The organic component of the earliest sulfur cycling

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The chemistry of the Early Earth is widely inferred from the elemental and isotopic compositions of sulfidic sedimentary rocks[1,2], which are presumed to have formed globally through the reduction of seawater sulfate or locally from hydrothermally supplied sulfide. Here we argue that, in the sulfate-poor ferruginous oceans of the Archean eon[3], organic sulfur must have played an important and previously unrecognized role in the formation of sulfides. In the anoxic ocean, mineralization of organic sulfur generated hydrogen sulfide, which provided a pathway to pyrite that bypassed the microbial reduction of sulfate, while organic-sourced sulfite could fuel microbial S reduction in the absence of ambient sulfate. Reaction transport modeling suggests that, for sulfate concentrations up to tens of micromolar, organic sulfur would have supported 20 to 100% of sedimentary pyrite precipitation and up to 75% of microbial sulfur reduction. By offering an alternative explanation for the low range of δ^{34}S in Archean sulfides, these effects alter the presently accepted picture of the Early Earth sulfur cycle, with a significant proportion of oceanic sulfur throttled through living cells. They also raise a possibility that sulfate scarcity in the anoxic

mid-Archean oceans delayed the evolution of dissimilatory reduction of sulfate until the initial ocean oxygenation around 2.7 Ga.

Since the beginning of Life, sulfur has cycled between the geosphere and biosphere as an essential component of all living matter. Organic S-bearing molecules, such as amino acids cysteine and methionine, have been ubiquitous throughout the planet's history[4,5] and even have been detected on Mars[6]. In modern oceans, however, the petagram inventory[7] of dissolved organic sulfur and the estimated 0.2-0.4 Pg of particulate organic sulfur[7] are dwarfed by the 10^9 Pg of inorganic sulfate, which at 28 mM is the second most abundant anion in seawater. At these concentrations, the geologically important cycling of sulfur through sulfate reduction, precipitation of pyrite, and reoxidation of sulfides is carried out overwhelmingly by inorganic sulfur. Abundant sulfate, however, was rare through most of the Earth's history. Proterozoic oceans were likely characterized by sub-mM to low mM concentrations[8], and low-sulfate conditions returned episodically throughout the Phanerozoic[9]. In the Archean, before the beginning of ocean oxygenation 2.7-2.5 billion years ago[10,11], marine sulfate was scarce in coastal and surface pelagic ocean, at no more than tens of μM[3,11], and likely absent in ferruginous deep waters. The cycling of sulfur under these conditions was very different from the one in the modern ocean, and freshwater systems, particularly stratified lakes, are commonly used as better analogues[3]. Recent work[12] has demonstrated that in low-sulfate lakes (<100 µM), mineralization of organic sulfur (OS) supplies a significant portion of the substrates for microbial sulfate reduction[13], and a significant fraction of sulfide is traceable to an organic source[14,15]. In the well-oxygenated sediments of oligotrophic Lake Superior[12], for example, mineralization of the settled particulate organic sulfur causes accumulation of sulfate in the upper oxidized layer, often in excess of the water column concentrations, and supports over 80% of sulfate reduction in the deeper anoxic sediment. Paradoxically, the organic component has not been considered in reconstructions of the Early Earth sulfur cycling. The histories of atmospheric oxygen and oceanic sulfate are widely inferred from the records of sulfur isotopes preserved in pyrites[1,11], but non-hydrothermal pyrite formation was considered only from seawater sulfate[3,16] or elemental sulfur[17]. Here we argue that organic sulfur must have been a significant component of the early biogeochemical cycling, and that its effects may alter the presently accepted interpretations of the geochemical and isotopic proxies.

