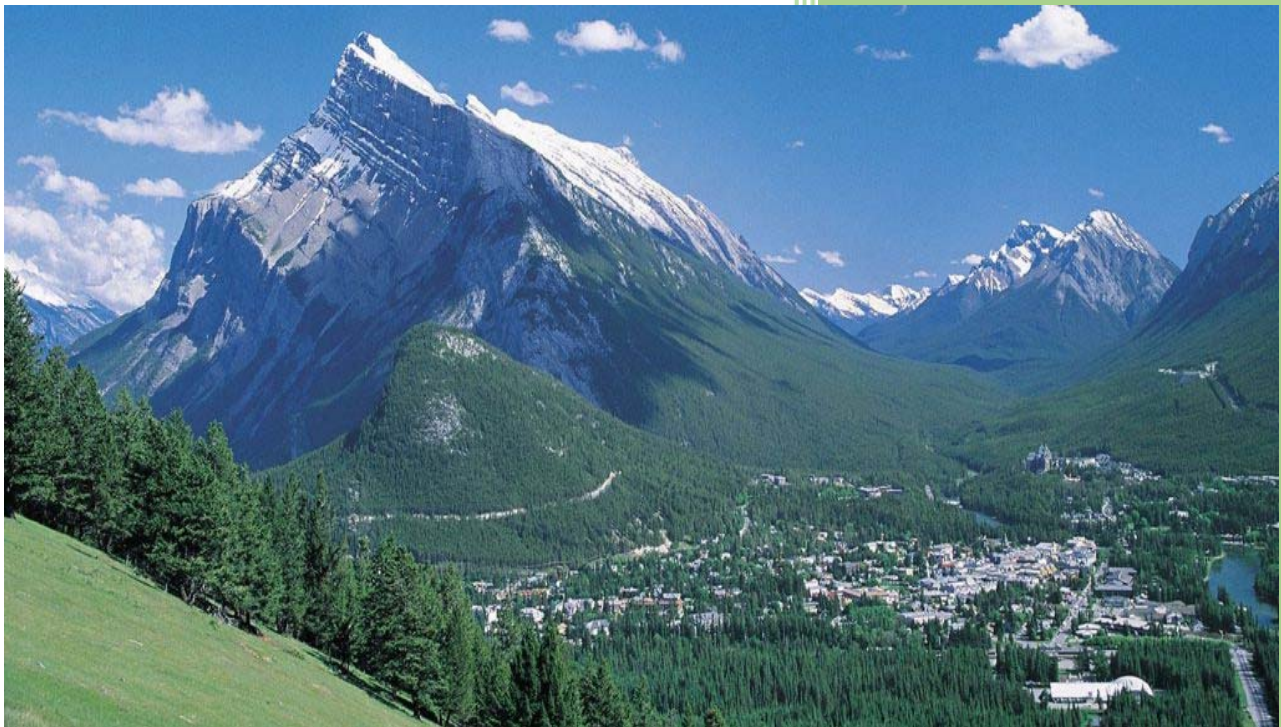




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# Growth rates and sulfur metabolism pathways of purple sulfur bacteria using biogenic metal sulfide nanoparticles as electron donors

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## Abstract:

The current study focuses on illuminating how purple sulfur bacteria may interact with metal sulfide nanoparticles (MNPs) formed via bacterial sulfate-reduction. The major questions to be addressed include, if PSB can grow on MNPs as the electron donor source, and further, what mechanisms are involved in the MNPs-driven bacterial growth. Motivations for this work arise from our knowledge gaps of both ancient and modern systems. A most direct one relates to the global-wide transition of ancient oceans from sulfidic to ferruginous conditions in early Neoproterozoic and how anoxygenic sulfide-oxidizers (green/purple sulfur bacteria) might have adapted to the deprivation of aqueous sulfide and the occurrence of relatively high concentrations of iron sulfide nanoprecipitates during that period. In modern systems, it remains largely elusive how the PSB communities respond to variations in sulfide concentrations, mainly regulated by metal cation availabilities in the same niche. We have chosen *Allochromatium vinosum* and *Halorodospira halophila* two model strains for this work and studied their growth and sulfur metabolism using different sulfur sources. For each type of bacteria, we have set up identical systems, whose difference only lies in the provided electron donors (i.e., aqueous sulfide versus nickel sulfide NPs), and adopted a comparative approach to analyze the collected aqueous chemistry and genomic/transcriptomic data. Time-resolved concentrations of dissolved sulfide, sulfate and nickel in each system were monitored using ICP-MS and colorimetric assays. Both *A. vinosum* and *H. halophila* cells showed healthy growth patterns using the MNPs as electron donors. The nickel concentrations were noticeably increased in the cell-negative solution for both types of cell cultures although orders of magnitude lower compared to those in the cell culture solution. Further work is being conducted to determine if the growth is mainly driven by the dissolution effect and if additional mechanisms have been enabled by the exposure to MNPs that contribute to the bacterial growth. Specifically, the *dsrC*, *dsrL*, *fccB*, and *HiPIP* expression will be quantitatively determined in the MNPs-negative vs. -positive samples using RT-PCR. We also plan to sequence the transcriptomes of the control and reacted bacterial cells for overall landscapes of sulfur metabolism.

## A bacterial role in Paleoproterozoic clay formation

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### Abstract:

Microorganisms are capable of precipitating and transforming clay minerals as a result of their high surface reactivity and metabolic activity. Perhaps one of the most striking examples is the neoformism of hydrated smectite to illite (known as illitisation) through a process that involves the microbial release of structural Fe(III) via dissimilatory iron reduction. Illitisation also requires potassium (K) incorporation to the smectite precursor, a process akin to reverse weathering. In the modern Amazon Delta, this process has been implicated to consume nearly 10% of the global riverine K<sup>+</sup> supply, however, it remains unclear if microbes facilitate K<sup>+</sup> uptake to the sediment pile, and whether illitisation was important in the geological past. The 2.1 billion-years-old Francevillian Series of Gabon has been shown to host diverse mat-related structures, and in this regard, these rocks offer a unique opportunity to test whether ancient microbes also induced illitisation. High K content are localized in well-crystallized illite particles that are abundant in the MRS, but not in the host sediments (sandstone and black shale). This suggests that microbial biofilms trapped K<sup>+</sup> from the seawater and released it into the pore-waters during respiration resulting in illitisation. The biological processes captured by the development of K-rich illite minerals exclusively in the fossilised biofilms could provide insight for the search of biosignatures preserved in sediments derived from K-feldspar-depleted rocks, such komatiites, tonalite-trondhjemite-granodiorites, that were abundant components of the early upper crust on Earth and Mars.

# Trace element geochemistry of carbonates from hyperalkaline groundwater springs at two sites of modern continental serpentinization

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## Abstract:

Studies of hyperalkaline groundwater and springs at sites of continental serpentinization have touch on a diverse transect of biogeochemistry. The hyperalkaline, ultrabasic (pH 11-12), reducing, and low bioessential element and electron acceptor abundance makes a harsh but unique environment for microbial life<sup>1</sup>. The springs are a source of CH<sub>4</sub>, among other gases, which are predominantly abiogenic but also incorporate a complex mixture of thermogenic and potential microbial sources<sup>1-3</sup>. Sites of continental serpentinization are being evaluated as carbon sequestration sites and provide analogues for water-rock interactions on other terrestrial planetary bodies<sup>4</sup>. Most studies have focused on gas fluxes and groundwater biogeochemistry, whereas this study has targeted the carbonates precipitated upon mixing of groundwater and meteoric waters at the springs with the aim to explore their potential as a window into subsurface geochemical reactions and bioessential element availability.

Two sites of continental serpentinization, the Tablelands in NL, Canada and the Cedars in California, US, were selected for this pilot study to represent different groundwater fluid-rock interaction dynamics with contrasting geochemical fluid characteristics and inferred microbial contributions. The carbonates, precipitated at the surface of ponds and on rock surfaces, were analyzed for major (Ca, Mg) and trace elements after careful picking to remove admixed detritus and gentle pre-leaching to remove organic coatings. Samples were digested in dilute HNO<sub>3</sub> and measured with He-kinetic energy discrimination quadrupole ICP-MS to minimize Ca-based polyatomic interferences. This contribution provides preliminary results on various controls on the trace element geochemistry and relationships to inferred or previously constrained groundwater fluid-rock pathways.

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# The dynamics of the Lomagundi-Jatuli carbon isotope excursion and implications for early life

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## **Abstract:**

Temporal constraints on the rise of atmospheric oxygen have fundamental implications for the trajectory of biological evolution, yet the rate of change of atmospheric O<sub>2</sub> in the aftermath of the ~2.33 Ga Great Oxidation Event is uncertain. Following this rise, the Lomagundi-Jatuli positive carbon isotope excursion (LJE) documents a massive and anomalous disruption to the global carbon cycle (sustained  $\delta^{13}\text{C} > 10\%$ ) for as long as ~260 Ma. The long-term distinctly positive carbon isotope values recorded in marine carbonates throughout the Lomagundi-Jatuli excursion have been interpreted to correspond with a surge in atmospheric O<sub>2</sub>, however, the driving mechanisms and the duration of the LJE perturbation are poorly understood. Furthermore, possible global variation of  $\delta^{13}\text{C}$  signatures throughout this interval are largely undefined. These age models have different implications for the operation of global biogeochemical cycles in the Paleoproterozoic and thus it is important to discern between them in order to understand the development of complex life in response to increasing levels of atmospheric oxygen. We use the Re-Os geochronometer to provide direct radiometric age constraints for sedimentary sequences in the Fennoscandian Shield (the Zaonega, Seidorechka, and Polisarka formations) and Botswana (the Sengoma Argillite). These sections currently have age uncertainties of several 100 Ma and therefore our improved age constraints critically refine the Lomagundi-Jatuli  $\delta^{13}\text{C}$ -time record. Additionally, these new ages coupled with Os isotope stratigraphy will enable us to assess cause-and-effect relationships with significant changes to the style of chemical weathering and nutrient delivery to the oceans and the evolution of complex life.

## Sulfur cycling in the terrestrial deep subsurface

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### **Abstract:**

Olkiluoto, an island in south-west Finland, has been selected as the site for a deep geological repository for the final storage of spent nuclear fuel. An understanding of the geomicrobial processes occurring within the groundwater at this site is therefore important to ensure long-term, safe storage of the fuel. Of particular concern is the generation of sulfide, as it can induce corrosion of the waste-bearing copper canisters. Sulfide is detected in relatively few drillholes at Olkiluoto despite sulfate being present in the groundwater up to ~300 m depth. To determine what electron donor(s) drive sulfidogenesis we investigated three different groundwaters where sulfate is available but the concentration of sulfide differs from 0–1.5 mM. Geochemical and isotopic data indicated that sulfate reduction was ongoing in two of the three groundwaters. However, combining these analyses with metaproteogenomics revealed that sulfate reduction was active in all three groundwaters. In the groundwater with geochemically undetectable sulfate reduction, a community of sulfate-reducing and sulfide-oxidising bacteria mediate a cryptic sulfur cycle. Hydrogen and small organic compounds provide electron donors for sulfate reduction. The produced sulfide is then cycled to sulfate by the activity of sulfide-oxidising bacteria. The ability of sulfide-oxidising bacteria to limit the accumulation of sulfide was further demonstrated in groundwater incubations amended with sulfide and nitrate. In all instances sulfide was fully removed. The results shed light on the drivers of sulfidogenesis at Olkiluoto and highlight a potentially beneficial sink for sulfide. They also contribute towards our understanding of microorganisms in deep terrestrial subsurface ecosystems and their role in geochemical cycling.

# Calcium isotope fractionation during bacterially mediated carbonate precipitation

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## Abstract:

The metabolic activity of microbial communities in marine sediments changes the local chemistry and thus influences mineral precipitation and dissolution within sedimentary environments. In particular, the activity of sulfate-reducing bacteria generates alkalinity and can raise local pH, driving sedimentary carbonate precipitation. To better understand the link between calcium carbonate precipitation and sulfate-reducing bacteria metabolism, we have explored the calcium isotope fractionation during the precipitation of calcium carbonate in pure cultures of the marine sulfate-reducing bacteria *Desulfovibrio bizertensis*. We show that there are different calcium isotope fractionation factors during bacterially mediated carbonate mineral precipitation that are calcium carbonate polymorph specific.

Then, bacterial growth was modulated using an antibiotic (ampicillin) and the evolution of  $\delta^{44}\text{Ca}$  in solution was monitored under several different growth rates. The resulting calcium isotope fractionation shows that the growth rate of the bacteria controls the oversaturation of the fluid with respect to calcium carbonate, and this growth rate influences the calcium isotope fractionation factor during carbonate mineral precipitation.

The rate of calcium isotope exchange between the precipitated mineral solid and the fluid phase, which occurs in the latter stages of the incubation, has been modelled. The modelling reveals high rates of calcium isotope exchange between the solid and fluid phase, which suggests there can be a rapid overprinting of the original calcium isotope signature from precipitation in microbially mediated carbonate mineral precipitation.

# Constraining potential sources of 24-isopropylcholestane biomarkers through functional analysis of sterol 24-C methyltransferases

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## Abstract:

24-isopropylcholestane (24-ipc), a C<sub>30</sub> sterane with an isopropyl moiety at the C-24 position, has been found in Cryogenian rocks >635 million years old and interpreted as a demosponge biomarker given that demosponges are the only known extant organisms to produce 24-ipc precursors as their major sterols. This is significant considering the oldest unambiguous morphological sponge fossils are ~535 million years old and this biomarker evidence, if correctly interpreted, pushes the sponge signal in the geologic record back ~100 million years. While a Neoproterozoic origin of derived sponges is consistent with molecular clock estimates, the interpretation of 24-ipc as a demosponge biomarker remains controversial. Trace amounts of 24-ipc have also been identified in certain Rhizaria and pelagophyte algae, and critics have suggested these organisms are the more plausible sources of Cryogenian 24-ipc biomarkers. Additionally, we identified sterol 24-C methyltransferases (SMTs), the proteins required to alkylate the sterol side-chain, in demosponge metagenomes, suggesting bacterial symbionts may contribute to 24-ipc biosynthesis in these early-evolving animals. To determine if alternative sources affect our interpretations of 24-ipc biomarkers, it is necessary to obtain a complete understanding of how 24-propyl sterols are synthesized in extant organisms. We therefore assessed the functionality of both demosponge and bacterial SMTs through heterologous expression and lipid analyses. SMTs from three demosponges alkylate the sterol side-chain in our system, providing the first experimental evidence of sponge SMT functionality. Further, ten of the bacterial SMTs tested thus far alkylate the sterol side-chain, including four SMTs identified in demosponge metagenomes. These results provide the first evidence of sterol side-chain alkylation in the bacterial domain and suggest bacterial symbionts may contribute to 24-propyl sterol biosynthesis in the demosponge holobiont. Future work will focus on identifying SMTs capable of adding the third carbon at the C-24 position of the sterol side-chain and assessing the functionality of pelagophyte and Rhizaria SMTs. Identification and characterization of these enzymes will inform molecular clock analyses used to determine which taxonomic groups likely had the genetic capacity to synthesize 24-ipc in the Neoproterozoic, improving our interpretation of Cryogenian 24-ipc biomarkers and our understanding of early animal evolution.

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# Genomic and transcriptional evidence for physiological responses to burial of the dominant carbon-fixing clade Woeseiaceae in Arctic fjord sediment

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## Abstract:

Dark carbon fixation within marine sediments is performed largely by chemoautotrophic gammaproteobacteria. The most abundant and widely-distributed of these is the clade JTB255<sup>1</sup>, which were recently classified as being a member of the Woeseiaceae. Although single cell genomic sequencing and metagenomic binning of this group showed the potential for both chemolithoautotrophy and heterotrophy, the only cultured representative of the Woeseiaceae was identified as an obligate chemoheterotroph. This highlights that uncultured Woeseiaceae clades may have fundamentally different physiologies compared to this isolate. Further, although community composition studies suggest that the Woeseiaceae are extremely abundant in marine sediments worldwide, very little is known about their transcriptional activity *in situ*. We used 16S rRNA sequencing, metagenomic binning, and transcriptomics (at 1 cm depth intervals) to uncover the *in situ* abundance, genomic content, and activity of Woeseiaceae populations in fjord sediments of Svalbard (79°N). We reconstructed 5 Woeseiaceae genomes that were unique to previously described genomes, which we placed phylogenetically into the Steroidobacterales, updating previous phylogenies which placed them into Chromatiales. The genomes encode a truncated Sox pathway for the oxidation of diverse sulfur intermediates linked to a reverse dissimilatory sulfide reductase (rDSR) pathway. In addition, sulfur oxidation could generate ATP for the reduction of inorganic carbon with a complete Calvin Benson Cycle. With increasing sediment depth, anoxic conditions stimulate the transcription of nitrite reductase (*nirS*) involved in denitrification. The cytochromes encoded in the genome span a vast redox potential, suggesting that Woeseiaceae have flexible redox preferences within microaerobic to anoxic conditions. Importantly, as Woeseiaceae continued to be buried, they increased transcription of genes related to stress-mitigation and sporulation while simultaneously decreasing transcription of genes related to growth. Sequencing at high depth resolution allowed us to capture nuanced changes that highlight the delicate interplay between redox conditions and transcriptional activity of redox-sensitive enzymes and the strategies Woeseiaceae use for subsisting after burial for future population re-seeding.

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## Probing the biogenicity of jarosite with analytical methods

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### Abstract:

Jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), a potassium and iron hydrous sulfate, is a mineral formed abiotically in a wet, acid and oxidizing environment [1]. The mineral also can be formed biotically by the metabolism of the gram negative *Acidithiobacillus ferrooxidans* bacteria, which can act oxidizing  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in a still poorly known extracellular mechanism [2]. Jarosite is important for astrobiological issues, once the mineral was discovered at the Meridiani Planum landing site and in Noctis Labyrinthus Region of Mars, showing to be a common mineral on the planet. Once bacterial processes can act in biomineralization processes by controlling the nucleation of the crystals intra or extracellularly, sometimes the mineral product can present ultrastructure, spectral characteristics and analytical responses different from those abiotic minerals. To discover how to differentiate them can be a tool for to test the biogenicity of some deposits from Mars. Here, we present the results from the comparison of biogenic and abiogenic controls precipitated in laboratory, using the bacteria *A. ferrooxidans* in the biotic synthesis, and the hydrogen peroxide in the abiotic pathway. In addition, the experiment was replicated with the addition of neodymium nitrate in order to observe some possible incorporation of the REE in the crystal lattice by the biotic process, using the Nd as a biomarker. The results derived of synchrotron-based X-ray fluorescence, X-ray diffraction and X-ray absorption, complemented by SEM/EDS analysis, showed parameters which can be useful to differentiate the biogenic and the abiogenic minerals. The Nd seems to have incorporated to the crystal lattice in the biotic synthesis, in which some Fe atoms were replaced by Nd. The same did not occur in the abiotic processes. The incorporation of Nd in the abiotic synthesis are being now better investigated in order to understand the mechanisms of biomineralization of jarosite by the *A. ferrooxidans*, as well as the variables which can control these bacterial processes.

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# The dose makes the poison: Cyanobacterial photosynthetic mechanisms in balance with defensive strategies against arsenic, salinity, and UV radiation in a high-altitude microbial mat system.

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## Abstract:

Cyanobacteria bridge the evolutionary transition between anoxygenic and oxygenic photosynthesis as the only prokaryotes capable of performing oxygenic photosynthesis. Lithifying cyanobacteria are considered “living fossils” and the resulting stromatolites are often studied as model organisms of ancient Earth. Before atmospheric oxygenation, cyanobacteria could have used a variety of reduced substrates as electron donors for photosynthesis. Among these is arsenite, the most common reduced form of arsenic, which was found abundantly in ancient Earth due to extensive volcanic activity<sup>1</sup>. Despite the toxicity of arsenic, arsenite-based photosynthesis has been reported in bacteria<sup>2</sup>. Moreover, Nagy et al.<sup>3</sup> proposed the co-regulation of genes involved in membrane transport of arsenic and those encoding for a key enzyme in photosynthetic sulfide oxidation in cyanobacteria.

We used microsensors to investigate the protective and metabolic strategies of cyanobacteria in stratified, lithifying microbial mats in Pozo Bravo, an arsenic-rich, hypersaline lake. This lake forms part of the evaporitic basin Salar de Antofalla, located in the volcanically influenced Argentinian Andes (3300 m.a.s.l.). In-situ measurements through the diel cycle showed photoinhibition of oxygenic photosynthesis and downward migration of oxygenic phototrophs in the afternoon. Ex-situ addition of up to 500  $\mu\text{M}$  arsenite to the mats did not affect oxygenic photosynthesis. Yet, after the second addition within 24 hours, it induced an increase in gross rates of sulfide-driven anoxygenic photosynthesis in the cyanobacterial layer. Analysis with  $\mu\text{XRF}$  showed no detectable mineral-phase-associated arsenic naturally present in the microbial mats in February 2019. Therefore, Pozo Bravo cyanobacteria were not exposed in-situ to the high concentrations of inorganic arsenic added during ex-situ measurement.

The surprising resilience of oxygenic photosynthesis by cyanobacteria to arsenite could be a result of constitutive expression of enzymes involved in the excretion of arsenic. As total arsenic in the mats and sediment have previously been reported to reach up to 15.5  $\text{mg L}^{-1}$ <sup>4</sup> the phototrophic community might be adapted to pronounced seasonal changes in arsenic abundance. Additionally, the delayed increase in gross photosynthetic rates supports the regulatory coupling of arsenic resistance to sulfide oxidation.

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# The Paleoenvironmental implications of an oncolite and stromatolites from early Miocene Lake Manuherikia, New Zealand

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## Abstract:

During the Early Miocene (~19 Ma), New Zealand's Central Otago region was covered by Lake Manuherikia, an extremely large (5,600 km<sup>2</sup>) fresh water body. Fossils, including stromatolites and oncolites, are preserved in sedimentary strata of the Manuherikia Group. This study aims to reconstruct aspects of the lake's paleoenvironment by analyzing the internal structures of these fossils, notably their pebble-sized cores, as well as the chemical composition of the biologically mediated layering. The oncolite core consists of a sedimentary pebble, whose angular shape and shale composition is indicative of a low-energy environment. A setting with minimal tidal activity allowed cyanobacteria to attach and grow on the surface of the pebble, forming a spherical shape as the unfixed core was gradually displaced in the lake. The core of the stromatolites consists of freshwater sponges, characterized by the presence of spicules and gemmules, which observed were in thin section under an optical microscope. Several types of fragments are also recognized, including plant debris and tubular structures, tentatively identified as Leptoceridae caddisfly larvae shells. Leptoceridae caddisflies prey on freshwater sponges, impeding their growth and providing an ideal surface for cyanobacteria in the lake to bind and accumulate. Micro X-ray fluorescence and Laser Ablation ICP-MS reveal that the fossilized microbial layers are likely composed of a variety of minerals, such as clay, silt, biotite, illite, dolomite, and ankerite. Strong and anti-correlated variations between Ca and Fe, and between Ca and Sr, and are identified across the layers using Micro X-ray fluorescence imaging. Their variation may indicate fluctuating environmental conditions with time scales of months to years. Future research should address the possibility that the Ca/Sr fluctuations represent temperature fluctuations, as has been proposed for marine corals.

