The evolution of the Ediacaran sulfur cycle: A paired sulfate-pyrite $\delta^{34}S$ approach

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An anomalous enrichment in marine sulfate $\delta^{34}S_{SO4}$ is preserved in globally-distributed latest Ediacaran – early Cambrian strata. The proximity of this anomaly to the Ediacaran-Cambrian boundary and the associated evolutionary radiation has invited speculation that the two are causally related. Here we present a high resolution record of paired sulfate ($\delta^{34}S_{SO4}$) and pyrite ($\delta^{34}S_{pyr}$) from sediments of the Ara Group, Sultanate of Oman. An enrichment in $\delta^{34}S_{pyr}$ coincides with the interval of enriched $\delta^{34}S_{SO4}$, beginning at ca. 550 million years ago (Ma) and continuing through at least ca. 540 Ma. These data are evaluated using a new approach based on paired $\delta^{34}S_{SO4}$-$\delta^{34}S_{pyr}$ data that enables us to calculate both $\delta^{34}S_{in}$, the isotopic composition of the sulfur flux entering the ocean, and f_{pyr}, the fraction of sulfur buried as pyrite. It appears that basal Ediacaran $\delta^{34}S_{in}$ was significantly enriched beyond bulk Earth composition and became progressively more enriched through at least the earliest Cambrian. The rise in $\delta^{34}S_{in}$ is correlated with the known record of increasing Ediacaran $^{87}Sr/^{86}Sr$, indicating a tectonic control on riverine sulfate delivery. The ~30permil decline in $\delta^{34}S_{SO4}$ observed in the Paleozoic is interpreted as representing in part the return of $\delta^{34}S_{in}$ toward bulk Earth values. Against this background of increasing Ediacaran $\delta^{34}S_{in}$, the Ara $\delta^{34}S$ enrichment is caused by an additional increase in f_{pyr}, which is most likely driven by enhanced primary production and increased sedimentation rates associated with the assembly of Gondwanaland. The data presented here constrain the changes in biogeochemical cycling that caused the Ara sulfur anomaly and serve as a contextual framework for understanding the E-C boundary, as well as biological and environmental change into the Paleozoic.

Micron-scale resolution of sulfur cycling in a microbial mat

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Microbial mats consist of finely laminated layers of diverse microbial communities. Mat organization is thought to result from strong spatial gradients in light intensity and redox in the uppermost few millimeters Optical examination reveals microbial laminations on scales between 5mm and 5um throughout the thickness of the microbial mat. However, such fine laminations at depth have usually been regarded as a 'relict architecture' inherited from an older mat surface. To further our understanding of microbial processes within this laminated architecture, we have investigated sulfur cycling (as recorded by sulfide production) within a benthic microbial mat.

We present a high-resolution spatial profile of sulfide abundance and isotopic ($\delta^{34}S$) composition on the micron-scale through a microbial mat community analyzed using a Cameca NanoSIMS 50L ion microprobe. We find a fine-scale (0.1-2mm) banding of sulfide throughout the mats as visible to the naked eye. In addition, there are micron-scale (~4μm) laminations observed using the NanoSIMS both in optical CCD and element scanning mode. We have mapped the sulfide $\delta^{34}S$ profile from the mat surface down to a depth of ~1cm at ~100μm resolution with a typical analytical error of ±0.5‰ (1σ). $\delta^{34}S$ varies over ~25‰ as a function of depth through the mat. An apparent oscillatory behavior in $\delta^{34}S$ exists over ~4mm, which approximates the spacing of the coarsest mat laminations. This result suggests that the deeper mat architecture reflects ongoing microbial activity rather than inherited architecture. At any given depth, there can be up to ~5-10‰ variability in $\delta^{34}S$ in immediately adjacent (~10μm apart) locations. High-resolution images (6-20μm squares) of elemental abundance and isotopic composition indicate that the ubiquitous banding in sulfide abundance appears to control the $\delta^{34}S$ variability, with the offset between high- and low-sulfide regions up to ~10‰. Control experiments in standard solutions did not reveal any banding or the same scale of isotopic variability as observed in the microbial mat. We therefore believe that the banding and isotopic variability observed in the microbial mat are not an analytical artefact, but rather reflect very-fine-scale lamination in microbial activity preserved at depth within the mat, as is supported by microscopic observations. The environmental conditions that maintain such rigid laminations at depth (~1 cm), far from the sharp redox gradients of the mat surface, remain poorly constrained.; however, our results suggest that the full scope of sulfur cycling with microbial mats remains far from being completely understood or fully appreciated.