The MIF-Sulfur record suggests the oxygenated atmosphere and sulfate-rich oceans through geologic time

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The presence of mass-independently-fractionated sulfur isotopes (MIF-S) in Archean-aged sedimentary rocks, and the scarcity of MIF-S in younger rocks, have been accepted by most geoscientists as unequivocal evidence for an anoxic Archean atmosphere and the G.O.E. at ~2.5 Ga. This theory has been based on an (unspoken) assumption that the MIF-S was created mostly near the Earth surface by the UV photochemical reactions of volcanic SO_2. UV with wave lengths 190-350 nm, which are responsible for the photochemical reactions of SO_2, would be largely blocked by the ozone shield if the P_{O2} had been greater than 10^{-5} PAL in the troposphere[1]. Here I suggest that the MIF-S signatures in Archean-aged sedimentary rocks were generated by: (1) the UV photochemical reactions in the stratosphere (> ~15 km above sea level) over an oxygenated troposphere of the SO_2 emitted by Plinian-type explosive volcanic eruptions, and/or (2) high temperature (> ~150°C) heterogenous reactions between SO_4^{2-} and highly-reactive organic matter (solid or liquid) in marine basins where abiotic, cell-free organic matter was abundantly produced by submarine hydrothermal processes. Both processes (atmospheric and oceanic) for MIF-S creation would have been important on early Earth when the Earth was hotter and magmatism was more intensive and extensive on land and in oceans than today.

The above suggestions are based on the following discoveries: (i) the MIF-S in sulfates associated with volcanic ashes from Plinian-type explosive volcanic eruptions (e.g., Mt. Pinatubo and Mt. Agung)[2]; (ii) the abundance of ash layers in MIF-S-bearing Archean shales[3]; (iii) the abundance of MIF-S-free Archean-aged sedimentary rocks[4]; (iv) the experimental evidence for the creation of MIF-S by UV-induced photochemical reactions of SO_2 in O_2-rich atmospheres[5]; (v) the evidence in 2.7 Ga-old Fe-micro meteorites of an O_2-rich upper atmosphere[6]; (vi) the MIF-S in sulfate associated with aerosols that were generated from the burning of pyrite-rich coals[7]; (vii) the experimental evidence for the creation of MIF-S during thermochemical sulfate reduction by amino acids[8]; (viii) the sub-nanometer-sized particles of hydrothermally-synthesized organic matter in 3.46 Ga-old jasper beds[9]; and (ix) the various lines of evidence for an O_2-rich atmosphere and O_2- and sulfate-rich oceans during the Archean[10], including, but not restricted to the following: (a) the abundance ratios of redox-sensitive elements in paleosols, sedimentary rocks, and deep-submarine volcanic rocks; (b) the abundance of pyrite and barite in sedimentary rocks and submarine hydrothermal deposits; (c) the $d^{34}S$ and $D^{33}S$ records of submarine hydrothermal deposits and sedimentary rocks; (d) the scarcity of detrital kerogen in Precambrian-aged sedimentary rocks; (e) the $d^{13}C$ records of carbonates and kerogen; and (f) the abundance of magnetite-series (i.e., oxidized-type) granitoids.

References: 1: Farquhar et al. (2000), Kasting et al. (1989). 2: Savarino et al. (2003), Baroni et al. (2007). 3: Unpublished data. 4: Ohmoto et al. (2009). 5: Whitehill et al. (2015). 6: Tomkins et al. (2016). 7: Romeo & Thiemaens (2003), Han et al. (2017). 7: Watanabe et al. (2008), Oduro et al. (2011). 9: Graham et al. (2018). 10: Ohmoto et al. (in prep.).

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