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# The role of temperature, pH, and geranylgeranyl reductase expression in *Sulfolobus islandicus* GDGT lipid cyclization

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## Abstract:

Archaea occupying environments characterized by extreme heat, acidity, or energy limitation produce distinctive isoprenoid membrane lipids called glycerol dialkyl glycerol tetraethers (GDGTs). These lipid structures may contain 0 to 8 cyclopentyl rings (GDGT-0, GDGT-1..., GDGT-8) and up to one cyclohexyl ring (crenarchaeol). A higher degree of cyclization is thought to confer greater membrane stability at extreme conditions. The biochemical mechanism(s) by which Archaea modify the number of rings in their GDGT lipids remains undescribed, though environmental factors such as low pH, high temperatures, or electron donor/acceptor availability are known to affect the degree of GDGT cyclization in both environmental and lab-cultured organisms. We have also found that over-expression of the gene encoding for the essential lipid biosynthesis enzyme geranylgeranyl reductase (GGR), shifts GDGT profiles in the model thermoacidophilic archaeon, *Sulfolobus islandicus*.

To better understand how *S. islandicus* GDGT cyclization responds to sub-optimal environmental conditions and genetic manipulation, we induced shifts in GDGT cyclization to compare with protein and transcript profiles. We performed temperature and pH stress experiments with three *S. islandicus* strains: 1) REY15A, wild-type strain, 2) Sis/pOE-GGR, strain containing an over-expression vector for the GGR-encoding gene, and 3) Sis/pOE, a control strain containing an empty over-expression vector. All strains grew significantly slower at sub-optimal temperature or pH relative to optimal conditions, but Sis/pOE-GGR consistently grew slowest among strains and across all culture conditions. Lipid profiles from optimal culture conditions showed that the degree of GDGT cyclization over the course of growth subtly decreased in Sis/pOE-GGR and subtly increased in the control strain, Sis/pOE. Corresponding quantitative proteomics confirmed GGR over-expression in Sis/pOE-GGR relative to Sis/pOE and showed that GGR over-expression co-occurred with differential expression of a cluster of oxidative stress response proteins and several hypothetical proteins. Based on previous cultivation studies, we predict that sub-optimal temperature and pH conditions will induce higher degrees of GDGT cyclization and differential expression of stress response proteins in *S. islandicus*. The effect of sub-optimal temperature and pH conditions combined with over-expression of the GGR-encoding gene is less certain. Quantitative proteomics and RNA-Seq transcriptomics are in progress across all growth experiments. We will compare protein and transcript expression with growth rates and GDGT profiles for a comprehensive analysis of potential biochemical mechanism(s) and regulatory systems contributing to GDGT cyclization under various sub-optimal environmental conditions.

## Diagenetic evolution of iron sulfides produced by sulfate-reducing bacteria

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### Abstract:

Iron sulfides are widespread at Earth's surface, and among them, pyrite (FeS<sub>2</sub>), the most stable one, is found throughout the whole geological record. At modern Earth's surface, sulfides are mainly produced upon the activity of sulfate-reducing microorganisms. Thus, pyrite is assumed to be a good candidate in the search for biosignatures. However, we lack a detailed understanding of the role of sulfate-reducing bacteria (SRB) versus diagenesis in the formation of pyrite.

Here we explored the nature of iron sulfides formed in pure cultures of *Desulfovibrio desulfuricans* grown in the presence of nano-particulate Fe<sup>III</sup>-phosphate, as well as their evolution upon pressure and temperature. Whereas most studies only show the formation of metastable mackinawite (FeS) or greigite (Fe<sub>3</sub>S<sub>4</sub>) in SRB cultures, pyrite formed in our cultures in the presence of nano particulate Fe<sup>III</sup>-phosphate after only 1 month. At earlier stages (10 days) however, only FeS and Fe<sup>II</sup>-phosphate (vivianite) were obtained. Diagenesis was simulated by heating these 10-day old culture samples at 75°C or 150°C for 1 or 10 days under strictly anoxic conditions. All products were characterized by X-ray diffraction, Scanning and Transmission Electron Microscopy. Whereas vivianite evolved into highly crystallized iron phosphate oxide-hydroxides at the highest temperature, amorphous FeS transformed into around 100-nm to few μm spheres or octahedrons of pyrite whatever the thermal treatment. Comparison with the thermal evolution of abiotic controls (Fe sulfides and phosphates) allows us to discuss the roles of organic matter, microbial activity and temperature in the formation of pyrite in our system.

# Rice soil microbial communities respond to incorporation of silicon-rich soil amendments

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## **Abstract:**

Biogeochemical cycling in rice paddy soil is driven by microbial activity. Use of plant-based silicon amendments—which decrease arsenic uptake in rice—have the potential to impact the microbial community. In this study, we added plant-based and synthetic Si amendments of calcium silicate, silicon-rich rice husk, and charred rice husk to 2m<sup>2</sup> rice paddy mesocosms, and compared them to nonamended paddies to investigate the impact of silicon amendments on the microbial community (3 replicates per treatment, 12 paddies total). Over the course of the growing season, we collected porewater for chemical analysis (redox, iron(II), arsenic speciation), methane gas flux measurements, and rhizosphere and bulk soil from each paddy. We sequenced the 16S ribosomal subunit gene from 120 rhizosphere and bulk soil samples from 5 timepoints, and assessed changes in microbial diversity and relative abundance of microbial groups known to be involved in biogeochemical cycling of iron and methane. Our preliminary results demonstrate that rice husk amendment lowered porewater redox, and increased porewater iron(II). We identified iron-oxidizing bacteria, iron-reducing bacteria, methanogens, and methanotrophs. Understanding the microbial community of iron cycling bacteria in flooded rice paddies is important in predicting arsenic uptake in rice, because iron-oxides are largely responsible for sorbing arsenic in soil. Additionally, flooded rice paddies are a major anthropogenic source of methane, and agronomic practices should not exacerbate these greenhouse gas emissions.

# Paleosol phosphorus record shows continental weathering not directly responsible for oxygen rise

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## Abstract:

It has been argued that phosphorus supply to the ocean (via continental weathering) has been a primary control on marine productivity and oxygen production<sup>1,2</sup>, and that during the late Precambrian, the terrestrial biosphere expanded and increased oxygen through intense weathering and nutrient delivery to shallow marine systems<sup>2,3</sup>. Here, we compile a 3 Ga record of paleosol phosphorus measurements (n = 2977) to assess whether the terrestrial geologic record supports either of these hypotheses. Rather than recording a Neoproterozoic state change, we show that the P/Ti ratios from paleosols are stable after the exposure of subaerial continents at ca. 2.8 Ga. Within the dataset, peak times of paleosol occurrences correspond closely to peaks in zircon abundance<sup>4</sup> from the global rock record, which we interpret to reflect periods of maximum subaerially exposed, weatherable surfaces, which would theoretically produce maximum weathering fluxes into the oceans. By comparing the paleosol P record with marine shale<sup>5</sup>, continental igneous<sup>6</sup>, and diamictite P records<sup>7</sup>, we demonstrate that terrestrial and marine nutrient cycles are decoupled following the Neoproterozoic, with all terrestrial records reflecting the average crustal P content (0.2 weight percent). While marine shale P increases, terrestrial records remain constant, supporting a change in marine nutrient recycling<sup>5</sup> rather than variable terrestrial weathering fluxes<sup>1-3</sup> being responsible for the decoupling. Additionally, zircon peaks and paleosol distributions do not correlate directly with major state changes in atmospheric oxygen. With the marine biosphere linking marine and terrestrial records, variable continental weathering alone cannot explain changes in marine productivity and oxygen production.

The lack of a state change in terrestrial phosphorus record during or after the Neoproterozoic supports the presence of an expansive terrestrial biosphere with active phosphorus cycling prior to the Phanerozoic, as has been suggested based on multiple lines of evidence, such as sedimentary structures<sup>8</sup> and organic material<sup>9</sup>. Pervasive terrestrial ecosystems, likely dominated by microbial mats, would have had important effects on terrestrial nutrient cycling and the production of subaerial oxygen oases (or at least biosignatures that would indicate oxidative conditions), but would represent a constant background flux in terms of the atmosphere.

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# Surviving Archean UV-fluxes: The role of iron-silicate minerals and DOC in attenuating UV for early iron-metabolizing microbial life

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## Abstract:

During the Archean, Earth's surface was subjected to UV radiation levels 10-1000 x greater than current<sup>1</sup> due to the combined effects of higher energy emissions from a rapidly rotating young Sun<sup>2</sup>, and the absence of an oxygenated atmosphere that could attenuate the high energy UV rays. Radiation wavelengths from 200-300 nm are known to kill cells within minutes of exposure. In addition, the wavelength of 254 nm causes irreparable damage to DNA. It has been demonstrated that both individual silicate and Fe(III) (oxyhydr)oxide mineral phases<sup>3,4</sup> as well as Si-Fe-aggregates<sup>5</sup>, can attenuate UV radiation, ultimately allowing cells to survive. However, the characteristics of these mineral particles, especially when present as nanophases and colloids, and how their properties might influence the survivability of iron-metabolizing microbial life is not well constrained. Specifically, it remains unclear what levels of attenuation would be necessary to allow cells to survive, and what this would imply about the Archean cellular environment. In this experimental study we investigate Archean-ocean relevant Fe-silicate-organic-carbon nanoparticles and colloids using a combined approach of microscopy, UV spectroscopy, geochemical characterization, and microbial cultivation. The aims are to determine: (1) the chemical and physical properties of these aggregates, such as aggregate size, morphology, surface charge properties, and particle chemistry; (2) how well these properties affect the attenuation of light from a UV source, and (3) whether a phototrophic Fe(II)-oxidizing microorganism can survive prolonged UV exposure when cultured with suspended Fe-silicate-carbon particles.

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## Implications of recycling flowback and produced water on microbial community composition and scale formation

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### Abstract:

Hydraulic fracturing is a water intensive process to recover oil and gas from tight geologic formations. An average of 15,000 m<sup>3</sup> of water, typically freshwater, is used per well to make the injected hydraulic fracturing fluid (HFF). After fracturing, between 30-80% of the injected volume returns to the surface as flowback and produced water (FPW). The FPW often has high total dissolved solids (10,000 mg/L to >300,000 mg/L) and is a complex mixture of hydrocarbons from the geologic formation, compounds from the HFF and compounds that form as the product of secondary downhole reactions. This water intensive process has led to a variety of concerns ranging from the allocation of freshwater for mixing HFF to the treatment and disposal of the FPW. One proposed means of addressing both is through reuse of FPW in the makeup of new HFF. However, this may pose risks related to the seeding of sulfate reducing and hydrogen sulfide producing bacteria, as well as promoting scale formation, in wells fractured with recycled FPW. In this study, we analyzed the inorganic composition of the FPW and microbial communities of two different wells in the Duvernay Formation of Alberta, Canada over the first 100 days of fracturing. One well used solely freshwater for HFF and the other well used a portion of FPW to make HFF. Using geochemical modelling and 16S rRNA analysis, we observed minimal changes in the inorganic geochemistry; however, the recycling of FPW encouraged the growth of *Halanaerobium*, which is known to produce hydrogen sulfide. In both wells the FPW had saturation indices (>1) indicating conditions favourable for barite precipitation within the first hour and for quartz precipitation starting at 9 days. While celestine and SiO<sub>2(Am)</sub> were undersaturated in the FPW for the duration of the time studied in both wells. This indicates that in the FPW for the Duvernay formation there is a risk of barite scale formation regardless of the source water used to mix the HFF and with the use of recycled FPW the risk of souring and corrosion may increase as halotolerant hydrogen sulfide producing bacterium, such as *Halanaerobium*, may be introduced into the well. Ultimately, these results enhance our understanding of the potential risks related to the recycling of FPW.

## **Harnessing microbial iron cycling for a pilot-scale attempt at iron duricrust re-formation.**

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### **Abstract:**

High grade iron ore deposits in tropical areas are capped by a hard, erosion-resistant iron duricrust that protects the friable ore below<sup>1</sup>. Geochemical evidence suggests that biogeochemical cycling of iron has played a critical role in the formation and ongoing evolution of these duricrusts even until the present day<sup>2</sup>. Hotspots for microbial activity in pools perched on iron duricrusts in Brazil indicates that extensive microbial iron cycling is occurring, with 5-25 ppm soluble iron typically measured, and up to 1000 ppm soluble iron detected in one instance. A novel iron reducing culture was enriched from one of these microbial hotspots in the iron duricrust ecosystem. The consortium was effective at goethite dissolution (up to 20% goethite reduction) coupled to fermentation and was used in a pilot scale attempt to drive iron cycling and promote iron duricrust re-formation from iron mine waste material in Brazil. Effective microbial iron reduction was observed in all treatments (*i.e.*, with and without plants, with and without the microbial inoculum, and closed bioreactor vs *in situ* conditions). Over the 15-months of the pilot scale experiment almost all treatments were dominated by deep branching candidate phyla radiations (e.g. OD1, OP11) suggesting these microbial lineages may play a role in fermentation and/or metal reduction. At end-harvest of the pilot scale experiment, the strongest aggregation of the iron duricrust fragments was observed in treatments that involved *in situ* microbial iron reduction (compared to *ex situ*). This proof of concept shows that harnessing microbial iron cycling holds promise for re-formation of iron duricrusts and accelerated remediation of iron ore deposits post-mining.

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# Assessing Ediacaran paleoecology using computation fluid dynamics

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## **Abstract:**

The Ediacara biota are a paraphyletic group of macroscopic eukaryotes (including some animals) that represent the first radiation of structurally complex life. Reconstructing their paleoecology is therefore pivotal to understanding origins of the modern, animal-dominated biosphere. In particular, reconstruction of feeding mode, reproduction, and motility provide fundamental information for assessing nutrient cycling and quantifying ecosystem engineering in the latest Ediacaran. Computational fluid dynamics (CFD) is a powerful analytical tool that provides answers to many of these questions. Here we highlight our recent studies that have advanced our understanding in Ediacaran paleoecology, discuss important caveats of fluid studies, and provide future research avenues and conceptual models for how to move forward in this subfield of Ediacaran paleontology.

# Abiogenic digitate structures in hot spring silica sinters of the El Tatio geothermal field, Chile: Implications for biosignatures on ancient Earth and Mars

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## Abstract:

Digitate silica sinters from the El Tatio geothermal field in Chile closely resemble ancient hydrothermal silica deposits that were recently identified in the Home Plate Formation, Gusev Crater on Mars<sup>1</sup>. The digitate sinters at El Tatio have been interpreted as a potential macroscopic biosignature, containing stromatolitic laminae and living microbial communities. The presence of Martian digitate sinter therefore requires an unambiguous test of biogenicity, which can be provided by examination of the El Tatio structural analogues and their growth patterns. Here we show that El Tatio digitate silica structures are subaerial formations that have all grown tilted into the prevailing eastward wind direction, and exhibit laminar growth patterns that coincide with day-night cycles of wind- and thermally-driven evaporation and rewetting. In contrast, filamentous cyanobacteria only inhabit subaqueous cavities that cross-cut the primary laminations. These observations imply that the digitate sinter structures found on the ancient surface of Mars can be explained as purely abiogenic features resulting from the evaporation of silica-rich hot spring waters influenced by strong Martian surface winds. Our results also have wider implications on interpretations of stromatolitic growth structures in ancient silica deposits on Earth. We report non-isopachous stacking of layers and detrital grains trapped well beyond the angle of repose in the digitate sinters of El Tatio. Both features are typically interpreted as strong evidence for the past presence of microbial mats, as upward growth of photosynthetic microorganisms during sediment trapping causes non-isopachous stacking of layers, while adhesive microbial mats enable the trapping and binding of sediments beyond the angle of repose. In contrast, non-isopachous El Tatio sinters are produced by wind-driven sand deposition, non-uniform capillary delivery of silica and salts and silica precipitation on uneven nodular surfaces, while grain adhesion on vertical surfaces is caused by rapid wind- and thermally-driven silica precipitation. Overall, our study improves the distinction between biogenic and abiogenic textures in subaerial hydrothermal systems, with critical geobiological implications for ancient silica deposits on Earth and Mars.

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# **Coupled paleoenvironmental and redox state analysis of 1 billion-year-old black shale units from the Fury and Hecla Group, Nunavut**

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## **Abstract:**

Thick sedimentary successions exposed in the eastern Arctic archipelago, Nunavut, and Western Greenland, offer critical insight into the tempo and influence of the rise of eukaryotes in the terminal Mesoproterozoic Era (ca. 1000 million years ago). Recent geochronological, chemostratigraphic and paleontological studies from the late Mesoproterozoic Bylot Supergroup of the Borden Basin in northern Baffin and Bylot Islands shed light on the evolution of a late Mesoproterozoic intracratonic basin system comprising the Borden, Fury and Hecla, Hunting–Aston, and Thule basins, collectively known as the Bylot basins. The Fury and Hecla Group comprises a relatively understudied succession of presumably late Mesoproterozoic sedimentary rocks interpreted to be broadly correlative with the Bylot Supergroup.

Detailed sedimentological studies of black shale units from the Fury and Hecla Group offer an opportunity to study mid- to outer-ramp depositional environments with known microfossil assemblages. Coupled with new iron speciation data from the shale rich units of the Fury and Hecla Group, these data will enable comparisons to be made between redox state and the diversity of microfossil assemblages. These paired paleobiological and paleoecological studies, in corroboration with rhenium-osmium geochronology on these black shale units from the Fury and Hecla Basin, can then be directly compared to presumably equivalently-aged successions in the Borden and Thule basins.

## Functional overlap between microbial mat morphotypes

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### Abstract:

In the fossil record, microbial mats are morphologically diverse and temporally and geographically ubiquitous. The appearance and structure of mats are used to infer paleoenvironmental conditions at the time of their formation, but even in modern mats relating macromorphology of mats to metabolisms and geochemical cycles within them remains a challenge. In this study, we evaluated the community composition (16S rRNA gene and metagenomics), function (metagenomics and metaproteomics), and biogeochemistry (microsensors) of microbial mat morphotypes in Middle Island Sinkhole, Michigan. The low-O<sub>2</sub> sulfate-rich submerged sinkhole environment hosts flat white mat, flat purple mat, uplifted purple mat (“fingers”), and variably pigmented purple/brown mat (“giraffe”), all overlying organic-rich sediment. White mat was the most biogeochemically distinct from the other mat types, with undetectable photosynthesis, high rates of O<sub>2</sub> consumption and highly variable sulfide exposure. While white mat was dominated by diverse sulfide-oxidizing bacteria and sulfate-reducing bacteria (SRB), flat purple, finger, and giraffe mats additionally hosted abundant cyanobacteria. All three cyanobacterial mat types had similar rates of net O<sub>2</sub> production during high light conditions in the afternoon, but finger mat experienced less sulfide due to physical separation from sediment-hosted SRB and lower within-mat sulfide production rates. Anoxygenic photosynthesis using sulfide was observed in finger and some flat mats, and based on similarities in functional profiles, is likely operating in other mat morphotypes. The cyanobacterial community differed the most between finger mat (dominated by *Phormidium* and *Planktothrix*) and giraffe mat (*Pseudanabaena* and *Spirulina*). We observed functional overlap in genes encoding oxygen, sulfur, and nitrogen metabolism within the pairs of metagenome-assembled-genomes of *Phormidium* and *Pseudanabaena*, and of *Planktothrix* and *Spirulina*. In addition, the identity of key SRB and sulfide-oxidizing bacteria differed between white, giraffe, and finger mat, as did their genetic potential for O<sub>2</sub> tolerance (SRB) and N and S metabolisms (sulfide-oxidizing bacteria). Proteomic data showed that a relatively small number of proteins from a few key groups (*Phormidium*, gammaproteobacterial sulfide oxidizers, and SRB) were significantly differentially abundant between mat morphotypes. However, many proteins were observed in similar abundances across morphotypes, suggesting core functions are shared between these mats. Our study uncovered variability in taxonomic composition yet conservation in key metabolic functions across distinct morphotypes of Middle Island Sinkhole microbial mats. The presence of core functional groups and metabolisms across these mats, and the consistency in geochemical fluxes, complicates our interpretation of the biogeochemical role of different mat morphotypes in Earth history.

# Understanding the role of clay minerals in the three-dimensional fossilization of erniettomorphs from the Ediacaran Wood Canyon Formation, Nevada

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## Abstract:

Global Ediacaran sandstones, including the mass flow deposits in the Wood Canyon Formation in the Montgomery Mountains, Nevada preserve three-dimensional fossils of *erniettomorphs*, soft-bodied organisms with uncertain taxonomic affinities. This unusual mode of fossilization can maintain a three-dimensional morphology of non-recalcitrant body parts in the absence of obvious replacive minerals, such as pyrite, carbonate, or clay cements. To better understand this mode of fossilization, we analyzed *erniettomorphs* from the Wood Canyon Fm. and the surrounding matrix. Petrographic analysis of thin sections revealed abundant clay mineral grains in and outside of the fossil. Larger quartz grains are more abundant within the fossil than on the outside, smaller grains of clay minerals filled the spaces between the quartz grains. Electron dispersive X-ray spectroscopy (EDS) revealed a strong compositional similarity between the material within the fossils, the surrounding rock matrix, and the interface that preserves mm-scale ridges, although the ridge surfaces contain more oxidized iron. The clay minerals were enriched in magnesium, iron, potassium, and aluminum. These enrichments, and their spatial distributions, were consistent with the presence of chlorite, smectite, illite, and kaolinite. Least-square linear combination fitting of Fe K-edge X-ray absorption near edge structure (XANES) spectra confirmed chlorite as a major iron-containing phase, and suggested the presence of minor phases that contain Fe(II) such as pyrite, siderite, and biotite. Chlorite is a likely diagenetic/metamorphic product of a clay mixture that originally contained smectite and kaolinite. As the sediment was buried deeper, dioctahedral smectite transitioned to illite, releasing iron and magnesium into the pore water and enabling the chloritization of kaolinite at lower green schist facies. Based on these data, we propose that quartz and clay grains that were originally present in the organism helped maintain the three-dimensional structure during the decay of the organic material, whereas some of the more abundant clay minerals may have helped inhibit the microbial activity. This allowed enough time for the formation of minor secondary precipitates that cemented the sand grains within the fossil. Taphonomy experiments will further test this scenario by investigating the delayed decay of a scallop's adductor muscle buried in smectite-rich or poor sand, the associated microbial activity, and the formation of early diagenetic mineral phases within and outside of soft tissues.



# Acid weathering, clay transport and enhanced phosphate supply to early Paleoproterozoic oceans following the Great Oxidation Event

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## Abstract:

Following the Great Oxidation Event (GOE) at ca. 2.5–2.3 billion years ago, oxygenation of the atmosphere led to increased rates of chemical weathering, unprecedented acid production from oxidation of crustal pyrite, and enhanced levels of nutrient transport to the oceans<sup>1</sup>. Higher levels of terrestrial phosphate supply would then have boosted marine primary production and facilitated the burial of more organic carbon than in any previous time in Earth's history. This is inferred to have led to a further rise in atmospheric oxygen and a sustained positive carbon isotope excursion between ca. 2.22 and 2.06 Ga—events collectively known as the Lomagundi Event (LE)<sup>2,3</sup>. Although phosphate was initially sourced from the dissolution of crustal apatite<sup>4</sup>, the mechanisms by which it was transported to the oceans and then concentrated into P-rich deposits are unclear. Here we show that phosphate is readily adsorbed onto clay particles at freshwater conditions (pH 4, ionic strength=0.01 M) but that phosphate is released in marine aquatic environments (pH 8, ionic strength=0.56 M). We thus propose a new nutrient delivery mechanism that was activated by the GOE: during terrestrial weathering, phosphate was carried by suspended clay particles into estuarine environments where it was desorbed, released into seawater as ionic phosphate species and then utilized by photosynthetic plankton. Upon death of the plankton, shoaling would have concentrated the biomass, leading to the deposition of the first commercially important phosphorites. Our research provides a novel mechanistic link between the rise in atmospheric O<sub>2</sub> and the LE.

