Sulfate interacts with carbon and oxygen in global biogeochemical cycles that regulate Earth’s surface chemistry and biology (1). At 28 mM, sulfate is abundant in modern seawater, fueling extensive sedimentary microbial sulfate reduction (MSR) (2). At these concentrations, MSR typically imparts large sulfur isotope fractionations (3), allowing the use of sulfur isotopes to reconstruct past global change (4, 5). Small sulfur isotope fractionations preserved in bulk pyrite from Archean (~2400 million years ago) rocks led to the original conclusion that the Archean oceans contained <200 μM sulfate, or ~1% of modern seawater (5). The distribution of mass-independent sulfur isotopes in Archean sediments (4, 6–8) and box models of global sulfur cycling (9) imply even lower Archean seawater sulfate of <60 to 80 μM. Paradoxically, microscale sulfur isotope data from Archean pyrites (~10–12) reveal large sulfur isotope fractionations of up to 40 per mil (%), only seen at hundreds to thousands of micromolar sulfur in modern environments (13–15). Electron-donor availability (3, 16) and MSR rate (3, 16, 17), however, also exert influence, with larger fractionation typically imparted when electron donors limit sulfate-reduction rates, allowing the
unexplored possibility for large fractionations in low-sulfate (<100 μM) environments.

We explored sulfur isotope fractionation in Lake Matano, Indonesia, an extremely low-sulfate analog for the Archean oceans (18). Lake Matano is a persistently stratified ferruginous (Fe2+-rich) lake, where dissolved ferrous iron (Fe2+) accumulates below a chemocline located at ~115 m depth (Fig. 1A). The upper waters of Lake Matano have sulfate concentrations of less than 30 μM (Fig. 1B), far lower than that of the natural environments studied for sulfur isotope fractionation thus far (23, 14) and lower than previous upper limits for Archean seawater (5, 8, 9). MSR is active within Lake Matano’s water column, and peak rates of 30 to 40 nM d−1 are reached at sulfate concentrations of between 5 and 10 μM (22) (Fig. 1C).

We measured the δ34S values of sulfate and sulfide in Lake Matano’s water column (Fig. 1D) and in the underlying sediments (19, 20). The δ34S values of sulfate ranged from 8.1‰ within the surface waters to 39.1‰ in the lower reaches of the chemocline, where sulfate is present at barely detectable concentrations (Fig. 1D). Sulfate reduction in the chemocline thus leads to strong isotopic fractionation, despite extremely low-sulfate concentrations, favoring the incorporation of 34S into the sulfide produced. Measurements of water-column sulfides reveal δ34S values from ~13.2 to 5.4‰ (table S1), demonstrating that they record large fractionations with a range in δ34S of up to 18.6‰. Depending on the depths considered, the δ34S value of water-column sulfides translates to an appreciable isotopic difference (Δ34S SO4(2−)3 sulfide) between water-column sulfide and the surface-water sulfate pool of up to 23‰.

We used both a Rayleigh distillation model and a one-dimensional (1D) reaction-diffusion model to calculate sulfur isotope fractionation factors. Rayleigh models underestimate fractionation in open systems (21, 22) like Lake Matano and therefore provide minimum estimates of the true fractionation. Using the Rayleigh model, we obtain a fractionation factor (εδ34S(34S−32S)) of 21 ± 1‰ (16) (Fig. 2A). To further assess the true magnitude of fractionation during MSR, we constructed an open-system, reaction-diffusion model. As expected, applying the fractionation factor obtained from the Rayleigh model to the reaction-diffusion model underestimates the fractionation observed (Fig. 2B), whereas fractionations ranging between 20 and 70‰ encompass our entire sulfur isotope data set (Fig. 2B). The best fit with constant fractionation, independent of sulfate concentrations, comes from a fractionation factor of 35‰. As MSR proceeds, sulfate concentrations decrease (Fig. 1B), probably shifting MSR from organic matter limitation, which allows expression of large isotope fractionation, to sulfate limitation, which progressively mutes fractionation as sulfate concentrations decrease (3, 16). We therefore also tested a model with fractionation of 70‰ at sulfate concentrations of >6 μM, with a linear decrease to 0‰ when sulfate is exhausted, obtaining an equally good fit. Regardless of the model used, these trends in the δ34S values of sulfate illustrate large isotope fractionations down to sulfate concentrations below 6 μM (Fig. 2, A and B), confirming that MSR can produce large isotope fractionations at sulfate concentrations more than one order of magnitude lower than previously demonstrated (5, 14, 15).

