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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

21   **mid-Archean oceans delayed the evolution of dissimilatory reduction of sulfate until the**

22   **initial ocean oxygenation around 2.7 Ga.**

23   Since the beginning of Life, sulfur has cycled between the geosphere and biosphere as

24   an essential component of all living matter. Organic S-bearing molecules, such as amino acids

25   cysteine and methionine, have been ubiquitous throughout the planet's history[4,5] and even

26   have been detected on Mars[6]. In modern oceans, however, the petagram inventory[7] of

27   dissolved organic sulfur and the estimated 0.2-0.4 Pg of particulate organic sulfur[7] are dwarfed

28   by the 10^9 Pg of inorganic sulfate, which at 28 mM is the second most abundant anion in

29   seawater. At these concentrations, the geologically important cycling of sulfur through sulfate

30   reduction, precipitation of pyrite, and reoxidation of sulfides is carried out overwhelmingly by

31   inorganic sulfur. Abundant sulfate, however, was rare through most of the Earth's history.

32   Proterozoic oceans were likely characterized by sub-mM to low mM concentrations[8], and low-

33   sulfate conditions returned episodically throughout the Phanerozoic[9]. In the Archean, before

34   the beginning of ocean oxygenation 2.7-2.5 billion years ago[10,11], marine sulfate was scarce in

35   coastal and surface pelagic ocean, at no more than tens of μM[3,11], and likely absent in

36   ferruginous deep waters. The cycling of sulfur under these conditions was very different from

37   the one in the modern ocean, and freshwater systems, particularly stratified lakes, are

38   commonly used as better analogues[3]. Recent work[12] has demonstrated that in low-sulfate lakes

39   (<100 μM), mineralization of organic sulfur (OS) supplies a significant portion of the substrates

40   for microbial sulfate reduction[13], and a significant fraction of sulfide is traceable to an organic

41   source[14,15]. In the well-oxygenated sediments of oligotrophic Lake Superior[12], for example,

42   mineralization of the settled particulate organic sulfur causes accumulation of sulfate in the

43 upper oxidized layer, often in excess of the water column concentrations, and supports over

44 80% of sulfate reduction in the deeper anoxic sediment. Paradoxically, the organic component

45 has not been considered in reconstructions of the Early Earth sulfur cycling. The histories of

46 atmospheric oxygen and oceanic sulfate are widely inferred from the records of sulfur isotopes

47 preserved in pyrites[1,11], but non-hydrothermal pyrite formation was considered only from

48 seawater sulfate[3,16] or elemental sulfur[17]. Here we argue that organic sulfur must have been a

49 significant component of the early biogeochemical cycling, and that its effects may alter the

50 presently accepted interpretations of the geochemical and isotopic proxies.

51   Sulfur makes up about 1% of dry weight of aquatic organisms[18]. It occurs at lower

52 oxidation states in proteins such as amino acids cysteine and methionine, in coenzymes (e.g.,

53 coenzyme A, biotin, thiamine), as iron-sulfur clusters in metalloproteins, and in bridging ligands

54 (e.g., in cytochrome c oxidase)[5]. Higher oxidation state compounds, such as sulfonates $R-SO_3-H$,

55 sulfones $R-SO_2-R$, and organo-sulfates, can be found in lipids (e.g., Sulfoquinovosyl

56 diacylglycerols) and are components of cell walls and photosynthetic membranes. Molar S:C

57 ratios in modern plankton[18] typically range between 0.003 and 0.01, with freshwater values[19]

58 being more varied than in marine environments because of a wider range of geochemical

59 conditions. Archean S:C ratios likely spanned a similar range, or were even higher if sulfolipids

60 could be used in place of phospholipids[20,21] to alleviate P limitation[22]. The Archean organic

61 sulfur pool was likely dominated by reduced compounds[2], which are thermodynamically easier

62 to assimilate under anoxic conditions[23]. Assimilation of sulfate requires energy even at the

63 stage of cellular uptake by sulfate-binding proteins[23], and sulfate (+6) is rare in prokaryotic

64 cells[23], whereas key molecules contain sulfites (+4) or sulfonates (+4)[24,25]. Reduced sulfur

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65   appears in evolutionary key molecules such as methionine, cysteine, cystine, coenzymes M and

66   acetyl CoA, aromatic sulfur and disulfides, and in primitive metabolic processes such as S

67   oxidation in anoxygenic phototrophs. Hydrothermally supplied hydrogen sulfide (+2) in the

68   presence of CO_2 could form thiols, critical coenzymes, CS_2 and dimethyldisulfide[4,26,27].