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# New isotopic perspectives on carbonate geochemistry from the Gunflint Iron Formation

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## Abstract:

Fluid chemistry encoded in Precambrian chemical sedimentary rocks can improve understanding of how habitable environments are created and maintained on the surfaces of terrestrial planets early in their geologic history. Proterozoic iron formations are a potential indicator of ancient marine chemistry, as they contain minerals that record depositional chemistry and host some of the oldest traces of life on Earth<sup>1,2</sup>. The 1.88 Ga Gunflint Iron Formation in Ontario, Canada is an example of a relatively pristine banded iron formation and is rich in minimally-altered carbonates ranging from sideritic to ankeritic compositions, with calcite and dolomite becoming more common as metamorphic grade increases<sup>3</sup>. Targeting carbonates as paleoclimatic recorders using stable isotopes is well-established in these Gunflint rocks<sup>4,5</sup>, though interpretations are equivocal. In response to this, we conducted boron and clumped isotope measurements on the least-altered Gunflint carbonate facies to determine whether these rocks preserve primary pH and temperature signals. Boron isotopes have been applied as a pH proxy in Ca-carbonates due to the dependence of boron speciation and isotopic composition on pH<sup>6</sup>, but to our knowledge have not been examined in Fe-carbonates. The carbonate clumped isotope paleothermometer exploits the thermodynamic preference of heavy C and O isotopes (<sup>13</sup>C-<sup>18</sup>O) to bond with each other, rather than with lighter isotopes, as the temperature of precipitation decreases<sup>7,8</sup>. Preliminary clumped isotope measurements of Gunflint carbonates likely reflect temperatures of burial diagenesis, ranging between 80 and 130°C. While dubious for paleoenvironmental interpretation, these results are consistent with thermal maturity indices that suggest these samples did not experience burial temperatures above 150°C [3-5].  $\delta^{11}\text{B}$  in Gunflint carbonates ranges from +4 to -38‰, which is substantially depleted relative to modern marine carbonates (~-22.1‰) [6], and is consistent with B-isotope alteration during burial diagenesis<sup>9</sup>. Due to the sensitivity of clumped isotopes to solid-state bond reordering<sup>10</sup> and the lack of understanding of B-isotope systematics in Fe-carbonates of any age, our results underscore the necessity of determining (1) the kinetics of bond reordering and (2) the behavior of boron isotopes in siderite to improve interpretation of natural Fe-carbonates in deep-time.

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# Regulation of N<sub>2</sub> production rates and pathways by trace O<sub>2</sub> in a persistently anoxic fjord, Saanich Inlet, British Columbia

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## Abstract:

The oceans are losing oxygen (O<sub>2</sub>) due to warming climate and increasing nutrient fluxes from land to the sea. As O<sub>2</sub> declines, microorganisms shift to anaerobic metabolisms supported by nitrogen substrates, such as anammox and denitrification, which both involve the reduction of oxidized nitrogen compounds (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>) and production of N<sub>2</sub> gas. It is unclear how these competing anaerobic metabolisms, and their distinct environmental impacts, are regulated in the transition from oxic to anoxic conditions. To determine how trace amounts of O<sub>2</sub> may differentially regulate rates of anammox and denitrification, we used <sup>15</sup>N-labeling incubations to measure process rates in Saanich Inlet, BC, a persistently anoxic fjord that experiences periodic oxygenation events. Using environmental samples collected both immediately following an oxygenation event and again after the fjord returned to anoxic conditions, we measured how potential process rates respond to spatial geochemical gradients in the water column as well as experimental manipulation of trace (0-10 μM) O<sub>2</sub>. We found that rates of anammox and denitrification follow distinct patterns over geochemical gradients. While anammox persists at lower but relatively constant rates across a range of conditions and redox potentials, denitrification occurs at much higher rates but only in isolated portions of the water column, likely due to higher sensitivity to specific geochemical conditions. Furthermore, from experimental manipulation of O<sub>2</sub> levels, we found that trace amounts of O<sub>2</sub> differentially affect rates of anammox and denitrification, suggesting that O<sub>2</sub> directly regulates these processes along environmental oxyclines. While denitrification was inhibited by 4-6 μM O<sub>2</sub>, anammox persisted in the presence of up to 8 μM O<sub>2</sub>. Notably, however, lower amounts of O<sub>2</sub> (0.1 – 2.5 μM) stimulated rates of denitrification without affecting rates of anammox. These findings are consistent with previous long-term studies on rates of anammox and denitrification in Saanich Inlet, which have found persistent but low rates of anammox throughout the year and isolated peaks of high denitrification following oxygenation events. Collectively, these findings highlight the importance of trace O<sub>2</sub> in regulating the transition from aerobic to anaerobic metabolisms, which can be used to build more accurate predictive models of the geochemical outcomes of ocean deoxygenation.

## A pre-Proterozoic origin for a cyanobacterial CCMs

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### **Abstract:**

The carbon isotopic difference between carbonate rocks and organic carbon provides a comprehensive record of the mode and variety of microbial carbon fixation through Earth history. This anabolic record could, in principle, be used to identify the dominant primary producers in ancient ecosystems, for example determining ecological role of cyanobacteria in Proterozoic oceans. While the Paleoproterozoic accumulation of atmospheric oxygen known as the Great Oxidation Event places a minimum age constraint on the emergence cyanobacteria, direct evidence for the role of cyanobacteria preceding the ecological shift towards photosynthetic eukaryotes is limited. Two hurdles exist in using the carbon isotope record to determine the ecology of Proterozoic primary producers including i) accounting for fractionations that occur as the primary substrates of carbon fixation are preserved in ancient rocks (1) and ii) the possibility that extant cyanobacteria are physiologically distinct from Proterozoic cyanobacteria. Here we present a new evaluation of the primary carbon isotope fractionation associated with carbon fixation during the Middle Proterozoic (1.8-1.0 Ga) using a bootstrap resampling scheme and account for the transformation of dissolved CO<sub>2</sub> and primary biomass into carbonate minerals and organic carbon. In concert, we use a genetic system in the model cyanobacterium *Synechococcus* sp. PCC 7002 to investigate net carbon isotope fractionation by analogs of ancient cyanobacteria with varying physiologies under relevant *p*CO<sub>2</sub> and pH levels. Comparing net carbon isotope fractionation by cyanobacteria with and without a CO<sub>2</sub> concentrating mechanism (CCM) reveals cyanobacteria without CCM can only explain a small fraction of the carbon isotope record during the Middle Proterozoic. In contrast, net carbon isotope fractionation by cyanobacteria with a CCM can explain > 95% of the carbon isotope record during this time, suggesting a pre-Proterozoic origin for the cyanobacterial CCM.

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# Geomicrobiology of five hot springs in the Culex Basin thermal complex, Yellowstone National Park

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## Abstract:

Yellowstone National Park, USA (YNP) contains the world's highest concentration of geothermal features (~14,000) and serves as a natural laboratory to explore habitats that are geochemically analogous to conditions on early Earth or on those found on other planets. The geobiology of five hot springs were investigated in the understudied Culex Basin Thermal Complex of YNP by environmental (metagenomic) sequencing coupled to thorough geochemical analyses. The temperature and pH ranges of the study sites spanned 37.5-72.5 °C and 3-9, respectively and were characterized by the presence of dissolved methane (20-570 nM) and organic carbon (35-300 μM). Microbial communities were composed of both archaeal and bacterial populations, except one site which was dominated by bacteria, as was determined by 16S rRNA gene analysis and the identification of numerous (30-200) genomic bins. Specifically, archaeal populations consisted of several cultured and uncultured phyla including *Aenigmarchaeota*, *Aigarchaeota*, *Bathyarchaeota*, *Crenarchaeota*, *Diaforarchaea*, the DPANN superphylum, *Euryarchaeota*, *Geoarchaeota*, *Hadesarchaea*, *Korarchaeota*, *Thaumarchaeota*, *Verstraetearchaeota* and other undescribed phyla. Bacterial diversity was broad and included many novel candidate phyla only recently reported (*e.g.* the Candidate Phylum Radiation CPR, *Fervidibacteria*, *Atribacteria*, *Kryptonina*). Functional analyses revealed the presence of genes likely involved in the cycling of major geochemical constituents. For example, multiple methyl coenzyme M reductase (McrA) genes related to archaeal phyla implicated in methane cycling (*i.e.* *Verstraetearchaeota*, *Korarchaeota*, *Bathyarchaeota* and *Euryarchaeota*) were identified in hot springs ( $\geq 45$  °C) with methane concentrations  $\geq 100$  nM. The identification and inferred metabolic potential of predominant microbial populations in these geothermal systems will facilitate the selection of specific phylogenetic groups for targeted enrichment and cell labeling experiments to gain better insight into the physiology of uncultured microbes *in situ*.

# Fraction distribution and risk assessment of heavy metals in sediments of North Saskatchewan River

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## **Abstract:**

Sequential extraction technique developed by Tessier was used to select different fractions (exchangeable fraction, carbonate fraction, Fe/Mn oxide fraction, organic fraction, and residual) in both suspended sediment and bedload sediment collected in North Saskatchewan River. 9 heavy metals (Cu, Cd, Mn, Cr, Pb, Sr, Co, Mo, V) were analyzed to determine their bioavailability and subsequent toxicity. The distributions of heavy metals at 8 different sampling sites along the river are showing no significantly spatial differences from upstream of Edmonton to downstream. However, values vary between bedload and suspended sediment due to their different chemical and physical composition. Majority of Mn is observed as carbonate bound, which may result due to its special affinity towards carbonate and co-precipitation with its minerals. Cd is mostly bound to the first two fractions, while more than 90% of V is bound to the residual fraction. In bioavailable phases (exchangeable and carbonate phases), the percentages of Cu in bedload sediment are almost three times than those in suspended sediment, while the average proportion of Sr in bedload sediment is 30%, which is nearly half of that value we got from suspended sediment. Colloids of Fe-Mn oxides act as efficient scavengers for trace metals like Cr and Pb. According to the Risk Assessment Code (RAC), Mn and Cd are posing high–very high risk to the environment both in suspended and bedload sediment. Cu concentration in bedload sediment represent very high risk, while that in suspended sediment are much lower, posing medium risk. And the Sr concentration shows a different pattern, higher percentages in suspended sediment and lower percentages in bedload sediment. V and Cr fall in low risk category in most of the sites. Stable isotope analysis was used to determine the source of TOC, which points out several possible anthropogenic waste input sites. Various physicochemical parameters such as Ph, anions, alkalinity, TOC, TN, carbonate, particle size, mineral composition, etc. were also analyzed.

# Connecting the spheres: interactions between the fluid and solid Earth in the Precambrian reveal limited emergent continental crust

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## **Abstract:**

The oxygen isotope composition of the oceans through time integrates changes in ocean temperature, nutrient cycling, and water-rock interaction over Earth history. However, marine chemical sediments do not provide clarity on this record, and their oxygen isotope compositions are typically cast in terms of two end-member environmental interpretations: either the oceans have had a constant oxygen isotope composition through time, and were much hotter deep in the past, or the oceanic oxygen isotope composition has evolved through time in the face of more moderate and less variable oceanic temperatures. Here we use an alternative archive of ocean chemistry, hydrothermally altered ocean crust, and inverse geochemical modeling to constrain the oxygen isotopic composition of seawater that infiltrated the 3.2-billion year old Panorama District in the Pilbara craton of Australia. Our inverse approach uses whole rock oxygen isotope measurements and temperature estimates from fluid inclusions to estimate a time-integrated mass balance and fluid flux through altered rock. We validated the approach against oxygen isotope patterns in recently altered oceanic crust, and find that the incoming seawater  $\approx$  3.2 billion years ago had an oxygen isotope composition that was more enriched than modern, with a  $\delta^{18}\text{O}$  of  $0.9 \pm 0.1\%$ . In the context of other isotopic records from oceanic crustal rocks, these results suggest that there has likely a decrease in ocean  $\delta^{18}\text{O}$  through time, opposite in sign and magnitude to the large increases seen in carbonate sediments. If this decrease reflects the development of a significant  $^{18}\text{O}$ -enriched continental reservoir between  $\approx$  3 – 2.5 Ga, Earth's oceans may have gone through two separate phases of steady-state behavior before and after continental emergence.

## The world according to Li

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### **Abstract:**

The evolution of carbon (C) and silicon (Si) cycles directly control the Earth's climate. At the same time, both cycles are intertwined via the silicate weathering, which we can track using lithium (Li) isotopes. We generated new extensive carbonate Li isotopes record spanning the last three billion years, which we use to reconstruct the seawater Li isotope values and decipher the evolution of C and Si cycles. The global Li isotope mass balance is controlled by both the fractionations that occur during incongruent silicate weathering in the terrestrial realm and during authigenic clay formation (i.e., reverse weathering) in the marine realm as well as by the sizes of the input and output fluxes of Li. Our new Li isotope record indicates that for the majority of Earth's history the terrestrial silicate weathering was more congruent and the reverse weathering was significantly more extensive relative to modern levels, implying that profoundly different C cycle persisted during that time. The transition to the modern-like Li isotope mass balance occurred sometime in the mid-Paleozoic and is likely linked to the transition to a biologically controlled marine Si cycle and the radiation of land plants. Once the Si-secreting organisms became ecologically important they depleted the ocean from Si, significantly reducing the rate of authigenic clay formation in the sediment column and, thus, affecting the fractionation of Li. However, riverine Li isotopes must have also changed dramatically, which can be linked to the occurrence and proliferation of land plants, perhaps, more specifically, the deep-rooted trees. It is generally agreed upon that the evolution of the deep-rooted trees considerably affected the terrestrial silicate weathering and that the radiation of land plants has reshaped the river systems. The effects of these important ecological changes and their tremendous impact on the ocean chemistry, and reciprocally on the global C and Si cycles, are clearly recorded by the Li isotopes.



## Geochemical association between the surface and deep oceans on the formation of REY-rich mud in the Pacific Ocean

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### Abstract:

Deep-sea sediments containing greater amount of rare-earth elements and yttrium (REY), called REY-rich muds, have received much attention as a new resource of REY because of their great economic potential exceeding the world's current reserves on land <sup>1</sup>. However, geochemistry responsible for such a huge accumulation of REY into the deep-sea sediments is still ambiguous. In this study, we extensively performed speciation of multiple elements including REY, Fe, and P in the REY-rich muds to clarify the carriers of REY and their associated geochemical processes during the formation of REY-rich muds. Samples are collected from the two regions of the Pacific Ocean, the eastern South Pacific and the central North Pacific, where the significant variations in hydrothermal influences are observed. Our XAFS analyses revealed that REY is commonly hosted by apatite in the two Pacific regions. In the eastern South Pacific, a strongly hydrothermally-affected region, the formation of REY-rich mud is geographically coincident with the occurrence of apatite, which seems to be authigenically formed below CCD derived from phosphate ion adsorbed on hydrothermal Fe-Mn (oxyhydr)oxides. Although hydrothermal activity has been considered as an important marine process controlling the REY accumulation into the sediments, our results also indicate its potential role in the formation of apatite combined with carbonate dissolution on the deep water depth. In contrast, biogenic apatite such as fish debris seems to be the important carrier of REY into the deep-sea floor in the central North Pacific with less hydrothermal influences, as shown in the REY-rich muds in other regions. A series of our findings indicate that apatite is of specific importance as the eventual host of REY for the widespread formation of the REY-rich muds, and various geochemical processes account for the origin of apatite and its accumulation of REY<sup>2</sup>.

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## Uncultured ANME-1 archaea gain energy from either methanogenesis or anaerobic oxidation of methane

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### **Abstract:**

Uncultured archaea in the Methanomicrobia (ANME-1) perform the anaerobic oxidation of methane (AOM), or reverse methanogenesis. The majority of marine sediments lack advective transport of methane, so AOM occurs in the sulfate methane transition zone (SMTZ) where sulfate-reducing bacteria make methanogenesis exergonic in the reverse direction by consuming hydrogen. When sulfate is depleted, fermentative hydrogen increases and forward methanogenesis becomes energy-yielding. However, it is not known whether ANME-1 can switch between methanogenesis and AOM, depending on which process is exergonic. We found that ANME-1 comprised 99.24% of 16S rRNA genes from Methanomicrobia in the SMTZ and 99.95% in the methanogenesis zone in White Oak River estuarine sediments. Each of the 16 ANME-1 OTUs (97%) had peaks in the SMTZ that coincided with peaks of sulfate reducing bacteria *Desulfatiglans sp.* and SEEP-SRB1. In the methane production zone, ANME-1, but no putative sulfate-reducing bacteria, increased with depth. We re-analyzed public genomic DNA to show that ANME-1 was the only potential methanogen present in hydrogen-dependent methane-producing enrichments. We conclude that ANME-1 reverses between AOM in the SMTZ and methane production the methanogenic zone of non-seep marine sediments. This may give ANME-1 a competitive advantage over cultured methanogenic clades in marine sediments, explaining their dominance in methanogenic sediments worldwide.

# Causes and consequences of high burial efficiency in the Archean ocean

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## Abstract:

A wealth of geological and geochemical evidence suggests that the Archean ocean was largely devoid of dissolved oxygen. This stands in stark contrast to the modern ocean, which is well-oxygenated even at depth. In order to understand the dynamics of organic matter remineralization, oxygen consumption and nutrient cycling in the Archean ocean, we must therefore consider the characteristics of modern reducing environments. In these settings today – ranging from anoxic, silled basins (such as the Black Sea) to oxygen-depleted sedimentary porewaters underlying mildly oxygenated seawater – the oxidation of organic matter utilizes alternative electron acceptors<sup>1</sup> (namely dissolved nitrate and sulfate as well as particulate Fe & Mn oxides), and organic matter is often buried at greater rates than in oxic, open-ocean settings<sup>2,3</sup>. This points to two ways in which Archean organic matter cycling was likely markedly different than in the modern ocean: anaerobic remineralization pathways were likely dominant, and burial efficiency was likely higher than it is today. This different system of organic matter cycling has important implications for redox and nutrient cycling in the Archean ocean. For instance, sluggish recycling of biomass would have made organic burial a more efficient sink for macronutrients, such as phosphorus. This could have kept marine P levels quite low<sup>4</sup>, thereby limiting net primary productivity. On the other hand, efficient organic burial may have enabled atmospheric oxygenation, and thus must be considered in terms of the Archean redox budget<sup>5</sup>. Finally, the important role of anaerobic remineralization pathways in maintaining a dissolved P reservoir may have tied biological productivity to geophysical source fluxes such as hydrothermal inputs of iron and volcanic outgassing of sulfur<sup>4</sup>. Here a range of evidence for high burial efficiency in the Archean is reviewed, and the implications for ocean redox and nutrient cycling are discussed, particularly in the context of transient surface ocean oxygenation events recorded in Late Archean sediments.

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## **Spinning down to oxygenation – *Role of daylength in O<sub>2</sub> export from microbial mats***

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### **Abstract:**

The length of day on Earth has undergone a gradual, and sometimes marked, increase towards the modern 24 hours due to interactions in the Earth-Moon system. We recognized a remarkable similarity between the patterns of postulated changes in daylength and atmospheric oxygen levels, especially in the Proterozoic.

We tested the relationship between daylength and oxygen export from benthic ecosystems using reaction-diffusion modeling and direct measurements of modern cyanobacterial mats analogous to those that dominated Proterozoic ecosystems. We found that increased daylength boosts net oxygen export to overlying waters, and thus the atmosphere. Mass transfer limitation by diffusion represents the fundamental mechanistic basis behind the daylength dependency of oxygen export. Considering greater complexity of metabolic regulations and microbial behavior in our modeled and measured mats further increased the strength of the effect. Our study indicates that decrease in Earth's rotation rate would have impacted global benthic oxygen export and atmospheric accumulation, and that this mechanism could have contributed to major turning points in the history of Earth's oxygen.

# Zetaproteobacteria pan-genome reveals candidate genes for Fe-biosignature formation

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## **Abstract:**

Fossilized signatures in form of microbially produced Fe(III)-biominerals in the geologic record are indicators for the presence and activity of Fe(II)-oxidizing bacteria on early Earth, and could serve as unique biosignatures on Mars or other exoplanets. Extant members of the lithotrophic, microaerophilic Fe(II)-oxidizing Zeta- and Betaproteobacteria produce putative modern equivalents of respective microfossils in form of organic nanofibers that encrust in Fe(III) oxyhydroxides, also known as twisted stalks. Analyzing the genetic and physiological controls on stalk formation in modern Fe(II)-oxidizers is a promising venue to decipher the mechanisms underlying Fe(III) biosignature genesis, and to understand the environmental conditions under which one of the first aerobic metabolisms emerged and diversified on Earth.

Here we present a Zetaproteobacteria pan-genome comprising of 14 isolate genomes, of which 9 isolates representing 5 operational taxonomic units (OTUs) produce stalks, while the other 5 belong to 4 OTUs that do not show the stalk-trait. We identified the Zetaproteobacteria pan-genome to be open, revealing a high genetic diversity between its members. Conducting a trait-based genome-wide association study, we identified 8 conserved gene clusters shared only among stalk-forming Zetaproteobacteria. These mostly contained flagellum biosynthesis genes and *cbb3*-type cytochrome genes that are missing in non-stalk-forming Zetaproteobacteria. Overall, our results imply stalk-formers to have diverged genetically from non-stalk-formers, particularly through the acquisition and conservation of a set of genes that potentially play an important role in the synthesis of twisted stalks and Fe(II) oxidation. The conservation of flagellar genes is suggestive of either (1) a modified flagellar type III secretion system for the export of the stalk organic backbone, or (2) directed flagellar-based motility in geochemical gradients as part of their microaerophilic lifestyle, where stalks function as anchors in environments with optimal gradients of Fe(II) and O<sub>2</sub>.

## **Enrichment of potential methanogenic Korarchaea from terrestrial hot springs**

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### **Abstract:**

Environmental metagenomics has recently expanded the predicted phylogenetic and metabolic diversity of archaeal methane and alkane metabolism. Experimentally determining the metabolic capacities of these uncultured archaea in situ remains challenging and enrichment-based studies have been key in investigating novel alkane-metabolizing archaea. In this study we focus on enriching methanogenic archaea from Washburn springs, a terrestrial hot spring ecosystem in Yellowstone National Park, characterized by high methane, sulfate, carbon dioxide and hydrogen concentrations, and known to harbor a unique diversity of Methyl coenzyme M reductase (Mcr) encoding archaeal lineages. We incubated hot spring material with synthetic media based on the hot spring chemistry but without sulfate and supplemented with methanogenic substrates. Continuous transfers over several months resulted in sediment-free enrichment cultures which we evaluated using 16S rRNA and mcrA gene amplicon sequencing, microscopy, fluorescence in situ hybridization and methane measurements. Our data show an enrichment of predicted methanogenic Korarchaea. To test the genomic potential of Korarchaea to perform methanogenesis and to reveal their metabolic interdependencies with co-enriched organisms, we will employ substrate and inhibitor tests as well as stable isotope probing combined with Raman spectroscopy for single cell analysis. Our study demonstrates that traditional enrichment cultivation can be used to test first insights from metagenome-based metabolic predictions and is an essential step towards deciphering metabolic traits in experiments under defined laboratory conditions.