Sediments under the chemocline record the integrated δ34S values of sulfate exported from the water column and exhibit a range of δ34S values from −4.2 to 6.6‰, with a mean of 2.5 ± 2.5‰ (Fig. 2C). These isotopic compositions are consistent with the range of δ34S values observed in the water column and predicted by our fractionation models (Fig. 2, A and B) and are up to 14.9‰ lower than that of sulfate in the surface waters of the lake (table S1). Reaction-diffusion models with either a constant fractionation of 35‰ or a variable fractionation of 70‰ that decreases below 6 μM sulfate yield integrated sulfide export with δ34S values of 3.8 and 2.7‰ (Fig. 2C), respectively. These δ34S values are similar to the mean of measured sediment sulfides, in contrast to the model with a 20‰ fractionation, which yields a sulfide export flux at the far maximum range of the sediment δ34S values (6.5‰) and outside of the standard deviation of the sediment mean.

The lack of a full expression of water-column sulfur isotope fractionation in bulk δ34S measurements of sedimentary sulfides is due to the depletion of sulfate to low concentrations in the chemocline and the development of a strong water-column gradient in sulfate concentration and isotopic composition. As a result, δ34S values of sulfate increase with decreasing sulfate concentrations (Fig. 1, B and C), leading to a reservoir effect and the production of correspondingly 34S-enriched sulfide, despite the strong fractionation imparted during sulfate reduction. In the
end, the net isotopic fractionation between lake-
surface sulfate and sedimentary sulfide is only
~7.5‰. A similar effect has been observed in oth-
er lakes, albeit at much higher sulfate concentra-
tions (14, 15).

Compilations of the S-isotope composition of
Archean sulfides from bulk sediment analyses
suggest that the expression of S-isotope fraction-
ation in the Archean was typically less than ~10‰
(Fig. 3). Though most Archean sulfides display
observed in the similar to our observations in Lake Matano.

fractionations, possibly more than 40
the Archean was accompanied by large sulfur iso-
data around the Archean MIF-S array (Fig. 3). We also assume
that the expression of this isotope fractionation
were possible (10–12). The scatter of sulfur isotope
data around the Archean MIF-S array (23) sup-
ports the idea that microbial sulfate reduction in
the Archean was accompanied by large sulfur iso-
tope fractionations, possibly more than 40‰, but
that the expression of this isotope fractionation
at the scale of bulk sedimentary sulfides was muted, similar to our observations in Lake Matano.

To test possible upper limits on Archean sea-
water sulfate concentrations, we have adapted
our reaction-diffusion model to simulate a strati-
fied Archean ocean water column. Like in Lake
Matano, we expect that pelagic MSR would have
ensued under the ferruginous ocean conditions
dominating marine chemistry throughout much
of the Archean eon (24). In an approach similar
to previous models for sedimentary S-isotope frac-
tionation (3), we varied seawater sulfate con-
centrations and computed the integrated δ34S
do the water column to un-
derlying sediments (Fig. 4). We also assume
that MSR would take place in sediments, so we modeled
the δ34S of diagenetic sulfides formed under a
range of overlying seawater sulfate concentrations.

Our water-column model shows that at mod-
est MSR rates, comparable to those measured in
the Chilean oxygen minimum zone (25), appreci-
ciable sulfate drawdown occurs with surface sea-
water sulfate concentrations in the low micromolar
range (Fig. 4, A and B). Fractionation factors
similar for marine environments (30‰), and jus-
tified as a conservative estimate based on micro-

scale measurements of δ34S in Archean pyrites, translate to a large range in the δ34S of pelagic sulfate and sulfide (Fig. 4C), showing that res-
vour effects similar to those in Lake Matano
develop under conditions typical for stratified
marine environments. Due to a combination of
sulfate drawdown, reservoir effects, and decreased
isotope fractionation at low sulfate concentra-
tions, the integrated sulfide exported from the
modeled Archean water column has δ34S values
closer to seawater sulfide than would be ex-
pected due to the isotope fractionation imparted.

The imparted fractionation is best reflected by
the sulfide produced in the upper regions of the
water column.

Application of a constant fractionation factor
of 30‰ in our models results in large differences
between the δ34S values of seawater sulfate and bulk pyrites of 15 to 23‰ (Fig. 4D). Comparing
these modeled δ34S values for sulfide with the
low sulfur δ34S values of seawater sulfate, we have adapted models for sedimentary S-isotope frac-
tionation factors similar to those in Lake Matano
brings modeled differences between the δ34S of seawater sulfate and bulk pyrites into a range supported by the Archean
bulk pyrite record (Fig. 4D). Under this sce-
nario, both water-column and sediment models
predict that MSR would impart bulk sediment
sulfide δ34S values of more than 10‰ lighter than
seawater sulfate at concentrations more than ~5 µM (Fig. 4D). Comparison under this sce-
nario suggests that more than half of the mea-
sured sulfide δ34S values could be described by
deposition at seawater sulfate concentrations be-
 tween 1 and 2.5 µM, and more than 90% deposited
at seawater sulfate concentrations <5 µM (Fig.
4D). Taking into consideration that the δ34S va-
ue of seawater sulfate may have reached up to
15‰ in the Neoarchean, and that δ34S values in pyrite may also include contributions from δ34S-
enriched photochemical sources (29), the con-
centration window may have extended as high as
10 to 15 µM. Higher seawater sulfate concentra-
tions would have left bulk sulfide δ34S values
much lighter and are therefore not supported by
the sedimentary δ34S sulfide record. The ~30‰
variability observed at the scale of some bulk
sediments could be imparted by dynamic pro-
cesses that cause changes in the concentration
of sulfate, the rate of sulfate transport into the
sulfate-reduction zone, the rate of MSR (17),
electron-donor availability (16), or the δ34S of
seawater sulfate. These could include variability
in depositional depth of sediments analyzed, fluc-
tuations in the depth of mixing, shifting organic
matter availability, or variable contributions of
atmospheric versus riverine sulfur fluxes to the
oceans. Overall, both the limited sulfur isotope
fractionation measured at the bulk sediment