69   Mineralization of organic sulfur compounds would recycle a significant portion of this

70   organic pool as inorganic sulfur, making it available for processes that in the modern oceans are

71   supported by seawater sulfate. Hydrolysis and mineralization of oxidized organic sulfur (R-SO_3-

72   H) would generate sulfite (SO_3^{2-}), which in Archean oceans would add to the pool generated by

73   the dissolution of volcanic SO_2 (Fig. 1). While in the modern environments sulfite is efficiently

74   converted to sulfate by oxidation or disproportionation[28,29], in an anoxic ancient water column

75   such conversion could take substantially longer, especially if disproportionation[30,31] was limited

76   by low concentrations or low capacity for microbial catalysis. Mineralization of oxidized organic

77   fractions would supply sulfite throughout the ocean depths that were reached by the inefficient

78   Archean carbon pump[32], but also, importantly, would generate it in sediments from any

79   exported organic matter. Sulfite is readily utilized by sulfur reducing bacteria for dissimilatory

80   reduction, and thermodynamically provides more energy for cell metabolism than sulfate[33]. Its

81   liberation in a sulfate-depleted ocean would make it available as a substrate for sulfur reducing

82   metabolisms. In a world that lacked a strong oxidant like molecular oxygen, the redox cycling of

83   sulfur could potentially rely on sulfite as the dominant oxidized species. This possibility is

84   supported by genetic evidence that points to the evolution of sulfite reducing metabolisms as

85   early as 3.7 Ga, while genes for sulfate reduction appear later[2,34]. Some Archaea are known to

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86   reduce sulfite while not being able to reduce sulfate, and some auxotroph bacteria are known

87   to utilize sulfonate OS directly[7,35].

88   Mineralization of the reduced organic S pool (R-SH) would provide an even more

89   important input of inorganic sulfur. Such mineralization generates hydrogen sulfide, which

90   under ferruginous Archean conditions would react with dissolved iron (Fe^{2+}) to form iron

91   sulfides, bypassing the traditionally assumed pathway of sulfate reduction.

92   The geochemical fluxes and transformation rates sustained by the mineralization of

93   organic sulfur must have been quantitatively significant. The inventory and cycling rates of

94   organic matter are poorly constrained for the Archean, but assuming, as an order of magnitude

95   estimate[32,36], that respiration in the anoxic Archean water column was 5% of the value found in

96   the modern ocean below the photic zone[37], mineralization rates were ~100 Tmol C yr^{-1},

97   regenerating 0.3-1 Tmol S yr^{-1} of inorganic sulfur. This is higher than the estimated flux of sulfur

98   from hydrothermal settings[38] (0.2 - 0.5 Tmol S yr^{-1}) and comparable to the estimated Archean

99   pyrite burial flux[39,40] (~0.1-1 Tmol S yr^{-1}). Through reduction of oxidized OS and direct release of

100   hydrogen sulfide from reduced OS, followed by a nearly quantitative conversion to pyrite under

101   ferruginous conditions, this re-mineralization could generate a significant portion of the pyrite

102   that was eventually preserved in Archean sediments. Like sulfate reduction, pyrite precipitation

103   likely occurred primarily in organic rich coastal regions, including microbial mats[41], where the

104   contributions from organic sulfur could have been high. For a concentration of total inorganic

105   sulfur in the ocean water on the order of 10 μM^3, mineralization at the rate of 0.3-1 Tmol S yr^{-1}

106   implies that the entire oceanic pool of sulfur could cycle through the organic pool in under

107   10,000 years. In surface sediments (e.g., at ~0.1% organic carbon content and the S:C ratio of

108 0.003), the abundance of organic sulfur (~100 μmol S per liter of sediment, assuming typical

109 porosity and bulk sediment density) would compete with the low μM availability[3] of inorganic S

110 from the overlying water column, and could be the only source of reactive sulfur in deeper

111 sediment.

