Transient euxinia in the Archean ocean?

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Ancient sulfidic black shales are often, incorrectly, taken as evidence for euxinic seawater conditions. This is particularly problematic with regard to Archean pyrite-rich sediments whereby, prior to the rise in atmospheric oxygen, the widespread deposition of iron formations coupled with independent evidence for low oceanic sulfate concentrations, implies predominantly ferruginous seawater conditions. There are several ways in which sedimentary enrichments in pyrite may occur, including diagenetic pyrite formation during conditions of very slow sediment deposition, extensive bacterial sulfate reduction close to the sediment-water interface below a ferruginous water column, secondary overprints, and true euxinic water column conditions.

Here, we present Fe-S-C data and microscopic observations for sediments from the Late Archean Transvaal Supergroup, South Africa. The sediments contain several horizons with abundant macroscopic pyrite in the form of nodules, layers, and lenses with early diagenetic compaction fabrics. However, Fe speciation results for pyrite-rich horizons from the lower part of the succession do not support sediment deposition from an euxinic water column. Instead, these pyrite-rich horizons likely represent environments with low sedimentation rates and a transient redox boundary between sulfidic porewater and an overlying ferruginous water column, with porewater sulfide and Fe(II) diffusing towards this boundary. However, particularly further up the succession, microscopic enrichments in fine-grained pyrite are commonly observed overlying horizons containing coarse-grained pyrite. Here, Fe speciation data suggest deposition of the fine-grained pyrite from a water column which was transiently euxinic. In addition, S isotope results suggest increases in seawater sulfate immediately prior to the deposition of massive pyrite, but subsequent rapid consumption of seawater sulfate after initial development of euxinic conditions. We conclude that the occurrence of temporally and spatially restricted euxinia was possible in the Late Archean ocean but, in terms of the search for euxinia, robust redox indicators need to be combined with detailed petrological evidence.

Early Paleoproterozoic fluctuations in biospheric oxygenation

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The Early Paleoproterozoic was a time of immense environmental change, characterised by at least 3 major glaciations and the first development of a persistently oxic atmosphere. However, the details surrounding the history of oxygenation at this time and the causes and consequences of the glaciations, remain vague. We have applied Fe-S-C systematics to a variety of successions deposited from ~2.45 to 2.2 Gyr ago, in order to investigate the detailed nature of oxygenation events and to evaluate potential implications for climate and ocean chemistry.

Sulfide S and organic C isotope values suggest fluctuations in atmospheric oxygen across the glacials, and in particular, the occurrence of oxygenation events in the run-up to each glaciation. This, in turn, implies that oxidation of atmospheric CH_4 to CO_2 may have been the driving force for the glaciations.

Despite these oxygenation events, the aftermath of the lower two glacial cycles are characterised by a continuation of anoxic ferruginous water column conditions. An exception occurs in the immediate aftermath of the second glacial cycle, where a transient period of ocean euxinia is recorded. By contrast, there is no evidence for anoxic oceanic conditions after the final Paleoproterozoic glaciation and prior to the Lomagundi C isotope excursion starting ~2.2 Gyr ago. We suggest that this period experienced a widespread increase in the spatial extent of oxic oceanic conditions, although it is as yet unclear whether this represents the first development of a globally oxic deep ocean. Such conditions would likely have resulted in a dramatic transient decrease in organic C burial and hence CO_2 drawdown, helping to maintain atmospheric CO_2 levels above the threshold required to prevent further glaciations. In addition, oxic conditions would allow build-up of nutrients such as nitrate and Mo, ultimately leading to an increase in productivity that might be responsible for the Lomagundi isotope excursion and the associated return to anoxic oceanic conditions.