Sulfur makes up about 1% of dry weight of aquatic organisms[18]. It occurs at lower oxidation states in proteins such as amino acids cysteine and methionine, in coenzymes (e.g., coenzyme A, biotin, thiamine), as iron-sulfur clusters in metalloproteins, and in bridging ligands (e.g., in cytochrome c oxidase)[5]. Higher oxidation state compounds, such as sulfonates R-SO_3-H, sulfones R-SO_2-R, and organo-sulfates, can be found in lipids (e.g., Sulfoquinovosyl diacylglycerols) and are components of cell walls and photosynthetic membranes. Molar S:C ratios in modern plankton[18] typically range between 0.003 and 0.01, with freshwater values[19] being more varied than in marine environments because of a wider range of geochemical conditions. Archean S:C ratios likely spanned a similar range, or were even higher if sulfolipids could be used in place of phospholipids[20,21] to alleviate P limitation[22]. The Archean organic sulfur pool was likely dominated by reduced compounds[2], which are thermodynamically easier to assimilate under anoxic conditions[23]. Assimilation of sulfate requires energy even at the stage of cellular uptake by sulfate-binding proteins[23], and sulfate (+6) is rare in prokaryotic cells[23], whereas key molecules contain sulfites (+4) or sulfonates (+4)[24,25]. Reduced sulfur appears in evolutionary key molecules such as methionine, cysteine, cystine, coenzymes M and acetyl CoA, aromatic sulfur and disulfides, and in primitive metabolic processes such as S oxidation in anoxygenic phototrophs. Hydrothermally supplied hydrogen sulfide (+2) in the presence of CO_2 could form thiols, critical coenzymes, CS_2 and dimethyldisulfide[4,26,27].

Mineralization of organic sulfur compounds would recycle a significant portion of this organic pool as inorganic sulfur, making it available for processes that in the modern oceans are supported by seawater sulfate. Hydrolysis and mineralization of oxidized organic sulfur ($R\text{-}SO_3\text{-}H$) would generate sulfite (SO_3^{2-}), which in Archean oceans would add to the pool generated by the dissolution of volcanic SO_2 (Fig. 1). While in the modern environments sulfite is efficiently converted to sulfate by oxidation or disproportionation[28,29], in an anoxic ancient water column such conversion could take substantially longer, especially if disproportionation[30,31] was limited by low concentrations or low capacity for microbial catalysis. Mineralization of oxidized organic fractions would supply sulfite throughout the ocean depths that were reached by the inefficient Archean carbon pump[32], but also, importantly, would generate it in sediments from any exported organic matter. Sulfite is readily utilized by sulfur reducing bacteria for dissimilatory reduction, and thermodynamically provides more energy for cell metabolism than sulfate[33]. Its liberation in a sulfate-depleted ocean would make it available as a substrate for sulfur reducing metabolisms. In a world that lacked a strong oxidant like molecular oxygen, the redox cycling of sulfur could potentially rely on sulfite as the dominant oxidized species. This possibility is supported by genetic evidence that points to the evolution of sulfite reducing metabolisms as early as 3.7 Ga, while genes for sulfate reduction appear later[2,34]. Some Archaea are known to reduce sulfite while not being able to reduce sulfate, and some auxotroph bacteria are known to utilize sulfonate OS directly[7,35].

Mineralization of the reduced organic S pool (R-SH) would provide an even more important input of inorganic sulfur. Such mineralization generates hydrogen sulfide, which under ferruginous Archean conditions would react with dissolved iron (Fe^{2+}) to form iron sulfides, bypassing the traditionally assumed pathway of sulfate reduction.

The geochemical fluxes and transformation rates sustained by the mineralization of organic sulfur must have been quantitatively significant. The inventory and cycling rates of organic matter are poorly constrained for the Archean, but assuming, as an order of magnitude estimate[32,36], that respiration in the anoxic Archean water column was 5% of the value found in the modern ocean below the photic zone[37], mineralization rates were ~100 Tmol C yr^{-1}, regenerating 0.3-1 Tmol S yr^{-1} of inorganic sulfur. This is higher than the estimated flux of sulfur from hydrothermal settings[38] (0.2 - 0.5 Tmol S yr^{-1}) and comparable to the estimated Archean pyrite burial flux[39,40] (~0.1-1 Tmol S yr^{-1}). Through reduction of oxidized OS and direct release of hydrogen sulfide from reduced OS, followed by a nearly quantitative conversion to pyrite under ferruginous conditions, this re-mineralization could generate a significant portion of the pyrite that was eventually preserved in Archean sediments. Like sulfate reduction, pyrite precipitation likely occurred primarily in organic rich coastal regions, including microbial mats[41], where the contributions from organic sulfur could have been high. For a concentration of total inorganic sulfur in the ocean water on the order of 10 μM[3], mineralization at the rate of 0.3-1 Tmol S yr^{-1} implies that the entire oceanic pool of sulfur could cycle through the organic pool in under 10,000 years. In surface sediments (e.g., at ~0.1% organic carbon content and the S:C ratio of

0.003), the abundance of organic sulfur (~100 μmol S per liter of sediment, assuming typical porosity and bulk sediment density) would compete with the low μM availability[3] of inorganic S from the overlying water column, and could be the only source of reactive sulfur in deeper sediment.