112 Generation of sulfite and dissolved sulfide from organic S within the sediments and

113 water column radically changes the picture of the Archean sulfur cycling. Traditional view and

114 previous numerical models[3,11,16] assumed that sulfate was transported from the surface ocean

115 into the deep waters or sediments where it underwent microbial reduction to sulfide, which in

116 the presence of ferrous iron precipitated to eventually form pyrite. In contrast, the oxidized

117 inorganic sulfur compounds produced from the oxidized fraction of OS could support S

118 reduction even when sulfate was absent from ambient water. Likewise, the hydrogen sulfide

119 produced from the reduced OS could generate pyrite even in the absence of sulfate reduction.

120 To illustrate the potential role of organic sulfur, we used a vertically resolved diffusion-

121 reaction model, which we adapted from Ref. (12) and applied to Archean conditions[11] (*see*

122 Supplement). For the sake of concreteness, we performed simulations in sediments. While the

123 transport mechanisms in water column may be more varied and three-dimensional, similar

124 arguments should apply, at least qualitatively, to a water column where sulfate and particulate

125 OS reach the anoxic ferruginous deep waters from the surface mixed layer[3]. For a more

126 straightforward comparison with previous models that did not consider sulfite, and to extend

127 the results to potentially oxygenated conditions of the Neoarchean, the model uses sulfate as

128 the oxidized form of inorganic sulfur; this does not change the generality of the argument.

129 Mineralization of reduced OS was assumed in the model to generate hydrogen sulfide. The

130   ratio of oxidized to reduced OS within organic matter was set to 40%:60% as a reference value

131   and varied in a sensitivity analysis (*see* Supplement). Similarly to previous work[12], the model

132   calculated the fraction of the sedimentary sulfate reduction that was supported by OS

133   mineralization, and the fraction of pyrite that was formed through the mineralization of

134   reduced OS (Fig. 2). These fractions were calculated from the respective ratios of the depth-

135   integrated rates for OS mineralization, sulfate reduction, and pyrite precipitation (*see*

136   Supplement).

137   Simulations reveal that, for <50 µM of sulfate in Archean seawater[3,11], between 20 and

138   100% of all pyrite precipitated in sediment would originate from organic sulfur (Fig. 2). For <10

139   μM, a significant fraction of pyrite may form from OS even at low organic S:C ratios and for

140   organic carbon concentrations as low as 0.1% (Fig. S3). Mineralization of oxidized OS supports

141   between 5 and 75% of the total sedimentary S reduction. The OS contributions remain

142   significant for sulfate concentrations up to >100 μM (Figs. 2, S1), at which point the seawater

143   sulfate becomes the dominant source. If these sulfate concentrations were not achieved in the

144   oceans until the later stages of the Great Oxidation Event[11], the organic component of the

145   sulfur cycle must have remained important throughout the Archean eon. At low sulfate

146   concentrations, the presence of oxygen enhances the organic sulfur contribution to sulfate

147   reduction (Fig. 2). Though oceans throughout the Archean Eon are thought to have been

148   predominantly anoxic, Neoarchean sediments in shallow coastal regions could have been

149   exposed to concentrations of up to tens of μM[10,11]. Being a more potent electron acceptor,

150   oxygen decreases the sediment demand for seawater sulfate, making the in-sediment

151   generation of oxidized S proportionately more important. The (percentage) contribution of OS

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152   to sulfate reduction increases also with the sediment organic matter content, as organic matter

153   supports OS mineralization rates, even though it also stimulates sulfate reduction and the

154   drawdown of sulfate from overlying water (Fig. S3). In the Neoarchean, environments with

155   higher oxygen concentrations and higher organic carbon fluxes could be found in oxygenated

156   oases in shallow coastal regions[10,42] where oxygenic photosynthesis fueled higher primary

157   productivity, sedimentation rates were high, and most pyrite is thought to have originated.

