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Reconstruction of secular variation in seawater sulfate concentrations

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Abstract. Long-term secular variation in seawater sulfate concentrations ([SO$_{4}^{2-}$]$_{SW}$) is of interest owing to its relationship to the oxygenation history of Earth’s surface environment. In this study, we develop two complementary approaches for quantification of sulfate concentrations in ancient seawater and test their application to late Neoproterozoic (635 Ma) to Recent marine units. The “rate method” is based on two measurable parameters of paleomarine systems: (1) the S-isotope fractionation associated with microbial sulfate reduction (MSR), as proxied by $\Delta^{34}$S$_{CAS-PY}$, and (2) the maximum rate of change in seawater sulfate, as proxied by $\partial^{34}$S$_{CAS}$/$\partial t$ (max). The “MSR-trend method” is based on the empirical relationship of $^{1}$34S$_{CAS-PY}$ to aqueous sulfate concentrations in 81 modern depositional systems. For a given paleomarine system, the rate method yields an estimate of maximum possible [SO$_{4}^{2-}$]$_{SW}$ (although results are dependent on assumptions regarding the pyrite burial flux, $F_{PY}$), and the MSR-trend method yields an estimate of mean [SO$_{4}^{2-}$]$_{SW}$. An analysis of seawater sulfate concentrations since 635 Ma suggests that [SO$_{4}^{2-}$]$_{SW}$ was low during the late Neoproterozoic (< 5 mM), rose sharply across the Ediacaran–Cambrian boundary (~5–10 mM), and rose again during the Permian (~10–30 mM) to levels that have varied only slightly since 250 Ma. However, Phanerozoic seawater sulfate concentrations may have been drawn down to much lower levels (~1–4 mM) during short (< ~2 Myr) intervals of the Cambrian, Early Triassic, Early Jurassic, and Cretaceous as a consequence of widespread ocean anoxia, intense MSR, and pyrite burial. The procedures developed in this study offer potential for future high-resolution quantitative analyses of paleo-seawater sulfate concentrations.

1 Introduction

Oceanic sulfate plays a key role in the biogeochemical cycles of S, C, O, and Fe (Canfield, 1998; Lyons and Gill, 2010; Halevy et al., 2012; Planavsky et al., 2012). For example, > 50 % of organic matter and methane in marine sediments is oxidized via processes linked to microbial sulfate reduction (MSR) (Jørgensen, 1982; Valentine, 2002). At a concentration of ~29 mM in the modern ocean, sulfate is the second most abundant anion in seawater (Millero, 2005). Its concentration is an important proxy for seawater chemistry and the oxidation state of the Earth’s atmosphere and oceans (Kah et al., 2004; Johnston, 2011).

Although there is broad agreement that seawater sulfate concentrations have increased through time, the history of its accumulation remains poorly known in detail. Archean and Early Proterozoic oceans are thought to have had very limited sulfate inventories (< 200 µM), as implied by small
degrees of sulfate–sulfide and mass-independent S-isotope fractionation (Shen et al., 2001; Strauss, 2003; Farquhar et al., 2007; Adams et al., 2010; Johnston, 2011; Owens et al., 2013; Luo et al., 2015). The accumulation of atmospheric O$_2$ during the “Great Oxidation Event” (∼2.3–2.0 Ga; Holland, 2002; Bekker et al., 2004) is thought to have resulted in a long-term increase in seawater sulfate concentrations (Canfield and Raiswell, 1999; Canfield et al., 2007; Kah et al., 2004; Fike et al., 2006). However, this increase was probably not monotonic and declines in pO$_2$ may have resulted in one or more seawater sulfate minima between ∼1.9 and 0.6 Ga (Planavsky et al., 2012; Luo et al., 2015). Estimates of Phanerozoic seawater sulfate concentrations are uniformly higher, although there is no consensus regarding exact values. Fluid inclusion data yielded estimates of ∼10 to 30 mM for most of the Phanerozoic (Horita et al., 2002; Lowenstein et al., 2003, 2005). However, recent S-isotope studies have modeled concentrations as low as ∼1–5 mM during portions of the Cambrian, Triassic, Jurassic, and Cretaceous (Wortmann and Chernyavsky, 2007; Adams et al., 2010; Luo et al., 2010; Gill et al., 2011a, b; Newton et al., 2011; Owens et al., 2013; Song et al., 2014), and a recent marine S-cycle model yielded low concentrations (<10 mM) for much of the Cretaceous and early Cenozoic before a rise to near-modern levels at ∼40 Ma (Wortmann and Paytan, 2012).