Generation of sulfite and dissolved sulfide from organic S within the sediments and water column radically changes the picture of the Archean sulfur cycling. Traditional view and previous numerical models[3,11,16] assumed that sulfate was transported from the surface ocean into the deep waters or sediments where it underwent microbial reduction to sulfide, which in the presence of ferrous iron precipitated to eventually form pyrite. In contrast, the oxidized inorganic sulfur compounds produced from the oxidized fraction of OS could support S reduction even when sulfate was absent from ambient water. Likewise, the hydrogen sulfide produced from the reduced OS could generate pyrite even in the absence of sulfate reduction.

To illustrate the potential role of organic sulfur, we used a vertically resolved diffusion-reaction model, which we adapted from Ref. (12) and applied to Archean conditions[11] (*see* Supplement). For the sake of concreteness, we performed simulations in sediments. While the transport mechanisms in water column may be more varied and three-dimensional, similar arguments should apply, at least qualitatively, to a water column where sulfate and particulate OS reach the anoxic ferruginous deep waters from the surface mixed layer[3]. For a more straightforward comparison with previous models that did not consider sulfite, and to extend the results to potentially oxygenated conditions of the Neoarchean, the model uses sulfate as the oxidized form of inorganic sulfur; this does not change the generality of the argument. Mineralization of reduced OS was assumed in the model to generate hydrogen sulfide. The ratio of oxidized to reduced OS within organic matter was set to 40%:60% as a reference value and varied in a sensitivity analysis (*see* Supplement). Similarly to previous work[12], the model calculated the fraction of the sedimentary sulfate reduction that was supported by OS mineralization, and the fraction of pyrite that was formed through the mineralization of reduced OS (Fig. 2). These fractions were calculated from the respective ratios of the depth-integrated rates for OS mineralization, sulfate reduction, and pyrite precipitation (*see* Supplement).

Simulations reveal that, for <50 µM of sulfate in Archean seawater[3,11], between 20 and 100% of all pyrite precipitated in sediment would originate from organic sulfur (Fig. 2). For <10 μM, a significant fraction of pyrite may form from OS even at low organic S:C ratios and for organic carbon concentrations as low as 0.1% (Fig. S3). Mineralization of oxidized OS supports between 5 and 75% of the total sedimentary S reduction. The OS contributions remain significant for sulfate concentrations up to >100 μM (Figs. 2, S1), at which point the seawater sulfate becomes the dominant source. If these sulfate concentrations were not achieved in the oceans until the later stages of the Great Oxidation Event[11], the organic component of the sulfur cycle must have remained important throughout the Archean eon. At low sulfate concentrations, the presence of oxygen enhances the organic sulfur contribution to sulfate reduction (Fig. 2). Though oceans throughout the Archean Eon are thought to have been predominantly anoxic, Neoarchean sediments in shallow coastal regions could have been exposed to concentrations of up to tens of μM[10,11]. Being a more potent electron acceptor, oxygen decreases the sediment demand for seawater sulfate, making the in-sediment generation of oxidized S proportionately more important. The (percentage) contribution of OS to sulfate reduction increases also with the sediment organic matter content, as organic matter supports OS mineralization rates, even though it also stimulates sulfate reduction and the drawdown of sulfate from overlying water (Fig. S3). In the Neoarchean, environments with higher oxygen concentrations and higher organic carbon fluxes could be found in oxygenated oases in shallow coastal regions[10,42] where oxygenic photosynthesis fueled higher primary productivity, sedimentation rates were high, and most pyrite is thought to have originated.