158   The contribution of organic component to pyrite formation profoundly changes the

159   accepted interpretations of the Archean isotopic signals. Microbial sulfate reduction depletes

160   the sulfide in ^{34}S, generating isotopic differences between the seawater sulfate and sediment

161   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

162   viewed as a consequence of low sulfate, which restricted sulfate reduction[3,16]. The $\Delta^{34}S_{FeS}$ range

163   is further limited by the Rayleigh distillation: the sulfate diffusing downward into the sulfate

164   reduction zone becomes isotopically heavier with depth and the $\delta^{34}S$ of the produced sulfide

165   trends towards the $\delta^{34}S$ of the original sulfate. The possibility of pyrite formation from the OS-

166   derived sulfur means that sulfidic rocks do not necessarily record the evidence of these

167   processes but instead reflect a more complex mixture of isotopic influences. Sulfite produced at

168   some depth within the sediment column may be reduced at the same depth, without

169   undergoing Rayleigh distillation[31]. As isotopic fractionations associated with the reduction of

170   sulfite are small[31,43] (13±7‰) compared with those for sulfate (>30‰), they are consistent with

171   observations of small $\Delta^{34}S$. The hydrogen sulfide produced from the more abundant reduced OS

172   compounds would generate solid sulfides, bypassing microbial reduction. Rather than carrying

173   an isotopic signature of redox processes, these sulfides could instead carry the isotopic signal of

174   hydrolysis. The magnitudes of the fractionations during hydrolysis of organic sulfur are

175   unknown, but thermodynamic considerations[44] limit them to less than 15‰, consistent with

176   small observed $\Delta^{34}S$. Small isotopic fractionations are similarly consistent with the evidence in

177   modern sediments where care was taken to analyze the hydrolyzable fraction of organic

178   sulfur[45,46]. In particular, depth variations in the isotopic composition of hydrolyzable organic

179   sulfur pool seem to indicate a preferential loss of isotopically light organic sulfur during the

180   early stages of diagenesis[45].

181   The ambiguity of isotopic interpretations calls for a re-evaluation of the ancient sulfur

182   cycling. Mineralization of S-bearing organic matter provided sulfur-reducing organisms not only

183   with an electron donor in the form of organic carbon, but also with an electron acceptor, while

184   mineralization of the reduced OS could supply hydrogen sulfide directly. As $\Delta^{34}S_{FeS}$ records are

185   equally consistent with sulfite reduction and formation of pyrite from reduced organic sulfur,

186   neither of which requires sulfate, the isotopic evidence for an early (3.47 Ga) onset of sulfate

187   reduction[47,48], suggested based on ~10‰ isotopic fractionations[49], may need to be re-

188   evaluated. Sulfur isotopes are the only reliable tracer for the sulfate reduction metabolism, as

189   preserved cellular structures are not readily identifiable for sulfate-reducers, while molecular

190   fossils (biomarkers) do not seem to survive over geological times[47]. In a low-oxygen world

191   where sulfate was produced in limited quantities by atmospheric photochemical reactions or

192   disproportionation of reactive sulfur intermediates[29], dissimilatory sulfate reduction could have

193   become globally competitive for the first time when sulfate concentrations increased in the

194   Neoarchean, following the initial marine oxygenation around 2.7 Ga[11]. The observed expansion

195   in $\Delta^{34}S_{FeS}$ beginning around that time[8,11] thus may reflect not only a more vigorous redox cycling

196   of sulfur but also increased isotopic fractionations[50] associated with the expanded range of

197   redox states. Similarly, while anoxygenic phototrophs nearly universally can oxidize sulfide to

198   elemental sulfur[23], evidence for the evolution of groups capable of completing the oxidation to

199   sulfate seems to appear first around 2.7 Ga[51]. As pyrite could be formed in non-hydrothermal

200   settings from relatively abundant reduced organic sulfur (Fig. 2), its presence may not

201   necessarily indicate active sulfate reduction, allowing a possibility of only trace amounts of

202   sulfate (sulfite) in oceanic seawater. The OS pathway under such conditions could generate

203   more pyrite than the reduction of seawater sulfate, and the geographic distribution of such

204   pyrite could be broader than for the pyrite formed from hydrothermal H_2S. The concentrations

205   of dissolved inorganic sulfur in ferruginous oceans thus could have been low enough to make

206   sulfur a co-limiting nutrient, consistent with the approximately similar S and P contents in living

207   cells.

