A Sulfur Isotopic Study of Neoproterozoic Evaporites in the Shaler Supergroup, Victoria Island, Northwest Territories, Canada

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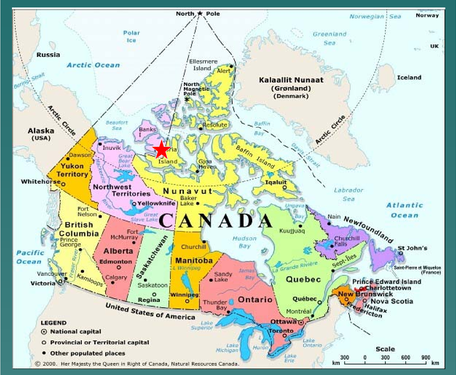
Abstract

Sulfur isotope distributions may yield valuable insight to microbial metabolisms, insofar as they are sensitive to the oxidation state of the Earth's surface. Considering sulfate's long residence time in the oceans, and subsequent isotopic homogenization, sulfate minerals formed in evaporitive environments are ideal reservoirs to examine the oxidative sulfur cycle. The Neoproterozoic (>723 Ma) Shaler Supergroup, which is located on Victoria Island in the Northwest Territories of Canada, is comprised of predominantly carbonates, shales, and notably, thick evaporites deposited on a broad tectonically stable low gradient, shallow marine platform within the intracratonic Amundsen Basin. These evaporites stand out as uniquely preserved windows to a critical transition in the oxidative sulfur cycle. In this study, sulfur isotope measurements (^{32}S, ^{33}S, and ^{34}S) of the bedded evaporites suggest the presence of active communities of sulfur disproportionating bacteria, revealing the presence of oxygen in the depositional environment. Positive excursions in $\delta^{34}S$ values in the uppermost evaporites in the Minto Inlet and Kilian formations coincide with negative excursions in $\delta^{13}C$ values of interbedded carbonates, suggesting a linkage between the carbon and sulfur cycling in the basin. The marked excursions in both isotope systems in the Kilian Formation, in particular, are consistent with earlier predictions that this unit formed in the prelude to Neoproterozoic glaciation, insofar as both isotope trends can be interpreted in terms of increasing oceanic anoxia.

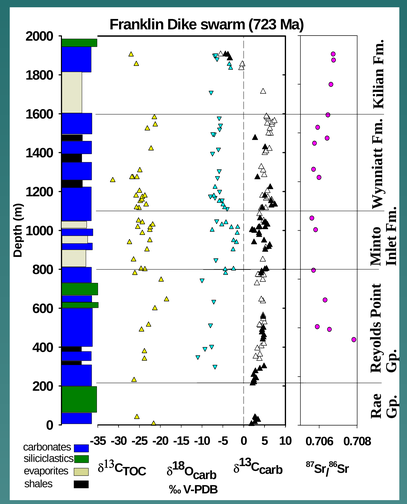
Hypothesis

- To test for the presence and relative importance of sulfur disproportionating reactions in the Neoproterozoic oceans, and their relation to large-scale environmental and climatic change.

Shaler Supergroup bedded evaporites



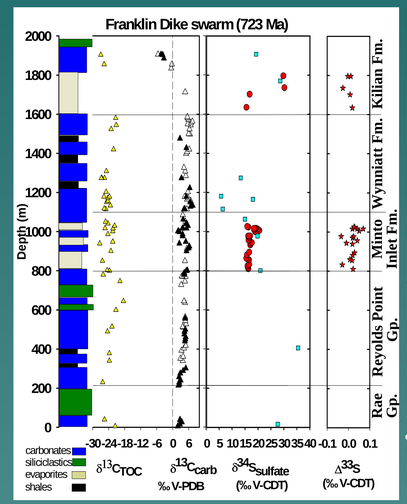
Chemostratigraphy



Previous Results

- Large negative carbon isotopic excursion in Kilian Fm.
  - Similar to pre-glacial trends elsewhere
  - Decrease in proportional burial of organic carbon
- Low $^{87}Sr/^{86}Sr$ values
  - Increase in flux of hydrothermal fluids and reduced elements (eg. iron) into oceans
  - Partial anoxic water column
- No systematic trends in the oxygen isotope data, suggesting that the samples are little altered