The contribution of organic component to pyrite formation profoundly changes the accepted interpretations of the Archean isotopic signals. Microbial sulfate reduction depletes the sulfide in ^{34}S, generating isotopic differences between the seawater sulfate and sediment pyrite $\Delta^{34}S_{FeS} = \delta^{34}S_{SO4} - \delta^{34}S_{FeS.}$ The limited range of $\Delta^{34}S$ <10‰ throughout the Archean is viewed as a consequence of low sulfate, which restricted sulfate reduction[3,16]. The $\Delta^{34}S_{FeS}$ range is further limited by the Rayleigh distillation: the sulfate diffusing downward into the sulfate reduction zone becomes isotopically heavier with depth and the $\delta^{34}S$ of the produced sulfide trends towards the $\delta^{34}S$ of the original sulfate. The possibility of pyrite formation from the OS-derived sulfur means that sulfidic rocks do not necessarily record the evidence of these processes but instead reflect a more complex mixture of isotopic influences. Sulfite produced at some depth within the sediment column may be reduced at the same depth, without undergoing Rayleigh distillation[31]. As isotopic fractionations associated with the reduction of sulfite are small[31,43] (13±7‰) compared with those for sulfate (>30‰), they are consistent with observations of small $\Delta^{34}S$. The hydrogen sulfide produced from the more abundant reduced OS compounds would generate solid sulfides, bypassing microbial reduction. Rather than carrying an isotopic signature of redox processes, these sulfides could instead carry the isotopic signal of hydrolysis. The magnitudes of the fractionations during hydrolysis of organic sulfur are unknown, but thermodynamic considerations[44] limit them to less than 15‰, consistent with small observed $\Delta^{34}S$. Small isotopic fractionations are similarly consistent with the evidence in modern sediments where care was taken to analyze the hydrolyzable fraction of organic sulfur[45,46]. In particular, depth variations in the isotopic composition of hydrolyzable organic sulfur pool seem to indicate a preferential loss of isotopically light organic sulfur during the early stages of diagenesis[45].

The ambiguity of isotopic interpretations calls for a re-evaluation of the ancient sulfur cycling. Mineralization of S-bearing organic matter provided sulfur-reducing organisms not only with an electron donor in the form of organic carbon, but also with an electron acceptor, while mineralization of the reduced OS could supply hydrogen sulfide directly. As $\Delta^{34}S_{FeS}$ records are equally consistent with sulfite reduction and formation of pyrite from reduced organic sulfur, neither of which requires sulfate, the isotopic evidence for an early (3.47 Ga) onset of sulfate reduction[47,48], suggested based on ~10‰ isotopic fractionations[49], may need to be re-evaluated. Sulfur isotopes are the only reliable tracer for the sulfate reduction metabolism, as preserved cellular structures are not readily identifiable for sulfate-reducers, while molecular fossils (biomarkers) do not seem to survive over geological times[47]. In a low-oxygen world where sulfate was produced in limited quantities by atmospheric photochemical reactions or disproportionation of reactive sulfur intermediates[29], dissimilatory sulfate reduction could have become globally competitive for the first time when sulfate concentrations increased in the Neoarchean, following the initial marine oxygenation around 2.7 Ga[11]. The observed expansion in $\Delta^{34}S_{FeS}$ beginning around that time[8,11] thus may reflect not only a more vigorous redox cycling of sulfur but also increased isotopic fractionations[50] associated with the expanded range of redox states. Similarly, while anoxygenic phototrophs nearly universally can oxidize sulfide to elemental sulfur[23], evidence for the evolution of groups capable of completing the oxidation to sulfate seems to appear first around 2.7 Ga[51]. As pyrite could be formed in non-hydrothermal settings from relatively abundant reduced organic sulfur (Fig. 2), its presence may not necessarily indicate active sulfate reduction, allowing a possibility of only trace amounts of sulfate (sulfite) in oceanic seawater. The OS pathway under such conditions could generate more pyrite than the reduction of seawater sulfate, and the geographic distribution of such pyrite could be broader than for the pyrite formed from hydrothermal H_2S. The concentrations of dissolved inorganic sulfur in ferruginous oceans thus could have been low enough to make sulfur a co-limiting nutrient, consistent with the approximately similar S and P contents in living cells.

Resolving the organic sulfur effects in the Archean rock record requires better understanding of the OS pathways and isotopic fractionations than is currently available. Some insight, however, may be obtained from the expected isotopic signatures (Fig. 3). Assuming that Archean microorganisms satisfied their sulfur requirements by assimilating sulfur with the isotopic composition similar to that of seawater sulfate, the $\Delta^{33}S/\delta^{34}S$ values in the resultant pyrites should fall closer to the SO_4-S^0 mixing line (Fig. 3) than those produced through microbial sulfate reduction, which generates stronger $\delta^{34}S$ fractionations. Earlier, organic-rich, or sulfate-poor deposits therefore would be expected to have higher pyritic $\delta^{34}S$ values than those that formed at higher sulfate concentrations, such as in the Neoarchean. While the small amount of Mesoarchean data does not yet allow firm conclusions, this trend seems to be indeed present (Fig. 3). Further insights are likely to be obtained through a combination of laboratory experiments and observations in modern low sulfate environments. In particular, mineral grain-scale signatures[17,41] of pyrite-forming OS mineralization may be potentially resolved when the OS pathways are better characterized for the conditions of low ambient sulfate, and the associated isotopic fractionations, including those during OS hydrolysis, are determined.

