A revised seawater sulfate S-isotope curve for the Eocene

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\textbf{A B S T R A C T}

The sulfur isotope ratio ($\delta^{34}S$) recorded in marine barite is commonly used to estimate secular changes in the sulfur isotopic composition of seawater sulfate ($\delta^{34}SSO_4$) throughout Earth's history. The Cenozoic record demonstrates a drastic 5‰ increase in seawater $\delta^{34}SSO_4$ during the Early Eocene. However, the gradient of this excursion is based on only a few data points. Taking advantage of a much improved biostratigraphic framework, we redefine the Eocene $\delta^{34}SSO_4$ data with a new high-resolution barite based $\delta^{34}S$ record between 60 and 30 Ma. Our results show that the rise of $\delta^{34}SSO_4$ starts about 3 million years later (~53 Ma) and lasts about 9 million years longer (until 38 Ma) than previously depicted. As such, the gradient of the $\delta^{34}S$ curve is ~0.4‰/Myr. The radiogenic strontium isotopic ratio in barite suggests that some of the samples used for the original barite record are affected by diagenetic alteration.

\textbf{1. Introduction}

The Earth system has experienced significant climatic and tectonic perturbations that affected the global biogeochemical sulfur cycle (Walker, 1986; Zachos et al., 2001; Kurtz et al., 2003; Newton et al., 2004; Hurtgen, 2012; Wortmann and Paytan, 2012; Owens et al., 2013; Sim et al., 2015; Jenkyns, 2018; Yao et al., 2018). Variations in the mass and isotopic composition of seawater sulfate ($\delta^{34}SSO_4$), the main S species in seawater at present, reflect changes in the sulfur fluxes delivered to and removed from the ocean and their respective isotopic values. Since the marine sulfur reservoir is large compared to its input and output fluxes, sulfate has a long residence time (~20 million years at present; Claypool et al., 1980), and hence sulfate is homogeneously distributed in the ocean (Ree et al., 1978; Claypool et al., 1980; Paris et al., 2013; Tostevin et al., 2014; but see Yao et al., 2018).

Seawater $\delta^{34}SSO_4$ records have been derived from marine evaporites, carbonate-associated sulfate (CAS), and marine barite (Claypool et al., 1980; Strauss, 1997; Paytan et al., 1998, 2004; Kampfchulte and Strauss, 2004; Rennie et al., 2018). The evaporite record is not continuous due to the intermittent occurrence of evaporites and often plagued by poor age control (Claypool et al., 1980; Strauss, 1997).

Beginning in the 1980's CAS has been used as an archive to reconstruct seawater sulfur isotopes ratios. The ubiquitous occurrence of carbonates allows the development of continuous records and a refined understanding of secular $\delta^{34}SSO_4$ variations (Burdett et al., 1989; Kampfchulte et al., 2001; Kampfchulte and Strauss, 2004; Rennie and Turchyn, 2014) and/or pyrite oxidation during CAS processing (Marenco et al., 2008) can modify the original isotope signal.

Marine barite, on the other hand, not only provides a continuous record, but is also stable under most diagenetic conditions (Paytan et al., 1998; Paytan et al., 2004). Barite continuously forms in the water column directly from seawater (Bishop, 1988; Dehairs et al., 1990; Ganeshram et al., 2003) with little S-isotope fractionation between barite and coeval seawater sulfate (Kusakabe and Robinson, 1977). Due to its low solubility at normal marine temperature and pH conditions, authigenic barite is stable during diagenesis as long as dissolved sulfate is not depleted in the interstitial water (Dean and Schreiber, 1977; Dymond et al., 1992; Paytan et al., 1993; Paytan et al., 2002).