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**Fig. 2. Sulfur isotope fractionation in Lake Matano.** (A) The
slope of the line taken from the
natural log of sulfate 34S/32S (R)
normalized to that of sulfate at the
top of the chemocline 34S/32S
(R0, 0.0446) versus the natural log
of the sulfate concentration (C)
normalized to the sulfate concen-
tration at the top of the chemocline
(C0, 16 µM). The slope of this relation
(m = −0.2075) is used to calculate the
Rayleigh fractionation factor
α = [(m + 1)−1 = 1.0211]. (B) Results from our 1D reaction-diffusion modeling with constant fractionation
factors (α) of 1.020, 1.035, 1.045, and 1.070, in addition to a variable fractionation factor with α of 1.070 at
sulfate concentrations >6 µM and a linear decrease of α from 1.070 to 1.000 below 6 µM. (C) Ranges in
δ34S observed (solid lines and circles) or computed (hollow lines and circles) for different sulfate pools in
Lake Matano. The shaded box outlines 1 SD from the anoxic sediment mean. AVS, acid volatile sulfide; CRS,
chromium reducible sulfide.
scale and the large isotopic fractionations at the microscale point strongly to sulfate concentrations less than 2.5 μM.

Our results suggest that Archean ocean sulfate concentrations were <0.01% modern seawater, implying very different global sulfur dynamics. With surface seawater sulfate concentrations in the low micromolar range, sulfate residence times (16) would have been on the order of 10^3 to 10^4 years, and sulfate could have been poorly mixed in the Archean oceans. Though homogeneity of S isotopes in some Archean barites has been taken as evidence for conservative sulfate behavior (29), such conservative behavior at these low seawater sulfate concentrations would imply smaller-than-estimated volcanic and weathering sulfate fluxes to the Archean oceans (30). Regardless, the short residence times would have rendered seawater sulfate and its isotopic composition extremely sensitive to perturbations in the global sulfur cycle.

At seawater sulfate concentrations up to 2.5 μM, sediment sulfate reduction would have contributed less than ~10% to sedimentary organic carbon degradation (16), leaving the balance to fuel other microbial processes. Organisms also require sulfur as a nutrient, using it for protein synthesis at a typical cellular ratio of 48C:1S:0.45P (31); cellular sulfur quotas are thus

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**Fig. 3.** Compilation of nearly 3000 individual measurements of the δ^{34}S values of bulk Archean sedimentary sulfides. The black line shows the normal distribution, and the general agreement between the data and the normal distribution suggests a single population. The vertical hatched band delineates the likely range of δ^{34}S for surface ocean seawater sulfate (26–28). The vertical gray band shows a 10‰ difference from seawater sulfate. Very few measurements extend beyond this 10‰ difference.

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**Fig. 4.** Models of marine sulfur cycling and isotope fractionation in the Archean eon. (A) Modeled rates of microbial sulfate reduction in a stratified Archean ocean water column with different surface seawater sulfate concentrations. (B) Resulting sulfate concentration profiles. (C) Sulfate (solid lines) and sulfide (dashed lines) δ^{34}S profiles generated using a variable ε of 30‰ at sulfate concentrations >6 μM that decreases to 0‰ when sulfate is exhausted. (D) Mean integrated δ^{34}S for sulfide produced and exported from the water column to sediments (blue) and diagenetic sulfide (red) at various surface seawater sulfate concentrations. The solid black line indicates the imposed sulfur isotope fractionation factor at different sulfate concentrations (ε ≤ 30‰, justified from microscale analyses of Archean pyrites), and the gray dashed line symbolizes a constant fractionation factor (ε = 30‰). The golden diamond distribution plot at left illustrates sedimentary δ^{34}S_{sulfate-sulfide} calculated from bulk Archean sulfides (from Fig. 3) and using 5‰ as a conservative value for δ^{34}S of seawater sulfate. The horizontal gray band delineates values between the 25th and 75th percentiles, whereas the horizontal dashed lines delineate the 5th and 95th percentiles, encompassing 90% of the Archean data. The arrow demarcates the previous 200 μM threshold for the full expression of sulfur isotope fractionation (5).
higher than those of phosphorus. At low concentrations, nutrients such as phosphorus tend to limit biological production, and by analogy, sulfur may have played a more important role as a biologically scarce nutrient.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/346/6210/735/suppl/DC1

