and +0.086 ‰. In a genetic framework, the S isotopic covariation occurring within the barite layer places firm constraints on the dynamic evolution of size and microbial influences on the post glacial marine sulfate reservoir. Furthermore this uniquely coupled data set allows us to explore the relative influence of pCO<sub>2</sub> and primary production on evolving  $\delta^{17}\text{O}$  values in the immediate aftermath of the Marinoan glaciation.

[1] Hoffman et al, (1998), Science 281, 1342-1346

[2] Bao et al, (2008), Nature 453, 504-506

[3] Killingsworth et al, (2013), PNAS

[4] Bao et al, (2011) Precambrian Research 216-219, 152-161

[5] Bao et al, (2009) Science 323, 119-122

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## **Protracted development of the mixed layer: Implications for substrate evolution and exceptional preservation in early paleozoic marine shelfal environments**

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The radiation of burrowing metazoans in the early Phanerozoic dramatically altered the properties of marine sediments, an event commonly referred to as the “Cambrian substrate revolution” or “agronomic revolution.” The advent of infaunalization and biogenically-mediated sediment mixing profoundly impacted the development of Phanerozoic biogeochemical cycling, including nutrient fluxes, organic carbon burial, seafloor oxygenation and sediment ecology. However, the timing of the development of mixing has, historically, not been well constrained. Mixing has long been assumed to occur at the Precambrian–Cambrian boundary with the appearance of the index fossil and three-dimensional burrow *Treptichnus pedom*. We present new ichnological, stratigraphic and taphonomic data, from a range of lower to middle Paleozoic siliciclastic successions spanning four paleocontinents, suggesting that shelfal sediments in the early Cambrian were essentially unmixed. Moreover, we demonstrate that even as late as the Middle–Late Silurian, nearly 120 million years after the Precambrian–Cambrian transition, infaunal mixing of shelfal sediments had still not attained modern reworking intensities. These data indicate that in spite of concurrent advances in infaunalization, mixed layer development was a protracted process, challenging assumptions that mixing occurred with the first appearance of three-dimensional burrows and holding important implications for the advent of modern-style biogeochemical cycling.



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## Multiple Equilibria of $pO_2$

Thomas Laakso\*, Daniel Schrag

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\*Presenter (laakso@fas.harvard.edu)

Atmospheric  $pO_2$  has changed by orders of magnitude over Earth history, punctuated by major oxidation events at either end of the Proterozoic. We propose that a single dynamical framework should be able to explain both these events, and the intervening steady state values of  $pO_2$ . The low oxygen Archean can be explained as a stable balance between organic carbon burial and oxidative reactions in a hydrogen-rich atmosphere maintained by slow Jeans escape of  $H_2$ . At substantially greater  $pO_2$  values, oxygen absorption of UV supports a warm thermosphere and fast escape, limiting the hydrogen sink for  $O_2$ . This defines the Proterozoic state, in which the regulating feedback is instead oxygen-dependent organic carbon burial. This feedback decreases organic burial as  $pO_2$  rises, preventing stabilization at higher oxygen values unless there is a compensating increase in primary production. Therefore, the high-oxygen Phanerozoic is only possible if there exists a positive feedback linking phosphorus inputs to  $pO_2$ . This relationship may arise from the kinetics of iron oxidation and P adsorption. These dynamics support three stable states for  $pO_2$ . Transitioning between the states requires large oxygen perturbations. These may be linked to the Snowball events in the Paleo- and Neoproterozoic through changes to humidity and air-sea gas exchange, respectively.

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## Metagenomics, single cell genomics, and steady-state free energy flux provide insight into the biogeochemical cycling of deep, meteoric water

Cara Magnabosco<sup>\*1</sup>, Kathleen Ryan<sup>1</sup>, Maggia Lau<sup>1</sup>, Greg Slater<sup>2</sup>, Esta van Heedren<sup>3</sup>, Barbara Serwood-Lollar<sup>4</sup>, Tullis Onstott<sup>1</sup>

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Here, I present an integrated analysis of steady-free energy flux and whole genome metagenomic data of 3.1 km deep water collected from a borehole (TT107) located in AngloGold Ashanti's TauTona Au Mine of South Africa and intersecting a fracture within a Witwatersrand Supergroup quartzite. The low salinity fracture water encountered at this depth is meteoric in origin and has a subsurface residence time on the order of a few thousand years. Aqueous geochemistry and estimated steady-state free energy flux values suggest that redox reactions are driven by the oxidation of abundant, energy-rich substrates including H<sub>2</sub>, CO, and propane. The majority of the metagenome's sequences related to the phyla Firmicutes, which contain several bacterial species that known to reduce sulfate and fix nitrogen. The methane at this site is of abiological origin ( $\delta^{13}\text{C-C1-3} = -43.5$  to  $-44.3$  VPDB;  $\delta^2\text{H-C1-3} = -345$  to  $-200$  VSMOW) despite the metagenome containing several sequences that are closely related to methanogens in the archaeal phyla Euryarchaeota. Sequences relating to methane monooxygenase are also present indicating the potential for aerobic oxidation of the abiogenic hydrocarbons at low pO<sub>2</sub>. Gene products involved in microbial denitrification and anammox are also present but in low abundance. Together, these results provide a new, multi-dimensional picture of the biogeochemical cycling and microbial communities within the Witwatersrand Supergroup and terrestrial deep subsurface

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## Sulfur isotope fractionation during reduction of sulfate by *Desulfovibrio fructosovorans*

David T Wang<sup>\*1,2</sup>, Shuhei Ono<sup>1</sup>, Tanja Bosak<sup>1</sup>

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\*Presenter (dtw@mit.edu)

Microbial dissimilatory sulfate reduction involves the oxidation of organic matter and concomitant production of isotopically-light sulfides. Constraining the physiological conditions that affect the magnitude of this isotopic fractionation ( $^{34}\epsilon$ ) is important because  $^{34}\epsilon$  is a critical parameter in historical reconstructions of the carbon and sulfur cycles. The largest known fractionations produced by sulfate reducers in pure culture have been associated with slow respiration of “refractory” organic substances (e.g., sugars and aromatic compounds). These substances have not traditionally been considered major carbon and energy sources for sulfate-reducing bacteria, and as a result, the sulfur isotope effects associated with degradation of complex organic material has received sparse consideration. To address this gap, we measured sulfur isotope fractionation factors in batch cultures of *Desulfovibrio fructosovorans* grown on fructose, pyruvate, and lactate. This bacterium fractionated sulfur isotopes by up to 31‰ when growing on fructose. The measured fractionation factors and cell-specific sulfate reduction rates displayed an inverse correlation. We compare our results to those obtained in previous studies on other bacterial strains, and propose further studies aimed at understanding the mechanisms responsible for the generation of large  $^{34}\epsilon$  during microbial sulfate reduction

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## **Contrasting the population structure of macroscopic benthic communities across the Precambrian-Cambrian boundary**

Simon Darroch

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USA 06511

\*Presenter (simon.darrach@yale.edu)

Previous authors have hypothesized a fundamental change in the particulate size of bioavailable carbon over the Ediacaran-Cambrian boundary. This model hypothesizes that the evolution of eukaryotic algae and mesozooplankton during the latest Neoproterozoic led to the formation of larger particular aggregates of organic matter, which would have been more readily exported to the ocean floor (coincidentally also bringing about profound and permanent change in the turbidity, oxygenation, and redox profile of the oceanic water column). Using the observation that seasonal flux of organic matter stimulates seasonal reproduction in deeper-water environments, I test this model using the population structure of macroscopic and benthic metazoan communities from either side of the Precambrian-Cambrian boundary. This work illustrates that community paleobiology and -ecology can be used to test broader geobiological models, and (in this case) potentially constrain the timing of global-scale step changes in ocean structure and dynamics



