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The triple oxygen isotope composition of marine sulfate and 130 million years of microbial control

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The triple oxygen isotope composition (Δ17O) of sulfate minerals is widely used to constrain ancient atmospheric pO2/pCO2 and rates of gross primary production. The utility of this tool is based on a model that sulfate oxygen carries an isotope fingerprint of tropospheric O2 incorporated through oxidative weathering of reduced sulfur minerals, particularly pyrite. Work to date has targeted Proterozoic environments (2.5 billion to 0.542 billion years ago) where large isotope anomalies persist; younger timescale records, which would ground ancient environmental interpretation in what we know from modern Earth, are lacking. Here we present a high-resolution record of the δ18O and Δ17O in marine sulfate for the last 130 million years of Earth history. This record carries a Δ17O close to 0‰, suggesting that the marine sulfate reservoir is under strict control by biogeochemical cycling (namely, microbial sulfate reduction), as these reactions follow mass-dependent fractionation. We identify no discernible contribution from atmospheric oxygen on this timescale. We interpret a steady fractional contribution of microbial sulfur cycling (terrestrial and marine) over the last 100 million years, even as global weathering rates are thought to vary considerably.

Significance

Stable isotopes in marine sulfate preserve information about Earth’s climate. Interpretations of geologic marine sulfate records infer changes in weathering states, microbial activity, volcanic events, and even atmospheric oxygen levels in Earth’s deep past. Here we construct a record of the minor 17O isotope in marine sulfate over the last 130 million years. In interpreting this new isotope record, we determine that the changes are consistent with a microbiologically dominated sulfate cycle over the last 100+ million years. Further, the 17O isotope composition of marine sulfate does not preserve a signal of atmospheric O2 over this interval.

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The authors declare no competing interest.

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As a means of bridging between the intellectual framework that has guided the reconstruction of Precambrian environments and that which is captured by the modern ocean, rivers, and recent past, here we report a high temporal resolution triple oxygen isotope record of marine barite (BaSO₄) minerals from 14 globally distributed sediment cores. Marine barite is precipitated in the open ocean water column during organic matter remineralization (27) and has been shown to faithfully capture the isotope composition of marine sulfate (10, 15, 26). By interpreting \( \Delta^{17}O \) alongside \( \delta^{18}O \) and \( \delta^{34}S \), together with independent estimates of critical environmental variables such as the pyritization flux, marine sulfate reservoir size, and sulfate inputs from volcanism, we provide a complete biogeochemical context for interpreting the marine sulfate oxygen isotope composition of marine sulfate across the last 130 million years.

Results

The oxygen isotope composition (\( \delta^{18}O \) and \( \Delta^{17}O \)) of seawater sulfate is inferred from measurements of marine barite minerals sampled from seafloor sediments collected from 14 globally distributed sites (SI Appendix, Table S1). Samples were screened for alteration based on scanning electron microscopy, X-ray diffraction (XRD), previously published Sr and S isotope data, and consistency with background temporal trends (see SI Appendix, Text for a full discussion). This screening affects the statistical treatment (i.e., regression CIs) but has no significant effect on the global interpretations. After filtering, samples of similar age yield statistically indistinguishable estimates for marine sulfate oxygen isotope composition; here we use a 1σ uncertainty interval based on the directly measured variability within modern core-top barite (±0.5‰ for \( \delta^{18}O \) and ±0.020‰ for \( \Delta^{17}O \)) (15, 26) as a conservative estimate. Oxygen isotope measurements from this study are compiled along with previous records of \( \delta^{34}S \) (Fig. 1A) (9–11, 15). We apply a previously calibrated offset between barite and seawater sulfate for \( \delta^{18}O \) of \(-2.7\% \) (15, 26), whereas the \( \delta^{34}S \) and \( \Delta^{17}O \) directly record seawater sulfate composition (10, 26).

