The Meso- and early Neoproterozoic deep ocean REE issue

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The sulphidic deep ocean model for the post-1.85 Ga Proterozoic elegantly combines several lines of evidence and reasoning, including: release of sulphate from land into the ocean; the increase in extent of S-isotope fractionation; the lack of significant Mo enrichment in black shales; and the absence of BIF. However, sediment redox proxies for the latest Neoproterozoic have more recently suggested that the deep ocean might have reverted from a sulphidic to a ferruginous state many 10 Ma before the Sturtian BIF deposition. In addition, little direct sedimentological or other geological evidence exists for the proposed sulphidic nature of Proterozoic deep ocean sedimentary rocks.

The present work aims to add to this debate from a rare earth element (REE) perspective. Archaean and Palaeoproterozoic hydrogenous sediments show very pronounced positive Eu anomalies. This well-established aspect of the seawater REE chemistry reflects the fact that the REE from high temperature hydrothermal fluids were not scavenged onto Fe-oxyhydroxides. In other words, hydrothermal vents were a significant source of dissolved REE to the ocean. By contrast, Phanerozoic seawater proxies consistently have either no or a slight negative Eu anomaly. The expectation from these observations for a sulphidic deep ocean, in which hydrothermal Fe combined with S (from sulphate) to form pyrite, is that the positive Eu anomly would persist. Pyrite cannot accommodate Eu in its lattice and the post-1.85 Ga deep ocean could thus be expected to still carry a strong Eu excess.

New data from the ≤711 Ma Rapitan Gp., the 845 Ma Little Dal Gp. and the 1040 Ma Arctic Bay Fm. (all Canada) will be presented. The deeper waters sampled by the Rapitan BIF show neither a negative Ce anomaly nor a positive Eu anomaly and are therefore consistent with a ventilated deep ocean. The carbonate facies of the Little Dal Gp. and the ca. 1040 Ma Arctic Bay Fm. sampled surface waters that were sufficiently oxygenated to generate a negative Ce anomaly. Corresponding black shales and deep water laminites, respectively, were deposited below a chemocline where Ce was re-released from particles. However, none of the deep water samples shows have a significant positive Eu anomaly. This observation is confimed by reactive Fe speciation in the Little Dal black shale, which rarely record sulphidic conditions. While supportive of a reduced deep ocean, these data cannot be explained if all hydrothermal Fe was sequestered as sulphide.

In summary, the redox evolution during the Neoproterozoic was likley very complex and may have involved a ventilated stage as well as ferruginous and sulphidic episodes. The lack of a strong positive Eu anomaly in Mesosproterozoic and early Neoproterozoic deep waters requires a more complex deep ocean redox in general, likley to have been influenced by the relative supply of Fe, S and C.

Application of PTR-MS to an incubation experiment of the marine diatom *Thalassiosira pseudonana*

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Emission of trace gases from the marine diatom *Thalassiosira pseudonana* (CCMP1335) was continuously monitored with a proton transfer reaction-mass spectrometry (PTR-MS) in an axenic batch culture system under a 13:11-h light:dark cycle. Substantial increases in the signals at *m*/*z* 49, 63, and 69, attributable to methanethiol, dimethyl sulfide (DMS), and isoprene, respectively, were observed in response to increases in cell density. Signals at *m*/*z* 69 showed diurnal variations throughout the experiment whereas those at *m*/*z* 49 were more pronounced at the beginning of the incubation. Interestingly, the signals at *m*/*z* 49 and 69 changed immediately following the light-dark and dark-light transitions, suggesting that light plays a crucial role in the production of methanethiol and isoprene. However, in the latter half of the experiment, methanethiol showed negligible diurnal variations regardless of light conditions, suggesting the production of methanethiol from enzymatic cleavage of DMS. The trend in signals at *m*/*z* 63 was similar to that of the abundance of senescent cells plus cell debris rather than vegetative cells. The results suggest that aging or death of phytoplankton cells could also substantially control DMS production in natural waters along with the other microbial processes related to bacteria and zooplankton.

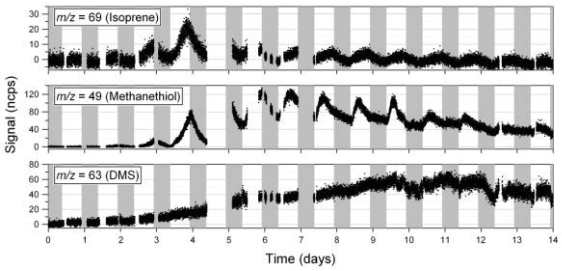

Figure: Time series of PTR-MS signals at *m*/*z* 69, 49, and 63