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**Poster Session 1: 12:30 pm - 1:40 pm**

Investigating paleoenvironmental and diagenetic controls on intrabasinal variability of stable isotope records in ancient limestones

*Ben Otoo\*, David Jones*

Deconstructing the dissimilatory sulfate reduction pathway: Isotope fractionation of a mutant unable to grow sulphate

*Emma Bertran\*, William D Leavitt, Andre Pellerin, Grant M Zane, Judy D Wall, David T Johnston, Boswel A Wing*

The multiple oxygen and sulfur isotope record of Phanerozoic oceans

*Benjamin R Cowie, David T Johnston*

Multiple sulfur isotope investigations of porewater sulfate profiles

*Andrew L Masterson\*, David T Johnston, Will Berelson, Robert C Aller*

Testing an anoxia-driven mass-extinction of the Ediacaran fauna: New geochemical data from the Nama Basin, Namibia

*Alexandra Morgan\*, Erik Sperling, David Johnston, Marc Laflamme*

Fluctuating atmospheric oxygen levels prior to the Great Oxidation Event (GOE): New insights from osmium isotopes

*Vivien M Cumming\*, David Selby, Simon Poulton, Andrey Bekker*

Enzymes drive the global S cycle and isotope fractionations therein

*William D Leavitt\*, Alexander S Bradley, Andre Santos, Sofia Venceslau, Inês C Pereira, David Johnston*

Large igneous provinces, True Polar Wander and the explosion of life

*Athena Eyster\*, Francis Macdonald, Richard O'Connell*

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A geobiological perspective on the evolutionary history of the terrestrial silica cycle

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Preservation of geochemical biosignatures in impact materials

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Characterizing the provenance of the North Slope subterranean and constraining its tectonic origin with Nd isotopes and sedimentary geochemistry

*Lyle L Nelson\*, Justin V Strauss, Francis A Macdonald, Grant M Cox, William C McClelland*

Morphological and Functional Diversity of Planktonic Foraminifera in the Atlantic Ocean

*Frances Liu\*, Pincelli Hull, Leanne Elder*

**Poster Session 2: 4:40 pm - 6:00 pm**

Clumped isotope systematics of biogenic methane

*Danielle Gruen\*, David Wang, Lucy Stewart, James Holden, Shuhei Ono*

Cyanobacterial calcification and silicification as probes of seawater chemistry through time

*Sharon Newman\*, Giulio Mariotti, Tanja Bozak*

Lipid biomarkers of Holocene, Miocene and Jurassic oolites

*Kelden Pehr\*, Roger E Summons*

Microbial shaping of wrinkle structures in siliciclastic deposits

*Giulio Mariotti\*, Taylor Perron, Sara Pruss, M O'Grady, Tanja Bozak*

Carbon isotopic composition of organic fossils across the isotopic extremes in Cryogenian carbonates

*Emily Matys\*, Katherine Freeman, Francis Macdonald, Laurence Bird, James Moran, Tanja Bosak*

Constraints on the Archean environment from mass independent sulfur isotopes signatures

*Andrew R Whitehill\*, Shuhei Ono*

Using high resolution sampling to reveal the geochemical environment across a chemocline at Fayetteville Green Lake, N.Y.

*Jeff R Havig\*, Michael McCormick, Aviv Bachan, Lee Kump*

Identifying weathering processes by Si isotopes

*G Steinhofel\*, J Breuer, F Von Blanckenburg, I Horna, M Sommer*

Evaluating dolomitization style and mechanism from configuration, stable isotope and trace element geochemistry - three case studies from the Mesozoic dolomites of the Levant margin

*Or M Bialik\*, John A Higgins, Itay Halevy*

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Mg and Ca isotope signatures of authigenic dolomite  
*Clara L Blätter\**, *Nathaniel R Miller*, *John A Higgins*

The co-evolution of energy metabolism and metal cofactor availability  
*Ben Jelen\**, *Yana Bromberg*, *Paul G Falkowsky*

**Poster Session 3: 6:40 pm - 8:00 pm**

Using uranium isotopes to reconstruct redox conditions in modern and ancient oceans  
*Amy M Anderson\**, *Silke Severmann*

Early Cambrian archaeocyathan reefs and phosphatized fossils of southwestern Mongolia  
*Camille H Dwyer\**, *Sara B Pruss*, *Emmy Smith*

Distribution, organic geochemistry and experimental constraints on ooid formation in modern Bahamian settings  
*Kiara Gomez\**, *Sara B Pruss*, *Tanja Bosak*, *Roger Summons*

Post-Sturtian Microfossils from Zambia and Namibia  
*Kelsey Moore\**, *Sara Pruss*

Benthic I/Ca records for the Paleocene-Eocene Thermal Maximum  
*Xiangli Zhou\**, *Ellen Thomas*, *Zunli Lu*

Diagenetic and biological processes influencing preservation in Mazon Creek Lagerstätte siderite concretions  
*Sarina Cotroneo\**, *UG Wortmann*, *M Laflamme*

Revisiting the latest Ediacaran small shelly fossils of Namibia  
*Sara J Mason\**, *Marc Laflamme*

Taphonomic variance in exceptionally preserved arthropods from the Mazon Creek Lagerstätten  
*Arjan Mann\**, *Christine Nguyen*, *Marc Laflamme*

The spatial pattern of surface uplift in the central Andes  
*Dave Auerbach\**, *Marc Brandon*

Stable Isotope Probing of microbial metabolic water using  $\delta^{18}\text{O}$  of DNA  
*Hui Li\**, *Ruth E Blake*, *C Yu*, *SJ Chang*

Paleoenvironmental change across the Meso-Neoproterozoic transition  
*Sarah Wörndle\**, *Galen P Halverson*, *Zunli Lu*



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## Investigating paleoenvironmental and diagenetic controls on intrabasinal variability of stable isotope records in ancient limestones

Ben Otoo\*, David Jones

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Stable isotope data from carbonate rocks are key to understanding paleoenvironmental conditions. However, syndepositional and early diagenetic processes alter geochemical proxies in modern environments; such variability might be predicted in the geologic record. We use Ordovician-Silurian limestones from Anticosti Island, Québec to test the hypothesis that  $\delta^{13}\text{C}_{carb}$  and  $\delta^{18}\text{O}_{carb}$  variability may be due to a) syndepositional processes in different depositional environments within the basin and b) differing diagenetic regimes across the basin. We examine two sample sets: one time series from a single section, and another set of coeval samples deposited in a range of paleoenvironments. Transmitted light and cathodoluminescence petrography constrain diagenetic history and supplement field-based interpretations of depositional environment. Variability of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and trace elements (Sr, Mn, Fe) in primary and diagenetic textures is statistically analyzed to characterize the effect of each on the bulk sample value. The time series records variation in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  but little environmental variation, having been deposited almost entirely on the outer ramp, below storm wave base. The coeval sample set records a progressive shallowing below the Ordovician-Silurian boundary and initial deepening above. The results will inform the interpretation of basin-scale variability in the stable isotope record through space and time.