208   Resolving the organic sulfur effects in the Archean rock record requires better

209   understanding of the OS pathways and isotopic fractionations than is currently available. Some

210   insight, however, may be obtained from the expected isotopic signatures (Fig. 3). Assuming that

211   Archean microorganisms satisfied their sulfur requirements by assimilating sulfur with the

212   isotopic composition similar to that of seawater sulfate, the $\Delta^{33}S/\delta^{34}S$ values in the resultant

213   pyrites should fall closer to the SO_4-S^0 mixing line (Fig. 3) than those produced through

214   microbial sulfate reduction, which generates stronger $\delta^{34}S$ fractionations. Earlier, organic-rich,

215   or sulfate-poor deposits therefore would be expected to have higher pyritic $\delta^{34}S$ values than

216   those that formed at higher sulfate concentrations, such as in the Neoarchean. While the small

217   amount of Mesoarchean data does not yet allow firm conclusions, this trend seems to be

218 indeed present (Fig. 3). Further insights are likely to be obtained through a combination of

219 laboratory experiments and observations in modern low sulfate environments. In particular,

220 mineral grain-scale signatures[17,41] of pyrite-forming OS mineralization may be potentially

221 resolved when the OS pathways are better characterized for the conditions of low ambient

222 sulfate, and the associated isotopic fractionations, including those during OS hydrolysis, are

223 determined.

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227 *Author contributions*: MF and SK conceived the ideas and co-wrote the manuscript. MF

228 performed the numerical simulations.

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230 *Data availability statement*: The datasets generated during the current study are available from

231 the corresponding author on reasonable request.

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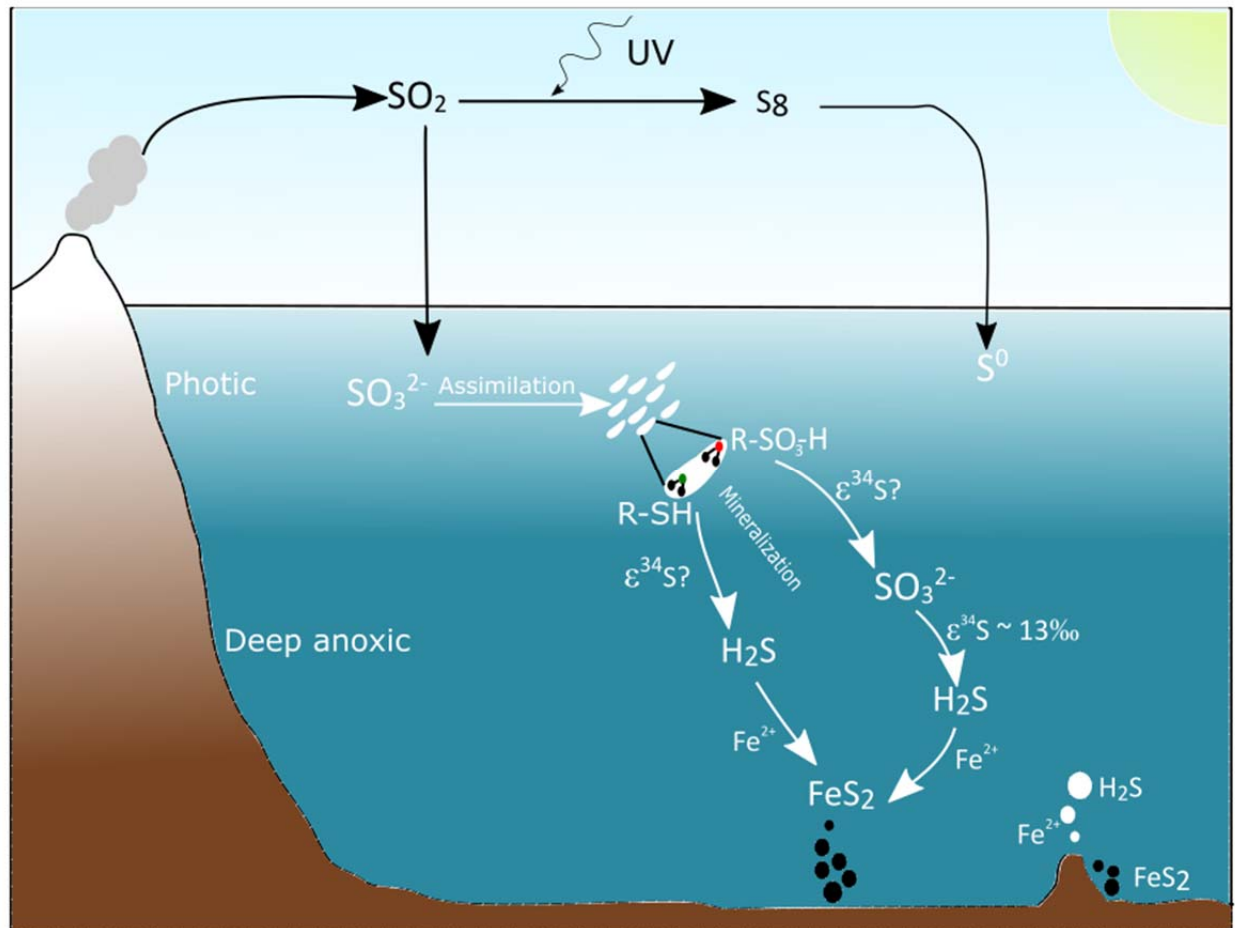359   (2003).