The \( \delta^{18}O \) and \( \Delta^{17}O \) of seawater sulfate both vary over the last 130 million years. In the Cretaceous (older than 65 million years), marine sulfate \( \delta^{18}O \) ranges from 11 to 18‰ and is noticeably more variable than younger records (Fig. 1B and C). Over the Cenozoic (65 million years to present), the \( \delta^{18}O \) of marine sulfate decreases steadily from 14 to 8.7‰. The \( \Delta^{17}O \) composition of marine sulfate (Fig. 1C) varies noticeably relative to a 1σ analytical uncertainty of 0.020‰. Here, compositions range between −0.042‰ and +0.063‰, with an overall positive trend toward the present (slope = 0.0003; R² = 0.23; p-val < 0.0001). Across our whole dataset, \( \Delta^{17}O \) correlates negatively with \( \delta^{18}O \) (slope = −0.005; R² = 0.24; p-val < 0.0001). Over the last 40 million years, marine sulfate \( \delta^{18}O \) correlates positively with \( \delta^{34}S \) (slope = 3.07; R² = 0.63; p-val < 0.0001). Between 40 million and 90 million years, \( \delta^{18}O \) does not significantly correlate with \( \delta^{34}S \) (slope = −0.19; R² = 0.114; p-val < 0.007). We tested the covariance of marine sulfate \( \delta^{18}O \) and \( \delta^{34}S \) through time (details in SI Appendix, Text and Fig. S5).

Discussion

The most striking feature of this >100-million-year time series is the apparent lack of an atmospheric \( \text{O}_2 \) signal. Although consistent with observations in the modern and recent past, this opens the question of just how sulfate comes to adopt an oxygen isotope composition through time. Further, the mechanisms often
discussed as the drivers of the $\delta^{18}O$ in sulfate—weathering, microbial activity (specifically, microbial sulfate reduction [MSR]) and volcanism—all carry consequences for the companion $\delta^{34}S$. Thus, there is also a simple requirement of internal consistency. In what follows, we consider all these features and work toward a better understanding of both what is controlling the barite record and how it could be different from on early Earth.

(De)Coupling S and O. Isootope studies of sulfate in modern rivers, marine sediment pore waters, and microbial experiments demonstrate that sulfate $\delta^{34}S$ and $\delta^{18}O$ are often positively correlated. In a global compilation of river sulfate isotope measurements (SI Appendix, Fig. S8 and Dataset S2, n = 919), this relationship, in part, arises from the relative contributions of cold, pyrite-rich, high weathering-rate catchments (often characterized by lower-$\delta^{18}O$ waters) that have low sulfate $\delta^{34}S$ and $\delta^{18}O$. This is then balanced by warm, wet catchments with thick soil mantles (where $\delta^{18}O \gg$ the observed slope of change in global rivers (40 years ago). However, the dramatic oscillations in sulfate $\delta^{18}O$, and its depositional age. In turn, previous studies have emphasized that sulfate $\delta^{34}S$ can better be preserved in the entire marine barite record, we do not observe the expected pulses of $\Delta^{17}O > 0$ as one might predict from the $\delta^{34}S$ derived LIP hypothesis (16). This could result from several scenarios. The $\delta^{34}S$ LIP hypothesis could be incorrect or overestimate volcanic sulfur fluxes, or a primary LIP-derived $\Delta^{17}O$ was overprinted via microbial activity, bringing the observed oxygen isotope composition back toward an equilibrium with water. This latter suggestion would allow LIPs to influence the $\delta^{34}S$ but not be preserved in the oxygen isotope records.

Interpretive Framework for the $\Delta^{17}O$ of Sulfate. Traditionally, the $\Delta^{17}O$ in marine sulfate is attributed to contributions related to local water and the partial incorporation of atmospheric $O_2$ (modern $O_2$ $\Delta^{17}O = -0.501 \pm 0.011\%$ (37)). With water assumed to be near zero in $\Delta^{17}O$, all (negative) nonzero $\Delta^{17}O$ compositions are interpreted to come directly from $O_2$ (18). The variance in an observed $\Delta^{17}O$ signal is then, at the geologic formation level, interpreted as differing fractional degrees of $O_2$ incorporation or water buffering via MSR (33, 38). On longer geological timescales, variability is attributed to changes in the influence of GPP on atmospheric composition. In parallel to simple two-component mixing between $O_2$ and water, kinetic and equilibrium isotope effects like those catalyzed via MSR can influence sulfate oxygen isotope composition (38). These effects are mass dependent, meaning they lead to much smaller $\Delta^{17}O$ effects than that generated in atmospheric $O_2$. As quantifications of kinetic effects in this system are lacking, we use, instead, theoretical predictions of equilibrium isotope effects to approximate the influence of microbial sulfur cycling (38, 39). Here we find the inclusion of mass-dependent fractionation crucial to the interpretation of the smaller-magnitude $\Delta^{17}O$ changes in marine sulfate from the Cretaceous to Cenozoic.