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## Deconstructing the dissimilatory sulfate reduction pathway: Isotope fractionation of a mutant unable to grow on sulfate

Emma Bertran<sup>\*1,2</sup>, William D Leavitt<sup>1</sup>, Andre Pellerin<sup>2</sup>, Grant M Zane<sup>3</sup>, Judy D Wall<sup>3</sup>, David T Johnston<sup>1</sup>, Boswel A Wing<sup>2</sup>

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Dissimilatory sulfate reduction significantly influenced the sulfur isotopic composition of sedimentary sulfides, which provide a record of Earth's surface redox history. Although net metabolic fractionations associated with sulfate reduction - the major metabolism in the sulfur cycle - have been well studied, unraveling the isotopic influence of each component of the pathway is still a challenge. The sulfite to sulfide reduction step is a particularly complicated one. Its biochemistry is not fully understood and its isotopic effect is largely inferred from net fractionation factors. Here, we investigated that redox transformation by studying a mutant strain of *Desulfovibrio vulgaris* Hildenborough in batch and continuous culture. This bacterium is missing its QmoABC complex, a principal enzyme in the reduction of adenosine phosphosulfate (APS) to sulfite, and is thus incapable of full sulfate reduction. In all experiments where sulfite is the terminal electron acceptor, sulfide and thiosulfate production occurred alongside sulfite and lactate consumption. In batch, the rates of inorganic thiosulfate production were one order of magnitude larger than in continuous culture. The  $\delta^{34}\text{S}$  isotopic difference between sulfite and sulfide was approximately -9 ‰ in batch and approximately -16 ‰ in continuous culture. Thiosulfate exhibited a large site-specific isotopic offset, with sulfane depleted by 30 ‰ in batch and 40 ‰ in continuous culture relative to sulfonate. The impact of these results, and the unexpectedly large effects associated with thiosulfate production, are discussed herein.

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## The multiple oxygen and sulfur isotope record of Phanerozoic oceans

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The triple oxygen and multiple-sulfur isotope records preserved in evaporite-derived sulfate minerals holds a rich, but largely untold story of Phanerozoic biogeochemical evolution. Oxygen-17 ( $\Delta^{17}\text{O}$ ) in sedimentary sulfate minerals (primarily gypsum, anhydrite and barite) track two important geochemical parameters, 1) the ratio of  $\text{CO}_2$  to  $\text{O}_2$  in the atmosphere ( $p\text{CO}_2/p\text{O}_2$ ) and 2) oxygen production in the biosphere (gross biosphere productivity, GBP). Popularized for application in the Neoproterozoic, application and further calibration of the  $\Delta^{17}\text{O}$  proxy in the Phanerozoic, where independent  $\text{CO}_2$  estimates are available, will allow for estimates of  $p\text{O}_2$  and gross primary production - a biogeochemical 'unicorn' of paleo-reconstructions. These changes are interpretable against a landscape of an ever-evolving community of primary producers in the oceans. Variation in the multiple sulfur isotope system ( $\lambda^{33}\text{S}$ ) through the Phanerozoic was recently demonstrated as a proxy for rates of microbial sulfate reduction (Leavitt et al., 2013) providing an indicator of electron donor availability in ocean sediments. Coupling a direct proxy for GBP ( $\Delta^{17}\text{O}$ ) with an indicator of sedimentary respiration rates ( $\lambda^{33}\text{S}$ ) may provide important constraints on biogeochemical cycling during Earth history. Here we present preliminary results and modeling constraints from this study.

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## Multiple sulfur isotope investigations of porewater sulfate profiles

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Remineralization of sedimentary organic matter via sulfate reduction leaves a characteristic isotopic imprint with the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of porewater sulfate. Sulfate concentration profiles, in concert with diagenetic, reactive transport models provide the information for extracting depth-dependent rates of OM remineralization. A multitude of sulfur-borne biogeochemical transformations and their overlapping isotope effects, however, complicates their direct interpretation. Utilizing the results of chemostat experiments exploring major ( $^{34}\text{S}/^{32}\text{S}$ ) and minor ( $^{33}\text{S}/^{32}\text{S}$ ) isotope rate/fractionation relationships for microbial growth, we construct a diagenetic model that aims to extract rates of sulfate reduction from the two fundamentally different geochemical environments (1) the California/Mexican borderland basins and (2) the tropical Amazon Delta from the  $\Delta^{33}\text{S}/\delta^{34}\text{S}$  reference arrays observed for the pore water sulfate. The four anoxic basins within the California Borderlands and Mexican margin (Alfonso, Mazatlan, Santa Monica and San-Blas) all exhibit linear sulfate profiles, used to infer rates of methanotrophy from flux balance models. We compare them to the results of a core extracted from the Amazon Delta, a fluidized sedimentary system, and the opposing geochemical endmember to the silled basins of the Cal- Mex margin. We highlight the differences in the minor isotope  $\Delta^{33}\text{S}/\delta^{34}\text{S}$  signatures between the two sites, and the importance of rates of sedimentary sulfate reduction in controlling that reference array.

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## Testing an anoxia-driven mass-extinction of the Ediacaran fauna: New geochemical data from the Nama Basin, Namibia

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The Ediacara biota, an assemblage of soft-bodied organisms, persisted in the fossil record for 93 million years before abruptly disappearing from the fossil record just prior to the Cambrian Explosion (542 Ma). Three explanations for this abrupt termination have been proposed: 1) a mass extinction event driven by environmental conditions, 2) a gradual and natural competitive replacement of Ediacara biota by Cambrian animals, and 3) the elimination of unique preservational settings that are necessary for biota to be preserved in the fossil record. While the Ediacara can be found in fossil assemblages around the world, few locations provide a continuous record. My work seeks to add to the conversation of this abrupt cessation of the Ediacara biota by providing new data on the paleoenvironmental conditions of this time period.

This past summer, I traveled with a Smithsonian-organized and National Geographic Society supported research team of sedimentologists, paleontologists, and geochemists to one of the few sections throughout the world that preserves the Ediacaran-Cambrian transition without a break in sedimentation. For two weeks at the Nama Basin in southern Namibia, Africa, we collected shale samples of the Swartpunt section to investigate what happened to the Ediacara biota. This unique and poorly studied stratigraphic section provides excellent sampling constraints because it has well-exposed outcrops crucial for sequence stratigraphy and carries abundant volcanic ash layers that provide radiometric dates (direct age constraints).

Since the beginning of summer of 2013, I have applied a multi-proxy approach to reconstruct redox sensitive metal budgets and biologically active major element cycles (carbon, sulfur, and iron cycles). My research methodologies include iron speciation chemistry (completed), small vial dissolutions (almost completed), and the chromium-reducible sulfur method (completed). I also have data produced from SGS about trace elements in my seventy-one shale samples.

From each of the geochemical tests performed on the collected Nama Basin samples, there are many indicators that the Ediacaran and Cambrian samples were deposited in oxic conditions, including low Mo concentrations,  $Fe_{HR}/Fe_T$  ratios far below 0.38, ratios of  $Fe_T/Al$  nearly equal to 0.5, higher percentages of iron oxides than other highly reactive iron forms, and essentially zero pyrite. Thus, the data I have produced does not support that a euxinic mass extinction event was responsible for the elimination of the Ediacaran Biota from the fossil record.

