Explaining the Structure of the Archean Mass-Independent Sulfur Isotope Record

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Sulfur isotopes in ancient sediments provide a record of past environmental conditions. The long–time-scale variability and apparent asymmetry in the magnitude of minor sulfur isotope fractionation in Archean sediments remain unexplained. Using an integrated biogeochemical model of the Archean sulfur cycle, we find that the preservation of mass-independent sulfur is influenced by a variety of extra-atmospheric mechanisms, including biological activity and continental crust formation. Preservation of atmospherically produced mass-independent sulfur implies limited metabolic sulfur cycling before ~2500 million years ago; the asymmetry in the record indicates that bacterial sulfate reduction was geochemically unimportant at this time. Our results suggest that the large-scale structure of the record reflects variability in the oxidation state of volcanic sulfur volatiles.

Most natural processes fractionate sulfur in proportion to the mass difference between the isotopes (J). Ultraviolet (UV) photolysis of atmospheric SO₂, however, produces a mass-independent fractionation (MIF) that is delivered to the surface only if atmospheric O₂ levels are very low (2–7). The presence of MIF in sedimentary sulfides and sulfates older than 2450 million years (My) and its absence from later sediments has led to the accepted view that atmospheric O₂ levels crossed a threshold value near the Archean-Proterozoic boundary (2–6). Beyond simply recording MIF, the Archean sulfur isotope record appears to carry a discernable temporal structure: moderate (~4 per mil [‰]) early Archean Δ³³S (~2) anomalies, followed by a mid-Archean minimum (~2‰) and a late Archean explosion in the magnitude of MIF (~12‰ in Δ³³S). Previous studies attribute this variability to changes in the composition and oxidation state of the atmosphere and the associated evolution of photochemical pathways (7–9). In addition, an asymmetry in the record, with strongly positive but only weakly negative isotopic anomalies, remains without a quantitative explanation.

Here we explore the effect of a variety of extra-atmospheric processes on the characteristics and preservation of MIF. We present an integrated model of the full surface-sulfur cycle, accounting for the production and translation of atmospherically derived MIF through a marine reservoir and its preservation in the geologic record (10). We use recent measurements and theoretical calculations of \( \Delta^{33}S \) for \( k = 2, 3, 4, 6 \) UV absorption cross sections to constrain atmospheric MIF production (10–12). By solving mass-balance equations for the steady-state reservoir sizes and isotopic compositions of four different oxidation states of sulfur (\( S^{6+} \) (sulfate), \( S^{4+} \) (sulfate, SO₄), \( S^2 \) (elemental sulfur), and \( S^2 \) (sulfide, \( H_2S \))), we track MIF from production to lithification.

Rates of volcanic supply, photolytic destruction, gas-phase reactions, and net deposition to the surface govern the atmospheric lifetime of SO₂. Any process that destroys atmospheric SO₂ at the expense of photolysis reduces the production, by mass, of MIF [for example, atmospheric oxidation (Fig. 1A)], but as long as photolysis rates are non-negligible relative to the other atmospheric SO₂ sinks, MIF is produced (though not necessarily preserved). In addition to nonphotolytic atmospheric sinks, which attenuate MIF by decreasing production, homogenization reduces MIF by remixing anomalous compositions back toward the original SO₂ value. Whereas atmospheric oxidation to sulfate has been discussed in this context (6), microbial processes, which can perform a similar function, have not been rigorously investigated (Fig. 1B). A quantitative model of MIF from SO₂ photolysis, cycling between the sulfur reservoirs (e.g., microbial activity) or transformation to one oxidation state [e.g., quantitative reduction to sulfide] must be minor, as not to erase the anomaly. An immediate implication is that low atmospheric O₂ is necessary but insufficient for preservation of MIF in the geologic record.

Our model results illustrate the sensitivity of MIF to a few key properties of the ocean-atmosphere system, as well as its relative insensitivity to several other properties. Atmospheric deposition of SO₂ leads to its speciation in seawater \( [SO₂] \) (aq) \( \rightarrow HSO₃⁻ + H²⁺ \rightarrow SO₄^{2⁻} + H²⁺ \), where subsequent oxidation by \( Fe^{3⁺} \) (13–15) leaves other aqueous oxidation pathways less important (for instance, \( Fe^{2⁺} \)-catalyzed oxidation by aqueous \( O₂ \) or by atmospherically produced \( H_2O₂ \)). This leaves vanishingly little marine \( S^{2⁺} \) (10⁻³ to 10⁻⁴ M) and only modest sulfate concentrations (10⁻⁶ M). Given these oxidation rates, the absolute magnitude of MIF is only moderately sensitive to the adopted rate of \( S^{4⁺} \) disproportionation (Fig. 1D) (10), although the symmetry of
the sulfate–elemental sulfur MIF is rate-sensitive. This is because the isotopic composition of SO₂ propagates to both sulfate and elemental sulfur when disproportionation is rapid, but only to sulfate when oxidation dominates. The negative–positive asymmetry of the MIF record suggests that oxidation, not disproportionation, was the dominant aqueous S⁴⁺ sink. Hydrated formaldehyde complexes S⁺, preventing its oxidation and disproportionation; however, this only affects MIF preservation at concentrations higher than those likely in an Archean ocean (Fig. 1E) (16).