# Lithium isotopic system as an advanced proxy for interpreting paleoenvironmental events

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## Abstract:

When estimating a continental silicate weathering, thus far the Sr isotopic composition of the oceans has been the primary source of information. However, during recent times, this proxy has been shown not to be suitable for every occasion (e.g.<sup>1,2</sup>) and attempts have been made to find new proxies for better the understanding of the link between climate and continental weathering. The stable Li isotopes is considered as one possible solution. So far, a number of previous studies have covered the Li in the seawater (e.g.<sup>3,4</sup>), showing it to be a conservative element with a residence time approximately one million years (e.g.<sup>5</sup>). The concentration of Li in the seawater and its isotopic composition is regulated by two main factors. Firstly, the input of Li from mid-ocean ridges and inflow of dissolved Li from rivers, and secondly, removal of Li into oceanic basalts and marine sediments. Riverine Li values reflect continental weathering processes, particularly preferred uptake of lighter isotope (<sup>6</sup>Li) into secondary minerals<sup>6</sup> and concentration of heavier isotope (<sup>7</sup>Li) into dissolved phase<sup>7</sup>. Li isotopes are not fractionated by biological processes or plant growth<sup>8</sup>. They are also not affected by carbonate weathering<sup>6</sup>. Therefore, lithium isotopes are the only tracer available, whose behavior is solely dominated by silicate weathering processes<sup>9</sup>. Lithium isotopic system could be a useful tool in palaeoenvironmental studies, such as investigating Hirnantian glaciation event in late Ordovician. Tests with Foraminifera show that the Li isotopic composition of seawater is best recorded in the low-Mg biocalcite<sup>10</sup>. Good preservation of the late Ordovician sedimentary structures in Estonia, consisting of carbonatic rocks and fossils, makes the area one of the best possible test polygons for that kind of study.

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**10. Vigier, N., Rollion-Bard, C., Levenson, Y., Erez, J. (2015). Lithium isotopes in foraminifera shells as a novel proxy for the ocean dissolved inorganic carbon (DIC). *C. R. Geosci.*, 347 (2015): 43–51. Carbon and nitrogen stable isotope signatures in the Devonian Canol Formation, Central Mackenzie Valley, Northwest Territories, Canada**

LaGrange, M.T.<sup>1</sup>; Li, L.<sup>1</sup>; Konhauser, K.O.<sup>1</sup>; Gingras, M.K.<sup>1</sup>

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**Abstract:**

The Middle to Late Devonian Canol Formation is an organic-rich mudstone succession present in the Central Mackenzie Valley and Mackenzie Mountains of the Northwest Territories, Canada. The environmental conditions that prevailed at the time when this interval was deposited remain poorly understood, and previous studies that characterized the type of organic matter present provide variable conclusions (e.g.<sup>1,2</sup>). This study examines carbon and nitrogen stable isotope compositions to gain information about the primary source of organic matter in the Canol Formation and interpret trends in biological productivity during deposition of this succession. A core from the Central Mackenzie Valley was sampled every 2 m through the Canol Formation and these samples were analyzed for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  compositions of organic matter.  $\delta^{15}\text{N}$  results range from  $-3.7\text{‰}$  to  $-0.6\text{‰}$  and show that  $\text{N}_2$  fixing cyanobacteria were the dominant primary producers at the time of sediment accumulation. This implies that nitrate ( $\text{NO}_3^-$ ) or ammonium ( $\text{NH}_4^+$ ) were likely limited in surface waters at that time because obtaining N by fixation of atmospheric  $\text{N}_2$  requires more energy than assimilation of the other N sources from surface waters<sup>3,4,5</sup>. Trends in  $\delta^{13}\text{C}$  from about  $-28\text{‰}$  to  $-30\text{‰}$  are interpreted to reflect decreasing productivity moving upwards through the Canol Formation, while a subsequent trend in  $\delta^{13}\text{C}$  increasing upwards from about  $-30\text{‰}$  to  $-26\text{‰}$  suggests increasing productivity when the overlying Imperial Formation was deposited. Gaining insight about the conditions that prevailed while this formation was deposited will enhance our understanding of controls on organic matter accumulation and preservation in organic-rich mudstones. Furthermore, an understanding of the nature and distribution of organic matter in the Canol Formation is essential to assessing the potential of this interval as an unconventional resource target.

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# Carbon isotope chemostratigraphy of the pre-Sturtian Ugab Subgroup, Otavi/Swakop Group, northwestern Namibia

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## Abstract:

The pre-Sturtian Islay anomaly is a negative carbon isotope excursion that has been documented globally, and recent work in northern Canada<sup>1,2</sup> and Scotland<sup>3</sup> has led to the suggestion that there may be two distinct late Tonian negative anomalies, an older one ca. 739 Ma and a younger one ca. 720 Ma, both being assigned to the Islay anomaly. Here we present the litho- and chemo-stratigraphy of the late Tonian Ugab Subgroup of the Otavi/Swakop Group in northwestern Namibia. We investigate the Ugab Subgroup in two separate outcrop belts where it is best exposed, the Summas Mountains and the Vrede Domes. We use closely-spaced detailed measured sections to develop a sequence stratigraphic framework for the Ugab Subgroup in each outcrop belt, and correlate strata across the two exposures to construct a composite carbonate  $\delta^{13}\text{C}$  record for the late Tonian in Namibia. This carbon isotope profile of the Ugab Subgroup shows two separate pre-Sturtian negative anomalies, and appears to be consistent with findings in northern Canada<sup>1,2</sup>, Scotland<sup>3</sup>, Svalbard<sup>4</sup>, and Ethiopia<sup>5,6</sup>. The additional evidence presented here for the existence of two discrete late Tonian negative carbon isotope anomalies has important implication for global correlations, the placement of the Cryogenian GSSP, and the formulation of models to explain the onset of the first Cryogenian snowball glaciation.

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## Archaeal lipid indicators of energy limitation in extreme environments

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### Abstract:

Archaeal lipids are commonly used as paleoenvironmental proxies. Biomarker temperature reconstructions are based on the principle that the relative abundance of cyclo-pentyl and -hexyl rings in core isoprenoid lipids produced by Archaea record the organisms' physiological response to environment in a predictable manner, both today and in the geologic past. The presence and abundance of these rings can affect the degree of membrane packing, allowing archaeal cells to maintain membrane function within a relatively narrow window of fluidity and permeability across wide thermal and chemical gradients. In a series of studies, we examined the role of different environmental parameters in influencing the degree of cyclization and stable hydrogen isotopic compositions of these membrane lipids.

In batch and chemostat experiments with the model thermoacidophile *Sulfolobus acidocaldarius* DSM639, we provoked the cells to shift isoprenoid lipid ring abundances in response to specific and controlled stimuli. We tested how ring distributions are influenced by shifts in temperature, pH, platform agitation speed, and electron donor or acceptor flux. The average degree of cyclization generally correlated with growth rate, with notable exceptions. In a separate series of experiments with a recently isolated and metabolically versatile thermoacidophile, *Acidianus* DS80, we examined whether membrane compositions can be driven by changing the type of central energy metabolism. DS80 was cultivated as a chemolithoautotroph on H<sub>2</sub>/S<sup>0</sup>, S<sup>0</sup>/Fe<sup>3+</sup>, and H<sub>2</sub>/Fe<sup>3+</sup>. DS80 showed lower average lipid cyclization when provided with H<sub>2</sub> as sole electron donor (H<sub>2</sub>/S<sup>0</sup> and H<sub>2</sub>/Fe<sup>3+</sup> pairs). Cells grown on S<sup>0</sup>/Fe<sup>3+</sup> exhibited significantly higher cyclization. We suggest the mechanism of substrate acquisition is important in regulating membrane fluidity and permeability when H<sub>2</sub> is involved as the energy source.

To further augment these observations of lipid type and relative abundance, we also quantified patterns of hydrogen isotopic composition among the different core archaeal lipids. Strikingly, the H isotope fractionation factor across different archaeal strains is fairly consistent within  $\sim\pm 80$  ‰. This implies that differences in H-isotopic signature of environmental archaeal lipids could reflect isotopic differences in the aqueous cultivation medium, and may be used to distinguish between distinct environmental settings. This is in stark contrast to the H-isotopic content of bacterial lipids, which varies widely with metabolic mode. Together, these observations provide a basis for clearer interpretations of experimental lipid data across the archaeal domain, while highlighting the need for further work with environmentally relevant strains to bolster interpretation of prior experimental and environmental records.

# Ironstones of the Katherine Group, Yukon: evidence for low oxygen surface waters in the early Neoproterozoic

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## Abstract:

Iron formations are an important tracer of the evolution of the Earth's oxidation state and ocean chemistry, and are rare in sedimentary successions younger than ~1800 Ma. The Tonian Period (1000–720 Ma) experienced significant eukaryotic diversification and biological innovation, yet our understanding of Tonian environments is limited. The discovery of shallow-water facies iron formation (ironstone) hosted by the ~850 Ma Katherine Group (Yukon, Canada) presents an opportunity to study shallow marine chemistry during this critical time in Earth's evolutionary history. The Katherine Group ironstones are hosted by a thick succession of quartz arenites and siltstones and are composed primarily of hematite (<75 wt% Fe<sub>2</sub>O<sub>3</sub>) with minor detrital quartz and clays. The ironstones feature mudcracks and fenestrae indicating a peritidal depositional environment. Abundant, large (<4 cm) hematitic oncooids demonstrate a microbial influence on deposition. Significant positive cerium (Ce) anomalies (average Ce<sub>n</sub>/Ce<sub>n</sub><sup>\*</sup> = 2.3) in the Katherine Group ironstones are interpreted to be the product of Ce scavenging by Mn-Fe oxyhydroxides and subsequent reductive dissolution in the presence of Fe(II). This evidence for a shallow redoxcline in the ferruginous oceans of the Tonian is suggestive of low atmospheric oxygen contents during this time. The upper Katherine Group is broadly correlative with ferruginous sediments in the Amundsen Basin (Northwest Territories, Canada), and other possible Tonian iron formations have been reported globally. This distribution may suggest that marine Fe(II)-oxidation deposition was a global phenomenon during the Tonian, warranting further investigation. The coincidence of shifts in iron cycling with leaps in ecosystem complexity may imply a link between changing ocean chemistry and biotic evolution during this time.

# Characterization and settling rate of cyanobacteria-ferrihydrite aggregates formed during oxygenic photosynthetic Fe(II) oxidation

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## **Abstract:**

Banded iron formations (BIF) are iron-rich (~20-40% Fe) and siliceous (~40-50% SiO<sub>2</sub>) sedimentary deposits that precipitated throughout much of the late Archean (2.7-2.5 Ga) and Paleoproterozoic (2.5-1.8 Ga). It is generally accepted that planktonic bacteria growing in the ancient ocean's photic zone were responsible for the oxidation of dissolved hydrothermally-derived Fe(II) into Fe(III), followed by the hydrolysis and precipitation of an amorphous ferric oxyhydroxide phase, such as ferrihydrite. The presence or absence of a strong association of cells with minerals or encrustation in minerals influences the rate and extent of sedimentation of the microbial cells, i.e., the biomass. To date, studies directed at understanding plankton cell-ferrihydrite aggregate formation have come exclusively from experimental work with photoferrotrophs. As a consequence, details of cyanobacteria-ferrihydrite aggregate formation remain unclear, specifically what is the size range of individual grains and aggregate and what fraction of cells become sedimented. Answers to these questions are significant in terms of explaining the presence and absence of minerals observed in BIF; the scarcity of organic carbon in BIF; and ultimately in using BIF as proxies for paleo-environmental conditions. Accordingly, in this work, we experimentally grew cyanobacteria in the presence of both dissolved Fe(II) and silica in anoxic environment to not only observe the size and morphology of the iron minerals produced by cyanobacteria, but as well the association of the cell surface and mineral products to assess the amount of biomass potentially buried when cyanobacteria may have been the dominant player in BIF deposition.

## The triple oxygen isotope composition of Precambrian chert

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### Abstract:

The temperature and chemistry of early seawater have both been inferred from the isotopic composition of Precambrian chert (SiO<sub>2</sub>), a precipitated mineral formed on or within marine sediments. The  $\delta^{18}\text{O}$  of chert shows a robust quasi-linear increase through time - a signal that has been interpreted in a number of conflicting ways. For example, changing  $\delta^{18}\text{O}$  has been hypothesized to reflect the product of cooling surface ocean temperatures, a signature of evolving seawater  $\delta^{18}\text{O}$  composition, or the product of later stage diagenesis (where measured  $\delta^{18}\text{O}$  reflects the composition of diagenetic fluids). We suggest this uncertainty can be resolved through the additional measurement and interpretation of the minor oxygen isotope <sup>17</sup>O (noted as  $\Delta^{17}\text{O}$ ) in conjunction with  $\delta^{18}\text{O}$ . In this study we present a suite of triple oxygen isotope data on stratigraphically constrained Precambrian chert (both peritidal chert nodules in carbonates and iron formation silica). These mineralogically well-defined data allow for the first stratigraphic tests of the fidelity of <sup>17</sup>O in SiO<sub>2</sub>. We apply a Monte Carlo resampling model approach to test the features of the competing hypotheses noted above but here include critical constraints from <sup>17</sup>O. The most parsimonious interpretation of these data suggests that secondary alteration with higher-temperature, meteoric-derived groundwater has skewed an original geochemical signature. Further, our <sup>17</sup>O measurements suggest limited (if any necessary) change in the isotopic composition of seawater itself and an equitable, modern-like Archean surface ocean temperature.

# Nitrogen cycling in cyanobacteria-dominated microbial communities in an alkaline soda lake in Cariboo Plateau, British Columbia

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## Abstract:

Nitrogen is one of the most common elements on Earth and plays important roles in both inorganic chemical and biochemical reactions that are essential to life. Several key roles in the nitrogen cycle are carried out by microbial metabolisms. In the past few decades, our understanding of nitrogen cycling in marine and lake environments has increased through the development of new analytical methods, discovering new microbes and uncovering new metabolisms<sup>1,2</sup>. However, few of those studies focused on soda lakes with high pH and alkalinity, dominated by highly productive cyanobacterial microbial mats. Revealing soda lakes' microbial nitrogen cycle will improve our understanding of this highly productive ecosystem, including microbial metabolisms, biodiversity and biogeochemical processes.

Our research unravels the nitrogen recycling rates of various nitrogen species in Goodenough lake, a soda lake in British Columbia, based on the recent research characterizing the lake's microbial community and metabolisms<sup>3</sup>. We identify the microbial groups carrying out specific nitrogen cycling processes, with novel methods that combine biogeochemical rate measurements using stable isotope (<sup>15</sup>N) probing and omics works including metagenomics and metaproteomics, using microbial community DNA and protein sequences, respectively. Experimental setups collected fresh microbial mats with lake water in serum bottles and added <sup>15</sup>N-labeled substrates (<sup>15</sup>N-urea, <sup>15</sup>N-N<sub>2</sub>, <sup>15</sup>N-NH<sub>4</sub><sup>+</sup> and <sup>15</sup>N-NO<sub>3</sub><sup>-</sup>), followed by an onsite incubation, tracking: urea, ammonium and nitrate assimilation and production; nitrification; denitrification and ammonia volatilization. Isotope ratio mass spectrometry and chemical measurements determined the assimilation rates of different nitrogen substrates and rates of substrate turnover, respectively. Tandem mass spectrometry, using an Orbitrap, will determine microbial proteins produced during the incubations. Proteomics software Calis-P (<https://sourceforge.net/projects/calis-p/>)<sup>4</sup>, using an established metagenomic database<sup>3</sup>, can further determine the identity of microbes incorporating specific <sup>15</sup>N substrates. So far, results from biochemical measurements point to an unexpected preferential uptake of urea by mat-forming microbes, compared to other substrates. The combination of biochemical measurements and omics work will help to identify the microbial populations in urea uptake and elucidate nitrogen cycling pathways in the highly productive soda lake environments.

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# Exploring microbial diversity and chemistry of geothermal features in Yellowstone National Park: Searching for methane cycling organisms

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## Abstract:

Methane (CH<sub>4</sub>) is a potent greenhouse gas and understanding its role in the global carbon cycle is imperative. Over the past year, we have collected an expansive biological and geochemical dataset from 100 geothermal features across four geothermal areas of Yellowstone National Park (YNP). Primary analyses of these samples includes over 40 geochemical measurements, PCR-directed 16S rRNA and *mcrA* gene sequencing, dissolved CH<sub>4</sub> gas measurements from eleven features, and shotgun metagenomic sequencing of DNA from five features potentially harboring novel methane-cycling microorganisms. Community profiling via 16S rRNA gene sequencing has revealed a promising number of features harboring members of archaeal phyla known or hypothesized to be involved in methane chemistry including *Euryarchaeota*, *Bathyarchaeota*, *Hadesarchaeota*, *Korarchaeota*, and *Verstraetearchaeota*. The presence of these phyla combined with preliminary dissolved CH<sub>4</sub> gas measurements suggest microbially mediated CH<sub>4</sub> cycling may be occurring within a subset of the analyzed hot springs. This study aims to provide direct experimental evidence of methane-cycling organisms to improve our understanding of anaerobic carbon cycling in YNP geothermal features. Metagenomic informed stable isotope probing experiments combined with 16S rRNA targeted fluorescence *in situ* hybridization (FISH) as well as visualization of cellular isotope uptake by Confocal Raman microscopy or nanoSIMS will be used to confirm these hypotheses.

# Investigation of laminae formation in Eocene Green River Formation stromatolites through combined micro-X-Ray fluorescence spectroscopy and petrography

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## **Abstract:**

Stromatolites are layered, lithified structures that may represent some of the earliest evidence of life on Earth. However, once lithified, unraveling the potential metabolisms of the microbes involved in stromatolite morphogenesis becomes difficult. Here, we employ micro-X-ray fluorescence spectroscopy ( $\mu$ XRF) coupled with light microscopy to investigate the elemental and morphological characteristics of stromatolite laminae, targeting redox-sensitive elements that are known to be cycled by microorganisms (e.g., Fe, S). The stromatolites were sampled from the Laney Member (LaClede Bed) of the Eocene Green River Formation, are finely laminated, and display several lamination styles (light micritic, dark micritic, sparry, etc.). The  $\mu$ XRF allows for elemental investigation at the scale of the lamination that can be directly compared to light microscopy. In addition to raw elemental abundances, measuring pertinent elemental ratios can help determine if the element is within the carbonate or in some accessory phase. For example, comparing the element of choice versus Ca (if calcite) or Ca+Mg (if dolomite) allows for the isolation of the element in question against the bulk carbonate chemistry of the stromatolite. Ratios with Ti and Al act as proxies for the presence of detrital siliciclastic grains that commonly become trapped in stromatolites along laminae and are unrelated to microbial processes involved in stromatolite growth. Ratios with S can account for the possible presence of trace sulfides (such as pyrite) in the stromatolite. Finally, by mapping out ratios of redox-sensitive elemental abundance compared to other, non-redox-sensitive elements commonly incorporated into carbonates (e.g., Na), we can evaluate whether variance in the element of interest is related to microbial redox processes associated with the stromatolite or is caused by external environmental change (such as lake level change). Ultimately this allows us to better understand the role of biology as well as the aquatic chemistry of the environment in which the stromatolite lithified. Preliminary analysis suggests enrichment of Fe in light versus dark micritic layers, hinting that Fe may have been cycled in some way during the formation of laminations.



# Macroalgae from the Tonian Dolores Creek Formation of the Wernecke Mountains, Yukon

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## Abstract:

The Tonian Period (1000-720 Ma) represents a critical transition in Earth history between the Mesoproterozoic Era (1600-1000 Ma) and the low latitude glaciations of the Cryogenian (720-635 Ma). Importantly, molecular clock analyses estimate that several key eukaryotic lineages evolved and began to diversify during the Tonian Period; however, the early Tonian Period is notoriously poorly understood and well-preserved exposures are rare. The Proterozoic inliers of Yukon present an opportunity to more accurately characterize the environmental conditions of the early Tonian and extract information on biospheric evolution at this time. Previously undocumented Tonian macrofossils were discovered in the ca. 900 Ma Dolores Creek Formation of the Wernecke Mountains in July 2018. The Dolores Creek Fm. is the oldest formation of the Hematite Creek Group, which forms the base of the Mackenzie Mountain Supergroup in eastern Yukon. The Dolores Creek Fm. in this studied location consists of ~1 km of dark grey to black siltstone with minor orange-weathering debrites grading upwards into stromatolitic bioherms. Ninety macrofossils samples were recovered from seven horizons from a nearly complete section of the Dolores Creek Fm. near the headwaters of Hematite Creek. We interpret the lower, fossiliferous portion of this section to represent relatively deep-water deposits in which the macrofossils were transported down-slope from coeval shallow marine environments in the photic zone, such as those recorded by overlying stromatolite bioherms. The macrofossils have an unbranched, filamentous structure and comprise repeated segments. There are clear taphonomic differences in the sampled specimens ranging from exceptionally preserved specimens with three-dimensional preservation to poorly preserved specimens that do not display clear segmentation. Analytical microscopy techniques were used to investigate the structure and taphonomy of the macrofossils so as to provide insight into their origin and phylogeny. Based on morphological analysis of the organisms, these macrofossils likely represent macroalgae. Preservation styles vary between specimens from Burgess Shale Type Preservation (with clays and pyritization) to poorly preserved specimens. These macroalgae with Burgess Shale Type preservation present a rare opportunity to add valuable paleontological data and gain insight into this crucial time period in Earth's biospheric evolution.

# Oxygenated oceans persisted after the Lomagundi Event: Evidence from the Zaonega Formation

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## Abstract:

The Lomagundi-Jatuli Event (LJE; ~2.22–2.06 Ga), the longest-lived C isotope excursion in Earth's history, is commonly viewed as associated with increased burial of organic matter that lead to a Paleoproterozoic "Oxygen overshoot"<sup>1</sup>. The end of the LJE is, conversely, associated with a recovery of anoxic conditions that might have arrested the evolution of complex life for the next billion years. The post-LJE Zaonega Fm. (ZF; ~2.0 Ga), an organic matter-rich carbonate-mudstone succession, is a linchpin in the study of Paleoproterozoic redox shifts. Geochemical data from the ZF has often been interpreted as prime evidence for an "O<sub>2</sub> crash" (e.g.,<sup>2</sup>), despite other authors including the ZF among well-oxygenated LJE-type successions (e.g.,<sup>3</sup>). Here, we present trace element analyses from several recent drill cores in the ZF that contain some of the highest Mo, U and Re concentrations reported to date in pre-Neoproterozoic shales (1009 μg g<sup>-1</sup>; 238 μg g<sup>-1</sup>; and 516 ng g<sup>-1</sup>, respectively). These enrichments are most parsimoniously explained through the establishment of an efficient trace metal trap in a highly bio-productive semi-restricted basin that was intermittently, but reliably, connected to a trace metal-rich ocean. Given that U and Re can only accumulate in an oxic water column, these data imply oxic waters overlying continental shelves during the deposition of the ZF and, therefore, undiminished levels of O<sub>2</sub> following the LJE. The temporal decoupling between the LJE and the O<sub>2</sub> overshoot, in turn, places doubt on our understanding of the mechanisms underlying some of the most profound environmental shifts in the Paleoproterozoic.

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# Preservation bias in silicified Proterozoic cyanobacterial mats

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## Abstract:

Modern marine/hypersaline marine environments that are analogous to peritidal environments during the Proterozoic contain microbial mats dominated by *Lyngbya* sp. and *Microcoleus chthonoplastes*<sup>1</sup>. The characteristic layering within a microbial mat is the result of distinct microbial communities that reflect changes in light quality and geochemical gradients, where cyanobacterial communities dominate the upper, photosynthetic layers of the microbial mat and provide organic carbon for microbial communities in the lower portion of the mat<sup>2-4</sup>. In the lower portions of the mat, cyanobacterial communities are more degraded and consist predominantly of empty sheaths<sup>5</sup> that were abandoned by their trichomes<sup>6</sup>. Without the active metabolism of the cyanobacteria, the sheaths become more susceptible to degradation<sup>7, 8</sup> and the physical structure of the mat is lost.