Materials and Methods
Supplementary Text
Figs. S1 and S2
Tables S1 to S5
References (31–68)
Data S1

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References

19. Materials and methods are available as supplementary materials on Science Online.


Mass-independent fractionation of sulfur isotopes (reported as δ33S) recorded in Archaean sedimentary rocks helps to constrain the composition of Earth’s early atmosphere and the timing of the rise of oxygen ~2.4 billion years ago. Although current hypotheses predict uniformly negative δ33S for Archaean seawater sulfate, this remains untested through the vast majority of Archaean time. We applied x-ray absorption spectroscopy to investigate the low sulfate content of particularly well-preserved Archaean carbonates and mass spectrometry to measure their δ33S signatures. We report unexpected, large, widespread positive δ34S values from stratigraphic sections capturing over 70 million years and diverse depositional environments. Combined with the pyrite record, these results show that sulfate does not carry the expected negative δ34S from sulfur mass-independent fractionation in the Neoarchaean atmosphere.

The sulfur isotopic composition of Archaean (~3.8 to 2.4 billion years ago (Ga)) sedimentary rocks provides critical evidence that Earth’s atmosphere contained very little, if any, free O2 before the rise of oxygen ~2.4 Ga (1–6). Most processes on Earth fractionate sulfur isotopes proportionally to their relative mass differences [δ34S = 0 (7)], yet Archaean pyrite (FeS2) commonly deviates from this relationship, skewed toward positive δ34S values (1, 8). This mass-independent fractionation (MIF) pattern is widely attributed to photodissociation of SO2 by ultraviolet (UV) light allowed by the extremely low levels of O2 and O3 in Earth’s atmosphere at that time (1, 6). In this scenario, coeval sulfate aerosols ultimately deposited in the ocean as dissolved sulfate carry the complementary negative δ34S anomalies required by isotopic mass balance (1, 2, 5, 8, 9). Recent experiments (10–12) and models of the Archaean atmosphere (2) show a much wider range of MIF patterns, including positive δ34S anomalies in sulfate instead of lower-valent S species. Sulfate minerals that would provide a test of the distribution of MIF signal are absent from Archaean evaporite sequences—bedded sulfate deposits occur only after the rise of oxygen (13). Paleooceanic barites (3.5 to 3.2 Ga) are a notable exception. They carry small, negative δ34S values [0 to −1.5% (14–16)] but have an enigmatic petrogenesis (17). No such sulfate record exists for the billion-year interval from Mesoarchean time through the Paleoproterozoic rise of oxygen. Consequently, the notion of an Archaean marine sulfate pool with negative δ34S values remains largely untested.

Sulfate minerals are not the only portal into the past marine sulfate pool. Small quantities of carbonated-associated sulfate (CAS) have become an important archive for studying marine sulfate in younger successions (18). However, the very low sulfate concentrations of Archaean carbonates have kept this archive largely out of reach for conventional analytical methods. Two studies measuring Archaean CAS suggested that Archaean sulfate carried positive δ34S (4, 19). However, both studies used large sample sizes (>100 g of CaCO3), raising the risks of lower preservation as well as contamination by pyrite. We recently developed a technique using inductively coupled plasma mass spectrometry to measure both δ34S and δ33S using a few tens of milligrams of low-CAS carbonate (20). Greater sensitivity allows the measurement of sulfur isotopes from specific petrographic and sedimentary fabrics with different diagenetic histories, coupled with light and electron microscopy (Fig. 1 and fig. S4), to directly assess sample quality based on the presence of additional S-bearing phases (e.g., organic sulfur, pyrite). In parallel, we applied synchrotron x-ray absorption spectroscopy (XAS) to measure sulfate speciation in these samples. We examined three sedimentary sections from a range of marine paleoenvironments across the Neoarchean Campbellrand carbonate platform (21). Section W1 (aragonite sea-floor fans, precipitated laminae, preserved as early diagenetic fabric-retentive dolomite) captures shallow subtidal environments, whereas sections GKP01 and W2 (herringbone, an early marine calcitic cement (22), microbial laminae, dolomite, and calcite spar) capture deep subtidal and slope environments (22). The CAS data preserve positive δ34S values and unambiguously positive δ33S values and display significant variability, sometimes at very small scales (Fig. 2 and additional data table S1). The carbonate fabrics contain 5 to 70 parts per million (ppm) sulfate—two orders of magnitude lower than typical Phanerozoic carbonates. Because of such low levels, we consider the potential impacts of contamination and/or sulfide oxidation.
Supplementary Materials for