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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).
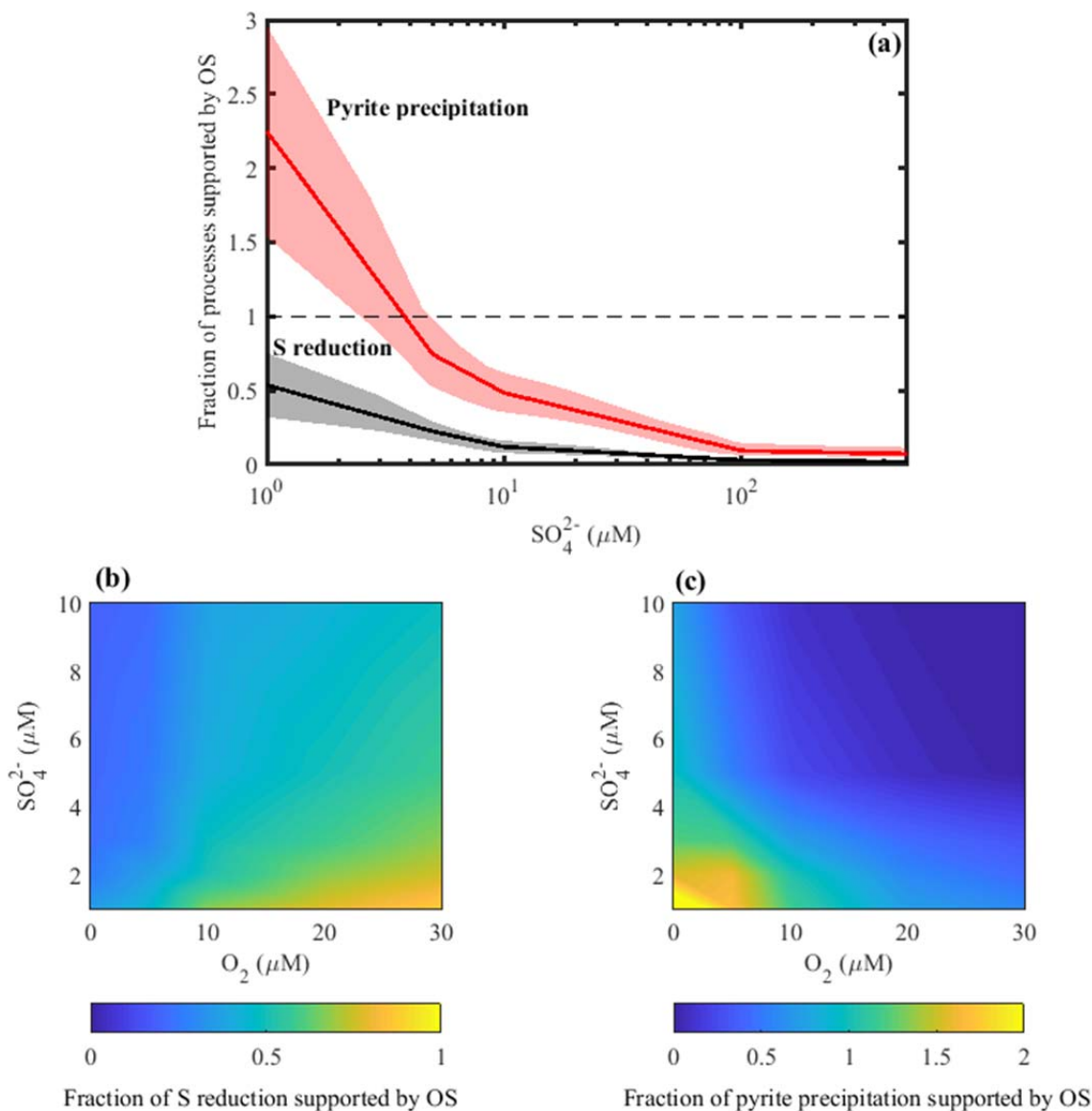
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Fig. 2. Support of sulfate (or sulfite) reduction and iron sulfide formation by organic matter-sourced sulfur (OS), simulated with a sediment reaction-transport model. **(a)** As a function of sulfate (sulfite) concentration under anoxic conditions. 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.