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## Fluctuating atmospheric oxygen levels prior to the Great Oxidation Event (GOE): New insights from osmium isotopes

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The Paleoproterozoic Era records the first significant rise in atmospheric oxygen, the GOE, as well as concomitant global glaciations. The Huronian Supergroup of Ontario, Canada is one of the best-preserved sedimentary successions that span this period, being deposited between 2.45 and 2.32 Ga. Deducing the nature and timing of the GOE in the Huronian Supergroup is crucial for understanding the co-evolution of the geosphere and biosphere during this important period in Earth's history. We use osmium isotope systematics to assess the link between glacial events and changes in the redox state of the atmosphere-ocean system during the oldest Huronian glaciation. We find a post-glacial radiogenic spike in  $^{187}\text{Os}/^{188}\text{Os}$  values (0.8) in the Pecors Formation in contrast to unradiogenic pre-glacial values in the McKim Formation (0.1). The pre-glacial mantle-like values require either overwhelmingly large juvenile hydrothermal flux of Os or levels of atmospheric oxygen that were too low to oxidize crustal sulfides and induce sufficient riverine flux of radiogenic Os via continental weathering. During the post-glacial period, oxidative dissolution of glacial flour could have caused a major influx of radiogenic Os from the continents, suggesting oxidizing surface conditions in the immediate aftermath of the oldest Huronian glaciation prior to the generally accepted age for the initiation of the GOE.

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## Enzymes drive the global S cycle and isotope fractionations therein

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The global biogeochemical sulfur cycle is set in motion and maintained by the microbiological reduction of marine sulfate to sulfide. The enzymatic cascade of redox reactions induces a distinct range of sulfur and oxygen isotope fractionations between the initial reactant sulfate and terminal product sulfide. What controls the magnitude of that fractionation, however, is the efficiency of that biochemical machinery in response to the organisms' environment. To better understand how variable fractionations are produced we utilize recent advances in microbial sulfate reducer (MSR) genetics and enzymology to determine the influence of the terminal step in MSR, the formation of hydrogen sulfide by the enzyme DsrC. DsrC couples the soluble cytoplasmic reduction of sulfite by DsrAB to the membrane potential that ultimately allows these cells to generate ATP. Here we employ three mutants in a background model MSR, *Desulfovibrio vulgaris*, to disrupt the efficacy of intracellular DsrC redox cycling and sulfide production. We compare disrupted strains to wildtype, both in terms of growth and specific sulfate reduction rates, biomass yield, magnitude of S isotope fractionation and DsrC activity. Implications for the MSR metabolic network, both as the key metabolism in the reductive branch of the sedimentary S cycle and driver of S isotope discrimination, are discussed.

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## Large igneous provinces, True Polar Wander and the explosion of life

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Ediacaran-Cambrian strata record the diversification of animals, large changes in ocean chemistry, and rapid shifts in paleomagnetic poles. Paleomagnetic studies have attributed observations of such changes in paleomagnetic poles to true polar wander. True polar wander (TPW) is the motion of the crust and mantle relative to the spin axis due to changes in the Earth's moment of inertia. Two TPW events have been proposed in the Ediacaran from 610-590 Ma and 590-560 Ma (Mitchell et al., 2011). Cambrian TPW has been proposed in the interval 535-505 Ma (Kirschvink et al., 1997). A large TPW event would reposition continents relative to the equatorial oceanic bulge and the ecliptic, causing changes in relative sea level, potentially altering Earth's global oceanic circulation patterns and biogeochemical cycles. Large TPW has been proposed as a trigger for the geochemical and biological events during the Ediacaran-Cambrian interval (Raub et al., 2007). Plumes, linked to large igneous provinces, can affect Earth's moment of inertia, causing TPW. I present results of modeling experiments for plumes and TPW. I explore whether plumes associated with the Ediacaran central Iapetus igneous events and the Cambrian Antrim igneous province could have acted as triggers for TPW that may have contributed to the Cambrian Explosion.



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## The global record of local iron geochemical data from Proterozoic through Paleozoic basins

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Iron-based redox proxies represent one of the most mature tools available to sedimentary geochemists. These techniques, which benefit from decades of refinement, are based on the fact that rocks deposited under anoxic conditions tend to be enriched in highly-reactive iron. However, there are myriad local controls on the development of anoxia, and no local section is an exemplar for the global ocean. The global signal must thus be determined using techniques like those developed to solve an analogous problem in paleobiology: the inference of global diversity patterns through time from faunas seen in local stratigraphic sections. Here we analyze a dataset of over 4000 iron speciation measurements (including over 600 de novo analyses) to better understand redox changes from the Proterozoic through the Paleozoic Era. Preliminary database analyses yield interesting observations. We find that although anoxic water columns in the middle Proterozoic were dominantly ferruginous, there was a statistical tendency towards euxinia not seen in early Neoproterozoic or Ediacaran data. Also, we find that in the Neoproterozoic oceans, oxic depositional environments—the likely home for early animals—have exceptionally low pyrite contents, and by inference low levels of porewater sulfide. This runs contrary to notions of sulfide stress on early metazoans. Finally, the current database of iron speciation data does not support an Ediacaran or Cambrian oxygenation event. This conclusion is of course only as sharp as the ability of the Fe-proxy database to track dissolved oxygen and does not rule out the possibility of a small-magnitude change in oxygen. It does suggest, however, that if changing pO<sub>2</sub> facilitated animal diversification it did so by a limited rise past critical ecological thresholds, such as seen in the modern Oxygen Minimum Zones benthos. Oxygen increase to modern levels thus becomes a Paleozoic problem, and one in need of better sampling if a database approach is to be employed.

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## A geobiological perspective on the evolutionary history of the terrestrial silica cycle

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The modern silica cycle is dominated by biomineralization within two clades of photosynthetic organisms, grasses and diatoms. However, neither group displays a long evolutionary history: diatoms evolved in the Jurassic Period but radiated in the Cenozoic Era, whereas grasses evolved no earlier than the Late Cretaceous Period. We employed a combined bioinformatics and geobiological approach to identify the origin and diversity of silicon accumulation in land plants. We identified heretofore unknown silicon transport proteins and assessed their likelihood of function through computational resolution of protein structure. We sampled tissue of living plants, from liverworts to angiosperms; assessed silicon abundance using wet ashing; and verified results using EDAX. Our results indicate pervasive silicon accumulation across terrestrial plants, particularly within early-diverging lineages with substantial diversity in the geologic past, including liverworts, lycophytes, and ferns, with a loss in the gymnosperm lineage and convergent evolution within the angiosperms. Comparing the diversity and abundance of silicon-accumulating fossil plant groups points to high terrestrial biological silicon accumulation during the Middle and Late Paleozoic Era, dropping in the Late Triassic Period, not to reach Paleozoic Era highs until the Cenozoic Era.

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## Preservation of geochemical biosignatures in impact materials

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Impact materials represent understudied microbial substrates with the potential to preserve evidence of life from early Earth as well as the potential for life on other planets. Meteorite impact events create unique microbial niches that may have been significant habitats on early Earth and are important astrobiological targets on other rocky bodies such as Mars. Given the probable ubiquity of impact products in post-impact environments throughout the Solar System, it is important to understand the biological components and potential of such systems on Earth. Recently, we described microbial ichnofossils in meteorite impact glass from the Ries impact structure, Germany. Using synchrotron based X-ray spectromicroscopy, we show distinct patterns of reduced iron surrounding the tubule features in the Ries glasses suggestive of microbial iron reduction. A series of culture-based experiments is proposed to assess the viability of impact lithologies as substrates for lithotrophic microorganisms. A subset of these experiments will be carried out anaerobically with iron-reducing autolithotrophs to test the hypothesis that such metabolism induces geochemical changes that can be preserved and detected in the rock record.