Sulfate was a trace constituent of Archean seawater

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Materials and Methods
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Other Supplementary Material for this manuscript includes the following:
(available at www.sciencemag.org/content/346/6210/735/suppl/DC1)

Data S1
Materials and Methods

Measurements of $\delta^{34}$S were made by Isotope Ratio Mass Spectrometry following sulfur conversion to either SF$_6$ or SO$_2$. Measurements of $\delta^{34}$S values at low sulfate concentrations were made by MC-ICP-MS (20). The isotope fractionation factor ($\alpha$) was calculated as $\ln(R/R_0)=(1/\alpha-1) \times \ln(S/S_0)$, where $R$ is $^{34}$S/$^{32}$S, and $S$ is sulfate concentration. The subscript ‘0’ indicates the sulfate concentration and isotopic composition of the surface water. The fractionation factor ($\alpha$) is related to $\varepsilon$ by $\varepsilon = (\alpha - 1) \times 1000$ and $\varepsilon \approx (\delta^{34}$S-SO$_4$ – $\delta^{34}$S-HS). Residence times were calculated by multiplying the sulfate concentration in a compartment by the volume of that compartment and dividing by the sulfate removal flux, which at steady state is equal to the sulfate addition flux. We used published ranges for sulfate addition fluxes (30).

Supplementary Text

Lake Matano 1-dimensional reaction-transport model

To model S-isotope fractionation in an open system, we setup a 1-dimensional reaction-transport model in which the profiles of the individual S-isotopes were described independently. Similar models have been constructed in marine sediments (22). The model predicts sulfate distributions under steady-state conditions by describing changes in sulfate concentrations with depth as a function of rates of vertical transport and bacterial reduction of sulfate to sulfide as:

$$K_z \frac{d^2[SO_4^{2-}]}{dx^2} - R_{SR} = 0$$

where $K_z$ is the eddy diffusion coefficient (0.1 m$^2$d$^{-1}$ in the redoxcline of Lake Matano, (33)), $x$ is the depth in the water column, and $R_{SR}$ is the sulfate reduction rate.

Rates of sulfate reduction ($R_{SR}$) in the model were set with an explicitly specified depth distribution function to generate modeled sulfate profiles that fit the measured sulfate profiles. Sulfate reduction rates were thus set for a normal distribution:

$$R = R_0 \frac{1}{\sigma \sqrt{2\pi}} e^{\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2}$$

where $\sigma$ is the variance (0.8 m), $x-\mu$ is depth subtracted from a reference depth, and $R_0$ is the maximum rate of 0.03 $\mu$M d$^{-1}$. The values chosen for $\sigma$ and $R_0$ reproduce the measured sulfate profile and yield volume specific and depth-integrated rates similar to those directly measured in the water column. Minor discrepancies between the depth distributions of the modeled and measured sulfate reduction rates are most likely attributable to seiching, given that sulfate reduction rates and the sulfate profiles were measured at different times and that seiching has an amplitude of 4-10 meters and a period of several hours (33). Additional differences can arise from vertical variability in $K_z$ (33), which we cannot account for in the current model. Gradients in sulfate concentration were computed by integrating the sulfate reduction rates, and concentrations were then computed through integration of the gradients.
Specific rates of $^{34}\text{SO}_4^{2-}$ and $^{32}\text{SO}_4^{2-}$ reduction and concentrations of $^{34}\text{SO}_4^{2-}$ and $^{32}\text{SO}_4^{2-}$ are related by a fractionation factor ($\alpha$):

$$\alpha = \frac{R_{32\text{SR}}[^{34}\text{SO}_4^{2-}]}{R_{34\text{SR}}[^{32}\text{SO}_4^{2-}]}$$

At fractionations of between 20 and 70 ‰, the rate of $^{32}\text{SO}_4^{2-}$ reduction ($R_{32\text{SR}}$) ≈ 0.96$R_{34\text{SR}}$ to within one percent, so $R_{32\text{SR}}$ was calculated as 0.96$R_{34\text{SR}}$. For our calculations, an initial approximation of $R_{34\text{SR}}$ was thus taken as 0.04$R_{34\text{SR}}$. The differential equations required to determine steady-state values of $[^{34}\text{SO}_4^{2-}]$ and $R_{34\text{SR}}$, were solved numerically. The model was highly sensitive to the initial $R_{34\text{SR}}$, and model convergence was only possible within a narrow range of initial $R_{34\text{SR}}$ values. The values for $[^{34}\text{SO}_4^{2-}]$ and $R_{34\text{SR}}$ were obtained iteratively until the model converged on an $\alpha$ within ± 0.0001 of the specified value. For example, if the specified $\alpha$ were 1.02, convergence was deemed acceptable at a modeled $\alpha$ of between 1.0199 and 1.0201. In other words, modeled fractionations were accurate to within ±0.1 ‰ $\delta^{34}\text{S}$.