Throughout the Proterozoic, chert deposition was common in peritidal carbonate strata. These deposits formed during early diagenesis, and likely penecontemporaneously with decaying microbial mats cf.<sup>9</sup>. Early silicification commonly preserves exceptional microbial morphologies at various taphonomic states<sup>10-12</sup>. The research presented here investigates the extent to which cyanobacterial mats are preserved by early diagenetic chert using a combination of taphonomic and petrographic observations and organic geochemical data from silicified mats within the ~1.0 Ga Angmaat Formation.

The Mesoproterozoic strata of the Angmaat Formation, Bylot Supergroup, records strata deposited within a hypersaline microbial flat<sup>13</sup>. Early diagenetic silica occurs as lenses, beds, and nodules in the Angmaat Formation and record microbial growth and decomposition across a range of peritidal environments, which contain several discrete filamentous and coccoidal mat types<sup>14</sup>. Filamentous mats within these chert deposits lack preserved trichomes and only empty sheaths were observed in a taphonomic assessment<sup>9</sup>. We propose that the process of silicification—particularly the formation of a silica gel— may cause environmental stress that promotes the migration of cyanobacterial trichomes and may bias the types of information able to be preserved in microbial mats.

Microbial morphologies within these mats are preserved in a primary silica phase that is distinct from the silica phase that in-fills constructional voids. Petrographic analyses indicate that the primary phase started as a silica gel. Despite the well-preserved taphonomy, lipids, including alkanes, hopanes, and steranes, are not preserved in these samples. This is likely a reflection of the lack of trichomes. Sheaths are composed of polysaccharides and therefore would not be expected to preserve lipid biomarkers.

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# Taphonomy and paleoecology of the early Jurassic Ya Ha Tinda Lagerstätte

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## **Abstract:**

*Konservat-Lagerstätten*—deposits containing ‘exceptionally preserved fossils’—provide the most complete snapshots of ancient organisms and communities. In the Mesozoic, *Konservat-Lagerstätten* are rarely found in marine facies outside Oceanic Anoxic Event (OAE) intervals, suggesting that low oxygen levels fostered exceptional fossil preservation during OAEs. Anoxia, however, does not guarantee survival of non-biomineralized tissues or articulated skeletons, so the prevalence of such fossils may reflect other OAE phenomena (e.g., fluctuating oxyclines). Here, we test this hypothesis with a taphonomic analysis of the Ya Ha Tinda *Konservat-Lagerstätte*, found in Lower Jurassic (Pliensbachian and Toarcian) black shales and siltstones (Fernie Formation, Alberta, Canada). The faunal assemblage of this deposit includes articulated vertebrates (fish, ichthyosaurs), crinoids, crustaceans, brachiopods, abundant mollusks (coleoids with soft tissues, ammonites, gastropods, and bivalves), wood, and microfossils. The fossils were preserved when euxinic conditions were common in the area, in part, due to the Toarcian OAE (~183 Ma); further, there was a significant faunal turnover during the Toarcian OAE. Some of the fossils contain carbonaceous material, but the majority consist of apatite minerals, indicating that they were preserved through secondary phosphatization. Phosphatization generally occurs within phosphate-rich sediment; however, oceanic anoxia causes sediment to release phosphorus and prevents animals from colonizing seafloor habitats. Accordingly, we propose that the fauna colonized the seafloor and were preserved during brief episodes of bottom water oxia and/or dysoxia, when the environment would have been most favorable to benthic communities and phosphate mineralization. In this setting, phosphatization may have been fueled by phosphate delivery from continental weathering in response to climatic warming, ocean upwelling of eutrophic water, and/or nutrient trapping by anoxia in the basin.

## Redox inverted cold seeps: Chemotrophic sulfur-oxidizing microbial mats growing on oxidant seeps in the euxinic basin of a meromictic lake

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### Abstract:

We report the discovery of chemotrophic sulfur-oxidizing microbial mats in a novel redox setting, the interface of oxidant bearing seeps or fracture springs discharging into the aphotic sulfide-rich waters of meromictic Green Lake, Fayetteville, NY. Using a small ROV in the spring of 2013, we explored the lake basin walls below the redoxcline under the thrombolite assemblage known as Dead Man's Point. In these dark euxinic waters we observed white vertically striated mats draped over the lake sediments, a morphology we later termed *Lacey veil*. In subsequent dives between 2013 and 2017, a variety of additional mat morphologies were observed, including *Yellow stripe*, *Casper* and *Hanging gardens*. These deeper mats are patchy in location and vary in thickness from milky translucent veneers only a few millimeters thick (*Lacey veil* and *Yellow stripe*) to white translucent mats that rise ~4 cm above the sediment-water interface (*Casper*). Oxidation-reduction potential measurements confirm that the interior or ventral sides of the mats are more oxidizing than the sulfide-rich water column. Metagenomic analyses of two *Casper* mats revealed low diversity communities dominated by a single *Epsilonproteobacteria* (up to 75% relative abundance). We constructed a near complete genome for this dominant phylotype (95.8% complete with 0% contamination, length = 2.01 Mb, 1946 coding genes) that is phylogenomically basal to the *Sulfuricurvum* genus. Functional annotation by BLASTKOALA showed the presence of sulfide-quinone reductase (*sqr*), indicating the capacity for H<sub>2</sub>S oxidation to polysulfides, the presence of high-affinity reductases for O<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, *cbb3* and *nap*, and a complete rTCA cycle for carbon fixation. We suggest this single species is the primary producer associated with the *Casper* assemblages. The community composition of the other mat morphotypes remains unexamined. These unusual communities expand our understanding of the range of redox settings that support chemotrophy and provide a rare example of aphotic oxidant oases in euxinic water that may have relevance to our understanding of life on Earth in the late Archean and early Proterozoic and perhaps our search for life elsewhere in the solar system.

# Disentangling the darkness: Light absorbing particulates as albedo lowering agents on the Greenland Ice Sheet

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## Abstract:

The western sector of the Greenland Ice Sheet (GrIS) has experienced increased surface melting in recent decades<sup>1</sup>, which in part corresponds to decreased surface albedo caused by light absorbing particulates (LAPs). While LAPs on the GrIS are known to comprise pigmented glacier algae, black carbon (BC), and mineral dust, the contribution of each of these constituents to the measured albedo reduction is incompletely understood. Here we characterize surface LAPs as a means of understanding the biogeochemical links between particulate types and their collective role in darkening the GrIS. The microbial community is dominated by glacier algae, namely *Ancylonema nordenskiöldii* and *Mesotaenium* sp.<sup>2</sup>, which ‘bloom’ on the ice surface and produce albedo-lowering photoprotective pigments<sup>3</sup>. Microbes are intermixed with fine grained mineral dust that accounts for 94% of the total LAP mass in the form of major rock forming minerals (quartz, feldspars, actinolite, pyroxenes, and phyllosilicates). Measured solid phase C:N:P ratios suggest P is a limiting nutrient. Spatial trends in the mineralogy, meltwater chemistry, and algal biomass indicate that nutrient limitation is overcome via biomineralization of trace nutrients from mineral dust. BC becomes entrapped in microbial biomass and thus is present in concentrations orders of magnitude higher than those measured in clean ice surfaces. Solid sample characterization combined with field spectroscopy measurements and an updated radiative transfer model indicate that glacier algae are the primary LAP driving albedo reduction in this sector, accounting for 5.5-8.0 Gt (10-15%) of the surface runoff observed in 2016<sup>4</sup>. These results indicate that constraining the controls on algal bloom development, including the availability of mineral derived nutrients, is necessary in order to account for this biogeochemical process in predictive models of ice sheet melting, runoff and sea level contribution.

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# Efficient electron transport over centimeter-scale distances in cable bacteria

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## Abstract:

Long-distance electron transport enables a novel type of microbial metabolism, whereby long, multicellular cable bacteria are capable of transporting electrons from cell to cell along their centimeter-long filamentous bodies. By establishing such electrical circuitry, cable bacteria are able to exploit spatially segregated pools of electron acceptors and donors, equipping them with a competitive advantage for survival in natural redox gradients. The electron transport induced by cable bacteria exceeds the known length scale of biological electron transport by orders of magnitude. So somehow, cable bacteria must have evolved a proficient mechanism for long distance electron transmission, but presently, neither the mechanism of charge transfer nor the identity of conductive structures have been identified. Here, we present a model of long-distance electron transport, where cells act as cathodes/anodes and periplasmic fibers in the cell envelope function as conductive structures. The model is based on newly collected microscopy and spectroscopy data, in combination with detailed electrochemical and electrical measurements. Resonance Raman spectroscopy of cytochromes confirms that electrical currents run through individual living cable filaments<sup>1</sup>. Electron microscopy reveals the three-dimensional architecture of the periplasmic fiber network that forms the prime candidate for the conductor<sup>2</sup>. Electrode recordings demonstrate that these periplasmic fibers are indeed the conduits of electron transport<sup>3</sup>. Overall, our research shows that biological electron transfer can occur across centimeter-scale distances with a low dissipative loss. In the geological past, the process may have been widespread in seafloor microbial mats in the Ediacarian or the early Trias, when oceans were oxygenated and bioturbation rates were low.

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## Coupled laboratory and field investigations resolve microbial interactions that underpin persistence in hydraulically fractured shales

Borton, M.A.; Hoyt, D.W.; Roux, S.; Daly, R.A.; Welch, S.A.; Nicora, C.D.; Purvine, S.; Eder, E.K.; Hanson, A.J.; Sheets, J.M.; Morgan, D.M.; Wolfe, R.A.; Sharma, S.; Carr, T.R.; Cole, D.R.; Mouser, P.J.; Lipton, M.S.; Wilkens, M.J.; Wrighton, K.C.

### Abstract:

Hydraulic fracturing of shale is the industrial process behind the surging natural gas output in the United States. This technology inadvertently creates an engineered microbial ecosystem thousands of meters below Earth's surface. Here, we show that persisting microbial communities in fractured shales converge to a similar membership and structure, despite differences in operators, shale formations, and input communities/chemistries. Based on the detection of the metabolite glycine betaine across all Appalachian Basin produced fluids sampled to date, we used laboratory reactors to manipulate persisting shale microbial communities that are currently not feasible in field scenarios. Metaproteomic and metabolite findings from the laboratory were then corroborated using regression-based modeling performed on field metagenomic and metabolite data from more than 40 produced fluid samples from five hydraulically fractured shale wells. Collectively, our findings show that *Halanaerobium*, *Geotoga*, and *Methanohalophilus* strain abundances predict a significant fraction of carbon and nitrogen metabolites at the field scale. Our combined laboratory and field results revealed that microorganisms persisting in hydraulically fractured shales must maintain osmotic balance in hypersaline fluids, gain energy in the absence of electron acceptors, and acquire carbon and nitrogen to synthesize cell building blocks. We provide evidence that co-fermentation of amino acids and their derivatives, like glycine betaine, meets these organismal needs and thus Stickland fermentations function as a keystone metabolism conserved across hydraulically fractured shale communities. These research findings likely extend across subsurface ecosystems, both marine and terrestrial, where amino acid fermentation and viral predation are increasingly recognized as important drivers of community structure.

# Geochronology, geochemistry and stratigraphy of the Neoproterozoic Hecla Hoek Succession, Svalbard, Norway

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## Abstract:

The Tonian Period (1000-717 Ma) was a time of global upheaval with dynamic oceanic redox conditions, the diversification of early eukaryotes, and biological innovations such as eukaryavory and biomineralization. All of these changes were set against the backdrop of tectonic reorganization and magmatism associated with the formation and breakup of the supercontinent Rodinia. However, the current lack of temporal constraints for the Tonian hinders our ability to answer first-order questions surrounding the timing and causes of these biospheric and biogeochemical events. The ca. 950-600 Ma<sup>1</sup> Hecla Hoek succession of Svalbard, Norway, consisting of the early-mid Tonian Veteranen Group, mid-late Tonian Akademikerbreen Group, and the Cryogenian-Ediacaran Polarisbreen Group, represents one of the most complete and well-preserved Neoproterozoic sedimentary successions worldwide. This succession provides a unique opportunity to construct a temporally-calibrated geochemical, biological, and geological framework in which to assess Tonian biogeochemical change and the timing and triggers of early eukaryotic evolution; however, despite containing assemblages of well-preserved microfossils that were initially reported over three decades ago<sup>3,4</sup>, mixed carbonate and siliciclastic strata of the Veteranen Group remain poorly studied with no detailed sedimentological, geochemical, or geochronological studies. We present major and trace element data from mudrocks spanning an ~4 km thick, near-complete section of the Veteranen Group from northeastern Spitsbergen. Basal carbonate units of the Veteranen Group are, however, only exposed on the neighboring island of Nordaustlandet, where stratigraphic correlations are tentative. In addition, we implement new sedimentological and stratigraphic analyses, in conjunction with carbon isotope chemostratigraphy, to make preliminary correlations between the Tonian strata of Spitsbergen and Nordaustlandet. Preliminary Re concentration data suggest that organic-rich shale horizons from the Veteranen Group are suitable for Re-Os geochronology and may provide the first radiometric depositional age constraints on these strata. Combined with future radiometric age constraints on fossiliferous strata, this framework will permit us to evaluate the tempo and drivers of eukaryotic diversification during the Tonian.

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## Novel eukaryotic picoplankton in a seasonally anoxic fjord

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### **Abstract:**

Picoeukaryotes (microbial eukaryotes 1-3  $\mu\text{m}$  in diameter) are by far the most abundant eukaryotes in the modern oceans. Photosynthetic picoeukaryotes (PPE), slightly larger in size than cyanobacteria, can account for up to 60-80% of biomass and primary production among picoplanktonic in the open ocean. Heterotrophic picoeukaryotes (HPE), through the phagocytosis and assimilation of bacteria and archaea (i.e. bacterivory), as well as PPE and other small eukaryotes, help regulate marine primary productivity and channel fixed carbon to larger protists ( $>3 \mu\text{m}$ ) (i.e. eukaryovores) and animals, as part of the microbial loop. How dissolved oxygen availability influences the distribution, diversity, and trophic specialization of picoeukaryotes remains poorly known, and informs our understanding of both the evolution of modern marine food webs, as well as the economic and ecological impact of modern marine deoxygenation on fisheries and other eukaryotic populations. By using time-series observations of ITS and 18S rDNA diversity over a 12-month period at Saanich Inlet, a seasonally anoxic fjord in Vancouver, BC, we identified a variety of picoeukaryotes from every depth and  $\text{O}_2$  concentration. In particular, we identified novel picoeukaryotic lineages at the phylum level below the oxycline where unclassified taxa comprise up to 92% of all picoeukaryotic diversity. At greater depths, other eukaryotic phyla, such as the ciliophora, make up to 82% of the picoeukaryotic diversity, and potentially play key roles in the anaerobic grazing of bacteria and other small planktonic cells. Overall, characterizing this unknown diversity of picoeukaryotes under anoxia sheds light on how eukaryotic food webs shift as a function of oxygen availability, and help us reconstruct the ecological consequences of an increasingly oxygenated atmosphere during the earliest stages of eukaryotic evolution.

# Investigating the preservation of the oldest cyanobacterial fossils

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## Abstract:

Silicification preserved many Proterozoic microbial mats and fossils, including the oldest cyanobacterial fossils. However, both marine silica concentrations during this time and the mechanisms that drove preservation in tidal flats where seawater may have been undersaturated with respect to silica remain unclear. Here, we use experimental taphonomy to investigate silicification of the benthic cyanobacterium *Entophysalis* sp., the modern analog to the silicified fossil *Eoentophysalis*. Experiments are conducted in a microfluidic flow through system at room temperature and 1 atm pressure, and investigate silicification using artificial seawater with silica concentrations that are below saturation (1.5 mM or less). During these 30 day experiments, the photosynthetic mats either exposed to light (light experiments) or shielded from light (dark experiments), and both mats and medium are sampled at regular intervals to assess changes in dissolved silica concentration and the distribution of silica accumulation in the biomass. These experiments address three main questions: 1) Can initial silicification occur under these conditions in seawater that is undersaturated with respect to amorphous silica? 2) Can cyanobacterial cells bind and concentrate silica to promote fossilization? and 3) What microbial compounds can facilitate this preservation process?

Scanning electron microscope (SEM) images and energy dispersive x-ray spectroscopy (EDS) of samples from dark experiments do not show silica accumulation in the biofilms. In contrast, the light experiments in which biofilms continued to grow show that silica begins to accumulate around cells after 1 day. This silica signal increases between days 1 and 5, and persists over the course of a month. Elemental maps generated with nanoSIMS demonstrate that silica accumulates preferentially in the exopolymeric substances (EPS) surrounding cells and cell clusters. The EPS also contains high levels of sulfur, suggesting a role for sulfated polysaccharides in silicification. Our results demonstrate that it is possible to initiate silicification of cells at room temperature and 1 atm pressure with seawater medium that is undersaturated with respect to silica. We reveal that *Entophysalis* sp. can sequester silica and promote initial fossilization under these conditions only when the biofilm is living and producing EPS, and that sulfated organic molecules may play a role in this process. These results inform our understanding of preservation in peritidal environments during the Proterozoic, suggesting that living, EPS-producing cyanobacteria may have promoted the early stages of fossilization even when marine silica concentrations were below saturation with respect to amorphous silica.

# Zonation of silica and associated microbial communities bounding high-temperature channel outflows at El Tatio Geysir Field, Chile

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## Abstract:

The local physical dynamics of geothermal outflows influence the mode and morphology of silica precipitating from neutral to alkaline hot springs. Microorganisms with thick sheaths such as filamentous cyanobacteria are widely known to influence sinter fabrics in distal, low temperature (<35°C) zones of geothermal outflows by acting as passive templates for silica nucleation<sup>1</sup>, resulting in features such as terraces and recognizable textures such as palisades<sup>2</sup>. In contrast, the morphology of sinter precipitated from high- (>60°C) and medium-temperature zones (35-59°C), such as lily pads and high-temperature digitates, are thought to be dictated by the local environment and hydro-dynamics and the influence of microorganisms on sinter precipitation is argued to be negligible<sup>3,4</sup>. Despite the ubiquitous observation of silicified microbial filaments at all temperatures, there remains considerable debate about whether organisms play any role in silica precipitation and resulting textures, especially at high temperatures where microorganisms are not often preserved<sup>5-8</sup>. El Tatio is a high-elevation, extremely arid environment; despite undersaturation of silica in waters has the highest observed precipitation rates of any hot spring setting<sup>6</sup> and therefore may be the ideal environment to preserve non-cyanobacterial organisms in high-temperature silica deposits. Whereas cyanobacteria dominate most mats below 72°C at other localities, cyanobacteria are not observed in mats at or above 55°C throughout El Tatio, due to both physico-chemical and phylogenetic constraints<sup>9</sup>. The strong influence of extremely rapid evaporation is apparent in the formation of high-temperature sinter at El Tatio; however, the local structure, color, and texture of closely-associated biofilms coated by flocculated amorphous silica precipitates exhibit macroscopic characteristics that follow the shape of sinter precipitates and appear to be templated by systematic biofilm textures that are linked to microbial community composition. Here we characterize the local geochemistry, microbial community composition, and micro-structure of biofilms in close association with sinters along high-temperature channel outflows at El Tatio, Chile and attempt to constrain any possible relationship of textured, silica-coated biofilms to the formation of adjacent mature sinter fabrics.

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# Co-diagenetic development of Carbonaceous material and silica in the ca. 1.0 Ga old Angmaat Formation, Baffin Island, Canada.

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## Abstract:

The ca. 1 Ga old Angmaat Formation of the Bylot Supergroup in northern Baffin Island is primarily composed of inter- to supratidal dolomitic carbonates with subordinate siliciclastics, evaporites and chert that formed in microbially populated flats<sup>1</sup>. Black chert beds of early diagenetic origin show often an excellent preservation of coccoidal and filamentous microfossils<sup>1,2</sup>. However, a high variability is observed in the taphonomy of individual microfossils<sup>3</sup>. The detailed processes leading to these variations are not fully understood yet.

Here we present a detailed petrographic and Raman spectroscopic mapping study of several microfossil occurrences in the Angmaat Formation. Micronodular growth with numerous 10 to 30  $\mu\text{m}$  large spheres at the nodules edges shows that the chert formed initially as opal from brines in the shallow subsurface of the supratidal flats. Ubiquitous silicified dolomite rhombs and rare microfossils preserved within dolomite indicate its early diagenetic to syn-sedimentary formation. Therefore, the formation of both, opal and dolomite took place within surficial microbial mats and directly below them. Our observations indicate that the preservation state of the Angmaat microfossils is mostly dependent on the earliest diagenetic processes like bio-mineralization during microbial mat growth. Most carbonaceous material was displaced by micronodular growth by few mm to cm. Densely packed carbonaceous material surrounding nodules and filling pocket spaces between them is preserved as opaque black mush without distinguishable microfossil individuals or populations. Carbonaceous material of lesser density was captured in chert nodules showing some of the best-preserved microfossil individuals with preserved cell walls and intercellular textures.

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# Mg and Sr isotope results from Paleozoic dolomites in the Williston Basin: Implications for the process of dolomitization

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## Abstract:

Dolomitized carbonates of the Williston Basin are abundant below the Devonian Prairie Evaporite. For this reason, and others, brine reflux dolomitization is the most common cited model in the Williston Basin. To evaluate this hypothesis, strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) of two prominent dolomite bodies, the Ordovician Red River and Devonian Winnipegosis Formations, were measured. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of both dolomite bodies are higher than contemporaneous seawater ratios<sup>1,2</sup>, suggesting that dolomitizing fluids moved upwards from the Cambro-Ordovician aquifer in the deep basin where present-day formation waters are known to be quite radiogenic<sup>3,4</sup>.

In this study, Mg isotopes ( $\delta^{26}\text{Mg}$  values) are coupled with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios to investigate the process of dolomitization in the Winnipegosis and Red River dolomites. In contrast to  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios,  $\delta^{26}\text{Mg}$  values may directly trace paleofluid movement during dolomitization, resulting from light isotopes of Mg preferentially sequestering into the precipitating mineral (e.g.,<sup>4</sup>). Therefore, it is hypothesized that Mg in the dolomitizing fluid, and by extension the dolomite itself, will evolve to progressively enriched  $\delta^{26}\text{Mg}$  values along the dolomitizing fluid flow path. We investigated the existence of spatial gradients in  $\delta^{26}\text{Mg}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that may be preserved in the aforementioned dolomites.  $\delta^{26}\text{Mg}$  values increased from the deep basin center ( $-1.9\text{‰}$ ) to the edge ( $-1.4\text{‰}$ ), in all directions. Measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios exhibit a similar radial pattern to that of  $\delta^{26}\text{Mg}$  values. We interpret these findings as evidence that the dolomitizing fluids of both Formations ascended, rather than descended, through the Paleozoic carbonate succession.

The Williston Basin burial history is punctuated by heat flow anomalies, in the Carboniferous and Cretaceous, indicated by resetting of thermal remnant magnetizations in dolomite and evaporite minerals. We speculate that one of these heating events may have triggered Mg-bearing formation waters to ascend from the crystalline basement, flowing laterally along permeable sedimentary units to the basin margins. If this interpretation is correct, dolomites in the Williston Basin are related to the tectonic and thermal history of deep basinal fluids migrating upwardly during a heat flow anomaly.

