

# Evolution of the oceanic sulfur cycle in the early Paleoproterozoic

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The 2.4-2.2 Ga Huronian Supergroup contains evidence, in the form of three glacial diamictites, for widespread glaciations. The driving force for these glaciations is widely debated, with several recent studies invoking oxidation of atmospheric CH<sub>4</sub> to CO<sub>2</sub>, linked to a rise in atmospheric O<sub>2</sub> at ~2.4 Ga, as a potential cause of lower surface temperatures [e.g. 1]. It has also been suggested that the presence of three discrete glaciations may relate to high atmospheric CH<sub>4</sub> throughout the interval, with pulsed oxidation events leading to surface cooling [2]. We have analysed 242 marine shale and diamictite samples from throughout the Huronian succession, in an attempt to ascertain whether sulfur isotope compositions can shed light on the nature of Earth surface oxidation at this time.

Our results indicate a significant change in the magnitude of sulfur isotopic fractionations in shales deposited after each glacial diamictite, likely reflecting a step-wise increase in Earth surface oxidation. For almost the entire succession, however, the range of fractionations in each unit is remarkably narrow, only reaching values of up to 20‰ towards the top of the succession. These observations suggest extremely low oceanic sulfate concentrations, with an increase to slightly higher levels occurring some time after the last glacial episode. These results are consistent with only a modest rise in surface oxidation at this time. Fe speciation results additionally suggest the persistence of anoxic, Fe-rich oceanic conditions, at least until prior to the final glacial episode, but with evidence for oxic surface waters throughout the succession.

## References

1. Pavlov, A.A. et al., 2000, *J. Geophys. Res.*, 105, 11981-11990.
2. Bekker, A. et al, 2005, *Precamb. Res.*, 137, 167-206.