The model was run with $\alpha$ values of 1.020, 1.035, 1.045, and 1.070. In addition, variable fractionations were investigated whereby $\alpha$ was set at 1.070 in the upper reaches of the chemocline, and a linear decrease in $\alpha$ was imposed at concentrations of 8, 6, and 4 µM sulfate. The fit of the modeled $\delta^{34}\text{S}$ sulfate values to the measured $\delta^{34}\text{S}$ sulfate profiles was assessed visually, and of the fractionations tested, a variable fractionation with initial $\alpha$ of 1.070 decreasing linearly below 6 µM sulfate appeared to fit the data best. Lower values for $\alpha$ did not improve the fit, and a better fit would likely require variable $K_z$ and possibly a non-normal distribution in sulfate reduction rates. These factors can be explored in future modeling efforts. Overall, our modeling shows that fractionations higher than 20 ‰ and possibly as high as 70 ‰ are needed to reproduce the measured S-isotope compositions.

The $\delta^{34}\text{S}$ of sulfide produced was calculated by subtracting the instantaneous fractionation ($(\alpha - 1)*1000$) at a given depth from the $\delta^{34}\text{S}$ of sulfate at the same depth. The $\delta^{34}\text{S}$ values, averaged over the water column, for the sulfide exported to the underlying sediments were calculated by integrating $\delta^{34}\text{S}*R_{34\text{SR}}$ over depth. An implicit assumption in this model is that the sulfide produced through microbial sulfate reduction is quantitatively scavenged by reaction with Fe and precipitated as FeS and FeS$_2$ without recycling through oxidation. There is some evidence for oxidative sulfur cycling in the upper reaches of Lake Matano’s chemocline, but as discussed below, this is unlikely to have a significant effect on the $\delta^{34}\text{S}$ of exported sulfide.

**Sulfide oxidation**

Sulfide oxidation and sulfur compound disproportionation reactions can contribute to the fractionations generated during sulfur cycling, and the influence of these processes can be revealed through the specific behavior of $^{33}\text{S}$ compared to $^{34}\text{S}$ (34, 35). Such a comparison from sulfate and sulfides in the Lake Matano chemocline produce no evidence for these alternative fractionation pathways (Table S1), implying that fractionations are exclusively due to microbial sulfate reduction. Furthermore, biological sulfur oxidation carries little fractionation (36, 37), and appreciable oxidation of
isotopically light sulfide all the way to sulfate would be directly recorded as a negative excursion in the δ\(^{34}\)S of sulfate. The δ\(^{34}\)S of sulfate at the upper margin of the chemocline, where sulfide oxidation would be most intense, is identical to the overlying water, while the δ\(^{34}\)S of sulfate becomes progressively heavier with depth, demonstrating a lack of isotopic effects from sulfide oxidation. If sulfide oxidation to sulfate were to operate cryptically, then the gradient in sulfate δ\(^{34}\)S values would be smaller than without sulfide oxidation, and sulfide oxidation would therefore cause us to underestimate the magnitude of fractionation from sulfate reduction based on sulfate profiles. Likewise, the sulfide exported would be isotopically lighter when oxidation operates, causing an overestimation of fractionation based on comparisons between δ\(^{34}\)S values of sulfide and sulfate.

**Archean ocean 1-dimensional reaction-transport models**

We constructed a model to explore how sulfate levels in the Archean oceans would influence the fractionation of sulfur isotopes in the ocean water column, and made predictions about how this fractionation would be recorded in the distribution of S-isotopes in marine sedimentary sulfides (pyrite). Like our model for Lake Matano, the model for the Archean ocean water column predicts sulfate distributions under steady-state conditions by describing changes in sulfate with depth as a function of vertical transport and bacterial reduction of sulfate to sulfide as:

\[
K_U \frac{\partial^2 [SO_4^{2-}]}{\partial x^2} - R_{SR} = 0
\]

where \(K_U\) is the vertical mixing coefficient (1.728 m\(^2\)d\(^{-1}\), (38)), \(x\) is the depth in the water column, and \(R_{SR}\) is the sulfate reduction rate. Sulfate reduction rates were calculated with a Michaelis-Menten description of sulfate reduction kinetics:

\[
R_{SR} = \frac{V_{max}[SO_4^{2-}]}{K_m + [SO_4^{2-}]}
\]