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Data availability statement: The datasets generated during the current study are available from the corresponding author on reasonable request.

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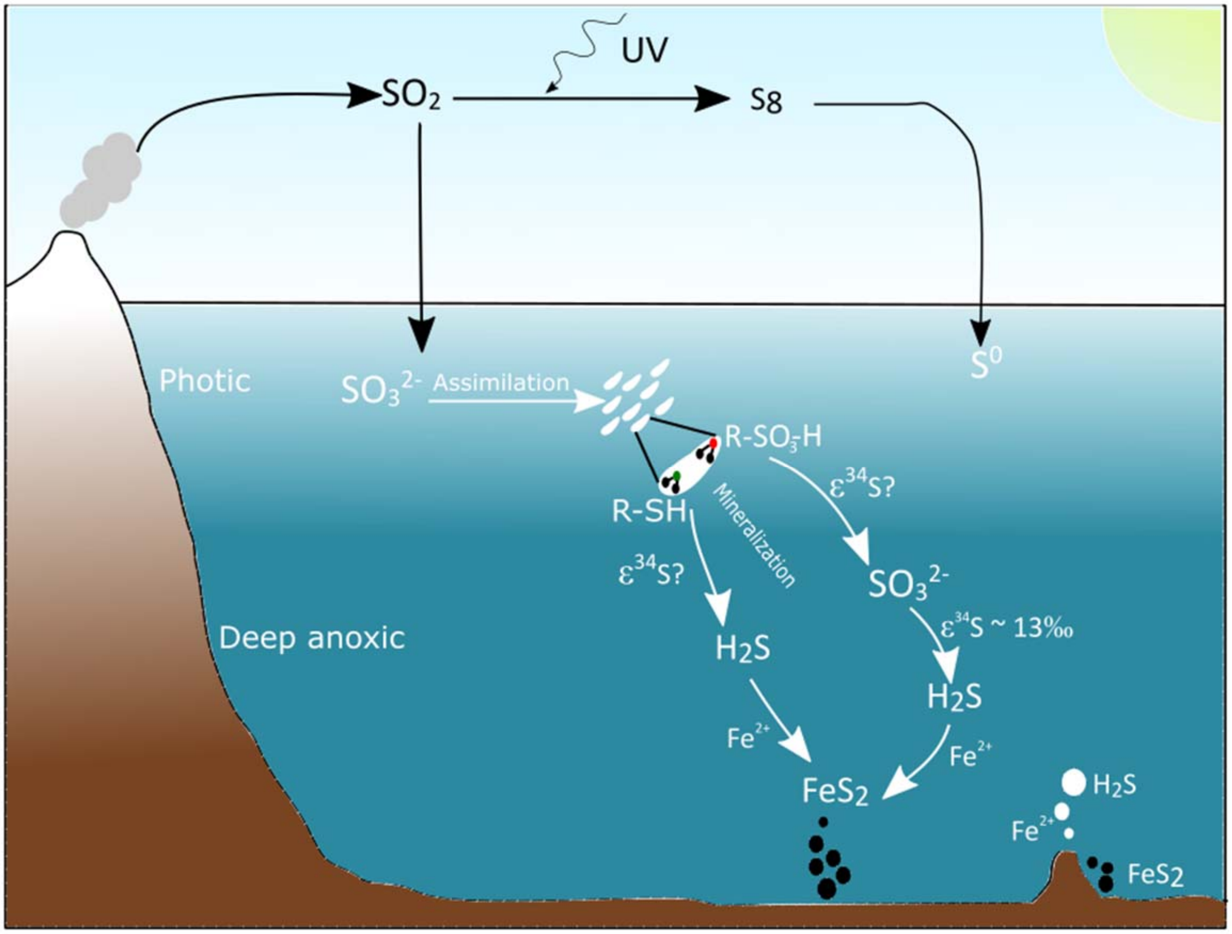

Fig. 1. Mediation of sulfur cycling by organic sulfur (OS) in anoxic ferruginous Archean oceans. Mineralization of OS serves as a source of both oxidized (up to +4) and reduced sulfur in the ferruginous deep water column and sediments. In the Neoarchean, the availability of free oxygen would increase the role of sulfate (+6).