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## Characterizing the provenance of the North Slope subterranean and constraining its tectonic origin with Nd isotopes and sedimentary geochemistry

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In the British Mountains of Yukon Territory, an extension of the North Slope subterranean of adjacent northeastern Alaska, much of the stratigraphy consists of a poorly understood late Neoproterozoic to the Devonian sequence of intensely deformed basinal siliciclastic and volcanic rocks. This strata has previously been grouped into the broadly defined Neruokpuk Formation and Road River Group and correlated as such throughout the region. In this study, epsilon Nd and major and trace element composition data are used to accomplish more detailed characterization and correlation of the stratigraphy. The Nd isotopic data shows three identifiable provenance signatures, which combined with paleontological and geochronological age constraints allow for the pre-Mississippian stratigraphy to be broken up into three sequences, each with distinct sediment sources. This data is also compared to similar Nd studies from the Yukon stable block, and elsewhere in the Arctic and North American Cordillera to better constrain the tectonic origin of the North Slope subterranean. The comparison presents complications due to juvenile sediment influx from local volcanism on both the North Slope and Yukon block. However, the timing of the major regional provenance shift suggests a potential link further East along the Arctic margin, more proximal to the Caledonian and Ellesmerian Orogenies.

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## Morphological and Functional Diversity of Planktonic Foraminifera in the Atlantic Ocean

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Planktonic foraminifera are used as a key tool for reconstructing the chemical and physical properties of past oceans. However, less is known about the dynamics of communities, in part due to the difficulty of measuring communities through time. Morphology can provide a direct window into the ecology of species and, as such, could provide a rapid, direct measure of biotic change. This project aims to examine the correlation between the morphological and ecological features of 34 species of extant planktonic foraminifera and their spatial distribution in the Atlantic Ocean to this end. We use the MARGO database, with over 900 core-top samples, and interpolate both the ecological and morphological richness patterns with ArcGIS. Results show differences among morphological and functional groups across open ocean habitats.

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## Clumped isotope systematics of biogenic methane

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Constraints on the biogeochemical cycling of methane have proven evasive, and it is often difficult to determine the sources of methane fluxes. In theory, the temperature at which methane forms should provide information about the source of the gas, because life is thought to only exist at an upper temperature limit of around 120°C and thermogenic methane often forms at temperatures greater than 150°C. We aim to determine whether the temperature of formation for methane, or temperature at which methane is equilibrated, is preserved in the multiply substituted isotopologue ( $^{13}\text{CH}_3\text{D}$ ) signature of biogenic methane. Methane produced in batch cultures of methanogens grown at a range of temperatures was analyzed using novel tunable infrared laser direct absorption spectroscopy. The relative abundance of  $^{13}\text{CH}_3\text{D}$  measured corresponded to higher than actual growth temperatures by 100°C or more. To understand the source of this discrepancy, we are carrying out a time series study for the clumped methane isotope fractionation of biogenic methane from batch cultures of *Methanocaldococcus* grown between 40°C and 90°C. We will report the results of this experiment and prospects of using  $^{13}\text{CH}_3\text{D}$  to understand the clumped isotope systematics of microbial metabolism and sources of natural methane

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## Lipid biomarkers of Holocene, Miocene and Jurassic oolites

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\*Presenter (kelden@mit.edu)

Oolites are sedimentary rocks formed from ooids, which are small (typically 2 mm or less in diameter) spherical to ellipsoidal, sand-sized grains composed of concentric layers of calcium carbonate and organic matter. Modern ooid sands are found at select beaches in the Atlantic and Indian oceans, including Exuma Sound, Bahamas and Hamelin Pool, Western Australia.

We analyzed oolite samples from three locals: a Holocene sample from Carbla Beach in Hamelin Pool, Western Australia; a Jurassic sample from Bath, England; and three Miocene samples from the Monte Carrubba Formation in Sicily. All samples displayed a similar lipid biomarker profile, dominated by C16 and C18 fatty acids and accompanied by normal and branched short chain (C12 - C19) fatty acids which can be attributed to a bacteria and/or cyanobacteria origin. A series of unusual long chain (C22 - C30) fatty acids with a strong even carbon number preference were also present. Trace amounts of hydrocarbons were detected, including long chain n-alkanes.

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## Microbial shaping of wrinkle structures in siliciclastic deposits

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Wrinkle structures are millimeter- to centimeter-scale elongated or reticulate sedimentary structures that resemble symmetric ripples. Sharp-crested and flat-topped wrinkle structures up to 1 cm wide occur on numerous bedding planes in the Neoproterozoic and Cambrian, as well as in some Archean and Phanerozoic siliciclastic deposits. Because similar, but unlithified structures occur in some modern, microbially-colonized sands, wrinkle structures are typically interpreted as microbially induced sedimentary structures. However, it is unclear if physical processes, such as the motion of suspended sand grains, can produce similar features in sand even before microbial colonization. We introduced mat fragments to the surface of silica sand in wave tanks and generated sharp-crested, flat-topped and pitted wrinkle structures. The abrasion of the sandy surface by rolling, low density, millimeter-size fragments of microbial mats produces wrinkle structures at extremely weak orbital velocities that cannot move sand grains in the absence of light particles. Wrinkle structures form in a few hours and can become colonized by microbial mats within weeks. Thus, wrinkle structures are patterns formed by microbially mediated sand motion at low orbital velocities in the absence of bioturbation. Once formed, wrinkle structures can be colonized and stabilized by microbial mats, but the shape of these mats does not dictate the shape of wrinkle structures. These experiments bolster the interpretation of wrinkle structures as morphological signatures of organic particles and early life in Archean and Proterozoic siliciclastic deposits.



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## Carbon isotopic composition of organic fossils across the isotopic extremes in Cryogenian carbonates

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Isotopically anomalous Neoproterozoic carbonate strata may preserve a record of major reorganization of biogeochemical cycles. Studies of these strata rely primarily on the bulk isotopic records of organic and inorganic carbon. We characterize fossil-specific C isotopic composition of organic-rich fossils from carbonate strata from the Cryogenian Tayshir Member of the Tsagaan Oloom Formation in Mongolia. These strata span a range of  $\delta^{13}\text{C}$  values, from +7 to -6 per mil. The morphology of fossil tests suggests a planktonic lifestyle of their precursor organisms. Thus, their isotopic composition should reflect that of the surface waters during the deposition of the Tayshir Member. Our preliminary results, obtained from the analysis of 8 samples of 15 individual tests by LA-IRMS and 8 samples of 75-125 individual tests by Nano-EA indicate that the carbon isotopic composition of fossil tests do not co-vary with the C isotopic composition of the host carbonate or bulk organic carbon. This implies the presence of isotopically heterogeneous organic matter within the carbonates characterized by large negative  $\delta^{13}\text{C}$  values. The isotopic heterogeneity will be tested by SIMS analysis of organic-rich material in thin sections and LA-IRMS analyses of bulk organic residues from fossiliferous samples.

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## Constraints on the Archean environment from mass independent sulfur isotope signatures

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The rise of oxygen during the Great Oxidation Event is one of the most remarkable changes in the Earth's surface environment. Mass-independent sulfur isotope signatures provide the best record of the low-oxygen conditions on the early Earth. Despite its profound implications, the processes responsible for the generation of the mass-independent sulfur isotope signatures are still poorly understood. We performed a series of experimental photochemical studies to provide experimental constraints on the systematics of mass-independent isotope fractionation during SO<sub>2</sub> photolysis. Results of these experiments allow us to begin to make interpretations about the conditions necessary for the production and preservation of sulfur mass-independent isotope signatures. We will present a summary of experimental results and some preliminary interpretations, and discuss the future directions of sulfur isotope mass-independent fractionation research and its implications for the Geobiology community.