In the context of the global biogeochemical sulfur cycle, the primary source of sulfate to the ocean is via terrestrial weathering of pyrite (FeS$_2$) and evaporite dissolution (CaSO$_4$) (40). Pyrite oxidation is traditionally thought to directly incorporate atmospheric $O_2$ (knowing also that anoxic oxidation via Fe$^{3+}$ is common), while evaporite dissolution reintroduces ancient seawater with a sulfate oxygen isotope composition reflective of its depositional age. In turn, previous studies have emphasized differing controls on the isotopic composition of riverine sulfate. The relative proportion of sulfate derived from weathered pyrite [estimated global average $\delta^{34}S = -17\%$ and $\delta^{18}O = +2\%$ (41)] to that of weathered evaporite [estimated global average $\delta^{34}S = +16\%$ and $\delta^{18}O = +12\%$ (41)] is a main factor thought to set the combined river sulfate isotope composition (23, 42, 43). More recent work demonstrates that the near-full range of $\delta^{34}S$ and $\delta^{18}O$ is also possible from weathering a single, fixed lithology, here emphasizing the role of MSR in addition to host rock in setting the composition of riverine sulfate (25). In general, MSR occurs in anoxic waters where sulfate serves as the electron acceptor during oxidation of organic matter. Reduced hydrogen sulfide can be sequestered as pyrite (FeS$_2$) where iron is available, or it can be reoxidized to sulfate, with a new oxygen isotope composition dependent on that of environmental water. 

![Fig. 2](https://www.pnas.org)
(33, 44) and the environmental oxidant. As discussed above, there is a characteristic isotope effect associated with MSR, where residual sulfate develops an enrichment in both \( \delta^{34}S \) and \( \delta^{18}O \). In marine sediment pore waters where MSR is the dominant process influencing the isotopic composition of sulfate, the residual sulfate pool can reach compositions of \( \delta^{34}S \) between +20‰ and +70‰ and \( \delta^{18}O \) from +22‰ to +26‰ higher than pure fluid \( H_2O \) (34). The maximum observed \( \delta^{18}O \) in pore water sulfate most commonly approaches the predicted equilibrium isotope offset from water (45). Enrichments in riverine sulfate are similar, but here sulfate \( \delta^{18}O \) is tied to a variable meteoric water \( \delta^{18}O \). In both settings, the simplest interpretation is that, albeit microbially catalyzed, the oxygen isotope composition of sulfate approaches that of equilibrium between sulfate and local water.

The \( \Delta^{17}O \) of sulfate can be used to test and extend the hypotheses noted above. For example, in the case where MSR is setting the oxygen isotope composition of sulfate, the \( \delta^{17}O \) and \( \delta^{18}O \) composition should evolve along a fixed slope reflective of a given mass law, noted as \( \theta \) (defined as the slope of \( \ln(\delta^{17}O/1,000 + 1) \) vs. \( \ln(\delta^{18}O/1,000 + 1) \)). This manifests as a straight line with a modestly negative slope in Fig. 3B, again where the magnitude of the imparted \( \Delta^{17}O \) is a function of \( \delta^{18}O \). Similar triple oxygen isotope relationships would result from various water–sulfate anion equilibrium effects. These could carry slight differences in \( \theta \) (see ref. 39). Conversely, if the composition of sulfate does, indeed, carry a memory of atmospheric \( O_2 \) incorporation, it is possible to deviate from these relationships. In the pyrite weathering–dominated Marsyangdi River system (25), the isotopic composition of sulfate covers a wide span (\( \delta^{18}O = -12.6‰ \) to +11.4‰ and \( \Delta^{17}O = +0.041‰ \) to +0.18‰) and is defined by a slope of \( \theta = 0.526 \pm 0.002. \) In the Mississippi River (47), sulfate oxygen isotope compositions evolve along a statistically indistinguishable slope from that of the Marsyangdi, \( \theta = 0.524 \pm 0.008. \)* It is then internally consistent that modern seawater sulfate [\( \delta^{18}O = 8.7 \pm 0.3‰ \) and \( \Delta^{17}O = 0.037 \pm 0.016‰ \)] are similar, but here sulfate \( \delta^{18}O \) is tied to a variable meteoric water \( \delta^{18}O \). Enrichments in riverine sulfate (red square, \( n = 24 \)) (5), interpreted as, in part, reflective of riverine inputs, lies statistically within the array defined by Marsyangdi River sulfate (Fig. 3). This framework naturally then extends to the entire Cenozoic–Cretaceous marine sulfate record, which again follows this same trajectory (with a statistically indistinguishable \( \theta = 0.525 \pm 0.003; \) Fig. 3). The commonality across modern river sulfate, modern seawater sulfate, and the Cretaceous to Cenozoic marine barite record suggests a shared set of controls.

