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Late Neoproterozoic to early Cambrian marine sulphur cycle, Yangtze Platform (China)

T. GOLDBERG AND H. STRAUSS

Geol.-Paläont. Inst., WWU Münster, Corrensstr. 24, 48149
Münster, Germany (tgold@uni-muenster.de;
hstrauss@uni-muenster.de)

The late Neoproterozoic to early Cambrian witnessed major changes in global climate and marine biogeochemical cycles, manifested in the form of snowball earth, Cambrian radiation and phosphogenesis. In the present work, we attempt to discuss these events with reference to sulphur isotopic perturbations across this time interval.

Sampling for this study was carried out across the Yangtze platform, South China. The diamictite bearing Nantuo Formation is overlain by Doushantuo and Dengying Formations consisting of carbonates, siliciclastics, bedded chert and phosphorite horizons. This is followed by the lower Cambrian Niutitang Formation comprising black shales and phosphorite horizons.

Sulphur isotopic compositions of structurally bound trace sulphate in phosphorite and carbonates, pyrite sulphur and organically bound sulphur (OBS) have been measured. $\delta^{34}S_{SO4}$ for the Doushantuo and Dengying formations ranges from 31 to 37 ‰. However, no systematic trend has been observed. In contrast, high values (41 to 54‰) of $\delta^{34}S_{SO4}$ have been recorded in basal Cambrian phosphorites. Compared to this, $\delta^{34}S_{pyr}$ and $\delta^{34}S_{OBS}$ range from -23 to +36 and -24 to +30 ‰ respectively. Positive correlations exist between $\delta^{34}S_{pyr}$ and $\delta^{34}S_{OBS}$. Pyrite sulphur shows a maximum fractionation of 55‰ relative to contemporary seawater sulfate. This can be attributed to diagenetic processes involving bacterial sulfate reduction and disproportionation. Influx of phosphorous into early Cambrian seawater might have caused a basinal anoxia resulting in extensive sulphate reduction and subsequent enrichment of $\delta^{34}S_{SO4}$ as recorded in the phosphorite beds of lowermost Niutitang Formation.

Assuming the Nantuo glaciation to represent a phase of Neoproterozoic snowball condition, very high $\delta^{34}S_{SO4}$ and $\delta^{34}S_{pyr}$ are expected from cap carbonates and shales immediately overlying the tillites (Gorjan et al.[1], Hurtgen et al.[2 and Zhang et al.[3]). However, $\delta^{34}S_{SO4}$ (+33‰) and $\delta^{34}S_{pyr}$.(-12 to +30‰) recorded in the cap carbonate overlying the Nantuo tillites do not comply with these models.

References

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4.1.46

Marine sulfur cycle dynamics; a new view through oxygen isotopes

A.V. TURCHYN AND D.P. SCHRAG

Department of Earth and Planetary Sciences, Harvard
University, 20 Oxford St., Cambridge, MA 02138
(avan@fas.harvard.edu; schrag@eps.harvard.edu)

Marine sulfate serves as the primary oxidant for much of the organic matter and nearly all the methane produced in ocean sediments, yet the biogeochemical cycle of sulfate is assumed to be relatively stable with a long residence time. However, the oxygen isotopic composition of sulfate is dominated by sulfate reduction and subsequent reoxidation in organic rich sediments on continental shelves and slopes, which in the modern ocean is nearly three times the riverine input of sulfate and ten times the hydrothermal input, yielding a much more dynamic geochemical cycle. In this context, the $\delta^{18}O$ of marine sulfate provides a more dynamic perspective on the biogeochemical sulfate cycle, and in particular changes in the processing of organic matter on continental shelves and slopes.

We present a record of the $\delta^{18}O$ in marine sulfate measured in marine barite over the Cenozoic extracted from several different DSDP and ODP sites. The $\delta^{18}O$ of marine sulfate exhibits large shifts, including a decrease of 5‰ during the Plio-Pleistocene. Using a numerical model, we explore these changes in the context of different types of environmental change. We argue that the sulfur cycle was affected by the periodic glaciations during the Plio-Pleistocene, which exposed continental shelf area, curtailing sulfate reduction and promoting oxidative pyrite weathering which is an isotopically light source of sulfate to the ocean. In addition, our data for the Plio-Pleistocene require that the pathways by which sulfide was reoxidized to change during glacial maxima, perhaps due to increased oxygen availability. Our data also require marine sulfate concentrations to increase over the Plio-Pleistocene, implying that sulfate concentrations were 10-20% lower in the Miocene.