where \(K_m\) is the half-saturation constant, which was taken as 5 µM for low sulfate environments (39, 5). \(V_{max}\) is the maximum sulfate reduction rate when sulfate supply is unlimited. When sulfate supply is unlimited, sulfate reduction rates are limited by the availability of organic matter. In the modern ocean, oxygen respiration rates are limited by the availability of organic matter, and we thus take modern open ocean respiration rates (40) as a starting point for the estimation of \(V_{max}\) (Table S2). Anaerobic respiration rates often appear to be slower than aerobic respiration and we have therefore decreased \(V_{max}\) correspondingly (41). Finally, primary production in the Archean oceans was likely lower than today, with model-based estimates suggesting a factor of 10 lower (42). The volume specific rates of sulfate reduction rendered by our model at low µM sulfate concentrations are well below those measured in Lake Matano’s water column, illustrating that such rates are within the physiological capacity of modern sulfate reducing bacteria. They are also much lower than rates of anaerobic nitrate respiration.
observed at comparable depths in modern oxygen minimum zones, indicating that marine systems today could support our modeled sulfate reduction rates.

Sulfate gradients, concentrations, as well as the $\delta^{34}S$ of sulfate and sulfide were computed as described above for Lake Matano. We conservatively imposed a fractionation factor of 30 ‰, which is typical for sulfate reducing bacteria (3) and also in line with micro-scale $\delta^{34}S$ values from Archean pyrites, and decreased this fractionation linearly below 6 $\mu$M, in line with our observations from Lake Matano. We note that higher imposed fractionations would lead to lower estimates for seawater sulfate concentrations. Likewise, if high fractionations persisted below 6 $\mu$M, this would also lead to lower estimates for seawater sulfate concentrations. The effect of surface seawater sulfate concentrations on depth profiles of the $\delta^{34}S$ of sulfate and sulfide, as well as the integrated $\delta^{34}S$ of sulfide exported was evaluated by systematically changing the surface seawater sulfate concentration in the model. Integrated pelagic sulfate reduction rates along with the $\delta^{34}S$ of sulfide exported at various surface seawater sulfate concentrations are tabulated below (Table S3).

We have evaluated the sensitivity of our model outputs to the availability of organic matter (Fig. S1). Since a greater availability of organic matter increases sulfate reduction rates, sulfate drawdown is more extensive, and the $\delta^{34}S$ values of exported sulfides are closer to surface seawater sulfate—all other factors being equal. Nevertheless, even at modern day levels of primary production and organic matter availability, fractionations greater than the 15 ‰ observed in the Archean record are expected at sulfate concentrations higher than about 10 $\mu$M. Lesser organic matter availability would lead to high fractionations at even lower seawater sulfate concentrations. Our model results then appear to be robust across at least an order of magnitude variability in organic matter availability. We also evaluated the effect of not decreasing fractionation below 6 $\mu$M sulfate at organic matter availability, corresponding to 5 times lower primary production than today. The $\delta^{34}S$ of exported sulfide in this case approaches 15 ‰, but remains greater than 15 ‰ to sulfate concentrations below 2.5 $\mu$M.

**Archean sediment 1-dimensional reaction-transport model**

The Archean sediment model was constructed in a similar fashion to the water column model. The reactivity of organic carbon was described by a power law as a function of time: $\log_{10} k = -(0.95) \log_{10} t + (0.81)$. Integrated sediment sulfate reduction rates along with the $\delta^{34}S$ of sulfide produced at various surface seawater sulfate concentrations are tabulated below (Table S4). Relevant sediment parameters are summarized in Table S5 below. Using a constant fractionation factor in the sediment model leads to high sediment sulfide isotope fractionations, even at 1 $\mu$M seawater sulfate (Fig. S2). Model runs at various porosities, as well as for porosities that decrease with depth (compaction), reveal a lack (<1.5‰) of sensitivity to porosity, given the same sedimentation flux of organic carbon. These results are consistent with the findings of earlier models of sulfur isotope fractionations. Model runs at various organic matter concentrations and sedimentation velocities also reveal a lack of sensitivity to these parameters.

**Biogeochemical implications for low seawater sulfate**

Global marine productivity in the Archean has been estimated at up to 5 x 10$^{14}$ mol C yr$^{-1}$ (42), and combining this with an ocean surface area of 3.61 x 10$^{14}$ m$^2$ yields
primary production of 1.39 mol C m⁻² yr⁻¹. Estimated fractions of organic carbon degradation through pelagic sulfate reduction are presented in Table S2. Sulfur is also required by organisms as a nutrient for protein synthesis, and typical modern marine organic matter has a C:S of 48:1 (31). In the absence of other sulfur sources, organisms would meet their nutrient S quotas through assimilatory sulfate reduction, which at primary production rates of 1.39 mol C m⁻² yr⁻¹ would occur at a rate of 0.013 mol S m⁻² yr⁻¹, (35.6 x 10⁻⁵ mol S m⁻² d⁻¹). At surface seawater sulfate concentrations of between 1 and 5 µM, assimilatory sulfate reduction would account for between 82 and 65 %, respectively, of total sulfate reduction. Under the high Fe concentrations predicted for the Archean ocean, the low solubility of FeS would limit sulfide concentrations to sub-µM concentrations (43), implying sulfate was the most available pool of sulfur. Elemental S may also have been present, but its concentration and availability are unknown at this time. Elemental sulfur is poorly soluble in water (44), so its concentration was likely in the sub-µM range.
Fig. S1.

