Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record

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Phanerozoic levels of atmospheric oxygen relate to the burial histories of organic carbon and pyrite sulfur. The sulfur cycle remains poorly constrained, however, leading to concomitant uncertainties in O2 budgets. Here we present experiments linking the magnitude of fractionations of the multiple sulfur isotopes to the rate of microbial sulfate reduction. The data demonstrate that such fractionations are controlled by the availability of electron donor (organic matter), rather than by the concentration of electron acceptor (sulfate), an environmental constraint that varies among sedimentary burial environments. By coupling these results with a sediment biogeochemical model of pyrite burial, we find a strong relationship between observed sulfur isotope fractionations over the last 200 Ma and the areal extent of shallow seafloor environments. We interpret this as a global dependency of the rate of microbial sulfate reduction on the availability of organic-rich sea-floor settings. However, fractionation during the early/mid-Paleozoic fails to correlate with shelf area. We suggest that this decoupling reflects a shallower paleo-oxygen boundary, primarily confined to the water column in the early Phanerozoic. The transition between these two states begins during the Carboniferous and concludes approximately around the Triassic–Jurassic boundary, indicating a prolonged response to a Carboniferous rise in O2. Together, these results lay the foundation for decoupling changes in sulfate reduction rates from the global average record of pyrite burial, highlighting how the local nature of sedimentary processes affects global records. This distinction greatly refines our understanding of the S cycle and its relationship to the history of atmospheric oxygen.
Results and Discussion

We conducted a suite of continuous-culture experiments with the model sulfate reducing bacterial strain Desulfovibrio vulgaris Hildenborough (DvH). Strain DvH is among the most well-studied sulfate reducers and is genetically tractable (36, 37). Although DvH is nominally a nonmarine strain, the concentration of sulfate in the chemostat was always near modern marine levels (28 mM) and well above known sulfate affinity constants (38). The sole electron donor (lactate) was always the limiting nutrient in these experiments and was provided at a stoichiometric 1:2 or 1:20 ratio with sulfate (Materials and Methods and SI Text).

These experiments show that MSR isotope fractionation is strongly inversely dependent on electron donor concentration (Fig. 1). In detail, mSRR follows a first-order nonlinear relationship to D (Fig. 1): as we decrease D, lactate availability and mSRR decline, whereas $^{34}_{\text{S}}$MSR increases. [The values of $^{34}_{\text{S}}$MSR and $^{33}_{\text{SGEO}}$ refer to the isotopic differences between the sulfate and sulfur from chemostat experiments (SI Text), whereas $^{33}_{\text{GEO}}$ refer to those differences calculated from sulfate and pyrite sedimentary records as time-binned averages (Dataset S1, Table S1, and Eqs. S4–S7). Further definitions are presented in SI Text.] These open-system experiments (Fig. S1 and SI Text) allow for the direct calculation of fractionation factors from the isotopic composition of output sulfate and sulfide (39), without having to apply Rayleigh distillation models addressing closed system (batch) dynamics (40).

We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40). We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40). We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40). We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40). We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40). We demonstrated conservation of elemental and isotopic mass balance throughout the entire experiment (Dataset S1) via the direct measurement of SO$_2$ gas (batch) dynamics (40).