If microbial metabolism (MSR and otherwise) catalyzes an isotopic equilibrium with water as predicted by \( \delta^{18}O \) studies (33), then theoretical equilibrium fractionation predictions can help refine a mechanistic understanding of the observed isotopic relationships. Quantum mechanical modeling, specifically, density functional theory, allows for calculations of specific triple oxygen isotope offsets tethered to local waters (meteoric or seawater itself) (39). The most parsimonious explanation of the Cretaceous–Cenozoic record is then contributions from both riverine sulfate and an MSR-catalyzed equilibrium with seawater. This is presented in Fig. 3B by the area bound by dashed lines and buttressed by the isotope equilibrium predictions of \( SO_2^- \) (dark gray field) and \( SO_3^-OH^- \) (light gray field). As expected, equilibrium with a seawater-like composition would fall along the right edge of this field. This result supports previous interpretations of the \( \delta^{34}S \) and \( \delta^{18}O \) records as reflecting a mixture of riverine contributions and marine recycling, a sulfur cycle under microbial control (48).

**Linking the Sulfur Cycle and Long-Term Weathering.** As noted above, perhaps the most striking feature of the data is the empirical consistency between the oxygen isotope compositions (\( \Delta^{17}O \) vs. \( \delta^{18}O \)) of riverine sulfate, modern seawater sulfate, and the record of the marine sulfate reservoir over the last 130 million years as they all relate to a microbially catalyzed equilibrium with water. The variability within the barite record can then be most simply interpreted as a balance of two contributions: that which is adopted from rivers (\( J_{riv} \)) and the degree to which MSR in marine sediments further resets the composition of sulfate (\( J_{bac} \)). This framework was initially used to describe the modern sulfate budget (5), but herein is applied to the entire Cenozoic–Cretaceous record (see SI Appendix, Text for full details). We do

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*The larger variability in the Mississippi slope is a function of less overall \( \delta^{18}O \) variability (\( \delta^{18}O = -3.6 \) to 8.8‰). The \( \Delta^{17}O \) is also slightly offset, as discussed in ref. 38. Finally, we note that the Mississippi may reflect additional mechanisms (i.e., contributions from anthropogenic sources).
so noting that this extension is imperfect, and fluxes outside of that included here could be contributing at lower levels, but try to note these uncertainties in turn.

The first question to address is the constancy of the equilibrium endmember and riverine sulfate over time; only after this can temporal changes in the sulfur cycle be meaningfully extracted and interpreted. For marine recycling and MSR, the isotopic composition of seawater H2O and/or environmental temperature may influence the oxygen isotope composition of Jbio. We do not consider any change in δ18O of seawater, but do vary temperatures between 4 °C and 15 °C, consistent with predictions for the last 100 million years (49–51). Further, the controls on isotopic equilibrium offset would also remain unchanged, together meaning that the “MSR equilibrium” end-member should remain relatively unique. In the case of rivers, it is certainly plausible that the globally integrated isotopic composition of riverine sulfate varies over time and as a function of features like exhumed lithologies, contributions from terrestrial/riverine MSR, and the isotopic composition of environmental water with which sulfate equilibrates. Although impossible to measure in the past, we propose that the heterogeneity of modern river systems serves as a useful proxy for the sort of changes one might see over time. To account for variation in δ18O of Jriv, we use the full interquartile range (25th to 75th percentiles) of a global riverine sulfate dataset (Dataset S2), or 1.3 to 10.4‰. Detailed riverine Δ17O sulfate data are, indeed, more limited, with uncertainty surrounding the source of positive Δ17O anomaly in headwater sulfates and the exact θ for MSR. As such, we move forward only using δ18O arguments, but note that the inclusion of Δ17O should be revisited as more constraints arise.