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## Using high resolution sampling to reveal the geochemical environment across a chemocline at Fayetteville Green Lake, N.Y.

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Fayetteville Green Lake (FGL) is a meromictic lake, with an upper oxic mixolimnion extending from the surface to a chemocline extending from roughly 15 m to 22 m. Previous studies have demonstrated a dramatic geochemical and redox (oxygenated to euxinic) transition across this boundary, but not at a resolution that captures the subtleties in concentration change. To better elucidate the geochemistry through the entire water column, we deployed an apparatus that allowed for near instantaneous water sampling from the surface through to the bottom (53 m) at 1 m intervals, and at  $\frac{1}{4}$  m intervals from 16 to 24 m, in conjunction with a Sonde equipped with sensors for measuring depth, pH, conductivity, temperature, turbidity, and dissolved oxygen content. We analyzed samples collected in November of 2012 and July of 2013 for over 25 physical and geochemical parameters. From this level of resolution, we can describe the dynamic and shifting geochemical environment which harbors the majority of biomass and productivity for the lake. Using geochemical tracers of different processes and water sources, we check the validity of previous modelling to describe the movement of water and nutrients through the system, and test the viability of using FGL as a proxy for Paleoproterozoic ocean conditions.

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## Identifying weathering processes by Si isotopes

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Stable Si isotopes are potentially an ideal tool to investigate the release or precipitation of Si during abiotic or biotic weathering processes which cause significant shifts in the isotope signature depending on the weathering intensity. In this study, we determine the Si isotope signature of water samples and of the principle Si pools in soils within two small catchments in the Black Forest (Germany).

The Si isotope data were obtained on a Neptune MC-ICP-MS in solution for the water samples and in situ by coupling a UV femtosecond laser ablation system for solid samples, respectively. Soil clay formation preserves initial Si isotope signatures of parental minerals. Biogenic mineral, i.e. phytoliths, exhibit  $\delta^{30}\text{Si}$  values of about -0.4 ‰. Springs and streams, sampled in spring and late summer, vary between -0.7 to 1.1‰ in  $\delta^{30}\text{Si}$  showing spatial and temporal variations. Whereas groundwater reveals constant isotope signatures water passing the soil zone shows very variable isotope compositions. Negative  $\delta^{30}\text{Si}$  likely reflects dissolution processes of clay minerals and phytoliths during spring. In late summer, positive  $\delta^{30}\text{Si}$  values expose the impact of Si uptake by plants. The results on these small catchments demonstrate that Si isotopes are a powerful tool to identify weathering processes and the sources of dissolved Si, which are valuable constraints to interpret the isotope signature of large river systems.

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## **Evaluating dolomitization style and mechanism from configuration, stable isotope and trace element geochemistry – three case studies from the Mesozoic dolomites of the Levant margin**

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The record of the Levantine margin provides a unique window into dolomitization through the Mesozoic and dolomitization in general. Carbonate sediments have accumulated through the Triassic, Jurassic and Cretaceous in this region, maintained at relatively shallow burial depth, and currently exposed at the surface. We examined the depositional configuration, and the geochemical and stable isotope compositions across several limestone-dolostone transitions, with the intention of inferring the paleoenvironmental trends leading to these transitions and the rocks' style of dolomitization.

Sequences were selected based on the presence of repeated interchanges between limestone and dolostone, in settings where the occurrence of the dolomite is likely to be derived from early diagenetic processes and interaction with marine or evaporated marine water. Three different settings were targeted for high resolution sampling: i) sub-tidal, open marine, evaporite-free (Cretaceous), ii) intertidal, open marine, evaporite-free (Jurassic), and iii) restricted lagoon, in association with sulphate evaporites (Triassic).

Sedimentary textures were investigated in field and lab. Mineralogical ratios in the carbonates were determined by XRD, isotopic ratios of carbon, oxygen and magnesium as well as trace elements were measured by mass spectrometry. The results of these analyses will be presented and their implications for mechanisms of dolomite genesis discussed

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## Mg and Ca isotope signatures of authigenic dolomite

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Authigenic carbonates are capable of generating anomalous carbon isotope values in marine sediments, but their contributions to ancient sedimentary sections are difficult to assess. In this study of dolomite from the Monterey Formation of offshore California, Mg and Ca isotopes are shown to vary with stratigraphic depth as they respond to early diagenetic processes. The relationship of  $\delta^{26}\text{Mg}$  and  $\delta^{44/42}\text{Ca}$  to traditional  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements represents a new geochemical tool for identifying authigenic carbonates in the geological record.

The dolomite of the Miocene-age Monterey Formation occurs as beds and nodules throughout the organic-rich, predominantly siliceous sequence. The dolomite is an early diagenetic (pre-compaction) phase, with  $\delta^{13}\text{C}$  ranging from -16 to +9‰. Light  $\delta^{13}\text{C}$  values were likely acquired from the sedimentary zone of microbial sulfate reduction and heavy  $\delta^{13}\text{C}$  from the zone of methanogenesis. Mg and Ca isotopes are roughly anti-correlated, with intervals of negative  $\delta^{13}\text{C}$  associated with low  $\delta^{26}\text{Mg}$  and high  $\delta^{44/42}\text{Ca}$  excursions that yield distinctly different values than primary marine carbonate.

The data can be explained either by variation in Mg and Ca isotope fractionation factors associated with changes in precipitation rate, or by changes in the depth distribution of dolomite formation within the sediment column. Regardless of the underlying mechanism, these data suggest that Mg and Ca isotopes can provide unique insights into the formation of authigenic carbonates which complement preexisting datasets of C and O isotope variability.

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## The co-evolution of energy metabolism and metal cofactor availability

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To gain a large-scale perspective on the relationship of biochemical pathways with transition metal cofactor usage, all fully-sequenced genomes at the National Center for Biotechnology Information were searched for presence of KEGG (Kyoto Encyclopedia of Genes and Genomes) pathways involving "Energy metabolism," and "Carbohydrate metabolism." Using Swissprot protein annotations, the KEGG pathways were annotated with their transition metal usage. Using genome metadata for "Oxygen requirement," the genomes were split into "Oxygen tolerant" and "Oxygen intolerant" groups. A technique to normalize and compare the pathways based on whether they were found in tolerant or intolerant organisms was used to rank the pathways. This ranking, using the Great Oxidation Event as a proxy to split "ancient" and "new" pathways, was used to look at which metals were preferentially used by the earlier (O<sub>2</sub> intolerant) life on Earth.