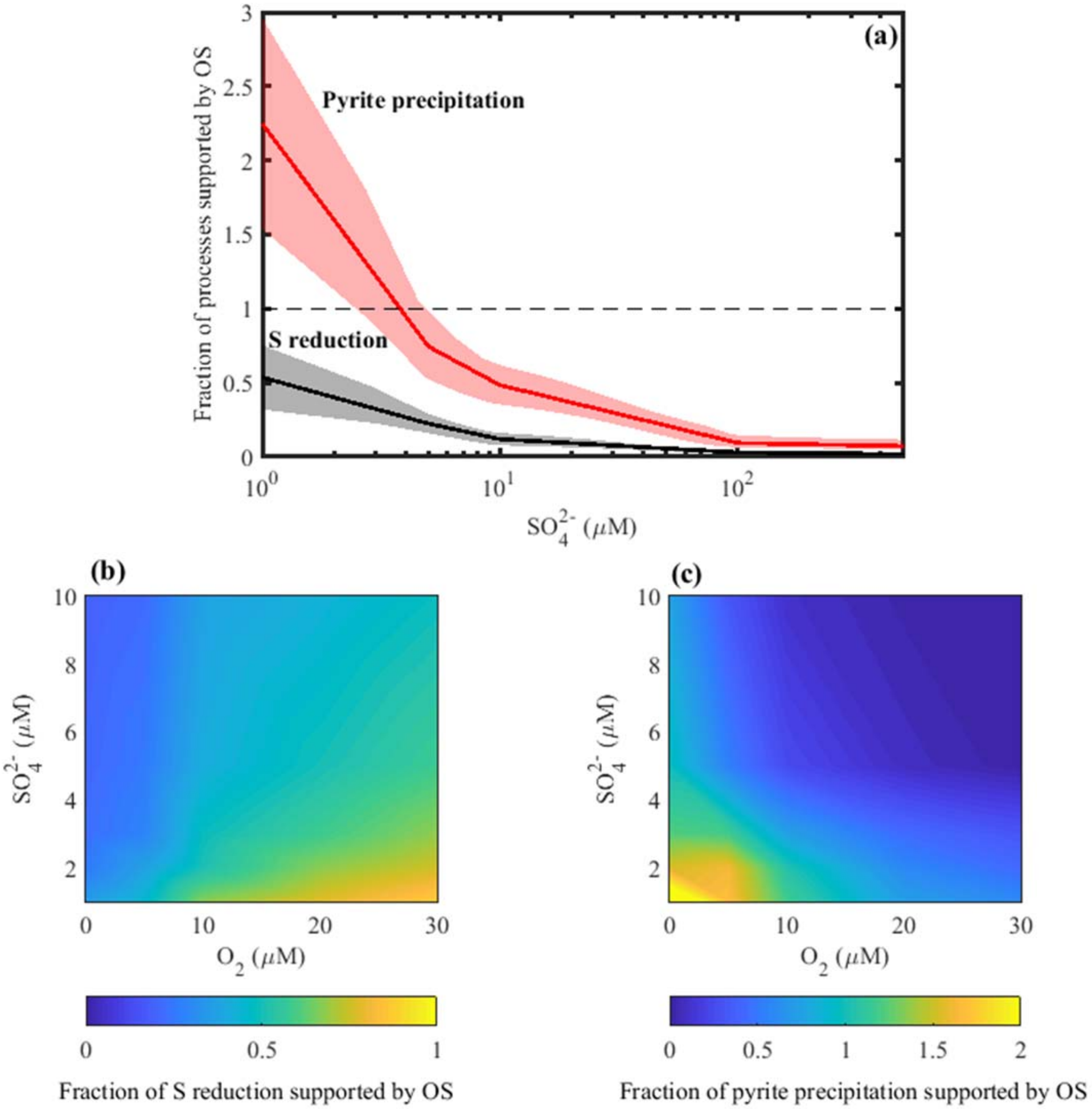

Fig. 2. Support of sulfate (or sulfite) reduction and iron sulfide formation by organic matter-sourced sulfur (OS), simulated with a sediment reaction-transport model. **(a)** As a function of sulfate (sulfite) concentration under anoxic conditions. Shaded bands reflect the corresponding ±1σ ranges obtained in the sensitivity analysis (see Supplement). **(b,c)** The same, in presence of oxygen. The fraction of supported S reduction was calculated as the ratio of the depth integrated rates of oxidized OS mineralization and sediment S reduction. The latter was corrected for the fraction of sulfate reduction supported by elemental S disproportionation and sulfide reoxidation. The fraction of supported pyrite precipitation was calculated as the ratio of the depth integrated rates of reduced OS mineralization and Fe sulfide precipitation. The ratio was corrected for elemental S disproportionation and the fraction of produced hydrogen sulfide that becomes unavailable for precipitation because of aerobic oxidation (see Supplement). Values greater than 1 correspond to a situation where excess hydrogen sulfide diffuses out of the sediment. Sediment was assumed to contain 0.3% of organic carbon by dry weight, with the molar S:C ratio of 0.005.

