Interpreting the ancient sulfur-isotopic signal from a metabolic pathway perspective.

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Sulfur-coupled metabolisms are some of the most important microbially-mediated processes. The rock record, while incomplete, provides the best framework for understanding the redox history of the Earth's surface, with sulfur isotopes (including the mass independent fractionation of sulfur, or MIF-S signal) providing convincing evidence for the timing of the transition from an oxygen depleted/reducing atmosphere to one with free oxygen. Here we work to merge the most up to date and comprehensive geochemical datasets from the literature with our current understanding of prokaryotic sulfur transformations in order to create testable hypotheses for the onset of microbial mediation of those transformations.

Based on observed trends in available geochemical data and using geochemical proxies, we divide earth history prior to 1.5 Ga into five periods (0 – 4), and putatively link each to development of microbially mediated sulfur transformations. (0) 3.9 to 3.7 Ga - Paucity of SO_4^{-2} minerals ($SO_{4(ppt)}$), lack of sulfide $\delta^{34}S$ fractionation ($\delta^{34}S\text{-}S^{-2}_{fract}$), small MIF-S signal preserved, exceedingly low SO_4^{-2} concentration ($[SO_4^{-2}]$), small subarial volcanism input of SO_2 to atmosphere ($SO_{2(volc)}$); SO_3^{-2} reduction and H_2S oxidation develop. (1) 3.6 to 3.2 Ga – More $SO_{4(ppt)}$ observed, increased $\delta^{34}S\text{-}S^{-2}_{fract}$, larger MIF-S signal preserved, increasing $SO_{2(volc)}$; development of sulfur disproportionation, anoxygenic photosynthesis linked to H_2S oxidation. (2) 3.2 to 2.7 Ga – Paucity of $SO_{4(ppt)}$, collapse of MIF-S signal, reduced $\delta^{34}S\text{-}S^{-2}_{fract}$, $[SO_4^{-2}]$ increases above the threshold for sulfate reducing bacteria, oxygen 'whiffs', increasing $SO_{2(volc)}$; SO_4^{-2}reduction develops. (3) 2.7 to 2.5 Ga - $SO_{4(ppt)}$, increase of $\delta^{34}S\text{-}S^{-2}_{fract}$, large MIF-S signal preserved, increasing $SO_{2(volc)}$, oxygenation of surface ocean; sulfolipid formation develops. (4) 2.5 to 1.5 Ga – Collapse of MIF-S signal, oxygenation of the atmosphere, increased $\delta^{34}S\text{-}S^{-2}_{fract}$, dramatic increase in $[SO_4^{-2}]$; modern sulfur cycle established.

Modelling of sulfur reservoirs coupled to sulfur isotopic signals in the rock record and incorporating the genomic record of the extant biogeochemical sulfur cycle will allow testing of these hypotheses, and result in a more complete understanding of the sulfur cycle through evolutionary time.