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## Using uranium isotopes to reconstruct redox conditions in modern and ancient oceans

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Isotopes of redox-sensitive trace metals can provide a tool to understand the extent of anoxic conditions within modern and ancient oceans. The evolution of the redox state of the ocean and atmosphere is linked to biological evolution throughout Earth history. Elements like uranium and molybdenum are soluble in oxidizing conditions and adsorbed to particulates for reducing conditions; thus dissolved oxygen concentrations control the solubility of transition metals. Adsorption processes remove elements to the sediments; this process is redox-dependent and influences the isotopic composition and elemental abundance. We are exploring whether the uranium isotope composition in the sediments will reflect the redox conditions of the water directly above the sediment layer at the time of deposition. For a transect across the Black Sea (containing both oxic and anoxic sites), bottom water and sediments were analyzed for their uranium isotope fractionation. By understanding the relationship between the sediment and bottom water, it will allow for a paleo-proxy to study past redox conditions of the oceans



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## Early Cambrian archaeocyathan reefs and phosphatized fossils of southwestern Mongolia

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Archaeocyathans, the first metazoan reef builders, and other small shelly fossils are uniquely preserved in phosphatic horizons in the Khairkhan Formation of the Zavkhan basin in southwestern Mongolia. Field samples were collected from the Orolgiin Gol locality. In the lab, eight limestone samples were dissolved in 10% buffered acetic acid and sieved to obtain acid-insoluble residue. All fossils were picked, and twenty representative fossils from each sample were imaged using the scanning electron microscope (SEM). Using these SEM images, I am reconstructing the ancient ecosystems to understand what organisms were preserved and to determine the diversity and abundance of fossil groups. Complementary thin section analysis of all dissolved samples is also yielding constraints on the origins for phosphate and conditions of phosphate precipitation. The primary goals of this work are to determine the morphological diversity of these organisms, to interpret the ancient environments in which they lived, and to understand the mechanism of phosphatization in these enigmatic Cambrian deposits of Mongolia.

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## Distribution, organic geochemistry and experimental constraints on ooid formation in modern Bahamian settings

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Ooids are small spherical to ellipsoidal coated grains, characterized by concentric layers of calcium carbonate. Despite the ubiquity of these grains in the geologic past, their formation is still the subject of debate. In 2013, a targeted collection of sand containing ooids was performed in subtidal and beach settings along Pigeon Creek Delta on San Salvador Island, The Bahamas. Thirteen samples were taken in the tidal channel at different locations to determine where ooids were most abundant. Dominant components were identified in thin section and included skeletal fragments and unidentified material, followed by ooids and peloids. The samples were further examined for their lipid biomarkers at MIT. Preliminary results indicate that these samples showed similar distributions of hydrocarbons and fatty acids as other Bahamian and Australian ooids [1]. To constrain the mechanisms of ooid formation in a laboratory setting, ooid collections from Cat Island, Bahamas were used to carryout accretion and erosion experiments. Scanning electron microscopy was also used to obtain images of these ooids to analyze surface destruction. Results from this multidisciplinary work will provide new petrographic, geochemical and experimental data to help explain the distribution, occurrence and formation of ooids in modern settings.

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## Post-Sturtian microfossils from Zambia and Namibia

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The fossil record of the Neoproterozoic has to date been scarce, with most examples of fossil material coming from shales and cherts. In recent analyses, several fossil groups have been identified in carbonates, particularly those that cap glacial deposits during Snowball Earth events [1,2,3,4]. Samples were recently collected from a drillcore in Zambia (by F. Macdonald, Harvard University), which includes both the Calcaire Rose Formation and the Kakontwe Formation (the cap carbonates of the Marinoan and Sturtian glaciations respectively). These samples, along with samples of equivalent age collected in Namibia of the Rasthof Formation, produce eukaryotic microfossils of possible agglutinated testate amoebae. These discoveries contribute to our knowledge of post-Snowball marine microbial ecosystems and demonstrate that testate microfossil were widespread in the glacial aftermath. This study provides insight into the morphology and composition of the Zambian and Namibia microfossils and allow for comparisons of similarly aged rocks from various localities.

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## Benthic I/Ca records for the Paleocene-Eocene Thermal Maximum

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The most severe benthic foraminifera extinction event occurred at roughly 55 Ma, when 30-50 % of deep sea species went extinct [1,2]. Both geochemical and modeling results indicate that OMZs expand [3,4] and oxygen concentrations may have decreased in intermediate-deep waters [5]. However, no solid geochemical evidence for global hypoxia or anoxia has been found, and biotic evidence commonly is not indicated for oxygen levels alone (e.g., indicating some combination of trophic, temperature and acidification stresses). A new redox proxy, carbonate-associated iodate has been used to reconstruct subtle redox changes in the upper ocean during the PETM, suggesting expanded OMZs or deoxygenation at multiple open ocean sites [6]. Here we aim to use single species benthic I/Ca ratios to detect potential deoxygenation in bottom waters. Preliminary data show lower I/Ca values of both epifaunal and infaunal species towards the onset of the carbon isotope excursion (CIE), but infaunal species have much lower I/Ca values than epifaunals, consistent with the assumption of pore water less oxygenated than the bottom water. At the Walvis Ridge (SE Atlantic), I/Ca values of the epifaunal species *N. truempyi* are higher at the deeper site 1262 than site 1263, indicating more oxygenated water at site 1262, which is consistent with the Mn enrichment factor [3]. More data from other regions will be obtained for comparison.

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## Diagenetic and biological processes influencing preservation in Mazon Creek Lagerstätte siderite concretions

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Remarkable preservation of soft tissues occurs in Pennsylvanian-aged (280 Ma) siderite concretions of Mazon Creek, Illinois. Concretion formation is thought to be associated with the decaying organism they encase, with the organism acting as a nucleation surface; however, many concretions exist in the absence of a fossilized organism. A crosssectional analysis of the mineralogical and isotopic composition of the concretions sheds light on the processes involved in mineral formation and the conditions under which exceptional soft-tissue preservation occurred. Mineralogical analyses employing Ramanspectroscopy, SEM/EDX, and XRD have confirmed that significant quantities of kaolinite are associated with the fossilized organism. Such analyses also reveal a transition from carbonate-dominated mineralogy to clays from the interior to the exterior of the concretion. Carbon and oxygen isotopes reflect the diagenetic processes and role of microbes in preservation, while sulfur isotopes will be instrumental in indicating the rate and mechanism of formation of sulfide minerals. This work represents the first-ever detailed geochemical analysis of the Mazon Creek concretions, and represents an important step toward broadening our understanding of exceptional fossilization in deep time.

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## Revisiting the latest Ediacaran small shelly fossils of Namibia

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The terminal Ediacaran “small shelly fossils” from Namibia are some of the earliest-known skeletonized organisms. Two genera are known: *Cloudina*, which is composed of a series of nested cones, and *Namacalathus*, which is shaped like a cup on a stalk. Reefs containing these calcified fossils occur at several stratigraphic levels in the latest Ediacaran Nama Group: a well-exposed succession deposited in a shallow marine environment. Preliminary investigations suggest that the diversity of forms is likely much larger than presently appreciated. We will use advanced X-ray microtomography, a non-destructive means of studying fossil morphology. The resulting 3D reconstructions will be instrumental in evaluating the true diversity of forms present, and will likely substantially increase the diversity of known Ediacaran calcareous life. These reconstructions will also allow for detailed studies of functional morphology, forming the cornerstone of proposed paleoecological studies on the relationships between the calcareous animals and the microbial reefs upon which they lived. We will also evaluate the original carbonate mineralogy of these fossils using carbonate petrology in conjunction with Sr isotope analyses. Understanding the original mineralogy of these organisms will have far-reaching consequences when interpreting the origin and early evolution of skeletonization and its relationship to Ediacaran ocean chemistry.

