

Challenges of modeling the marine sulfur cycle in deep time

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Much of our understanding of the oxygenation history of the Precambrian atmosphere and oceans has derived from analysis of S-isotopes in the marine system. Traditional modelling of S-isotopes has emphasized a single-reservoir model, in which the composition of the marine sulfate reservoir depends only on the magnitude and isotopic composition of input fluxes and output fluxes. Later use of a time-dependent variation of this single box model highlighted the effect of reservoir size on rapidity of isotopic variation, wherein small reservoir size facilitates more rapid changes in the isotopic composition of the marine sulfate reservoir.

Utilization of this time-dependent approach has been powerful, yet has specific limitations when it comes to interpreting the evolution of the marine sulfur cycle. Specifically, an inherent assumption in this model is that bacterially reduced HS^- is either extracted by reaction with available iron (as in an anoxic water column) or immediately reoxidized, through a range of intermediate sulfur phases, to sulfate (as in a well-ventilated water column).

Unfortunately, through much of the Proterozoic, and into the early Paleozoic, independent Fe speciation data suggests the presence of persistent marine euxinia, which indicates that Fe^{2+} was at least locally insufficient to strip the water column of bacterially produced HS^- . Such a scenario demands modelling the marine sulfur cycle as a dual-reservoir system, wherein marine SO_4^{2-} and HS^- are treated as distinct, reactive reservoirs, with their own input and output fluxes that affect both the behavior of the individual reservoirs as well as the degree of linkage between them. In this case, the isotopic composition of marine sulfate is affected directly by the magnitude and isotopic composition of traditional input and output fluxes that act over long time scales, as well as a suite of transitory input and output fluxes, including bacterial sulfate reduction and a combination of chemical and biological sulfide oxidation. The composition of marine sulfate will be influenced directly by the magnitude and isotopic composition of pyrite burial only when the transitory fluxes between the two reservoirs are in equilibrium.

Here we define, for the Proterozoic and early Paleozoic, a suite of critical environmental parameters involved in construction of S-isotope datasets, and highlight the predictable consequences of dual-reservoir modelling.