Here, we develop two approaches for quantitative analysis of seawater sulfate concentrations ([SO$_4^{2-}$]$_{SW}$) in paleo-marine systems. The first method calculates a maximum possible [SO$_4^{2-}$]$_{SW}$ based on a combination of two parameters that are readily measurable in most paleo-marine systems: (1) the S-isotope fractionation between cogenetic sedimentary sulfate and sulfide (δ$^{34}$S$_{CAS-PY}$), and (2) the maximum observed rate of variation in seawater sulfate δ$^{34}$S (δ$^{34}$S$_{CAS}$ / ∂t). This rate-based method is an extension of earlier modeling work by Kump and Arthur (1999), Kurtz et al. (2003), Kah et al. (2004), Bottrell and Newton (2006), and Gill et al. (2011a, b). The second approach yields an estimate of mean seawater [SO$_4^{2-}$] based on an empirical relationship between δ$^{34}$S$_{CAS-PY}$ and aqueous sulfate concentrations (the “MSR trend”) in 81 modern depositional systems. Conceptually, the MSR-trend method is related to the fractionation relationship given in Habicht et al. (2002, their Fig. 1). Although some earlier studies have made qualitative assessments of paleo-seawater [SO$_4^{2-}$], the significance of our methodology is that the [SO$_4^{2-}$] of ancient seawater can be quantitatively constrained as a function of measurable sediment parameters and empirical fractionation relationships.

We fully recognize that the marine sulfur cycle is controlled by myriad factors, many of which are only now coming to light thanks to detailed field and laboratory studies, and that not all such influences can be thoroughly considered and accommodated in the present study. While acknowledging the complexity of the sulfur cycle, this study attempts to identify broad first-order trends that potentially transcend these diverse influences and that are robust over significant intervals of geologic time. Our ultimate goal is to generate useful approximations of the long-term history of sulfate in the ocean. Our results suggest that large-scale empirical relationships may exist that are not highly sensitive to influences such as organic substrate type, sulfate reduction rates, strain-specific fractionation, and other factors. We envision such local influences, as they become more completely understood, being mapped onto, and thus integrated with, the broad first-order relationships documented in this study.
Methods of modeling paleo-seawater sulfate concentrations

2.1 The rate method

The marine S cycle has a limited number of fluxes with fairly well-defined S-isotope ranges (Holser et al., 1989; Canfield, 2004; Bottrell and Newton, 2006), making it amenable to analysis through modeling (e.g., Halyo et al., 2012). Sub-aerial weathering yields a riverine sulfate source flux ($F_Q$) of $\sim 10 \times 10^{13}$ g yr$^{-1}$ with an average $\delta^{34}$S of $\sim +6\%$, which is significantly lighter than the modern seawater sulfate $\delta^{34}$S of $+20\%$. Sulfate is removed to the sediment either in an oxidized state, as carbonate-associated sulfate (CAS) or evaporite deposits, or in a reduced state, mainly as FeS or FeS$_2$. The oxidized sink has a flux ($F_{\text{EVAP}}$) of $\sim 6 \times 10^{13}$ g yr$^{-1}$ with a S-isotopic composition that closely mimics that of coeval seawater ($\Delta^{34}$S$_{\text{SW-EVAP}}$ of $\sim 4$ to $0\%$). The reduced sink has a flux ($F_{\text{PY}}$) of $\sim 4 \times 10^{13}$ g yr$^{-1}$ with a composition that characteristically shows a large negative fractionation relative to coeval seawater ($\Delta^{34}$S$_{\text{CAS-PY}}$ of $\sim 30$ to $60\%$; Habicht and Canfield, 1997; Canfield, 2001; Brüchert, 2004; Brunner and Bernasconi, 2005). Secular variation in seawater sulfate $\delta^{34}$S is mainly due to changes in the relative size of the sink fluxes, with increasing (decreasing) burial of pyrite relative to sulfate leading to more (less) $^{34}$S-enriched seawater sulfate (Holser et al., 1989; Bottrell and Newton, 2006; Halyo et al., 2012).