Our data complement and significantly extend previous open-system experiments (8, 19, 27, 41, 42). Over a ~50-fold change in mSRR (Fig. 1 and Figs. S2 and S3), $^{34}_{\text{MSR}}$ ranged from 10.9 to 54.9‰ (Fig. 1A), whereas $^{33}_{\text{GEO}}$ varied from 0.5079 to 0.5144 (Fig. 1B). In addition to aiding in our understanding of environmental/geological records (discussed below), these data allow for an empirically derived fractionation limit for DvH under conditions of electron donor limitation. We apply a nonlinear regression model (43) based on a pseudo-first-order rate expression, appropriate for a reaction in which rate depends on the concentration of a single reactant (Eqs. S8 and S9) (26, 44). The results of the model illustrate the capacity of MSR to exceed the classic 47‰ limit for $^{34}_{\text{MSR}}$ (Fig. 2 and ref. 45), here suggesting an upper limit of 56 ± 2.6‰. The same nonlinear regression model (Eq. S9) predicts a minor isotope limit (in $^{33}_{\text{GEO}}$) at 0.5143 ± 0.0004. Great that our experiments were performed with an axenic population of sulfate reducers, we can definitively rule out contributions from intermediate S-oxidizing or disproportionate organisms (46). However, although the magnitudes of these fractionations exceed the canonical MSR limits ($^{34}_{\text{e}} = 47$‰), they do not reach the low-temperature equilibrium predictions between sulfate and sulfide in $^{34}_{\text{e}}$ [at 20 °C, $^{34}_{\text{e}} = 71.3$‰; ref. 40].

Decoupling the Isotopic Effects of Sulfate Reduction Rates from Pyrite Burial Rates. In modern marine sediments, OC availability is strongly tied to sedimentation rate (47–49). Faster sedimentation (such as in river deltas or on continental shelves) generally leads to more efficient delivery of OC below the depth of oxygen penetration, into the zone of sulfate reduction. (Extreme sedimentation rates deviate from this prediction and can lead to OC dilution.) The absolute flux of OC also scales directly with primary production. The balance of these processes dictates where sulfate reduction occurs with respect to the sediment–water interface, as well as how much sulfate ultimately is reduced (50). Because...
some fraction of the resulting sulfide will be buried as pyrite—with concomitant release of oxidant to the ocean-atmosphere system—it is critical to determine how the mSRR-dependent isotope fractionation ($^{34}e_{\text{MSR}}$ and $^{33}\lambda_{\text{MSR}}$) influences the S-isotopic records of pyrite relative to coeval sulfate ($^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$). Analogous to the influence of lactate on mSRR in our experimental system, the availability of greater quantities of more highly labile OC to the sulfate reduction zone in modern sediments translates to an increase in sulfate reduction rates, with a corresponding decrease in the magnitude of $^{34}e_{\text{MSR}}$ (24, 35, 51). Conversely, decreases in sulfate reduction rates down a sediment column owing to the modeled loss of OC quality and quantity are consistent with observations that $^{34}e_{\text{MSR}}$ increases (47, 52). Together these ideas describe the concept of net sedimentary sulfate reduction rate (sedSRR; moles of S per square meter per year). The sedSRR, because it integrates the depth-dependent rate through the entire zone of sulfate reduction, must encompass a depth-weighted average of the variable $^{34}e_{\text{MSR}}$ as well as be tightly linked to the initial OC delivery to the sediment–water interface. Data from the modern sea floor (18, 22, 53) confirm the expected inverse relation between bulk in situ sedSRR and the magnitude of the net sedimentary S isotope fractionation ($^{34}e_{\text{GEO}}$).

The concept of sedSRR also contains another important distinction from mSRR. In most environments, measures of microbial population density are lacking, as are measures of the metabolically available OC compounds. Our experimental system quantifies these parameters and enables direct calculation of mSRR. However, in the environment, the useful metrics are the bulk sedSRR and the global sulfate reduction rate (gSRR; moles of S per year). The sedSRR is converted to gSRR through an areal normalization and a reoxidation coefficient (1, 17); further details are presented in Table S2. It is gSRR that is necessary for determining long-term oxidant budgets and global pyrite burial.

We propose that it is possible to decouple the isotopic effects caused by variable sedSRR from the ultimate sedimentary record of S isotopes. For example, under iron-replete conditions, net pyrite burial may increase as a result of more sulfide production and/or an increased sulfide scavenging efficiency by iron (i.e., less oxidation), but at a constant sedSRR. Alternatively, pyrite burial could increase in response to a higher sedSRR, if it were driven by a higher flux of metabolizable OC to the sedimentary zone of sulfate reduction. This comparison can also be extended to include the roles for weathering and changes in the abundance of shallow-water environments (shelf area). We posit that it is possible to differentiate between these scenarios and determine the ultimate control (tectonics vs. OC) on pyrite burial at the global scale: The first case would maintain a constant $^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$, whereas varying sedSRR would be recorded by a change in the fractionation patterns.