We pair this two-component mixing model with a prediction for global weathering rate over the last 100 million years (52) to probe the relationship between riverine and microbial contributions. First, the flux of riverine sulfate input to the oceans is scaled to the total sedimentary weathering flux over the last 100 million years, following ref. 3, to solve for Jriv. From our mixing, with error propagated, Jbio can be directly constrained. Notably, this leaves riverine contributions dominating the oxygen isotopic composition of marine sulfate over much of this period, with Jbio estimates between 0 and 1.2·1012 mol/yr (Fig. 4). It is only in the mid-Cretaceous, where riverine fluxes are predicted to decrease to roughly 10% of present value, that biology exerts a more prominent control. This is consistent with an enriched δ18O and a depleted Δ17O at that time, indicating more MSR-equilibrated sulfate, perhaps related to the expansion of the Cretaceous interior seaway. Across much of the Cenozoic, the riverine sulfate flux is modeled as increasing by eightfold, while Jbio is roughly constant. These results suggest that the global rate of marine sedimentary MSR is decoupled from riverine sulfate inputs to the ocean. Ultimately, the combined effects of pyrite weathering and riverine biogeochemistry (specifically, MSR) come to largely set the isotopic composition of seawater sulfate.

All of these interpretations carry significance for previous storylines for the sulfate record. A consequence of the Cenozoic–Cretaceous barite record is that it stands in contrast with the canonical interpretation of direct O2 incorporation used for Precambrian pO2/pCO2 and GPP estimates. Recall that the pyrite weathering–dominated Marsyanndi River contributes sulfate with Δ17O > 0‰, the opposite in sign than would be expected if O2 were involved (25). The evolution of this signal downstream, the result of biogeochemistry (i.e., both recycling within MSR and HS− oxidation), falls along an array that is indistinguishable from equilibrium with water. Similarly, the Cenozoic–Cretaceous record of marine barite holds no (yet) resolvable fraction of atmospheric oxygen (the brown field in Fig. 3B). The question at hand then becomes what changed between the Proterozoic and more modern sulfur cycles. Further study is needed of the processes and environments that give rise to atmospheric O2 incorporation into sulfate.

Conclusions

The triple oxygen isotope composition of marine sulfate mineral records is a powerful tool for paleoenvironmental reconstructions. Here, we employed high-fidelity marine barite records from sediment cores to inform the evolution of the sulfur cycle over the last 130 million years. The data reveal a different sulfur cycle from that captured in the Precambrian, but strikingly consistent with that observed in modern rivers and seawater sulfate as well as previous work on the S cycle (9). Here, the triple oxygen isotope composition of sulfate is governed by an evolving balance between biogeochemical recycling and weathering, with continental weathering playing an outsized role. To this end, it is also clear that atmospheric oxygen does not significantly influence the oxygen isotope composition of sulfate. However, our result pointing to the importance of rivers, and noting that terrestrial ecosystems have changed dramatically over Earth history, poses an interesting and testable hypothesis about the capacity to impart a mass-independent effect in marine seawater sulfate.

Materials and Methods

The materials and methods are detailed here; further information is provided in SI Appendix. All data used in this study are reported in Datasets S1 and S2.
Sample Collection and Chemical Methods. Marine barite samples were collected from 14 Ocean Drilling Program and Deep Sea Drilling Project sites, and seven core-top locations, across the global ocean. Barite was first extracted from sediments following a sequential dissolution method (15, 53) and further cleaned by dissolution in sodium carbonate (15, 54, 55). In the sequential dissolution method, samples were immersed in a series of solutions in order to remove various nonbarite minerals. In sequence, the sediments sat in HCl to dissolve carbonates, sodium hypochlorite to oxidize organic matter, hydroxylamine hydrochloride to remove iron and manganese oxhydroxides, concentrated HF–HNO3 mixtures with ratios of 1:2, 1:1, and 2:1 to remove silicates, and aluminum chloride in 1M HNO3 to remove fluorides. After each dissolution step, the samples were rinsed and centrifuged three times in deionized (DI) water. Finally, the remaining barite was collected onto filter paper and heated at 750 °C in the furnace for 1 h to oxidize highly refractory organic matter. Following these steps, samples were weighed and added to Teflon (polytetrafluoroethylene) vials with a 0.5 M Na2CO3 solution in a ratio of 10 mg of BaSO4 to 2 mL of Na2CO3 solution. The sample mixtures were sonicated at room temperature for 60 min and then placed in an 80 °C oven for 16 h. The sodium carbonate step was performed three times. After the third collection, barium chloride was added (10% BaCl2 in 2M HCl) until samples reached pH < 2, to precipitate BaSO4. Samples were rinsed twice in 2N HCl and three times in DI water, and dried at 60 °C.