The rate method calculates a maximum seawater sulfate concentration ($[\text{SO}_4^{2-}]$$_{\text{SW}}$(max)) based on two parameters: (1) S-isotope fractionation between coegenetic sedimentary sulfate and sulfide ($\Delta^{34}$S$_{\text{CAS-PY}}$, as proxied by $\Delta^{34}$S$_{\text{CAS-PY}}$) and (2) the maximum observed rate of variation in seawater sulfate isotopes ($\partial\delta^{34}$S$_{\text{SO}}$/∂t(max), as proxied by $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max)) (Fig. 1). Rates of isotopic change for seawater sulfate are given by

$$\partial\delta^{34}$S$_{\text{CAS}}$/∂t = ((F_Q \times \Delta^{34}$S$_{\text{SO}-\text{SW}}$) - (F_{PY} \times \Delta^{34}$S$_{\text{CAS-PY}}$))/M_{SW},$$

where $F_Q \times \Delta^{34}$S$_{\text{SO}-\text{SW}}$ is the flux-weighted difference in the isotopic compositions of the source flux and seawater (SW), $F_{PY} \times \Delta^{34}$S$_{\text{CAS-PY}}$ is the flux-weighted difference in the isotopic compositions of the reduced-S sink flux and seawater, and $M_{SW}$ is the mass of seawater sulfate. The full expression represents the time-integrated influence of the source and sink fluxes on seawater sulfate $\delta^{34}$S. The maximum possible rate of change in the sulfur isotopic composition of seawater sulfate is attained when the source flux goes to zero:

$$\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max) = F_{PY} \times \Delta^{34}$S$_{\text{CAS-PY}}$/M_{SW}.  \quad (2)$$

Reorganization of this equation allows calculation of a maximum seawater sulfate concentration from measured values of $\Delta^{34}$S$_{\text{CAS-PY}}$ and $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max):

$$M_{SW} = k_1 \times F_{PY} \times \Delta^{34}$S$_{\text{CAS-PY}}$/\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max), \quad (3)$$

$$[\text{SO}_4^{2-}]_{\text{SW}}$(max) = $k_2 \times M_{SW}$, \quad (4)$$

where $k_1$ is a unit-conversion constant equal to $10^6$ and $k_2$ is a constant relating the mass of seawater sulfate to its molar concentration that is equal to $2.22 \times 10^{-26}$ mM g$^{-1}$. Kah et al. (2004) assumed $F_{PY} = 10 \times 10^{13}$ g yr$^{-1}$, which is the total sink flux for modern seawater sulfate, in order to model $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max). While this may be appropriate for intervals of widespread euxinia in the global ocean, $F_{PY} = 4 \times 10^{13}$ g yr$^{-1}$ (i.e., the modern sink flux) may better represent intervals with well-oxygenated oceans in which the sink fluxes of sulfate and pyrite S are both substantial (Fig. 1). Assuming $F_{PY} = 4 \times 10^{13}$ g yr$^{-1}$ and values of $\Delta^{34}$S$_{\text{CAS-PY}}$ and $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max) potentially representative of modern marine systems (e.g., 35 and 1.1% Myr$^{-1}$, respectively), Eq. 3 yields the modern seawater sulfate mass of $M_{SW} = 1.3 \times 10^{21}$ g and Eq. (4) yields the modern seawater sulfate concentration of $\sim 29$ mM.