**Interpreting Phanerozoic Records.** Phanerozoic compilations provide a context for evaluating the potential variability in sedSRR through time. Records of $^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$ from Phanerozoic sedimentary basins provide a time-series approximation of the mean isotopic difference between coeval sulfates and sulfides (Fig. 3 and Table S1) (13, 54). In parallel, we use recent estimates for the areal extent of continental shelf and abyssal ocean across Phanerozoic time (Table S1) (55, 56). Assuming that the physical processes dictating OC delivery to sediments today hold throughout the Phanerozoic, shelf environments are generally expected to be OC-rich and support higher sulfate reduction rates than deep-water settings (17, 22). This is reinforced by modern observations, where in shallow water sediments (<1,000 m deep), the area-weighted average sedSRR is 96 μmol SO$_4^{2-}$·cm$^{-2}$·y$^{-1}$, whereas in deep-water sediments (>1,000 m deep) it is $\sim$1 μmol SO$_4^{2-}$·cm$^{-2}$·y$^{-1}$.

It has long been appreciated that the $^{34}e_{\text{GEO}}$ record through the Phanerozoic carries a definitive structure (13, 57, 58)—the earliest Paleozoic has mean fractionations of $\sim$30‰ and transitions through the Permain and Triassic to a Meso-Cenozoic average near $\sim$45‰ (Fig. 3). This temporal distinction also exists for estimates of $^{33}\lambda_{\text{GEO}}$ (Fig. 3) (54). Interestingly, by comparing both isotope metrics ($^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$) with estimates of shelf area, we are able to resolve temporal patterns (Fig. 4 and Fig. S4). From our analysis of the compiled datasets (SI Text), we find that as shelf area increases, both $^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$ tend to decrease (Fig. 4 and Fig. S4). Closer examination of these data illustrates, however, that the statistical significance of these correlations rests largely on the tightly coupled behavior in the Meso-Cenozoic. In contrast, the Paleozoic has a less coherent relationship (Fig. 4 and Fig. S4). We thus interpret the multiple S isotope record as being divisible into two states offset by a transition. The first state is the early Paleozoic (540–300 Ma), where $^{34}e_{\text{GEO}}$ is lower, shelf areas are larger, and $^{33}\lambda_{\text{GEO}}$ is highly variable; the second state is the Meso-Cenozoic (200–0 Ma), where $^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$ are larger and associated with less shelf area. The transition spans at least the Permian and the Triassic (ca. 300–200 Ma).

Although there is relatively less sulfur isotopic variability in the Meso-Cenozoic compared with the Paleozoic, the interval from the Cretaceous to the present (ca. 100–0 Ma) shows increases in $^{34}e_{\text{GEO}}$ and $^{33}\lambda_{\text{GEO}}$ of 7‰ and $\sim$0.0002, respectively (Fig. 3). [The opposite trends, and by analogy the converse arguments, apply to the Mesozoic interval from 200 to 100 Ma (Fig. 3).] In our conceptual framework, this may represent a constant sedSRR...
with a decreasing shelf area (thereby decreasing both gSRR and pyrite burial), or it may represent a decrease in sedSRR with concomitant decline in shelf area. We first consider the case of constant sedSRR: Here, a ∼10% decrease in pyrite burial is required to accommodate the 7‰ increase in 34S_GEO (SI Text). Such a fluctuation in pyrite burial is reasonable. However, changes in pyrite burial cannot affect 33S_GEO, and as such, the observed variance in 33S_GEO means that a change in shelf area alone (as it relates to gSRR) cannot explain the Meso-Cenozoic S isotope record (i.e., sedSRR also must have changed).