The magnitude of MIF in pyrite, but not in sulfates, is very sensitive to the SO₂:H₂S ratio in volcanic volatiles (Fig. 1C). This is because the elemental sulfur that ends up in pyrite originates from both atmospheric SO₂ and H₂S, but H₂S photoreactions do not generate MIF. When the outgassing rate of SO₂ increases relative to that of H₂S, more of the elemental sulfur budget comes from SO₂ photolysis and, as a result, anomalously fractionated. Sulfate, on the other hand, is produced almost entirely from oxidation and photolysis of SO₂, and so its isotopic composition is insensitive to changes in the relative abundance of SO₂ and H₂S. Changes in the total sulfur (SO₂ + H₂S) outgassing rate with constant SO₂:H₂S produce no change in MIF magnitudes (Fig. 1F), but this may be due to the simplified nature of our atmospheric model; S₈ production in more detailed atmospheric models is sensitive to the total sulfur outgassing rate (7, 17). We note, however, that more rapid S₈ production does not necessarily translate into stronger MIF if the S₈ is derived from H₂S.

MIF depends critically on the partial pressure of CO₂ (pCO₂); increased pCO₂ results in stronger scattering and UV absorption, decreasing SO₂ photolysis rates (Fig. 2A). In more detailed atmospheric models, the relative abundances of atmospheric CO₂ and CH₄ also influence SO₂ oxidation rates and the efficacy of MIF export.

**Fig. 1.** The sensitivity of MIF in pyrite and sulfate, for pCO₂ of 0.01 and 0.1 atm, plotted as a function of (A) the fraction of outgassed SO₂ that is oxidized in the atmosphere, (B) microbial cycling, represented as a multiple of the sum of nonbiological sinks, (C) SO₂:H₂S in volcanic sinks, (D) the disproportionation rate constant, (E) the hydrated formaldehyde concentration, and (F) the total sulfur (SO₂ + H₂S) outgassing rate. Metabolisms included in (C) are sulfate reduction, elemental sulfur oxidation, disproportionation and reduction, and sulfide oxidation. Estimates of modern biological sulfur cycling and volcanic outgassing are also shown.

**Fig. 2.** The sensitivity of (A) the SO₂ column photolysis rate and (B) MIF in pyrite (black) and in sulfates (gray) to pCO₂. Dashed lines represent the response of MIF to changes in atmospheric opacity due to increased molecular absorption and scattering by CO₂ with pCO₂ held constant at 0.01 atm in the ocean. Dotted lines represent the response to changes in the ocean (pH, Fe⁺⁺ concentration, etc.), with pCO₂ held constant at 0.01 atm in the atmosphere. Solid lines show the combined effect.
(6, 7, 17). Our model highlights that, with a more acidic ocean (at high $P_{\text{CO}_2}$), the degree of pyrite precipitation decreases, and $H_2S$ partitions more strongly into the atmosphere. As the importance of $H_2S$ photolysis relative to pyrite precipitation increases, more $S^0$ is $H_2S$-derived. This does not affect the $\Delta^{34}S$ of sulfate ($\Delta^{34}S_{\text{sulfite}}$), but it decreases the $\Delta^{34}S$ of pyrite ($\Delta^{34}S_{\text{pyr}}$, Fig. 2B, dotted lines) and influencing the symmetry of the $\Delta^{34}S$ signal.

Four properties emerge as important for the preserved magnitude and symmetry of Archean MIF: (i) atmospheric $SO_2$ oxidation rates, (ii) redox transformations (including microbial cycling rates), (iii) $SO_2$-$H_2S$ in volcanic gases, and (iv) $P_{\text{CO}_2}$. The very presence of MIF in the rock record points to low oxidant availability, suggesting that atmospheric oxidation was not the dominant $SO_2$ sink (6, 7). With constraints from the geologic record on the remaining three properties, we explore their potential to explain the structure in the Archean MIF record using two quantities: $\Delta^{33}S_{\text{pyr}}$ and $R_{\text{asym}}$, a measure of the asymmetry ($\Delta^{33}S_{\text{pyr}}/\Delta^{33}S_{\text{sulfite}}$). A successful explanation of the record must account for early Archean $\Delta^{33}S_{\text{pyr}} \approx 4\%_{\text{o}}$ and $R_{\text{asym}} \approx 2$, mid-Archean $\Delta^{33}S_{\text{pyr}} \approx 2\%_{\text{o}}$ and $R_{\text{asym}} \approx 1$, and latest Archean $\Delta^{33}S_{\text{pyr}} \approx 11\%_{\text{o}}$ and $R_{\text{asym}} > 5$.