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# **An iron-rich carbonate tidal sequence, Cryogenian Angepena Formation, South Australia**

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## **Abstract:**

The Neoproterozoic Era is characterized by some of the most dramatic environmental change in Earth's evolutionary history. However, few studies have examined these early environments within a coupled sedimentologic and geochemical context, hindering our ability to understand this environmental change. The Cryogenian Angepena Formation of South Australia records deposition in an iron-rich peritidal environment landward of the Balcanoona reef complex. Marine cements from this environment are characterized by well-preserved non-bright cathodoluminescent zoning, strong negative and positive cerium (Ce) carbonate anomalies ( $Ce_{anom}$ ), and distinct hematite-rich beds with abundant iron oxides. These data indicate syn-sedimentary iron precipitation in an intermittently oxidized peritidal environment. Basinward, laterally equivalent subtidal Balcanoona Formation reef facies precipitated from ferruginous anoxic seawater. Coupled sedimentology and geochemistry suggests these Neoproterozoic tidal sediments represent depositional processes at the interface of an oxidizing atmosphere with an anoxic ferruginous marine system. In Adelaide Fold Belt basin, it appears that the peritidal environments of the Angepena Formation were one of the first oceanic environments to be oxidized. Future work in other Neoproterozoic peritidal settings may determine if this is a global phenomenon.

## A new framework for the study of the evolution of photosynthesis

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### **Abstract:**

The origin of anoxygenic photosynthesis predates the origin of oxygenic photosynthesis. This traditional interpretative framework underpins the study of the evolution of life's bioenergetics and the interpretation of the early geochemical record. However, the confidence placed in this premise exists in stark contrast with the historical ambiguity and controversial interpretation of molecular evolution and geochemical data regarding when and how oxygenic photosynthesis originated. To understand and clarify the tempo and molecular mechanism of the origin of oxygenic photosynthesis, we have studied in atomic detail the origin of the photosystems using extensive molecular evolution methods and comparative structural biology. As controls, we have compared their evolution with that of an ancient enzyme known to have emerged before the last universal common ancestor, V-/F-type ATP synthase; and with a more recent enzyme known to postdate crown group cyanobacteria, the heterohexameric FtsH protease involved in photosystem quality control. The data show indistinguishable distances, rates of evolution, and evolutionary dynamics throughout geological time between the core duplications of Photosystem II, which occurred after the origin of water oxidation to oxygen, and the duplication of ATP synthase's catalytic core. Conserved structural elements in Type II (quinone-reducing) and Type I (Fe<sub>4</sub>S<sub>4</sub> cluster-reducing) photosystems indicate that the origin of water oxidation started before or at their initial divergence. It is shown that the divergence of Type I and II photosystems occurred in the early Archean and long before the radiation events leading to the described groups of phototrophs. That water oxidation to oxygen drove the origin of photosynthesis not only explains the peculiar coordination sphere of the Mn<sub>4</sub>CaO<sub>5</sub> oxygen-evolving cluster and the chimeric structural nature of Photosystem II, but also it clarifies the numerous apparent paradoxical observations that emanate from the traditional interpretative framework: such as the absence of anoxygenic phototrophs using both types of photosystems in series or the convoluted biochemical derivations needed to make bacteriochlorophylls from a chlorophyll *a* precursor. It becomes apparent that anoxygenic photosynthesis originated twice from primordial transitional stages during the early evolution of oxygenic photosynthesis as ancient strategies to avoid oxygen toxicity and competition for visible light in early Archean microbial mats. These observations revive the long-abandoned yet little explored idea, first speculated in the late 50s, that water-splitting photochemistry might have been central to the origin and early evolution of life's bioenergetics.

# **Biotic recovery after the end-Permian mass extinction: the role of the monsoon cycle on biogenic silica deposition**

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## **Abstract:**

The end-Permian biotic crisis at 251 million years ago (Ma) was the largest mass extinction event in the Phanerozoic, with estimates of faunal species loss as high as ~90%<sup>1</sup>. This event was coincident with a number of changes, such as ocean acidification, vegetation loss and soil alteration, sea-level rise. In addition, slower ocean circulation and warmer oceans resulted in decreased levels of dissolved oxygen that led to marine anoxia, and ultimately ocean stratification. Despite the environmental calamities, there was an abrupt reappearance of warm-water taxa within 4 million years of the Permian-Triassic (PT) boundary. This abrupt reappearance suggests some biological activity persisted into the Early Triassic, albeit in isolated pockets. These marine refugia have been treated as unique, possibly ephemeral isolated enclaves of ecologically favorable conditions, such as sheltered near-shore environments, where marine biota was able to survive. Given that heterotrophic organisms require organic carbon for metabolic function, the establishment of such refugia should occur in regions enriched in both organic matter and oxygen. Here we examine the mechanisms whereby organic matter and nutrients were ephemerally deposited in near-shore environments during the Early Triassic, following the collapse of the trophic pyramid. Detailed geochemical and sedimentological analysis of a Permian-Triassic section from western Canada demonstrates systematic trends in weathering and palaeoproductivity proxies, as well as biogenic silica fluxes. These trends, when paired with sedimentological indicators of riverine input and storm episodes, suggest that seasonal monsoons produced wind-induced upwelling along the northwest margin of Pangea. These intervals of upwelling coincide with intervals of biogenic silica and occur anti-phase to indicators of increased weathering. This suggests that winter storms, in partnership with coastal runoff, were the major factor in supporting biotic recovery in the Griesbachian.

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# A recap of the geobiology of the Paleoproterozoic Belcher Group, Nunavut, Canada

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## **Abstract:**

The ~2.0-1.8 Ga Belcher Group on the Belcher Islands in Nunavut provide a unique opportunity for studying Paleoproterozoic geobiology. The Belcher Group includes a sequence of low metamorphic grade peritidal carbonate rocks that preserve putative microbiota, as first described by Hofmann and Jackson (1969). Additionally, morphologies possibly related to blue-green algae were first described in granular iron formation rocks of the Belcher Group by Moore (1918). The Belcher Group microbiota are a group of simple organisms, believed to be prokaryotic in nature. Microbiota morphologies include ellipsoids, spheroids, and filamentous chains of cells interpreted by previous workers to represent blue-green algae and acritarchs. Some microstructures are questionably biogenic and might be abiotic. The most significant field studies on the Belcher Group occurred from the late 1950's to the early 1980's, which provides the geological context for this study. This project aims to build on the previous work of H. Hofmann and others in the '60s and bring these microbiota into a modern context, drawing on the analytical advancements of the last 50 years. The main goal of the project is to determine if there is evidence that the microbiota are perhaps eukaryotic organisms, with the primary hypothesis of the project being that the microbiota are some type of transition group between prokaryotes and eukaryotes. To test the hypothesis, hand samples and thin sections have been taken from the microbiota-containing rocks that were collected on the Belcher Islands. Both light microscopy and a collection of modern analytical techniques will be used to obtain the highest resolution images and chemical signatures possible of the microbiota and their biosignatures. The analytical techniques include Scanning Electron Microscopy (SEM), Raman Spectroscopy, and X-ray Photoelectron Spectroscopy (XPS). SEM imaging will determine the surface topography and composition of the sample, while Raman spectroscopy will collect high resolution, micron-scale molecular and structural data in situ from the sample. XPS acts as a more detailed SEM analysis, with more precise chemical data being produced. Together, these techniques allow for the morphology and chemical nature of the microbiota to be distinguished to a very high degree, allowing for a proper characterization.

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# Organic matter sulfurization in redox gradients around mangrove roots

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## Abstract:

Mangrove sediments are frequently anoxic, which facilitates elevated organic matter (OM) burial via several mechanisms, including sulfurization – abiotic reactions between dissolved (poly)sulfide and OM that decrease its lability. Although sulfurization was estimated to account for roughly half of OM preservation in a Bermuda mangrove forest,<sup>1</sup> both its mechanisms and its global significance remain poorly understood. In this study, we investigate S cycling in mangrove forest sediments from Little Ambergris Cay, Turks and Caicos Islands, an environment with predominantly microbial OM inputs and no major source of terrestrial iron. We characterize the S- and C-isotope composition and organic S speciation of sedimentary OM fractions with varying degrees of resistance to acid hydrolysis, along with other inorganic S phases. Near the surface of a 3-mm-diameter, O<sub>2</sub>-releasing root, abundant organic and elemental S with a <sup>34</sup>S-depleted composition indicates microbial sulfur cycling and OM sulfurization. A mixture of pyrite, elemental S, and organic S form a plaque within the outer 50 μm of the root, which also contains strongly <sup>34</sup>S-depleted sulfate in its xylem. OM sulfurization products in the sediments include both the alkyl sulfides and disulfides associated with the root plaque and more oxidized forms, especially sulfonates. Hydrolysis-resistant organic S in the sediments is consistently 3–5‰ more <sup>34</sup>S-enriched than coexisting elemental S, matching the reported kinetic isotope fractionation factor for OM sulfurization via reaction with polysulfides. These sediments also contain a substantial pool of solid-phase, hydrolyzable organic S with a seawater sulfate-like isotope composition, largely in the form of sulfate esters, which may represent excretions from abundant gastropods. The coexistence of sulfurized OM and aerobic macrofauna highlights how understanding spatial scales and/or temporal cycles in local redox state is critical for predicting net OM preservation, especially in dynamic, coastal environments. Future attempts to mechanistically predict changes in carbon storage in coastal systems will benefit from incorporating OM sulfurization as both a sink for microbially produced sulfide and a mechanism for enhanced carbon sequestration.

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## **Bioorthogonal labeling as a high-throughput approach for screening microbial cultivation conditions**

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### **Abstract:**

To better understand the physiology and diversity of environmentally relevant microbes, we must be able to culture them in a laboratory setting. Many microbes remain yet uncultured due to unknown enrichment medium requirements and optimal growth conditions. Traditional studies to understand a microbe's activity rely on genomic predictions and incorporation of expensive isotopically labeled substrates but often lack *in situ* activity measurements. Bioorthogonal non-canonical amino acid tagging (BONCAT) is a nondestructive method to fluorescently label active, protein-synthesizing cells that can later be separated from a community using fluorescent activated cell sorting (BONCAT-FACS). Because the method is based on the incorporation of a synthetic amino acid, off the shelf substrates and variations to incubation conditions can be tested with ease. In this proof of principle study, material from a hot spring in Yellowstone National Park was collected and incubated in the presence of 25 substrate amendments or atmospheric conditions. After two days of incubation, active, protein-synthesizing cells were stained, sorted and identified through 16S rRNA gene sequencing. By analyzing which substrates stimulated microbial activity, cultivation medium can now be developed. BONCAT-FACS is a novel method that uses single-cell bioorthogonal labeling to profile microbial activity under a multitude of substrate amendments and conditions.

# Isotopologue fractionation during microbial methanogenesis near thermodynamic limits in a bioelectrochemical system

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## Abstract:

While the stable carbon and hydrogen isotope ratios as well as the clumped isotopologue (e.g.,  $^{13}\text{CH}_3\text{D}$ ) abundances help us identify the sources of methane, the effect of environmental and physiological conditions during microbial methanogenesis on methane clumped isotopologue fractionation is not well understood. For example, microbial methane from marine environments often indicates external equilibria with substrates (e.g.,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) and internal equilibria among methane isotopologues. In contrast, microbial methane from laboratory experiments is often characterized by strong kinetic isotope signals<sup>1-3</sup>. This apparent discrepancy has been attributed to the differences in hydrogen ( $\text{H}_2$ ) availability<sup>2,4</sup>, which is closely linked to the redox potential of the environment. So far, laboratory conditions explored in batch cultures, fed-batch bioreactors and co-cultures have not yielded equilibrium fractionation in D/H ratios or clumped isotopologue abundances<sup>4,5</sup>.

We present a new method to address this problem by culturing methanogens in a bioelectrochemical system (BES). In a BES, hydrogenotrophic methanogens can use  $\text{H}_2$  produced via the electrolysis of water at low redox potentials applied at the cathode or directly use electrons to produce methane. Either case provides a means to precisely control the supply rate of  $\text{H}_2$  or reducing equivalents to methanogens. We demonstrate the growth of a pure culture of methanogens in a BES at a range of redox potentials, including conditions close to the thermodynamic limit of hydrogenotrophic methanogenesis (ca.  $-240$  mV vs. standard hydrogen electrode, at  $25$  °C and pH 7). Methane production rate changed as a function of cathode potentials, with higher total methane production rates at lower potentials and vice versa. High coulombic efficiency (i.e., efficient current-to-methane conversion) was achieved in all experimental conditions explored. We will present the bulk and clumped isotope compositions of methane produced at a range of redox potentials and discuss potential implications for our interpretations of the isotopic signatures of microbial methane in the environment.

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# Can sediment trace metal geochemistry serve as a biomarker for microbial mat community structure in a low-oxygen Precambrian analogue?

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## Abstract:

It is critical to identify the presence and composition of microbial communities in the fossil record because microbes are implicated in both biogeochemical maintenance of the Earth system and as drivers of major environmental changes (e.g. cyanobacterial oxygenic photosynthesis as a major driver of the Great Oxidation Event<sup>1</sup>). There are a number of potential lines of evidence for ancient microbial assemblages including physical and geochemical evidence of their presence such as stromatolites<sup>2</sup> or organic biomarkers<sup>3</sup>. In addition, iron and trace metal contents have been used to infer how iron oxidizing bacteria had a major role in the development of Banded Iron Formations<sup>4</sup>. This work aims to test whether or not sediment trace metal geochemistry has the potential to serve as a biomarker for the presence of cyanobacterial microbial mats such as those inferred for the Proterozoic. The ferruginous Middle Island Sinkhole (MIS) in Lake Huron features low oxygen and high salinity waters, and microbial communities that exhibit diverse metabolic functions at the sediment-water interface. With water chemistry and microbial mat presence as inferred for the Proterozoic, MIS is considered a Proterozoic ocean analogue<sup>5</sup>, and can be contrasted with a fully oxygenated Lake Huron control site (LH) to infer mechanisms for abiotic and biotic controls on elemental burial. Notably, relationships between trace metals and sulfur do not follow expected trends based on our conventional understanding of how the trace metals are buried, and instead most closely track organic matter burial in both the oxygenated and ferruginous settings. For metals that serve as proxies for paleo-environmental redox chemistry, such as Mo, this has major implications for our interpretations of Mo abundance and Mo isotope systematics in the geologic record. Together, these results demonstrate that bulk sediment trace metal composition does not capture microbiological processes, and indicate that trace metal abundance cannot be used as a biosignature for the presence of cyanobacterial microbial mats in the fossil record. Instead, more robust trace metal geochemistry such as isotopes and speciation may be critical for understanding the intersections between microbiology and sediment geochemistry within microbial mats.

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# **My biogeochemical romance: Correlation of inorganic geochemical data and biomarker composition in the Late Ordovician Utica-Point Pleasant Formation**

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## **Abstract:**

The Middle to Late Ordovician was a period of significant restructuring and transition toward a ‘modern’ Earth system state as the geosphere and biosphere became more intimately linked. Here, we focus specifically on the middle Late Ordovician (Katian) for its unique juxtaposition as a relatively stable period – with respect to oceanic redox conditions – between a number of major environmental and biological transitions that may reveal clues about the overall state and dynamic nature of the Early Paleozoic Earth system.

This work aims to understand the development of Late Ordovician biogeochemical feedback mechanisms using a quantitative approach by correlating inorganic geochemical proxy data and biomarker composition through the Utica-Point Pleasant (U-PP) formation of the Appalachian Basin, most well known for its prolific source rock potential. The lithological development of the U-PP from carbonate platform-dominated facies to organic-rich calcareous black shales reflects a combination of both tectonically driven and glacioeustatic controls on sea level, providing the temporal and stratigraphic framework necessary for meaningful interpretation of any correlations in the geochemical data. Three cores have been logged and sampled across the western basin margin, and samples have been analyzed for Fe-speciation, major and trace element composition, and TOC. Preliminary results suggest that the U-PP can be characterized by 3-5 distinct facies, across which redox broadly transitions from an oxic to ferruginous (anoxic, Fe-replete) environment. Next, samples will be analyzed for organic geochemical parameters (e.g. biomarker composition,  $\delta^{13}\text{C}_{\text{org}}$ ) and the relationships of the inorganic and organic geochemical parameters quantified via multivariate statistical methods. Analysis of one sample returned a relatively low thermal maturity and an abundance of lipid biomarkers, reinforcing the utility of the U-PP interval for a study of this type.

Ultimately, the information that can be unlocked by the organic fraction may provide insight into both the evolution of the Late Ordovician Earth system as well as the mechanistic underpinnings responsible for Fe and trace elemental proxy values, such as the influence of terrestrialization on weathering, clay formation and diagenesis, and shelfal Fe cycling and transport to the deep basin.

## Estimating paleomarine pH from non-carbonate records

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### **Abstract:**

The ability of global climate models to accurately project future climate scenarios is largely dependent on calibrating these models against paleoclimate reconstructions. In turn, paleoclimate reconstructions are built upon the models' ability to replicate a variety of geochemical signals. Paleoclimate reconstructions, however, may be complicated by varied estimates for model parameters derived from different proxy records; for instance, CO<sub>2</sub> estimates derived from the carbonate-based records of boron isotopes in foraminifera or carbon isotopes in alkenones. Accordingly, there is a need for additional proxies, independent of the carbonate system, that can be used to refine estimates for atmospheric CO<sub>2</sub> concentrations and aid in resolving such discrepancies. Here, we describe two potential, novel methods for assessing marine pH based on the analysis of metal oxides, and that may be used to refine and calibrate pH estimates from existing carbonate-based proxies. While iron oxides have been used to examine paleomarine trace element concentrations, the metal oxide record has remained unexplored with regards to its potential as a pH proxy. Specifically, we evaluate the ability of boron isotopes in coeval iron and manganese oxides and the trace metal inventory of these deposits to track marine pH. These novel methods may ultimately help to resolve contrasting estimates for CO<sub>2</sub> concentrations, and establish new avenues for calibrating additional paleoclimate reconstructions.

# Evaluating the solubility product constant of dolomite through PHREEQC modelling of oilfield brines

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## Abstract:

Low-temperature (25°C) dolomites have an equivocal biologically-mediated petrogenesis. Though biotic processes may catalyse the reaction, thermodynamics dictate the feasibility of dolomite formation and thus a robust understanding of the low temperature solubility product constant is critical. This constant has proved elusive as dolomite reaction rates are relatively slow under Earth surface conditions. This study employs a groundwater-based approach to determine the solubility product. We use PHREEQC with the Pitzer database to calculate Mg:Ca activity ratios of a subset (n=11691) of the USGS Produced-Water Database (Blondes et al. 2016) after filtering to eliminate samples with a lack of lithological or geochemical data. At-formation depth temperatures are determined using the SMU Heatflow Database (Blackwell et al. 2011) and mean annual land surface temperatures over North America. Calcite-dolomite equilibrium appears prevalent for the majority of subsurface fluids and this study determines the dolomite  $pK_{sp} = 17.21$  (25°C) for waters spanning a temperature range 25-250°C. This value is close to the constant as experimentally determined by Benezeth et al. (2018;  $pK_{sp}=17.19$  (25°C)).

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# Uranium isotope evidence for a transition to well-oxygenated ocean conditions during the mid-Devonian (lower Eifelian)

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## Abstract:

The Devonian Period (419 to 359 Ma) represents a critical transition period in Phanerozoic Earth history, witnessing the diversification of vascular land plants, appearance of the first forests, and expansion of large predatory fishes. It has been hypothesized that the evolution of land plants was accompanied by a change the redox balance of the ocean-atmosphere system by changing the intensity of terrestrial weathering, organic carbon burial rates, and ultimately, atmospheric pO<sub>2</sub>. Prior work has suggested that a major pulse of global oxygenation occurred around 400 Ma, based on both geochemical evidence and modelling of long-term biogeochemical cycles (e.g.<sup>1-3</sup>). However, the existing data provide relatively low temporal resolution making it impossible to directly test the hypothesis that the evolution of land plants was accompanied by a major change in the redox conditions of the atmosphere-ocean system.

To test this hypothesis and pinpoint the exact timing and pattern of oxygenation, we present a new, high-resolution uranium isotope ( $\delta^{238}\text{U}$ ) dataset from limestones spanning most of the Devonian Period in the Great Basin, Nevada, USA. In our composite dataset,  $\delta^{238}\text{U}$  values are consistently less than -0.5 ‰ (and as low as -0.9 ‰) through the Emsian Stage, suggesting extensive marine anoxia during this interval. This is followed by a significant, progressive shift towards higher  $\delta^{238}\text{U}$  values (consistently greater than -0.3 ‰) in the earliest Eifelian Stage, suggesting that a major pulse of ocean oxygenation occurred around 395-398 Ma. These relatively high  $\delta^{238}\text{U}$  values generally persist through the Givetian and Frasnian stages.

This new high-resolution, carbonate-derived  $\delta^{238}\text{U}$  profile identifies points to a major shift in marine redox conditions in the earliest Eifelian coincident with evidence for increasing abundance of trilete spores during the lower Devonian<sup>4</sup> and may hint at a possible expansion of large terrestrial plants by this time.

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# Identifying microbial life in rocks: insights from population morphometry

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## **Abstract:**

The identification of microfossils in the Archean rock record is fraught with difficulty, since early life forms were simple cells that lacked sufficient morphologic complexity to be efficiently distinguished from abiologic features in rocks such as pore-fillings, botryoidal crystals, exfoliated crystals, and fluid inclusions. Such objects can contain or be coated by (a)biologic hydrocarbons, resulting in microstructures that mimic the remains of microbial cells. These uncertainties have led to many re-interpretations of individual microstructures in the ancient rock record. One critical aspect of unicellular life, however, is the occurrence of many identical, spatially associated specimens that reflect a microbial population. The question is whether such preserved biologic populations can be distinguished from populations of the objects mentioned above. Here we present a statistical approach on the quantitative morphological description of biologic and abiologic microstructure populations and the morpho-space they occupy. In order to do this, several pictures of modern microbial populations were compared to two relevant types of abiologic microstructures already discussed in the context of Archean micropaleontology: interstitial space fillings (in abiotic clastic sediments) and complex biomimetic mineral aggregates (silica-witherite biomorphs). The spatial organization, size and shapes of microstructures in the pictures were characterized and used to identify differences between populations of these biologic and abiologic entities. For bacteria, the polymodal size distribution was linked to the composite nature of a community, and the independence of shape and size was linked to the biological internal control of shape. Discriminant analyses were run in order to assess the potential of different sets of parameters to discriminate the three systems in 2-D morphospaces. Notably, parameters describing statistical distributions allowed a good discrimination between populations from these three systems. These results indicate the great potential of morphometric descriptions of populations in the context of life recognition in rocks, either on Earth or on extraterrestrial bodies. Besides, they show the need for a better understanding of the different controls of morphometric characteristics at the scale of populations.