As an alternative to a change only in shelf area, our experimental data provide a means to test the second hypothesis: variable sedSRR. The sediment data for 33S_GEO vs. 34S_GEO through the Meso-Cenozoic are statistically within the relationship extracted from our chemostat data (33S_MSR vs. 34S_MSR; Fig. S5). This suggests that the dominant control on fractionation is sulfate reduction, and that the geologic data can be interpreted in the context of where they fall on the slope-rate relationship of MSR (Fig. S5). The isotopic record of the Meso-Cenozoic corresponds to an estimated mean 83‰ variation in sedSRR if based on our experimentally determined 33S_MSR-rate relation, or a mean 43‰ variation in sedSRR if based on the 33S_MSR-rate relation [Fig. 5, Fig. S4, and SI Text]. 34S_MSR or 33S_MSR-derived mSRR is converted to sedSRR by using the Plio-Pleistocene as a reference and assuming that the scaling relationship is constant over time (SI Text).

We postulate that synergistic changes in sedSRR and shelf area work together to explain the Meso-Cenozoic S isotopic record. The pattern of change in sedSRR between 200 Ma and 0 Ma is also significantly correlated to the variability in shelf area over that same interval (Fig. 5 and Fig. S4). This implies that sedSRR and shelf area are at least partially inseparable variables, although the underlying coupling between them is not immediately clear. Importantly, an increase in sedSRR is not simply an increase in the molar flux of sulfate reduction, proportional to increased shelf area. An increase in sedSRR requires a change in the local mSRR integrated in a local sediment column. This must signal a response to availability of the limiting reactant—in this case, OC—either via its quantity or quality delivered to the sedimentary zone of sulfate reduction. We hypothesize that changes in the absolute flux of nutrients (59) to shelf environments is influencing the location and intensity of primary productivity, changing the delivery of OC to the sediments, and influencing the sedSRR. In this way, sedSRR joins the many other sedimentary biogeochemical processes known to respond to varying nutrient regimes (60). Further refining the structure of the Meso-Cenozoic record may provide critical insight into what processes are playing a prominent role in setting sedSRR, and we consider the consequences of this prediction below. However, we first consider the different patterns apparent in the Paleozoic records.

Our mechanistic understanding of the S isotope record of the last 200 Ma does not explain the 33S_GEO vs. 34S_GEO relationship of the Paleozoic. Compared with the mid-Cenozoic, the early-mid Paleozoic (540–300 Ma) records a similar variance in 34S_GEO values (∼6‰ around an era mean of ∼30‰), but three times the variability in 33S_GEO (a continuous decrease of ∼0.0008; Fig. 3). This results in a significant departure of the Paleozoic from the 3S to 34S slope-rate relationship that defines the last 200 Ma (Fig. 4 and Fig. S5). The lower overall 34S_GEO during the Paleozoic (~30‰), if paired with the lowest Paleozoic 33S_GEO from that same interval (Pennsylvanian; Fig. S4), may indeed relate to an elevated sedSRR and greater areal extent of shallower sea floor (Fig. 4). However, the failure of the Paleozoic data to plot on the 33S_MSR vs. 34S_MSR line (Fig. S5) not only undermines any confidence in applying our experimental calibration to this earlier interval (SI Text), it also is consistent with the observed weak relationship between the 34S_GEO and 33S_GEO data to shelf area (Fig. 4). This suggests that the general decoupling of 34S_GEO and 33S_GEO within the Paleozoic is not readily attributable only to changes in sedSRR. The breakdown of the observed relationships that applied in the Meso-Cenozoic suggests that, for the Paleozoic, a conceptual model that ascribes changes in 34S_GEO and 33S_GEO to a codependent relationship between sedSRR and shelf area is insufficient. Because fluctuations in 33S_GEO for the Paleozoic are largely independent of changes in 34S_GEO, there must be additional forcings.