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## **Taphonomic variance in exceptionally preserved arthropods from the Mazon creek lagerstätten**

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The Pennsylvanian Mazon Creek (Francis Creek Shale) fossil sites represent a rare instance of exceptional soft-tissue preservation from of northeastern Illinois. Rapid burial followed by diagenetic encapsulation within siderite concretions allowed for soft-tissue preservation. The Royal Ontario Museum (ROM) presently houses an extensive concretion collection, allowing for comprehensive studies of the preservational variance occurring within, and between, species. Over 2000 fossil individuals across a broad spectrum of arthropods including crustaceans *Belotelson*, *Acanthotelson*, *Anthracaris*, and *Anthrocauphosia*, insects *Thyloblatta*, *Testajapyx*, *Prochoroptera*, *Eucaenus*, *Herdina*, *Dasyonthus*, *Homaoneura*, myriapods and chelicerates were compared. Morphological and Taphonomic matrices were constructed to evaluate the preservational variance on a character-by-character basis, in addition to evaluating the overall preservational quality across hundreds of individuals. Ultimately, the construction of qualitative and quantitative taphonomic series of numerous anatomical structures between a large number of individuals may help constrain relative rates of decay, sequences of character loss, and allow inference of original tissue liabilities and taphonomic trajectories in extinct organisms

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## The spacial pattern of surface uplift in the central Andes

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Reconstructing the past surface elevations of mountain ranges offers us a chance to address questions of biological evolution, paleoclimate, and tectonics. Here we present stable isotope data and use them to derive a paleoelevation history for the southern part of the Altiplano Plateau in the central Andes. We focus on the record preserved in pedogenic carbonates from well-dated middle-late Miocene (16.3 to 7.1 Ma) sedimentary sections, which record paleoenvironmental conditions that can be used as proxies for elevation. We find that surface paleotemperatures ( $\Delta 47$ ) decreased by  $14^{\circ}\text{C}$  from 16 to 8 Ma in the southern Altiplano relative to low-elevation paleotemperatures, which remained stable through that interval. After considering effects of uplift on atmospheric circulation and temperature, this indicates a surface elevation increase of  $1.5 \pm 0.5$  km between 16 and 13 Ma and an additional  $0.5 \pm 0.5$  km by 8 Ma. These results show the southern Altiplano experienced a similar rate and magnitude of surface uplift as the northern Altiplano, but  $7 \pm 4$  Myr earlier. This temporal offset also appears in other metrics of surface uplift such as climate (aridity) and sediment accumulation. The consistency of these records suggests that the same mechanism(s) were responsible for the periods of rapid uplift in both parts of the Altiplano, but was active at different times in different regions.



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## Stable Isotope Probing of microbial metabolic water using $\delta^{18}\text{O}_\text{P}$ of DNA

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It is generally accepted that intracellular water is isotopically identical to extracellular water, due to the unimpeded transport of water across cell membranes. However, isotopic measurements of intracellular water extracted from microbial cells indicate that metabolism produces isotopically distinct water, which can account for as much as 70% of intracellular water. Our recent studies of the O isotopic composition of  $\text{PO}_4$  in DNA also indicate a significant contribution of nonextracellular water (e.g. metabolic water) to the intracellular water pool. Our observations are based on  $\text{PO}_4$  in DNA, which has been shown to be a powerful probe of intracellular water and like bioapatites (e.g., bones, shells, teeth), also records temperature and O-isotope exchange between  $\text{PO}_4$  and water. When *Marinobacter aquaeolei* was grown in media made using 3 different  $^{18}\text{O}$ -labeled waters, the  $\delta^{18}\text{O}_\text{P}$  value of  $\text{PO}_4$  in DNA plotted against  $\delta^{18}\text{O}$  values of extracellular water gave a slope of 0.65, indicating that 35% of O in DNA- $\text{PO}_4$  is not derived from the extracellular water in the growth medium. Results from these studies suggest the need to determine the percentage and isotopic composition of any possible metabolic water component of intracellular water for isotope probing studies of cellular processes and cellular biomass.

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## Paleoenvironmental change across the Mesoproterozoic - Neoproterozoic transition

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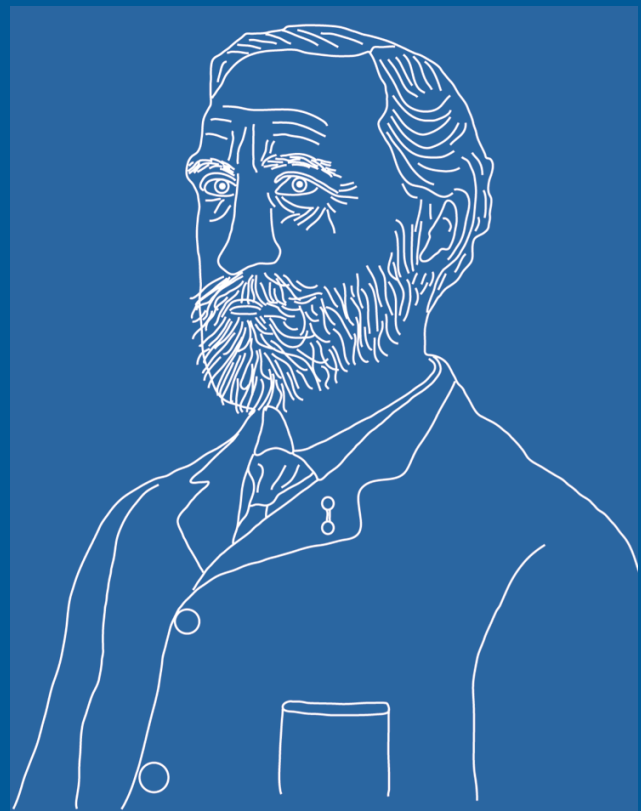
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The time interval spanning the Mesoproterozoic-Neoproterozoic boundary (c. 1.2 to 0.8 Ga) coincided with the final amalgamation of the supercontinent Rodinia, a pulse of eukaryotic diversification, and major changes in ocean chemistry. This study aims to evaluate the biospheric and geochemical changes across the Mesoproterozoic- Neoproterozoic boundary as record in carbonate platform environments. Prior work on microfabrics of carbonate rocks for this interval imply a first order shift in carbonate depositional styles. Mesoproterozoic silicified carbonates from the Angmaat Fm ( 1.267 Ga), in northern Baffin Island, Arctic Canada, contain chert with uncommon and well-preserved void-rich texture and microfossils. In contrast, early Neoproterozoic chert from the Draken Conglomerate Fm ( 800-750 Ma), in Svalbard, Norway, present remnants of dissolution and a great diversity of filaments, but lack the void-rich texture. This lack of voids in younger carbonates reflects a change in the environment and preservation. Most likely, at the end of Mesoproterozoic, carbonate precipitation occurred directly on the seafloor at the same time that the well-preserved filament-tufted fabric formed. Moreover, during early diagenesis, silica cement rapidly replaced carbonate and fragile textures were shielded from compression. The Mesoproterozoic-Neoproterozoic transition demonstrates that processes occurring during early diagenetic carbonate deposition evolved in the Proterozoic Eon, likely reflecting a secular change in the seawater chemistry, potentially closely linked to ocean redox conditions. To build upon this conclusion, I will develop a dataset of a new tracer for ocean redox: the iodine to calcium ratio (I/Ca) as preserved in marine carbonates. As an initial test of the viability of this technique on ancient rocks, we have analyzed a suite of well-preserved carbonates from Svalbard, dating from 820 to 740 Ma. This interval spans the 'Bitter Springs' carbon isotope anomaly, which is commonly interpreted to reflect a fundamental shift in the style of organic carbon production and burial, and hence ocean redox

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