# Assessing the reduction of selenite by filamentous fungi under anoxic conditions: implications for the evolution and future environmental impacts of fungi on Earth

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## Abstract:

Selenium (Se) is a redox-sensitive metalloid that is a micronutrient required by most life, including some groups of fungi, for the production of selenoproteins. However, elevated levels of Se in the environment can cause detrimental and severe biological repercussions. While most knowledge of biotic Se transformations is related to bacterial processes, some species of fungi, including two common fungal isolates, *Alternaria alternata* and *Paraconiothyrium sporulosum*, have evolved to transform Se from aqueous Se(+IV/VI) to elemental Se(0) or volatile Se(-II) under oxic conditions. In preliminary tests, these fungi also visibly reduced selenite (Se(IV)) to pink nanoparticulate Se(0) under anoxic conditions. This reduction may allow them to detoxify an environment to suit their needs. However, little is understood about the chemical or genetic mechanism(s) of this transformation over time, or how the fungi survive and grow under the anoxic conditions. Anoxic culture experiments of these two fungi were established with 0.1 mM selenite (Se(IV)) under N<sub>2</sub> headspace to characterize the geochemical and genomic responses to elevated Se concentrations and elucidate the mechanism(s) of anoxic mycogenic Se transformations. The fungi were grown for one month in a yeast extract media under anoxic conditions before 0.1 mM Se(IV) was added. At one week and one month post-Se addition, replicates were sacrificed for geochemical and genomic analyses. Aqueous selenite concentrations were determined by ion chromatography, and solid phase Se was determined by inductively coupled plasma optical emission spectroscopy. X-ray absorption spectroscopy will be used to identify the oxidation state of solid Se, and electron microscopy will be used to track the size and location of Se nanoparticles with respect to the cells. Lastly, transcriptomics analysis will elucidate which fungal genes are involved in Se reduction. By comprehensively examining Se transformations in these fungi from a combined geochemical and genomic approach, more accurate predictions for the cycling, transformation, and transport of Se in natural and contaminated environments will be achieved. Further, this study will lend insight to how fungal metalloid transformations have impacted past and may shape future global biogeochemical cycling of selenium.

# An ancient microbial origin for cyanide metabolism

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## Abstract:

Hydrogen cyanide (HCN) has long been considered a promising player in prebiotic and origins chemistry because of its potential to produce several key precursors of life—including nucleotides and amino acids—through anaerobic, abiotic chemical processes<sup>1-7</sup>. Previous work indicates various thermochemical, electrochemical, and UV-mediated processes that could form and sustain HCN on the early Earth<sup>6,8</sup>. However, limited evidence exists to directly support HCN's presence or abundance at that time. Phylogenetic analyses of HCN-metabolizing enzymes may help constrain the age and distribution of cyanide metabolisms, thereby supporting or challenging cyanide's hypothesized role as a resource for early life; such analyses may also help contextualize the role of cyanide metabolism in modern ecosystems. We present phylogenetic analyses of the HCN-metabolizing enzymes cyanide hydratase and cyanide dihydratase, closely-related members of the nitrilase superfamily<sup>9-12</sup>. Our early results indicate that these cyanide-degrading enzymes have an ancient origin, possibly as old as the Archaean eon. Contrary to previous hypotheses that suggested these enzymes evolved in plants<sup>9</sup>, the data clearly suggest a bacterial origin for HCN-degrading nitrilases. While a deep pattern of vertical inheritance is evident among these enzymes, extensive horizontal gene transfer is also evident between microbial groups, possibly reflecting sustained ecological advantages of cyanide metabolism. These early results provide motivation and material for performing molecular clock analyses, which will be used to quantitatively estimate the origin and diversification of cyanide metabolisms in prokaryotic and eukaryotic groups.

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# Using the boron-pH proxy to detect permanent El Niño conditions during the Pliocene

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## Abstract:

Warm sea surface temperatures (SSTs) in the eastern equatorial Pacific during the early and middle Pliocene (~5.3-3.6Ma) have been put forward as evidence of a collapsed meridional SST gradient and an overall El Niño-like background state persisting in the Pacific during this time<sup>1,2,3</sup>. More recent SST studies with new proxies (TEX<sub>86</sub>) have pushed back on this idea with evidence of the western equatorial Pacific warming equally during the Pliocene, maintaining the modern west-east, hot-cold temperature gradient observed today<sup>4</sup>. This disagreement amongst SST proxies has left the question of a Pliocene “Permanent El Niño” open-ended and in need of further investigation. Initial measurements of the boron isotopic composition ( $\delta^{11}\text{B}$ ) of planktonic foraminifera from two sites in the equatorial Pacific (east and west) provide the first evidence of reduced upwelling strength in the eastern equatorial Pacific during the Pliocene, an alternative and as-of-yet unconsidered signature of El Niño-like conditions. These results make use of the  $\delta^{11}\text{B}$ -pH proxy, in which the  $\delta^{11}\text{B}$  of foraminifera tracks the acidity of ambient ocean water. The acidity signal in the east Pacific is taken as a measure of upwelling strength (and thus of El Niño-like conditions) since deep water is expected to be more acidic than surface water. The relative difference in pH between the east and west Pacific is also taken as a marker of strength of El Niño-like conditions. Initial results show a distinct difference in pH between the east and the west Pacific at ~1Ma of similar magnitude to the modern day. At ~5Ma, however, this difference appears to have collapsed, with similar pHs in both the east and the west. pH is also reduced at both sites at ~5Ma, consistent with the equilibrium state of the atmosphere at ~400ppm<sup>5</sup> during the Pliocene. While further work is required to validate these results, they nonetheless represent a promising new line of evidence with which to investigate the question of a “Permanent El Niño” during the Pliocene.

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# Metagenomic analyses of pustular microbial mats from Shark Bay, Australia and Cat Island, The Bahamas reveal distinct cyanobacterial adaptations to stresses in peritidal environments

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## Abstract:

Modern cyanobacteria that form pustular mats in marine supratidal/intertidal zones experience ultraviolet radiation, high salinity (56-70 ppt), and periodic desiccation. These organisms are also direct ecological and morphological analogs of the oldest cyanobacterial fossils. To characterize the modern organisms and the genetic machinery that they use to cope with the harsh environmental conditions, we sequence, analyze, and compare the metagenomes of cyanobacteria from pustular microbial mats collected in the peritidal zone of Shark Bay, Australia, and an exposed part of a tidal channel in Cat Island, The Bahamas. Quality filtering of the metagenome-assembled genomes (MAGs) yielded cyanobacterial MAGs with >90% completeness and <3% contamination for both the Shark Bay and Bahamian samples. After quality control (>50% completeness; <10% contamination) of the whole microbial community, 84 MAGs and 16 MAGs were recovered from the Shark Bay and Bahamian communities, respectively. The Shark Bay metagenomes were comprised of 56% Alphaproteobacteria and Bacteroidetes, 40% Gammaproteobacteria, Planctomycetes, Verrucomicrobia, and Chloroflexi, and 4% Cyanobacteria. The less diverse Bahamian microbial community consisted of 50% Alphaproteobacteria, 19% Gammaproteobacteria and Planctomycetes, and ~31% Cyanobacteria. Cyanobacteria from both locations have genes that encode for the production of the UV-protective pigment scytonemin. A conserved cluster of genes that encode for polysaccharide transport and export proteins, glycosyl transferases, and sulfotransferases is also present in all 3 cyanobacterial genomes from Shark Bay and in 3 out of 5 cyanobacterial genomes from Cat Island. Furthermore, several genes adjacent to this operon encode for proteins involved in the metabolism and transport of fucose, suggesting that the sulfated polysaccharides are fucoidans. All Bahamian cyanobacteria and one of the three cyanobacteria from Shark Bay also contain a five-gene operon that encodes for the synthesis of glycine betaine from choline. The presence of the same conserved operon in pustular mats from the two locations, and its absence from freshwater cyanobacteria, suggest that choline monooxygenase has a role in a potentially novel glycine betaine synthesis pathway and osmoprotection. Thus, specific adaptations of cyanobacteria in pustular mats to UV, osmotic, and desiccation stresses in peritidal and hypersaline environments include the synthesis of UV-protective pigments, sulfated polysaccharides, and glycine betaine.

# Probing the iron speciation extraction using magnetic techniques and X-ray diffraction

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## Abstract:

Iron speciation is one of the most widely applied tools for understanding ancient oxygen and environmental conditions. The proxy utilizes a sequential geochemical extraction proportioning iron into distinct pools connected to mineralogy<sup>1</sup>; ratios of these pools are compared to empirical calibrations from modern sediments to make paleoredox interpretations, which have fundamentally altered our perspectives on Precambrian and early Paleozoic ocean chemistry. Beyond these Earth History applications, the formalized extraction sequence has been widely applied to understand Holocene to modern iron cycling and metal sequestration. Although tested on pure mineral mixtures, fundamental technique checks have not been performed to probe if these extractions are solubilizing the targeted mineral phases in natural sedimentary rocks and sediments. Our approach was to characterize the mineralogy of bulk powders as well as the residues taken after each sequential extraction step: acetate (targeting carbonates), hydroxylamine-HCl (targeting “easily reducible” oxyhydroxides), dithionite (targeting ferric iron (oxyhydr)oxides), and oxalate (targeting magnetite). Magnetic techniques and X-ray diffraction were used to identify and quantify iron-bearing minerals in twenty fine-grained siliciclastic samples dating from the Holocene to 1.5 Ga with diverse total iron contents, different proportions of iron from each iron speciation extraction, and distinct redox interpretations. The acetate extraction at least partially dissolves siderite as well as the majority of calcite and dolomite present. The dithionite extraction is the most robust at removing the targeted mineralogy; nearly all goethite is solubilized during this step. However, oxalate extracts one to three orders of magnitude more iron than is present in magnetite in the samples based on magnetic quantification. X-ray diffraction analyses suggest dissolution of iron-bearing clays, specifically berthierine/chamosite, could be causing this disparity. The solubility of minerals depends upon their grain-size, crystallinity, and coordination resulting in natural variation and complexity; studies of past and present iron cycling should utilize multi-pronged methodologies to provide more direct connections to mineralogy and thus natural processes.

## References

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## **Biogeochemical anomalies of forest ring edges – phenomena caused by microbial interactions**

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### **Abstract:**

Scattered across the landscape of Manitoba, Ontario, and Quebec, Canada, are numerous perfectly circular forest rings, observable from aerial photographs and satellite images. Historically, these rings have been a source of puzzlement as their appearance and geometry are not straightforwardly explained. Recently, several forest rings in Ontario have been better characterized using geophysical, geochemical, and microbiological techniques. Those investigations showed that their edges, up to 30m wide, host geophysical and geochemical gradients, that are expressed as dramatic changes in the soil electrochemical potential (redox), electrical fields, chemical composition, soil respiration and acidity. Here, we investigated the soil and groundwater using similar tools for understanding mechanisms responsible for those gradients. Our results indicate that while the groundwater has low pH outside the ring, the pH is higher within the confines of the forest ring. By contrast, electrical conductivity shows consistently low values within the ring and higher outside. “Anomaly zones” at the ring edges, where the major gradients are located, are 5m wide. Digestions and sequential extractions indicate that many trace elements (e.g., P, S, As, Ni, Co, and Cu) are leached from the peat and accumulate in the clay and sand below.  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  indicates that the soil respiration anomaly is caused by microbial activity with ubiquitous carbonate depletions within the ring edges. 16S rRNA and ITCgene sequencing, as well as the characterization of extracellular polymeric substances, indicate that certain substrates host very specific microbial communities working in close collaboration with fungal species at the surface. Using thermodynamic calculations, we propose that the “anomaly zones” are caused by an active community of saprophytes/fermenters overlying a syntrophic community of methanogens and aerobic and anaerobic methanotrophs. Enrichment cultures and SEM imaging further suggests that cable-like bacteria play a role in the creating and keeping the redox gradients. Furthermore, our investigations show that forest rings are sensitive and easily disturbed by invasive sampling and measuring techniques and it is difficult to repair the damage done by the multitude of sampling techniques. These studies provide valuable new insights and hypothesis to be proved into the microbial controls on the measured anomalies.

## **Paleoatmospheric conditions recorded in Paleoproterozoic weathering crust at the Karelian craton**

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### **Abstract:**

The composition of Earth's early atmosphere has been an intriguing research topic for long, though general consensus has not been achieved. Major changes in the development of Earth's geochemical system were taking place at a critical time coinciding with the Archean-Proterozoic transition when Earth's atmosphere became oxygenated, thus triggering a whole new set of chemical weathering reactions that are potentially recorded in weathering products. It has been argued whether the oxygenation of the atmosphere was a gradual or stepwise process. In this contribution we study a paleoweathering crust developed between 2.5 – 2.44 Ga, just before the Great Oxidation Event on the basalt of the Kuksha Volcanic Formation at the Imandra-Varzuga Paleoproterozoic Greenstone Belt, northwestern Russia. Kuksha weathering crust can potentially shed light on the paleoatmosphere composition and weathering modes of this time. The 3 m-thick paleoweathering profile tells us a story of intense weathering under seasonally contrasting climatic conditions. The crust is characterized by Al-phyllsilicate clay minerals that are typical products of strong chemical weathering. The mineralogy of the uppermost part of Kuksha weathering crust suggests its formation under elevated CO<sub>2</sub> partial pressures, which is consistent with previous estimates of  $p\text{CO}_2$  at the time interval. Estimates of the atmosphere CO<sub>2</sub> levels using the mass-balance modeling of Kuksha paleoweathering profile suggest  $p\text{CO}_2$  varying between 2-8 times of PAL (present atmospheric level). Several geochemical and mineralogical proxies applied also suggest that this intense acidic weathering occurred under low-oxygen conditions. Although not proven, the behavior of the element Cr and mineral siderite described in the Kuksha weathering crust possibly mark the presence of microbial activity in continental crust already before the GOE.

## Novel apparatus designed for continuous chemical monitoring of decay environments

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### Abstract:

Soft tissues are rarely found in the fossil record because their high susceptibility to decay leaves only a short window for preservation. Decay experiments provide a valuable tool with which to analyze the early chemical environments that could lead to soft-tissue fossilization. A novel apparatus has been designed to continuously monitor environmental conditions, thus removing the need for experiment termination upon measurement. Chemical sensors are mounted on the lid of a 3D-printed, sealed enclosure and connected to an Arduino microcontroller which records the sensor readings and relays them to a local computer. Currently, the following sensors are installed: two nondispersive infrared (NDIR) gaseous sensors, measuring carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), a temperature sensor, a humidity sensor, and two glass electrodes, measuring acidity (pH) and oxidation-reduction potential (ORP). This sensor combination was designed to investigate the early diagenetic environment of fossiliferous siderite (FeCO<sub>3</sub>) concretions from Mazon Creek, Illinois; however, different sensors can readily be installed to explore other diagenetic environments. Carbon dioxide and methane concentrations within the headspace of the decay vessel were monitored to give an indication of when aerobic decay and methanogenesis initiated, respectively. Methanogenesis has been related to siderite precipitation through the production of bicarbonate (HCO<sub>3</sub><sup>-</sup>), an important reactant in the formation of siderite. Acidity and ORP indicate changes in water chemistry and metabolic activity. Experiments have been conducted verifying the operation of this novel decay apparatus so that it can be used with confidence on future experiments. Current decay experiments require numerous replicates with planned termination dates upon which data is collected. This novel apparatus allows for continuous data recording without termination of experiments resulting in more detailed data, possibly revealing shorter trends not captured with current experiments.

## Microbial communities in Canadian coastal sediments

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### Abstract:

Coastal marine sediments are one of the largest habitats for microbial life on Earth, collectively harboring up to  $7.5 \times 10^{29}$  prokaryotic cells. Coastal sediments also support the vast majority of global organic carbon burial and thus play a critical role as biogeochemical reactors that modulate atmospheric O<sub>2</sub> and CO<sub>2</sub> concentrations over geological time. Despite their importance, however, the composition, diversity, and structure of microbial communities in coastal sediments remains underexplored and largely unknown. Biogeochemical data collected through decades of research reveals a canonical vertical stratification of metabolic pathways that sequentially utilize terminal electron acceptors according to their availability in order of progressively decreasing free energy yields. Vertical stratification in substrate supply and availability is expected to exert strong control on microbial community composition and, while this is observed in analyses of specific functional guilds (e.g. sulfate reducers), the broader expected stratification of the entire sediment community remains largely untested. To create new knowledge on coastal sediment microbial communities, we analyzed sediments recovered from four Canadian sites: Saanich Inlet; the Strait of Georgia; Jervis Inlet; and the Beaufort Sea. We found that the overall composition of coastal sediment communities is distinct from that of other large microbial habitats like seawater and soil, and that sediment diversity was extremely high, rivaling that of the most diverse known habitats like soils. We identified cosmopolitan microbial community members common to all sediments despite strong latitudinal differences between sites. These cosmopolitan organisms form a core microbial community, implying that they are key contributors to sediment metabolism and play an important role in global biogeochemical cycling. Each site also had a unique peripheral microbial community comprised largely of low abundance members, imparting biogeography to coastal sediments. We did not, however, observe the strong vertical stratification in the microbial community expected from biogeochemical information, implying that the availability of electron acceptors does not have a strong influence on microbial community composition, diversity, and structure. Overall, this work expands our knowledge of microbial communities in one of the largest habitats on Earth and represents a key step in linking biogeochemical cycling in coastal sediments to the underlying microbial community.

## Tiny spaces, busy places: Illuminating spatial organization of microbial activity in sediments from nanometer to centimeter scale

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### Abstract:

Microorganisms inhabiting marine sediments provide crucial ecosystem services through the cycling of carbon and essential nutrients. Previous studies have used whole community approaches at relatively large spatial scales to survey active microbes responsible for carrying out important transformation. However, the scales commonly used to assess microbes *in-situ* are too large to capture their intimate relationships with other microbes and mineral substrates. Here, we describe the combination of multiple approaches to quantify, identify, and visualize active microbes at sub-centimeter scale resolution in the sediment of Little Sippewissett salt marsh near Falmouth, MA, USA. Bioorthogonal non-canonical amino acid tagging (BONCAT) was used to fluorescently label translationally active cells *in-situ*. The BONCAT-labeled active cells were then quantified, sorted using fluorescence activated cell sorting (FACS), and identified using 16S rRNA gene sequencing to provide community data at sub-centimeter resolution. Preliminary results show that while only a fraction of the total microbial cells was translationally active (9.4% - 22.43%), nearly all bacterial genera residing in the sediment contained translationally active individuals (57.6% - 74.5%). Interestingly, the proportion of active microbial cells was highest in the surface sediment and decreased with depth, but the proportion of bacterial genera that contained active members demonstrated an opposite trend and generally increased with depth. The microbial composition of the active community differed markedly from the total community and also varied by depth in the sediment column. These results will be paired with microscale computed tomography ( $\mu$ CT) to identify zones of interest for further investigation of microbe-microbe and microbe-mineral interactions using fluorescence microscopy, secondary electron microscopy (SEM), and energy-dispersive x-ray diffraction (EDS). In summary, this study represents an innovative attempt to correlate the identification of anabolically active microbes with the visualization of their spatial organization at high-resolution, biologically relevant scales.

## Can microbial activity enhance chromium removal from industrial stormwater?

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### Abstract:

Treatment processes for metals in industrial stormwater can be cost prohibitive. Therefore, passive remediation strategies using natural materials and microbial processes have the potential to provide affordable solutions for removing metals from aqueous waste streams, which is important from regulatory and environmental quality perspectives. Our research explores the key chemical, biological, and physical processes promoting removal of hexavalent chromium (Cr) from an industrial stormwater treatment system by association with granular organic peat media. In this installation chromium is primarily in the water soluble and carcinogenic hexavalent form, chromate. Prior to treatment, chromate is converted to Cr(III) via an oxidation-reduction reaction using iron sulfate (Fe(II)SO<sub>4</sub>). The resulting Cr(III) is less water soluble than chromate, making Cr precipitation as hydroxides possible. The removal capacity for Cr(III) is much higher than expected for adsorption and filtration alone, suggesting other mechanisms, including microbially mediated attenuation may play a role. In addition to filtration of Cr(III) precipitates, the presence of Fe(III) (from the pre-treatment step) could yield Cr(III) co-precipitation with Fe minerals and/or serve as a terminal electron acceptor.

Samples were collected from the treatment site in Howell, MI USA, where Cr-laden stormwater is treated in large tank reactors filled with peat sorbent material. We sampled one reactor in four different locations at four depths for a total of 16 solid-phase peat material samples. DNA was extracted to collect metagenomic data and microbial coupons were installed in the tanks to harvest biofilm samples. Chemical digestions show total Cr concentrations ranging from 400-900 mg/kg peat dependent on depth and location. X-ray Fluorescence Microprobe (XFM) data reveal that Cr is heterogeneously distributed within the bioremediation media with diffuse and “hot spot” features on the micron to 10s of micron scale. Additionally, results show Cr(III)-bearing particles and metallic Cr bearing particles in the same sample.



# Moving from correlation to mechanism: testing the role of oxygen and temperature change in the Great Ordovician Biodiversification Event

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## **Abstract:**

The Great Ordovician Biodiversification Event, or GOBE, was one of the most rapid and dramatic diversity increases recorded in the Phanerozoic fossil record. Global cooling and atmospheric oxygenation have both been suggested to be important factors in driving the transition from the high-extinction regime of the upper Cambrian-Early Ordovician to the Middle-Late Ordovician diversification, but there are a number of competing hypotheses. The research presented here proceeds from 1) geochemical analysis of global ocean redox change to 2) calibration of Earth system models with geochemical data, and finally to 3) testing evolutionary hypotheses with an ecophysiological framework. The uranium isotope proxy is proposed to track global marine redox conditions in geologic time, with predictable isotope fractionations from seawater recorded in shallow-water carbonates. We present  $\delta^{238}\text{U}$  measurements of upper Cambrian through Middle Ordovician carbonates from the House and Confusion Ranges, Utah, to directly test whether there was a global marine oxygenation event coincident with the Ordovician radiation. We use a novel Monte Carlo uranium isotope mass balance model to provide error-bounded, quantitative constraint from  $\delta^{238}\text{U}$  measurements on the global extent of euxinic (anoxic, sulfide-dominated) bottom-waters through the Ordovician. These paleoredox estimates and a compilation of sea-surface temperature reconstructions are next used to calibrate a time-series of Ordovician ocean models from the cGENIE Earth system model. Finally, we use the Metabolic Index, a method developed to quantify the extent of viable aerobic habitat for marine ectotherms, to investigate the extent to which changes in habitat availability driven by temperature and oxygenation changes could have mechanistically driven the diversification observed in the fossil record. Specifically, we populate modeled oceans with a suite of ‘ecophysiotypes’, sampling from probability density functions summarizing the growing body of measured temperature-dependent hypoxia tolerances in modern marine ectotherms. The Metabolic Index approach thus allows us to model predicted changes in latitudinal diversification and migration gradients based solely on oxygen and temperature changes consistent with the geochemical record. We compare modeled biodiversity dynamics to those previously identified in the fossil record to establish the extent to which observed diversification patterns could have been driven by marine temperature and oxygenation changes.

# Trace metal interaction with ferrihydrite: Application to Precambrian biogeochemical cycles

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## Abstract:

Low atmospheric O<sub>2</sub> levels are thought to have led to a predominance of ferruginous conditions (Fe<sup>2+</sup> rich) in the Precambrian ocean, evidence for which is found in the sedimentary record of iron formations (IFs). IFs are thought to have formed by chemical precipitation of metastable Fe-bearing precursor minerals followed by diagenetic transformation to stable minerals. One of the suggested precursors to the minerals assemblages in IFs is ferrihydrite (Fh), a hydrous Fe<sup>III</sup> oxyhydroxide known to be reactive towards various trace metals. Thus, as long as Earth's oceans contained appreciable concentrations of Fe<sup>2+</sup>, up to the late Neoproterozoic or early Paleozoic oxygenation of the oceans' interior, Fh likely played a role in regulating the trace-metal budget in the early ocean.

To test this hypothesis, we conducted experiments of trace metal (Cu, Zn, Ni and Mo) uptake by Fh in ancient seawater-analog solutions, at a pH of 7.5 and at 25°C. To investigate both sorption and co-precipitation, experiments were conducted with Fh synthesized in advance and then exposed to the metals, or with Fh synthesized in the presence of the metals. The solids were identified by XRD, TEM and SEM, and trace metals were measured in both solids and supernatants on an Agilent 7700s ICP-MS.