Sulfur isotope chemostratigraphy



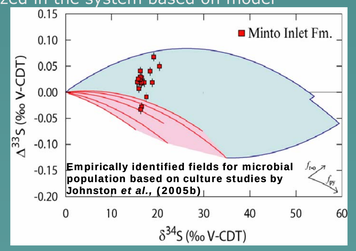
New Results

- Strong positive $\delta^{34}S$ excursions in the Kilian Fm.
  - Coupled with the large $\delta^{34}S$ positive isotopic excursion is the carbon isotopic data at the same stratigraphic level.
  - These two strong lines of isotopic evidence are indicative of a major environmental change, such as a glacial interval.
- CAS data consistent with evaporite data in Minto Inlet and Kilian intervals; variability in other intervals may be related to low sulfate concentrations.
- $\delta^{34}S$ and $\Delta^{33}S$ data suggest that the isotopic variability is due to an increase in the burial of pyrite in the system

Discussion

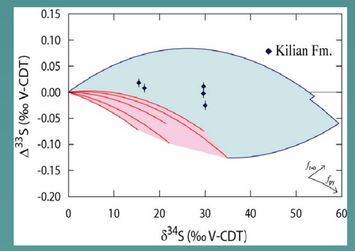
Minto Inlet Fm.

- Most samples plot within the sulfur disproportionation and sulfate reduction field (blue), which indicate that these bacteria were active.
- Values of $\Delta^{33}S$ from the Minto Inlet Formation suggest an increase in the amount of sulfide that is being reoxidized in the system based on model parameters.
- Increased reoxidation ($f_{r\text{-}o}$) is interpreted as an increase in biological activity (namely sulfur disproportionating bacteria).
- There is minimal change in the amount of pyrite buried (f_{py}) suggesting that the degree of basin anoxia did not change.
- This could be due to high seawater sulfate concentrations, or constant Fe fluxes to the basin, which could constrain pyrite formation and deposition.
- These observations favor a biologically-driven sulfur cycle.



Kilian Fm.

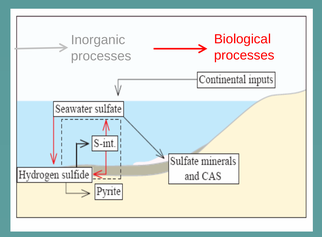
- All of the Kilian Fm. samples plot within the sulfur disproportionation and sulfate reduction field, which indicate that these bacteria were active.
- The trend in $\Delta^{33}S$ indicates an increase in pyrite burial.



- Increases in pyrite burial may suggest the onset of more reducing conditions.
- These observations lead to environmentally-driven changes in the sulfur cycle, which support the pre-glacial interpretation.

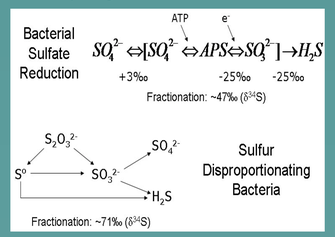
Surface Sulfur Cycle

- A box model of the surface sulfur cycle (from Johnston *et al.*, 2005b). The arrows represent fluxes of material between reservoirs, with biologically mediated reactions shown in red arrows, and inorganic reactions in grey.



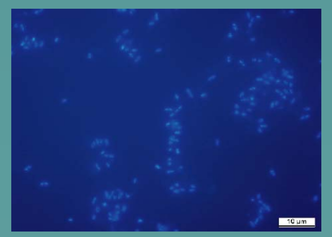
Microbial Metabolisms

- Sulfate reducing bacteria are obligate anaerobes that oxidize simple organic compounds with sulfate, yielding energy (ATP) and hydrogen sulfide
- Microbial sulfur disproportionation requires intermediate sulfur species (elemental sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), or sulfite (SO_3^{2-})) to produce both hydrogen sulfide and sulfate.



Sulfate Reducing Bacteria

Photograph of *D. autotrophicum* (sulfate reducing bacteria) after staining with DAPI (4'-6-Diamidino-2-phenylindole). Provided by D. Johnston



Conclusions

- Sulfur disproportionating bacteria were present in the Neoproterozoic Era
- Coupled carbon and sulfur isotopic data suggest anoxia in the oceans in the prelude to glaciation
- The drastic changes in the sulfur isotopic record could directly reflect deep ocean oxidation related to a step-wise change in pO_2.
- Development of sulfide oxidizers, starting with photosynthetic sulfide oxidizers and progressing to nonphotosynthetic sulfide oxidizers, could be a potential reason for the increase in fractionation in the sedimentary sulfide $\delta^{34}S$ record around 800 Ma.