Sensitivity of model outputs to organic matter availability. MP corresponds to modern levels of productivity, LP5x and LP10x correspond to 5 and 10 times lower production than today. The red line shows the imposed fractionation of 30 ‰, which is decreased linearly below sulfate concentrations of 6 µM. LP5x 1.03 constant illustrates the effect of not decreasing fractionation below 6 µM at 5x lower organic matter availability than today.
Fig. S2
Sensitivity of sediment model outputs to porosity and variability in the fractionation factor. Model runs include a constant porosity of 0.9 (blue line), variable porosity from 0.95 at the sediment-water interface to 0.9 at 20cm below the sediment-water interface (green line), and variable porosity from 0.95 at the sediment-water interface to 0.8 at 20cm below the sediment-water interface (purple triangles). The red line shows the imposed fractionation of 30 ‰, which is decreased linearly below sulfate concentrations of 6 µM. The cyan line illustrates the effect of not decreasing fractionation below 6 µM sulfate (i.e. a constant $\alpha$ of 1.03).
<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Year</th>
<th>Sulfate µM</th>
<th>Technique</th>
<th>Species</th>
<th>$\delta^{34}$S</th>
<th>$\Delta^{34}$S</th>
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<td>5</td>
<td>2009</td>
<td>29</td>
<td>SF$_6$</td>
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<td>SF$_6$</td>
<td>CRS</td>
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Table S2.
Values used to obtain estimates of sulfate reduction $V_{\text{max}}$.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Oxygen Respiration mmol m$^{-3}$ yr$^{-1}$</th>
<th>Sulfate reduction mmol m$^{-3}$ yr$^{-1}$</th>
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<tr>
<td></td>
<td>From(44) Scaled for anoxia(45) Modern OM 10x less</td>
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<tr>
<td>100</td>
<td>21.6 17.28 8.64 0.864</td>
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<td>150</td>
<td>10.1  8.08 4.04 0.404</td>
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<td>200</td>
<td>5.9   4.72 2.36 0.236</td>
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<td>250</td>
<td>3.9   3.12 1.56 0.156</td>
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Table S3.
Water column model results including integrated sulfate reduction rates (SRR), and integrated δ$^{34}$S.

<table>
<thead>
<tr>
<th>Surface seawater sulfate (µM)</th>
<th>1</th>
<th>2.5</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>1000</th>
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<tbody>
<tr>
<td>SRR mol S m$^{-2}$ d$^{-1}$ (x10$^{-6}$)</td>
<td>7.9</td>
<td>18</td>
<td>30</td>
<td>44</td>
<td>60</td>
<td>67</td>
<td>70</td>
<td>71</td>
<td>73</td>
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<tr>
<td>δ$^{34}$S (%)</td>
<td>2.2</td>
<td>5.7</td>
<td>12.5</td>
<td>22.7</td>
<td>25.9</td>
<td>27.7</td>
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<td>3.9</td>
<td>5.9</td>
<td>8</td>
<td>8.8</td>
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<td>9.8</td>
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Table S4
Sediment model results including integrated sulfate reduction rates (SRR), and integrated δ^{34}S.

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<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRR mol S m^{-2} d^{-1} (x10^{-6})</td>
<td>27</td>
<td>61</td>
<td>97</td>
<td>140</td>
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<td>236</td>
<td>256</td>
<td>268</td>
<td>321</td>
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<tr>
<td>δ^{34}S (%)</td>
<td>2.8</td>
<td>6.9</td>
<td>14.2</td>
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<td>24.6</td>
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<tr>
<td>% OM degradation</td>
<td>6</td>
<td>13</td>
<td>21</td>
<td>31</td>
<td>43</td>
<td>52</td>
<td>56</td>
<td>59</td>
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Table S5
Sediment model parameter values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Sedimentation rate</td>
<td>0.05 g cm(^{-2}) y(^{-1})</td>
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<tr>
<td>Organic carbon flux</td>
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<td>Sediment porosity</td>
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<td>K(_{mSO_4^-})</td>
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<td>Imposed fractionation (at sulfate &gt; 6µM)</td>
<td>30 ‰</td>
</tr>
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</table>

Additional Data table S1 (separate file)
Compilation of Archean sediment sulfur isotope data.
References and Notes


19. Materials and methods are available as supplementary materials on Science Online.