Modeling studies illustrate how such an isotopic decoupling can be produced, either through an increase in reoxidative fluxes and associated processes (61) or through non-steady-state behavior (62). The former may seem unlikely given lower estimated oxygen partial pressure (pO2) during the first two-thirds of the Paleozoic (63). However, lower pO2 also implies a sulfate reduction zone closer to the sediment–water interface, or perhaps within the water column. Under these conditions, the delivery of sulfate to the sulfate reduction zone is no longer diffusion-limited, and as a result reoxidation reactions may be fractionally more important despite lower overall pO2. This includes both classic sulfide oxidation [at the expense of oxygen, nitrate, manganese (IV) oxides, and iron (III) oxide-hydroxides] as well as disproportionation reactions. Both have been tentatively shown to produce a negative slope of the 33S_M-A vs. 34S_M-A isotope relationship (15, 61). The shallow slope of the Paleozoic 33S_GEO vs. 34S_GEO data suggests that this opposite isotopic directionality partially is expressed and preserved (64). A change in the location and flux through reoxidation reactions is also dependent on the proximity to iron (water column vs. sediment), given that pyrite formation is a terminal sink (i.e., reoxidation inhibitor) for aqueous sulfide (65). Non-steady-state behavior of the Paleozoic S cycle is also possible and necessarily relates to seawater sulfate concentrations; however, current estimates suggest Paleozoic sulfate was abundant enough to circumvent such direct, first-order microbial control on fractionation (29). We therefore favor the explanation that a fundamentally different zonation of the paleoredox boundary in the Paleozoic decoupled the controls on S isotopes from sedimentary processes (sedSRR) and shelf area effects. Although speculative, this idea is testable using modern environments with strong redox gradients.

Equally as intriguing as the difference between the early Paleozoic and the last 200 Ma is the isotopic transition captured during the Permian and Triassic (Fig. 3 and Fig. S4). The generally weak correlations between 34S_GEO and 33S_GEO within the
Paleozoic are followed by a 15% increase in average $^{34}$S_{GEO} and a 0.0005 increase in $^{34}$S_{GEO}. This implies a major state change to the global biogeochemical S cycle across 100 Ma spanning the Permo-Triassic boundary. Complementary geochemical metrics ($\delta^{13}$C, $\delta^{34}$O, and $\delta^{34}$Sr/$\delta^{34}$S) also record major changes as Earth transitioned from the later Paleozoic to late Triassic (66). A recent statistical treatment elegantly points to the assembly and breakup of Pangaea as the explanation for this state change (56). Pangaea formed during the end of the Paleozoic and began to rift during the Triassic (67). This clearly relates to shelf area (55), but also affects primary production (OC) through the effect of continental weathering on nutrient budgets (68). Although this transition in the S cycle encapsulates the Permo-Triassic boundary, it began tens of millions of years before the Permian–Triassic extinction. Such a protracted time scale for the isotopic transition (from 300 to 200 Ma) may implicate the possible cause as a change in the ratio of S to Fe from rivers (65) associated with a Carboniferous increase in $\text{PO}_2$ (63).

Conclusions

We propose that changes in sulfate reduction rates in marine sediments, rather than global pyrite burial, dictated S isotope records over the last 200 Ma. The post-Triassic geological record suggests that sedSRR increased to a mid-Cretaceous apex and then slowed again over the last 100 Ma (Fig. 5). What, then, controlled sedSRR? During this interval our estimates of sedSRR correlate strongly with estimates for shelf area (Fig. S4B). To the degree that global shelves capture weathering fluxes and modulate nutrient delivery to primary producers, they may not only dictate the quantity and quality of organic matter reaching the zone of sulfate reduction, but they also help dictate the position of this zone with respect to the sediment–water interface. Thus, if the combination of OC delivery and sedimentation rate controls sedSRR, marine sedimentary S isotope compositions may reflect a combination of Mesozo-Cenozoic productivity and shelf area. For this relationship to hold (i.e., to maintain the direct connection to shelf area), it requires that $\text{PO}_2$ be elevated in the Meso-Cenozoic (63), because it must regulate the locus of sulfate reduction to be (on average) below the sediment–water interface. Encouragingly, this provides a testable hypothesis, applicable to high-resolution datasets from Phanerozoic sections where multiple biogeochemical isotope proxies are measurable and interpretable (69).

