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Mass Independent Signals from Sulfur and Oxygen in Constraining Atmospheric Oxygen since the Great Oxidation Event

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There persists a three-order of magnitude uncertainty for the estimated partial pressure of atmospheric oxygen(pO_2) derived from various geochemical proxies during the mid-Proterozoic (1.8 Ga ~ 0.8 Ga) [1]. To reconcile this difference requires deciphering geochemical signals of direct and distinct atmospheric origin. The Sulfur Mass-independent fractionation (S-MIF) signature in sedimentary sulfur provides definitive estimates on the maximum pO_2 [2] before the Great Oxidation Event (GOE, 2.45-2.32 Ga), but cannot be used to infer pO_2 after the GOE under the current conceptual framework. Similarly, Oxygen-MIF in sedimentary sulfate carries distinct atmospheric signature [3-5], however its utility [6-7] in inferring atmospheric oxygen has been recently questioned by a more accurate photochemical framework [8]. Recent data compilation of Oxygen-MIF in Phanerozoic marine sulfate [9] also seems to suggest that a direct atmospheric signal from oxygen was missing.

We revitalize ancient sulfate as a direct proxy of atmospheric oxygen since the GOE through tracking the life cycles of atmospheric sulfur and oxygen. By developing a TIPO model (three isotopes photochemical model for oxygen) coupled with an existing S-MIF model, we are able to infer atmospheric oxygen levels since the GOE by examining both the oxygen-MIF and sulfur-MIF signal in geologic records. Considering uncertainties involving diagenesis, microbial recycling, SO_2 outgassing and pCO_2 levels, this new framework shows the potency of deciphering mid-Proterozoic pO_2 and demonstrated that the Phanerozoic sulfur and sulfate record also reflect a direct signal from atmospheric oxygen.

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