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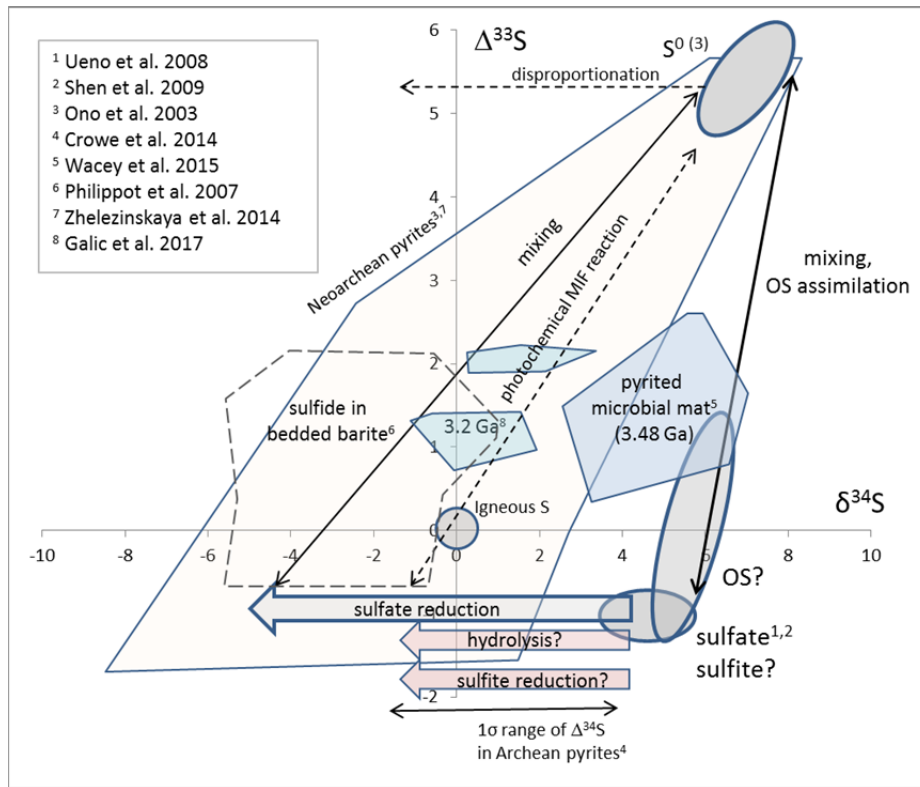
Fig. 3. Potential effects of organic sulfur reactions on the isotopic signatures in Archean pyrites. Assuming minor fractionations during hydrolysis, the isotopic composition of the pyrite produced from OS-sourced H_2S would be expected to deviate less from the seawater sulfate $\delta^{34}S$ values (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].