When imposed on a purely abiological early Archean sulfur cycle, metabolic cycling between the different sulfur pools can potentially explain portions of the Archean MIF record (Fig. 1B). Both microbial $S^0$ disproportionation and dissimilatory sulfate reduction may have existed since ~3500 million years ago (Ma) (18, 19). Adopting for the moment a scenario in which biological sulfur cycling is not important before ~3500 Ma, an increase in the role of microorganisms equivalent to ~10% modern cycling rates could drive a change in $\Delta^{33}S_{\text{pyr}}$ and $R_{\text{asym}}$ similar to that observed from the early to mid-Archean (Fig. 3B, i → ii). Difficulty arises, however, when microorganisms persist into the late Archean. Given that sulfate reduction delivers $\Delta^{34}S < 0$ to sulfide, a greater degree of symmetry (and even reversed asymmetry, $R_{\text{asym}} < 1$) would be expected for the late Archean; this is in marked contrast to the observed $R_{\text{asym}}$ of 5 to 6 and suggests that dissimilatory sulfate reduction only rises to geochemical importance between 2400 and 2500 Ma, when high MIF magnitudes and large asymmetry are no longer observed. A late Archean or early Paleoproterozoic onset of sulfate reduction is consistent with a reanalysis of traditional sulfur isotope ($\delta^{34}S$) records (10) and suggests an explanation for the persistence of nonzero and relatively symmetric MIF for 10 to 100 My postdating the major loss of MIF at ~2500 Ma in some locations (5), but not in others (20).

In the absence of biological sulfur cycling, we find that, with constant volcanic $SO_2$-$H_2S$, climatically reasonable changes in $P_{\text{CO}_2}$ (21–23) cannot alone produce the observed MIF history (Fig. 3A). If we adopt instead an evolving value for Archean $P_{\text{CO}_2}$, calculated to offset changes in solar luminosity and to maintain liquid water [together with ~10 parts per million by volume atmospheric methane maintained by about twice modern sea-floor serpentinization rates (21–24)], changes in volcanic $SO_2$-$H_2S$ well within observed values (25, 26) easily account for the histories of both $\Delta^{33}S_{\text{pyr}}$ and $R_{\text{asym}}$ (Fig. 3A, i → ii → iii). This result does not preclude further changes in $P_{\text{CO}_2}$ affecting the MIF signal [for example, through the effect of methanogens on $P_{\text{CO}_2}$ and $P_{\text{CH}_4}$ (21, 23)], though the asymmetry in the latest Archean almost by necessity indicates a substantial increase in volcanic $SO_2$-$H_2S$. Such an increase may be related to a major shift in the style of large igneous province eruption from submarine to subaerial in the late Archean (2700 to 2500 Ma), also suggested to have been the cause for the rise in atmospheric $O_2$ and the loss of MIF (25). Consistent with the sulfur isotope record, our results suggest that this loss would be preceded by a MIF spike due to the elevated volcanic $SO_2$-$H_2S$. A small clustering of plume events during the early Archean [3500
Contrasting Décollement and Prism Properties over the Sumatra 2004–2005 Earthquake Rupture Boundary


Styles of subduction zone deformation and earthquake rupture dynamics are strongly linked, jointly influencing hazard potential. Seismic reflection profiles across the trench west of Sumatra, Indonesia, show differences across the boundary between the major 2004 and 2005 plate interface earthquakes, which exhibited contrasting earthquake rupture and tsunami generation. In the southern part of the 2004 rupture, we interpret a negative-polarity sedimentary reflector ~500 meters above the subducting oceanic basement as the seaward extension of the plate interface. This predécollement reflector corresponds to unusual prism structure, morphology, and seismogenic behavior that are absent along the 2005 rupture zone. Although margins like the 2004 rupture zone are globally rare, our results suggest that sediment properties influence earthquake rupture, tsunami hazard, and prism development at subducting plate boundaries.

The 2004 moment magnitude ($M_w$) = 9.2 Sumatra earthquake initiated close to Simeulue Island and generated a regionally destructive tsunami (1, 2). The 2005 $M_w$ = 8.7 earthquake, immediately to the south across an apparently persistent rupture boundary, caused only a local tsunami (3). Both earthquakes initiated at similar depths (~30 to 40 km), but the 2004 rupture offshore North Sumatra propagated farther seaward than the 2005 rupture (1–3), with the latter more similar to other large subduction-zone earthquakes, including the 1960 Chile and 1964 Alaska earthquakes (e.g., (4–6)). The different rupture patterns of the two Sumatra earthquakes are likely controlled by rheology (sediment properties), stress state, and fault properties and will generate different tsunami by affecting both magnitude and water depth of the associated sea-floor deformation. Sediment properties, both before and after incorporation into the subduction zone, may also affect the morphology and deformation of the margin (e.g., (4, 7)), which in turn are linked to the dynamics of the earthquake rupture (8). On some other subduction margins [e.g., Nankai (9) and Barbados (10)], accretionary prism faults