The most prominent feature of the Cenozoic sulfur isotope record is a pronounced 5‰ increase in the early to middle Eocene (56–47 Ma; Paytan et al., 1998; Rennie et al., 2018). Previous studies interpreted...
this shift as evidence for increased pyrite burial rates which were caused A) by a change in the dominant locus of pyrite burial from shallow shelves to open oceans (Rennie et al., 2018), B) by moving pyrite burial from brackish to euxinic environments (Kurtz et al., 2003), or C) by increasing pyrite burial as a consequence of increasing marine sulfate concentrations (51–47 Ma; Wortmann and Paytan, 2012). Here we refine the barite δ34S record for this critical time interval with new data from Ocean Drilling Program (ODP) Leg 198 Site 1211, ODP Leg 199 Site 1219, and Integrated Ocean Drilling Program (IODP) Expedition 320 Site U1333 with a temporal resolution better than 0.5 million years.

2. Geological settings and methods

Paytan et al. (1998) obtained their Eocene barite samples from Deep Sea Drilling Project (DSDP) Leg 32 Site 305, Leg 85 Site 574 Hole C and Leg 86 Site 577 in the North Pacific Ocean, and Leg 41 Site 366 in the Equatorial Atlantic. For this study, we use samples from ODP Leg 198 Site 1211 Hole A at the Shatsky Rise in the Central Basin of the North Pacific Ocean and ODP Leg 199 Site 1219 Hole A and IODP Expedition 320 Site U1333 Hole C in the Equatorial Pacific (see Table 1). Sediments in sections sampled for this study consist of nannofossil ooze with claley radiolarian ooze. Sulfate concentrations in pore water at these sites are high (26–28.5 mM) throughout the cores (Bralower et al., 2002; Lyle et al., 2002; Pälike et al., 2010). Note that the seawater sulfate concentration in the present-day open ocean is about 29 mM (Horita et al., 2002). For comparison, we also re-measure barite samples which were separated again from the same cores and sections of the previously used sites (see Table S1).

Barite samples are separated using a sequential leaching method (Paytan et al., 1993). To test the presence of diagenetic barite (Paytan et al., 1998; Erhardt et al., 2013), we examine the morphology and compositions of barite samples with a scanning electron microscope (SEM), an AURIGA FIB- FESEM Carl Zeiss SMT microscope equipped with an energy dispersive X-ray detector system (Centre for Scientific Instrumentation, University of Granada). We additionally use strontium-isotope analysis to test whether barite has been affected by diagenesis. Strontium isotope ratios (87Sr/86Sr) of barite are measured following the methods of Paytan et al. (1993). The Sr-isotope measurements are done with a Thermo Fisher Scientific Triton Plus multi-collector thermal ionization mass spectrometer (TIMS) at Ohio State University. The 87Sr/86Sr values are corrected against NBS 987 (0.710248, McArthur et al., 2012). Instrument precision for NBS 987 is ± 0.000004 (1σ).

Additional bulk sediment samples are processed for Sr-isotope analysis by first removing the carbonate fraction using ultrapure 10% acetic acid and then digesting in ultrapure nitric, hydrochloric and hydrofluoric acids on a hot plate with hydrogen peroxide.

Sulfur isotopes ratios are measured with a continuous flow isotope ratio mass spectrometer system (CF-IRMS, Finnigan MAT 253) at the Department of Earth Sciences (University of Toronto), using a Eurovector Elemental Analyzer (EA3000 series) which is coupled via a Conflo III open split interface to a Finnigan MAT 253 mass spectrometer. We weigh approximately 200 (± 5%) μg barite powder plus ~600 μg vanadium pentoxide powder (V2O5) into a tin capsule. Tin capsules are then flash combusted at 1700 °C under oxygen atmosphere to release sulfur dioxide (SO2). We calibrate sulfur isotopic values of barium sulfate using three international barium sulfate standards with respect to Vienna Canyon Diablo Troilite (VCDT; Coplen et al., 2001): NBS 127 (21.12‰), IAEA-SO-5 (0.49‰) and IAEA-SO-6 (~ −34.05‰). Repeated measurements of our in-house BaSO4 standard yield an analytical error up to 0.28‰ (1σ).

We use the Neptune database to convert biostratigraphic zones into absolute ages (Lazarus, 1994; Spencer-Cervato, 1999). This curated database provides an extensive review of microfossil occurrence records from DSDP and ODP publications for each core and recalculates ages relative to a given timescale. Here, we opt to use the GTS2012 timescale (Gradstein et al., 2012). We estimate the barite δ34S value at any given time using a "local regression smoothing" module (LOESS; Cleveland, 1979) in the statistical software package R (R Core Team, 2012). All figures use a "span" value of 0.5. The 95% confidence interval is calculated for each datum point from the standard errors returned by the LOESS function.