The Paleozoic $^{34}$S_{GEO} vs. $^{34}$S_{GEO} relationship requires significant contribution from processes other than changing OC delivery rates or total shelf area. As such, building a quantitative understanding of the Paleozoic sulfur cycle remains difficult. The disagreement between Paleozoic sedimentary data and our experimental calibration leaves room for other S metabolisms to contribute significantly to the observed S fractionations (biotic and abiotic sulfate oxidation, as well as disproportionation). Indeed, if a major difference between the Paleozoic and Meso-Cenozoic is the locality and magnitude of sulfide reoxidation—the water column in the Paleozoic vs. the sediments in the Mesozo-Cenozoic—then the delivery of reactive iron to the zone of sulfate reduction (55, 70) will determine whether most iron sulfides are syngenetic or diagenetic. This in turn influences the net pyrite burial flux and the balance of global oxidants. Further measurements and modeling are required to define these fluxes over both eras. Still, we can state with some confidence that recent multiple S isotope records do not require changes in pyrite burial over the last 200 Ma. Recent sediments carry a detailed and rich repository of small-scale microbial activities, and the magnitude of overall S fractionations likely reflects global oxidant budgets working in tandem with possible tectonic changes.

Ultimately it is the reduction potential trapped in pyrite and organic matter—rather than the rate of sedimentary sulfate reduction—that influences Earth’s surface oxidant budget on billion-year time scales. Our hypotheses suggest that pyrite burial flux (and by extension its contribution to $\text{PO}_2$) has not changed dramatically in recent times. Conversely, changes in pyrite burial flux remain a potentially critical control on the oxidant budget during the first half of the Phanerozoic. Continued measurements of geological materials (marine pyrites, sulfates, and terrestrial deposits), coupled with additional microbial experimentation and biogeochemical modeling, promise to yield further insight into the behavior of the S cycle over Earth’s history.

Materials and Methods

An experiment with Dvit in a custom-built chemostat was run with lactate as the sole electron donor and rate-limiting nutrient for sulfate reduction. The dilution rate was varied over 43-fold ($D = 0 \text{mSRR}$), with measurements of the following biological, geochemical, and isotopic parameters on all samples (Dataset S1): temperature, pH, dilution rate, cell density, sulfide production rate (the sole detectable sulfate reduction product), acetate production rate, $\lambda^{34}$S and $\lambda^{33}$S of sulfate and sulfide, and cell density. By measuring the difference between the S-isotope compositions of sulfate and sulfide, and because S-mass balance is closed with these two pools alone (i.e., no thionates detected), we may directly calculate the $\lambda^{34}_\text{MSR}$ and $\lambda^{33}_\text{MSR}$. Specific growth rate is calculated by measuring the dilution rate and the rate of change in optical density between time points (Dataset S1). The nonlinear regression models (based on pseudo-first-order kinetics) are applied to the experimental data $\lambda^{34}_\text{MSR}$ or $\lambda^{33}_\text{MSR}$ vs. mSRR, allowing us to calculate theoretical $\lambda^{34}_\text{MSRmax}$ and $\lambda^{33}_\text{MSRmax}$ along with corresponding fitting parameters, SEs, and 95% confidence interval (Fig. 2). We compare between models by examining the goodness of fit from each model (Fig. S3). The resultant expressions relate a measured isotopic fractionation (Eqs. 58 and 59) to mSRR and the fitted kinetic constant ($k$) to extract fractionation limits (e.g., $\lambda^{34}_\text{MSRmax}$ and $\lambda^{33}_\text{MSRmax}$). Relative sedSRRs are calculated with Eqs. S12–S14. Phanerozoic data compilations and isotope mass-balance models are detailed in SI Text.

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