Isotope Notation. We use standard isotope notation throughout this work. The amount of a minor isotope (34S, 18O) relative to a major isotope (32S, 16O), is expressed as

\[ \Delta Y = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1,000 \%_{\text{o}} \]  \hspace{1cm} \text{[1]}

where \( R \) is the ratio of minor to major isotope in a sample or standard material. Standards are Vienna Canyon Diablo Trilite (VCDT) for sulfur and Vienna Standard Mean Ocean Water/Standard Light Antarctic Precipitation (VSMOW/SLAP) for oxygen. The triple oxygen isotope composition of sulfate describes the ratio 17O/16O relative to 16O/16O. This relationship is expressed in the form

\[ \Delta^{17}O = \left[ \ln \left( \frac{\delta^{17}O}{1000} + 1 \right) - \delta_{\text{air}} \ln \left( \frac{\delta^{16}O}{1000} + 1 \right) \right] \cdot 1,000 \%_{\text{o}}. \]  \hspace{1cm} \text{[2]}

We use \( \delta_{\text{air}} = 0.5350 \), which is also the theoretical high-temperature limit for the linear dependence of 17O/16O versus 18O/16O (56). All measurements are expressed in units of permil.


Isotope Measurements. Purified barite was then subjected to two different forms of isotope analyses. First, ≈250 ± 50 μg of clean dry barite was weighed in triplicate into silver capsules (Elemental Micronalysie; 4 × 3.2 mm) with AgCl and glassy Cadditive in an ~2:1 mass ratio. Before measurement, weighed sample capsules were dried at 60 °C in a vacuum oven overnight. All samples were run using a high-temperature conversion elemental analyzer (TC/EA) connected to a Thermo Scientific Delta V Plus isotope ratio mass spectrometer configured in a continuous flow mode. The δ18O data were corrected to accepted values for standards International Atomic Energy Agency (IAEA)-SO-5 and National Bureau of Standards (NBS)-127 and NBS-127 (57). Samples were corrected for 1) the amount of additive, which contributes <10% to the area of the CO2 peak; 2) drift over the course of the analysis; and 3) scale compression. All isotope ratios are reported in units of permil relative to VSMOW/SLAP. The long-term weighted 1σ for the standards is <0.6‰ (n = 282). For minor oxygen isotope analyses, barite was measured according to published protocols (58). Approximately 5 mg of purified BaSO4 was reacted in a pure F2 atmosphere by heating with a 50-W CO2 laser, which liberates O2 along with other fluorinated byproducts. Sample gas was passed through multiple cryoflow steps and an in-line gas chromatograph before being introduced, as pure O2, to a Thermo Scientific MAT 253 gas source isotope ratio mass spectrometer configured in dual-inlet mode. Each δ18O and δ17O were taken as the mean of four acquisitions of 10 cycles with a target of 3,000 mV to 5,000 mV on the m/z 34 cup. The measured δ18O and δ17O values were subsequently corrected for the fractionation associated with lasering and gas purification (58). This correction uses the fraction of original SO2 collected as O2, the δ18O and δ17O from the 253 analysis, and the true δ18O sample value from TC/EA analysis. Using a set of internal standards, we report a precision on sulfate of 0.02‰ for δ17O (n = 76). Information on tank gas calibration and potential Ar interference are provided in SI Appendix, as well as details on the applied three-point calibration (air O2, University of Wisconsin Garnet 2, NBS 28).

Data Availability. All study data are included in the article and/or supporting information.

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