3. Results and discussion

Our results confirm the overall shape and magnitude of the Late Paleocene to Eocene seawater δ34SO4 curve (Fig. 1, black symbols). Specifically, the barite δ34S value decreases from 18.1% to about 17% between 60 and 53 Ma, followed by a pronounced +5% increase to a

![Fig. 1](https://example.com/figure1.png)
peak value of 22.4% at ~38 Ma, which remains relatively constant and decreases gradually to 21.3% over the next 8 million years.

It is noteworthy that between 53 and 42 Ma the barite data from DSDP Site 366 show a markedly faster increase (0.69‰/Myr; Paytan et al., 1998), which could be a result of diagenetic alteration and sample inhomogeneity. Detailed information about samples from other sites in Table S1.

3.1. Comparison with the previous barite record

Paytan et al. (1998) measured the barite δ34S using offline conversion to sulfur hexafluoride (SF6), whereas our study uses a continuous flow method with barite conversion to SO2. We thus reanalyzed the original barite samples used by Paytan et al. (1998) and find a good agreement between both data sets (Fig. S1). The observed discrepancies between the two data sets are generally less than 1‰ (Fig. 2). Up to 0.4‰ differences can be explained by the isotopic inhomogeneity of the reference material Canyon Diablo Troilite (CDT; Beaudoin et al., 1994; Krouse and Coplen, 1997; Ding et al., 2001) used by Paytan et al. (1998), and the remainder is possibly caused by the different analytical approach and analytical uncertainty in the biostратigraphy of DSDP Site 366.

3.2. SEM analysis

SEM images show that the size of most barite crystals in Site 366 sediments is smaller than 5 μm (Fig. 3) and that their ellipsoidal morphology is consistent with the authigenic barite crystals that precipitate in the water column (Paytan et al., 2002). However, a few larger crystals (e.g., the circled crystal in Fig. 3) can also be seen in samples separated from sediments of 53 to 42 Ma, which are not typical of pelagic barite and have likely formed by diagenetic processes.

3.3. Sr-isotope analysis

We use Sr analysis to further explore the nature of the Site 366 barites in Cores 10 to 38 (Table S2). Our results show that the Eocene 87Sr/86Sr ratios vary between 0.70760 and 0.70900 (Fig. 4). With the exception of one sample from Section 10-2, the 87Sr/86Sr ratios of barites at the upper part of the record (e.g., Sections 12-2, 16-2, 18-2) are generally consistent with contemporaneous seawater values. However, barites from the lower part of the record show generally elevated 87Sr/86Sr ratios with two exceptionally high values measured in samples from Sections 23-2 and 33-2.
Indeed, the Sr-isotope data unequivocally suggest that some of the barites in Site 366 are not of authigenic marine origin, and these samples are specifically at the same interval as those with anomalous δ34S values seen in Fig. 1. The idea that the barite appears pristine in the SEM image (Fig. 3) but is affected by cryptic diagenesis, is further supported by the findings of Henkel et al. (2012), who show that barite crystals of similar size and appearance can have different origins.

3.4. Comparison between barite and CAS

Rennie et al. (2018) publish a Cenozoic seawater δ34S record based on carbonate-associated sulfate (CAS). Unlike previous studies, they base their record on single-species foraminifera and correct the data for offsets between species related to vital-effects (Rennie et al., 2018). Our barite record (Fig. 5, black symbols) tracks the species-adjusted CAS record (Fig. 5, red symbols) faithfully with respect to the magnitude and duration of the excursion. After mapping both data sets onto the same timescale (Lazarus, 1994; Spencer-Cervato, 1999; Gradstein et al., 2012), the previously observed 1‰ offset between CAS and barite data (Rennie et al., 2018), now extends past the Oligocene well into the Paleocene (Fig. 5; also see Fig. 1 in Rennie et al., 2018).