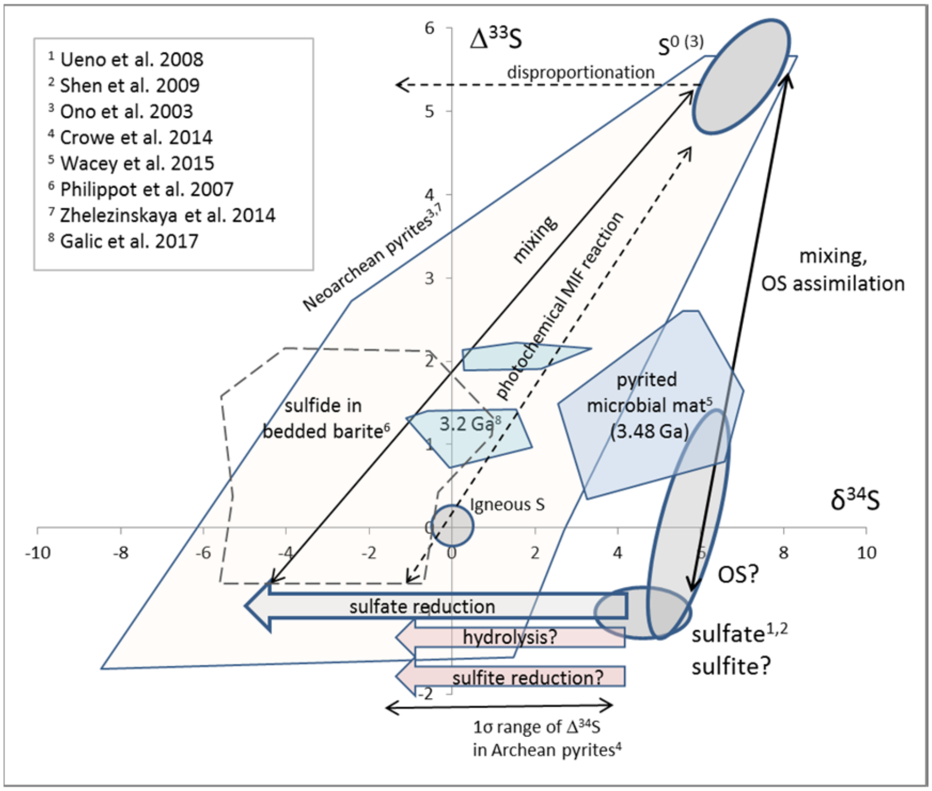

Fig. 3. Potential effects of organic sulfur reactions on the isotopic signatures in Archean pyrites. Assuming minor fractionations during hydrolysis, the isotopic composition of the pyrite produced from OS-sourced H_2S would be expected to deviate less from the seawater sulfate $\delta^{34}S$ values (small $\Delta^{34}S$) than for the pyrite produced by sulfate reduction, and would plot closer to the mixing line between the seawater sulfate and photochemically produced S^0. Increasing sulfate reduction, as hypothesized for the Neoarchean, would shift the isotopic signatures to the left. The microbial reduction of sulfite and disproportionation reactions would produce smaller shifts. The $\Delta^{33}S$/ $\delta^{34}S$ values of the OS pool could potentially vary along the sulfate-S^0 mixing line, depending on whether Archean organisms assimilated sulfur from seawater sulfate (sulfite) or from disproportionated atmospheric elemental sulfur. Shapes outline likely values for endmember pools (gray) and literature values for pyrite[3,17,41,52–56].