Emergence of large seawater sulfate reservoir without MIF-S at the early stage of the GOE

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Recycling of mass-independent fractionation of sulfur isotopes (MIF-S) from the upper continental crust could have masked the expression of the rise in atmospheric oxygen in the sedimentary rock record. Models suggest that seawater sulfate retained MIF-S for >100 Myr as sulfides from the Archean crust were oxidized [1]. This hypothesis requires that the Late Archean upper continental crust carried a positive $\Delta^{33}S$ value. To test these ideas, we measured multiple S isotopes of some of the oldest sulfate evaporites in the rock record (~2.4 Ga Duitschland Formation (DF), South Africa; 2.32 Ga Gordon Lake Formation (GLF) in Canada).

These units overlie the youngest (~2.45 Ga) sediments that contain detrital pyrites deposited in shallow-marine settings and were, therefore, formed shortly after Earth's surface redox conditions changes. Sulfate evaporites from both units have $\Delta^{33}S$ values from 0.02 to 0.08‰ (DF; n=30) and from 0.01 to 0.11‰ (GLF; n=16), inconsistent with a significant signal of recycled MIF-S in seawater sulfate during the early stage of the GOE. The same units have positive $\delta^{34}S$ values from 13.6 to 19.4‰ (DF; n=30) and 13.1 to 16.1‰ (GLF; n-16), which indicate a growing seawater sulfate reservoir responding to the isotopic consequences of microbial sulfate reduction and to a rise in atmospheric oxygen, marked by disappearance of detrital pyrite from the sedimentary record and glacial events linked to oxidation of atmospheric methane. Our data thus argues against recycling of the upper crustal MIF-S as a process to mask surface oxygenation in the S isotope record. More importantly, our study suggests that overwhelmingly positive $\Delta^{33}S$ values marking the Archean sedimentary rock record are not representative of the upper continental crust composition and that pyrite nodules, barren massive sulfide deposits, and other untapped reservoirs are underestimated in the mass balance of S in the Archean upper continental crust.

1 – Reinhard et al., 2013, Nature 497, 100-103.

Authors are listed in order of how strongly they believe the ideas presented here.