At present, the cause for this offset is unclear, but we can think of at least two possibilities. A) There is early diagenesis of the foraminiferal tests in sediments (e.g., Rennie and Turchyn, 2014). However, the fact that the observed offset is constant across a variety of species ranges and locations and for at least 60 million years back in time, suggests that this is unlikely. B) The formation of CAS may involve species-specific S-isotope fractionation. Indeed, Rennie et al. (2018) report species-specific offsets between seawater and core-top data using G. menardii, and up to ± 1‰ differences of the CAS δ34S between different foraminiferal species of the same age. Extrapolation of this offset back in time requires careful analysis of overlapping δ34S data for different foraminiferal species of the same age. Extrapolation of this offset back in time requires careful analysis of overlapping δ34S data for different foraminiferal species. A closer examination of the CAS data by Rennie et al. (2018) shows that the G. menardii data only extend back to 5.5 Ma, and the calibration for older δ34S rests on a single sample where G. menardii overlaps with D. venezuelana. Based on this datum point, Rennie et al. (2018) conclude that D. venezuelana has no offset relative to the coeval seawater and correct all other older foraminiferal species against this datum point. It thus seems at least possible that the 1‰ offset for all samples older than 5.5 Ma is simply a calibration artifact.

Clearly, more work is required to establish the precise deep-time relation between the CAS and barite δ34S record.

3.5. Implications to the Eocene sulfur cycle

The much-expanded data density between 55 and 35 Ma, allows for a much better biostratigraphic anchoring of the changing S-isotope ratio. Our dataset suggests that the onset of the rise starts about 3 million years later (~53 vs. 56 Ma) and ends about 9 million years later (38 vs. 47 Ma) than previously portrayed. In other words, the
gradually smaller, and changes occur over a 15-Myr period, rather than 9 million years. This may require revaluations of existing hypotheses which aim to explain the rise in the seawater S-isotope ratio. For instance, Wortmann and Paytan (2012) suggest that an intensified basin-scale evaporite dissolution event contributes approximately $2.0 \times 10^{19}$ mol CaSO$_4$ between 51 and 47 Ma. Using our new data, we can revise these estimates to $1.7 \times 10^{19}$ mol CaSO$_4$ between 51 and 42 Ma. Since the timing of the India-Eurasia collision is uncertain, the new timing is still consistent with this hypothesis but requires modifications to the flux estimate.

Alternatively, Kurtz et al. (2003) explain the rapid change in the marine $S$ isotopic ratio as a result of increased pyrite burial during the marine transgression in the Ypresian, whereas our new data show that the increase in marine $S$-isotope ratios is much broader (i.e., from the Ypresian to Lutetian). We also note that thus, the increasing $S$-isotope ratios correlate with a long-term trend of falling sea levels (Miller et al., 2005). Further revaluations of this hypothesis and other potential explanations to the change in the Eocene are needed.

4. Conclusion

This study significantly expands the barite $\delta^{34}S$ data set for the Cenozoic. The higher data density as well as the increase in sampling locations, results in much better-resolved biostratigraphy. This is particularly true for the most prominent feature of the marine S-isotope record - the Eocene $5\%$ increase. We show that the onset of this rise starts about 3 million years later than previously portrayed (~53 vs. 56 Ma) and lasts about 9 million years longer (38 vs. 47 Ma). This has two implications: A) the gradient of the S-isotope increase is now reduced to 0.4%/Myr (previously 0.69%/Myr), which will affect flux estimates used in geochemical models; B) the changing timing of the event requires revaluations of the geological processes that could have triggered this change.

While it has long been known that diagenetic fronts can drastically alter the isotope ratios recorded in barite, we do show that cryptic diagenesis, which is undetectable by SEM imaging, can affect the S isotope ratio recorded in barite as well. Moreover, our data also suggest that Sr-isotope analysis is a sensitive tool to detect these alterations. Finally, we show that the barite and CAS derived records track each other with astounding fidelity, supporting the idea that both archives record the actual seawater $S$-isotope ratio. The reason for the systematic 1% offset for samples older than 5.5 Ma is currently unclear and requires further investigation.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2019.119382.