Preliminary results indicate metal reactivity with Fh in the order Mo << Ni < Zn < Cu. Solid-aqueous equilibration times for these metals are about 24, 5, 0.5, 0.25 hours, respectively. Mo, present as molybdate ions, partitions negligibly onto Fh, irrespective of the uptake methods. Cu, Zn and Ni appear to partition more strongly into Fh under co-precipitation. A break in the slope of metal to Fe ratios (M:Fe) in the Fh versus M:Fe added to the solution suggests a switch in the association mechanism. At low M:Fe of Cu, Zn and Ni, the association appears stronger (slope closer to unity), consistent with co-precipitation or strong sorption. A weaker association (shallower slope) at higher M:Fe suggests saturation of the strong association mechanism and a switch to the weaker association. At geologically plausible concentrations of Cu, Zn and Ni, the association with Fh is strong, suggesting that in regions dominated by Fh formation, it may have had a role in regulating Precambrian concentrations of these trace metals. These findings have implications for our understanding of the chemical composition of Earth's oceans and biological activity, and for the application of geochemical proxies for the oxidation state of the ocean-atmosphere.

## Ferromanganese crusts as recorders of marine dissolved oxygen

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### **Abstract:**

The distinct triple oxygen isotope composition of tropospheric O<sub>2</sub> relative to seawater is the result of biogeochemical reactions (e.g. primary productivity, respiration), exchange with the stratosphere, and the relative size of different oxygen-containing reservoirs, namely O<sub>2</sub> and CO<sub>2</sub>. This difference in isotopic composition gives tropospheric O<sub>2</sub> utility as a record of these biogeochemical and atmospheric processes, and its anomalous oxygen-17 has utility for determining where in the rock record isotopic fingerprints of tropospheric oxygen may be preserved. The isotopic record of tropospheric oxygen is largely limited to analyses of gas trapped in continental glaciers and a patchwork of other proxies, most notably the triple oxygen signature of sulfate. Here we show the uppermost layer of hydrogenetic, deep-ocean ferromanganese crusts from each of the major ocean basins also exhibit a persistent triple oxygen isotope composition consistent with the direct incorporation of dissolved oxygen. The range of  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  in ferromanganese crusts suggests the Mn oxide endmember contains a near 50:50 mixture of oxygen from water and dissolved O<sub>2</sub> that undergoes minimal mineral-water oxygen isotope equilibration. We show this signal persists throughout the crusts, potentially preserving near 75 million years of the oxygen isotopic composition of the lower troposphere and subsequent deep-ocean respiration. Oxygen isotopic analyses and bulk chemistry suggest that ~25% of the oxygen atoms contained in a typical ferromanganese crust from the Pacific derive directly from dissolved O<sub>2</sub>. Although some analytical challenges remain, these widespread layered deposits of ferromanganese crust offer a tractable path for interrogating the oxygen cycle of the troposphere and deep ocean millions of years into the past.

## The biogeochemical impact of early Paleozoic bioturbation

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### **Abstract:**

Bioturbation—sediment mixing by burrowing animals—critically shapes seafloor ecology and sediment properties, as well as global marine biogeochemical cycling. Observation of strong bioturbation-biogeochemical feedbacks in modern marine environments suggests that the evolutionary development of bioturbation should have profoundly impacted contemporaneous biogeochemical (e.g., C, P, O and S) cycling. Stratigraphic archives indicate that the early Paleozoic development of bioturbation was a protracted process, and that the appearance of intensively and deeply mixed sediments lagged significantly behind relatively early advances in infaunal seafloor colonization. Recent modeling work has suggested that even limited extents of bioturbation may nonetheless have initiated an early Paleozoic productivity crisis and ocean-wide deoxygenation. It has also been proposed that the emergence of bioturbation would have operated as a stabilizing feedback, dampening C cycle perturbation. However, the precise biogeochemical impact of early Paleozoic bioturbation has remained debated.

To further address this question, we explore a new and more fully parameterized multi-component diagenetic model. We observe that the relationship between bioturbation and both C-P-O and S cycling is complex and non-linear, and that not only intensity but style of bioturbation (e.g., biodiffusion vs. bioirrigation) influence the magnitude of both P recycling and S oxidation. In this light, early Paleozoic bioturbation—which was likely bioirrigation-dominated and characterized by relatively muted and shallow biodiffusional sediment mixing—may have initially only weakly influenced net S oxidation, while simultaneously mediating increased P recycling. Moreover, we find that porosity—a parameter that, although rarely explored in diagenetic models, is substantially impacted by bioturbation—strongly influences both these systems. Additionally, in contrast to previous studies, we find that, rather than operating as a stabilizing feedback, bioturbation amplifies the sensitivity of the coupled C-P-O cycle to environmental perturbations.

## Seawater contamination in ODP/IODP porewater samples and its quantitative effects on studies of microbial sulfate reduction

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### **Abstract:**

Redox reactions at the seafloor determine how much organic carbon is buried and thus play vital roles in regulating the carbon and oxygen cycles on Earth. Studies usually reveal the extents and rates of these redox reactions by measuring concentrations of dissolved reactants or products in porewater, followed by modeling or using radioactive tracers. Measuring porewater chemicals has been a standard practice in expeditions of the International Ocean Discovery Program (IODP, and formerly the Ocean Drilling Program (ODP)). However, porewater is prone to contamination, especially to seawater which is used as the drilling fluid. As seawater contains a high content of sulfate (28 to 29 mM), a small quantity of seawater can already add a large amount of sulfate into porewater samples and impede the reliability of studies on microbial sulfate reduction. However, descriptions of such effects from contamination have largely been qualitative. Here we carry out quantitative analyses on how seawater contamination affects the interpretations of sulfate reduction rates and isotope fractionations and give suggestions to avoid or discern contamination.

## **Bistability in iron-sulphur cycling and redox shifts in anoxic marine systems**

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### **Abstract:**

Today, oxygen depleted marine environments are limited to oxygen minimum zones, restricted basins and sedimentary pore waters. Before the Phanerozoic Eon (more than 542 million years ago) however, the global ocean was characterised by extensive anoxic regions. In the absence of oxygen, seawater should become either rich in dissolved ferrous iron (ferruginous) or rich in dissolved sulphide (euxinic). It is commonly assumed that under a certain set of environmental conditions – delivery of iron oxides and sulphate or organic matter – only 1 stable state exists for anoxic seawater: ferruginous or euxinic.

Theoretically however, it can be shown that a bistability zone exists in the Fe-S cycle, where seawater can be euxinic or ferruginous for identical boundary conditions, and this is an inherent feature of all anoxic marine systems. Diagenetic modelling analysis reveals that this bistability zone arises for ratios of iron oxide delivery versus organic matter influx that are common in modern marine sediments. Furthermore, in a three-box ocean model, the iron-sulphur bistability zone appears for organic matter export fluxes that are expected in the Precambrian. We propose that Fe-S bistability is common in present-day marine sediments, and that this could have been a prominent feature of ocean redox chemistry before the Phanerozoic.

# Microbial community shifts due to U and Ni concentrations at the bottom of meromictic pit lakes

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## Abstract:

Mine pit flooding during decommissioning is a common alternative to backfilling to prevent oxidation of exposed rock. Two such open mine pits were flooded at the decommissioned uranium (U) mine at Cluff Lake, Saskatchewan<sup>1</sup>. Both pit lakes turned meromictic, and while one is shallow (28 m) and rich in iron and organic carbon, the other is up to 90 m deep and rich in calcium and sulfate<sup>2</sup>. Microbes in the sediments of those pits exist in the presence of elevated concentrations of U, As, and Ni. The deep sediment communities in the 90 m deep pit are specifically exposed to 1.7 mg/L U and 2.0 mg/L Ni in the aqueous phase and 1400 mg/kg U and 100 mg/kg Ni in the solid phase, both elements being relatively bioaccessible as determined by sequential extractions. These metals cause considerable shifts in the microbial communities, leading to a decreased species diversity and richness, as indicated by 16S rRNA gene sequencing. The pits are dominated by the classes Sphingobacteriia (family *Chitinophagaceae*), Alphaproteobacteria (order Rhizobiales), Actinobacteria (family *Microbacteriaceae*), and Betaproteobacteria. Data interpretation using Canonical Analysis of Principal Coordinates suggests that in terms of solid chemistry, U was the dominant driver of community structure. At the same time, increased U concentrations did not correlate with larger abundance of potential U reducers, such as members of *Geobacteriaceae*. Further in-depth studies on these communities that are anthropogenically exposed to unnatural chemical gradients will help to understand their adaptability and survival strategies, thus allowing for the development of more adapted bioremediation technologies.

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# Interpreting Phanerozoic changes in sulfate $^{17}\text{O}$ isotopic composition

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## Abstract:

The anomaly observed in triple oxygen isotopic composition ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ) of ancient seawater sulfate likely originates from mass-independent stratospheric chemical reactions, where the size of the anomaly reflects the atmospheric ratio ( $p\text{O}_2/p\text{CO}_2$ ). Phanerozoic marine sulfates have values of  $\Delta^{17}\text{O}$  as low as  $-0.339\text{‰}$ <sup>1</sup>, and these large depletions in  $^{17}\text{O}/^{16}\text{O}$  have been used as evidence of lower  $p\text{O}_2$  relative to  $p\text{CO}_2$  in past atmospheres. However, this isotope proxy has not yet been tested in the modern, so there is large uncertainty associated with atmospheric interpretations. This anomaly is believed to be incorporated during the oxidation of  $\text{FeS}_2$  by  $\text{H}_2\text{O}$  and  $\text{O}_2$ , however the degree of incorporation and the extent of competing sulfur cycle fluxes (largely microbial sulfate reduction) are underdetermined. Global rates of microbial sulfate reduction are unknown to within an order of magnitude.

Here we test the strength of the sulfate oxygen isotope proxy in the modern sulfur cycle. We present an updated sulfur cycle model and calibrate it with the measurement of  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of modern marine sulfate ( $\delta^{18}\text{O} = 8.67 \pm 0.21\text{‰}$ ,  $\Delta^{17}\text{O} = -0.016 \pm 0.017\text{‰}$ ). Included in the model are the two main processes that exert isotopic control of marine sulfate – (1) biological cycling during microbial sulfate reduction and (2) physical weathering of sulfur-bearing minerals. (1) We draw on the findings of an isotopic model of the microbial sulfate reduction metabolism rooted in thermodynamics to describe the averaged modern biological effect on sulfate. (2) The sulfate weathering flux carries a fraction of atmospheric  $\text{O}_2$  and associated isotope anomaly. We use a steady-state biosphere-atmosphere model of atmospheric  $\text{O}_2$  isotopic composition to interpret the isotopic composition of this weathered sulfate.

We use our findings from the modern sulfur cycle to revisit the Phanerozoic marine sulfate record and its implications for atmospheric compositions. Measurements of marine sulfate  $\Delta^{17}\text{O}$  show that the sulfates become increasingly depleted with age, but at any particular age compositions range to  $\Delta^{17}\text{O} > 0$ . The more depleted values are thought to directly reflect marine sulfate composition, whereas through the additional processes that cycle sulfur (i.e. microbial sulfate reduction), sulfate compositions move toward  $\Delta^{17}\text{O} = 0$  or even  $\Delta^{17}\text{O} > 0$ . As an example, we use a section of Upper Triassic evaporites to illustrate how this sequence of events can operate in a restricted marine basin. Finally, we use the compiled Phanerozoic marine sulfate record to draw conclusions about atmospheric compositions and the balance of sulfur cycle processes through time.

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## Phanerozoic radiation of ammonia oxidizing bacteria

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### **Abstract:**

The biogeochemical nitrogen cycle is central to the functioning of the biosphere. The modern nitrogen cycle involves a web of microbially mediated redox transformations necessary for supplying the nitrogen demand for primary productivity. The N cycle further provides electron donors and acceptors for diverse microbial metabolisms. Among the most crucial steps in this process is the oxidation of ammonia to nitrite, an obligately aerobic process with sluggish abiotic kinetics performed by a limited number of lineages of bacteria and archaea. While this process has an absolute requirement for molecular oxygen, it has been contested whether microbial ammonia oxidation evolved around the Great Oxygenation Event ~2.3 Ga or whether it arose much earlier in Earth history. In order to estimate the antiquity of bacterial ammonia oxidation, we performed phylogenetic and molecular clock analyses of ammonia oxidizing bacteria and proteins involved in this metabolism. Surprisingly, bacterial ammonia oxidation appears quite young, with crown group clades of ammonia oxidizing bacteria having originated during Neoproterozoic (or later) time with major radiations occurring during Paleozoic and Mesozoic time. The evolution of ammonia oxidizing bacteria is broadly coincident with the first extensive oxygenation of the deep ocean, potentially reflecting restructuring and increased vigor of the biogeochemical nitrogen cycle. The late evolution of crown group ammonia oxidizing bacteria challenges earlier interpretations of the ancient nitrogen isotope record, predicts a more substantial role for ammonia oxidizing archaea during Paleo- and Meso-proterozoic time, and may have implications for our understanding of the size and structure of biological nitrogen cycling through geologic time.

# Oxygen and pH gradients within silicifying microbial mats in El Tatio, Chile

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## **Abstract:**

The preservation of microbial communities as microbialites is essential to studies assessing the earliest evidence for life on Earth and major transitions in our planet's geosphere and biosphere. In particular, silicification has the potential to preserve fine-scale biosignatures in modern and ancient microbial deposits. Studies often focus on end-members of the microbial silicification process: initial silica precipitation on cellular scales, and the lithology of biogenic sinter deposits. In contrast, the effects of progressive silicification within in situ microbial mats remain unconstrained. Here, we present oxygen and pH micro-profiles and lateral transects from living mats with nascent silicification in Vicuna Stream, within the El Tatio hydrothermal fields of Chile. Vicuna Stream mats float at the air-water interface, with alternating subaqueous and subaerially-exposed surfaces. Silica precipitation is most prevalent on subaerial surfaces, forming brittle sub-mm sheets. While all mats produce oxygen, concentrations below silicifying surfaces are several times lower than within immediately adjacent subaqueous mats. The upper layers of silicifying mats are also more acidic (pH = 5-7.5) than adjacent subaqueous mats (8.5-10). Unsilicified subaerial mats form lateral gradients between subaqueous and silicifying subaerial surfaces, with intermediate oxygen concentrations and pH values. We propose a silicification model where diminished oxygenic photosynthesis in subaerially exposed mats facilitates increased silica precipitation as pH locally becomes more acidic.

# Remediation of metals by Mn-oxidizing fungi in Minnesota Soudan Iron Mine

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## **Abstract:**

Manganese (Mn) oxides are ubiquitous minerals that commonly control the uptake and release of heavy metals and nutrients through coprecipitation, adsorption, and redox processes. In nature, the oxidation of Mn(II)<sub>aq</sub> to form the sparingly soluble, nanocrystalline Mn(III/IV) oxide phases is largely driven by microbial activities. These biogenic Mn oxides are highly reactive and can act as natural sponges to adsorb many metals (e.g., Ni, Cu, Co, and Zn) from the water. During formation, the structure of biogenic Mn oxides can be altered in the presence of Mn(II)<sub>aq</sub> and other metals, which may in turn affect their ability to bind metals. Such processes are potentially controlled by the chemistry of the aqueous environments and the type microorganisms involved. For environmental remediation, mycogenic Mn oxides are of particular interest because diverse Mn-oxidizing fungi can survive in harsh (e.g., metal-rich and high salinity) environments and are prevalent in many metal-polluted sites. The Soudan Underground Mine, a former iron ore mine in northern Minnesota, emits wastewater containing high concentration of heavy metals and salts. Nickel (Ni) and cobalt (Co) are the major concerns in the wastewater and are actively being treated at great expense to the mine and State of Minnesota as it has been designated a state park. Thus, a cost-effective bioremediation strategy is valuable, but this requires the understanding of the interactions among metals, fungi, and biogenic Mn oxides. We have isolated three fungal species (phylogenetic analysis is currently ongoing) from the Soudan Mine wastewater, all of which are capable of oxidizing Mn(II)<sub>aq</sub> to form Mn(III/IV) oxides. We are conducting a series of experiments with fungal cultures grown under high salt conditions with various amount of Mn/Ni/Co. Elemental and spectroscopic analysis will be combined to determine the mechanisms of metal removal from the media. Results from this study will directly inform the development of a fungal bioreactor for removing these metal contaminants from high salt wastewaters. In addition, these co-contaminants are often found together with Mn in other mining and industrial wastewaters, so the information gained from this study will be transferrable to other sites.

# A hydrothermally induced $^{34}\text{S}$ enrichment in pyrite as an alternative explanation of the Late-Devonian sulfur isotope excursion in South China

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## Abstract:

The sulfur isotope record from the Late Devonian, mostly recovered from bulk analysis of pyrite in sedimentary rocks and sediment-hosted ores, is characterized by a global positive excursion, with some  $\delta^{34}\text{S}_{\text{pyrite}}$  values even higher than those of contemporaneous seawater  $\delta^{34}\text{S}_{\text{sulfate}}$ . Several possible explanations have been proposed to explain this  $^{34}\text{S}$  enrichment in pyrite, including low concentrations of dissolved sulfate in seawater system, or intense aerobic re-oxidation of dissolved sulfide within sediments under very low sulfate waters. Implicit to these previous models is the assumption of a biogenic origin for pyrite through microbial sulfate reduction (MSR). In South China, the Late-Devonian sulfur isotope excursion occurs in both the sedimentary rocks of the Lower Wuzhishan Formation and the overlain Xialei manganese deposit of the Middle Wuzhishan Formation. In this study, we carried out detailed texture and *in-situ* sulfur isotope examinations on the  $^{34}\text{S}$ -enriched pyrite grains in the Xialei manganese deposit. Our results show that the studied pyrite display two distinct generations, a “dirty” core and a relatively clean euhedral rim or independent overgrowth. The core, containing abundant rhodochrosite inclusions and showing negative  $\delta^{34}\text{S}_{\text{pyrite}}$  values from -7‰ to -2‰, was likely formed by microbial sulfate reduction (MSR). However, the overgrowth, which contain much less inclusions and show strikingly positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values from +5‰ to +38‰, was more likely formed as a result of secondary hydrothermal alteration, with the sulfur sourced from thermochemical sulfate reduction (TSR) of barite in the underlain Liujiang Formation. The TSR origin of the strongly positive  $\delta^{34}\text{S}_{\text{pyrite}}$  during the Late Devonian suggests that it is necessary to reappraise previously  $\delta^{34}\text{S}_{\text{pyrite}}$  profiles that display heavy values during this period of Earth’s history.

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# Mineral carbonation in smectite-rich kimberlite (diamond) mine tailings

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## Abstract:

Mineral carbonation is one of the promising methods for CO<sub>2</sub> sequestration and is part of a strategy for mining companies to offset their greenhouse gas emissions<sup>1</sup>. In this study, we investigated the reactivity of kimberlite ore and processed kimberlite (tailings) from the Venetia diamond mine (South Africa). Processed kimberlites from this mine consist of a clay-rich mineral assemblage dominated by serpentine and Mg-rich smectites<sup>2</sup>. Due to the crystallographic properties of smectites (i.e., swelling clays), these phases have a high cation exchange capacity and can act as Mg and Ca sources for carbonation reactions. Combining high concentrations of Mg and Ca in solutions generated by leaching mafic–ultramafic mine tailings with conducive biogeochemical conditions can result in mineral carbonation<sup>3</sup>. However, the most suitable treatments to extract cations from smectite-rich tailings, and determining how microbes in mine tailings provide nucleation sites for carbonate formation, are still not well understood.

Here, we report the results of laboratory-based experiments using sodium, ammonium and proton exchange and inoculation of leachates with cyanobacteria to accelerate carbonation of processed kimberlite from Venetia. Our first results show that hydrochloric acid (0.16 M) has the most efficient cation extraction capacity (30% of Ca and 20% of Mg extracted). Moreover, we show that trisodium-citrate can be used to preferentially select for Ca during leaching, with no extraction of Mg. Finally, analyses of the cation exchange capacity of different facies of kimberlites and tailings allow us to estimate that potential greenhouse gas offsets could be highly significant (around 20%) for the Venetia mine.

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# Responses of surface water microbial communities exposed to spills of flowback and produced water

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## Abstract:

Flowback and produced water (FPW) returned to the surface following hydraulic fracturing in shale oil and gas extraction. Surface spills of these fluids may cause detrimental effects to aquatic environments. In this study, we investigated responses of microbiota in surface waters exposed to FPW derived from fracturing of the Duvernay Formation, Canada. We used 16S rRNA gene sequencing to track the changes in microbial community structure and important bioindicators at the various simulated contamination scenarios which freshwater mixed 0% - 50% FPW concentrations over seven days under aerobic conditions. Our results showed three distinct shift pathways for microbial communities were identified at the three FPW concentration ranges tested: (1) from 0% to 0.5% FPW, indigenous surface water genera *Flavobacterium*, *Methylothera*, and *Caulobacter* were predominant, (2) from 2.5% to 5% FPW, microbial communities shifted to potential organics degraders such as *Pseudomonas*, *Rheinheimera*, and *Brevundimonas*, and (3) from 25% to 50% FPW, microbial shifts were not significant. Using these 16S data, these enriched genera were also identified by Random Forests (2% classified error in 1000 runs) as essential bioindicators to predict spill magnitude, information that was used to develop a machine learning-based model. Our study indicates that a few key microorganisms are likely to attenuate organics derived from FPW spills in surface waters, and that significant responses of the surface microbiota to FPW contaminants start at modest FPW to fresh water ratios.

# Carbon capture, utilization and storage potential of hydraulic fracturing flowback and produced water

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## Abstract:

Maintaining net zero carbon emissions to limit global warming is becoming an increasingly important global goal. Carbon sequestration through the production of Mg- and Ca-hydroxide and carbonate minerals, as well as carbonate-bearing hydrotalcite minerals, can be used to store excess atmospheric CO<sub>2</sub> in the structures of these minerals. Flowback and produced water from oil and gas wells is of environmental concern owing to its high concentration of anions, heavy metal cations and organic carbon; however, it can also be used as a source solution for synthesis of Mg- and Ca-hydroxide and carbonate minerals and carbonate-bearing hydrotalcites minerals. Our research investigates treatment of hydraulic fracturing flowback and produced brines for Carbon Capture, Utilization and Storage (CCUS) through the formation of carbonate minerals.

We titrated fracking flowback and produced brines with 1M NaOH to investigate the pH effect on precipitation of Mg- and Ca-hydroxide and carbonate minerals from the brines. Scanning Electron Microscope (SEM) images indicate that brucite [Mg(OH)<sub>2</sub>] and calcite (CaCO<sub>3</sub>) precipitated after titration of the brines to alkaline conditions. We also conducted an anion exchange experiment between a hydrotalcite group mineral, iowaite [Mg<sub>6</sub>Fe<sub>2</sub>Cl<sub>2</sub>(OH)<sub>16</sub>·4H<sub>2</sub>O], and petroleum brines to investigate the behaviour of iowaite in these solutions (i.e., 0.1 M HCl, 0.01 M HCl, 0.1 M NaCl and 1 M NaCl) under different conditions of pH and salinity. These 4-day long experiments were used to assess whether iowaite has the potential to trap CO<sub>2</sub> in brines. The pH of the solutions increased after 1 day of reaction with iowaite, which indicates hydroxyl groups from the iowaite structure were introduced to the solutions. Our ICP-MS results and laboratory observations indicate iowaite completely dissolved into the acidic solution (0.1M HCl) and partially dissolved into solutions with initial pH > 3. Phase identification with powder X-ray diffraction patterns indicates that exchange of interlayer Cl<sup>-</sup> for one or more other anions did occur during reactions, but the mechanisms of exchange need to be further investigated.