Relationships among the rate-method parameters are illustrated in Fig. 1 for $\Delta^{34}$S$_{\text{CAS-PY}}$ from 1 to 100% (ordinal scale) and for discrete values of $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max) ranging from 1 to 100% Myr$^{-1}$ (diagonal lines). $[\text{SO}_4^{2-}]_{\text{SW}}$ increases linearly with increasing $\Delta^{34}$S$_{\text{CAS-PY}}$ (at constant $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max)) and decreases linearly with increasing $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max) (at constant $\Delta^{34}$S$_{\text{CAS-PY}}$). The measured maximum $\partial\delta^{34}$S$_{\text{CAS}}$/∂t for a paleomarine unit is generally smaller than the theoretical maximum $\partial\delta^{34}$S$_{\text{SO}}$/∂t because the latter can be achieved only when the source flux of seawater sulfur is reduced (at least transiently) to zero (Kah et al., 2004), which does not routinely occur in nature. As a consequence, rate-method estimates of $[\text{SO}_4^{2-}]_{\text{SW}}$ are generally larger than actual seawater sulfate concentrations, so Eq. 4 yields the maximum likely $[\text{SO}_4^{2-}]_{\text{SW}}$ for a paleomarine unit of interest. This outcome can be illustrated by a calculation for the modern ocean, using $\Delta^{34}$S$_{\text{CAS-PY}}$ of $\sim 30$–$60\%$ and $\partial\delta^{34}$S$_{\text{CAS}}$/∂t(max) of $\sim 0.7$% Myr$^{-1}$ (based on the Cenozoic seawater sulfate $\delta^{34}$S record; Paytan et al., 1998). These inputs yield $[\text{SO}_4^{2-}]_{\text{SW}}$(max) values between $\sim 40$ and $80$ mM, which is modestly larger than the actual modern $[\text{SO}_4^{2-}]_{\text{SW}}$ of $\sim 29$ mM (Fig. 1). Overestimation of modern $[\text{SO}_4^{2-}]_{\text{SW}}$ is due to measured $\partial\delta^{34}$S$_{\text{CAS}}$/∂t values for the Cenozoic ($<0.7$% Myr$^{-1}$) being lower than the theoretical maximum for modern seawater ($\sim 1$–$2$% Myr$^{-1}$; Fig. 1). This situation is probably typical of marine units of all ages – measured rates of $\delta^{34}$S variation will be lower than the theoretical maximum because the source flux of sulfur to the oceans rarely if ever goes to zero.

The results of the rate method depend on the parameterization of the pyrite burial flux ($F_{PY}$). This method is likely to yield an accurate estimate of seawater sulfate concentrations only if $F_{PY}$ is inversely proportional to the residence time of sulfate in seawater ($t_{SO_4}$), which basically requires the ma-

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rine sulfate system to be in equilibrium. If a value for \( F_{PY} \) is chosen that is much larger or smaller than the equilibrium flux, then seawater sulfate concentrations will be overestimated or underestimated, respectively (see Appendix A1 for extended discussion). Second, the pyrite burial flux has almost certainly varied through time. Since pyrite burial flux is a component of Eqs. (2) and (3), variations in this parameter will influence calculated seawater sulfate concentrations. Phanerozoic variation in pyrite burial fluxes has been calculated in several global C–S-cycle models (e.g., Berner, 2004; Bergmann et al., 2004), although the details remain unpublished. We therefore explored the effects of variable pyrite burial fluxes on seawater sulfate estimates by using the [SO\(_4^{2-}\)]\(_{SW} \)–dependent pyrite burial flux relationship of Wortmann and Chernyavsky (2007). This procedure yielded Phanerozoic [SO\(_4^{2-}\)]\(_{SW} \) estimates that are close (± 10 %) to our original values (see Appendix A2 for extended discussion).

### 2.2 The MSR-trend method

An alternative approach to constraining ancient seawater sulfate concentrations is based on an empirical relationship to S-isotope fractionation associated with microbial sulfate reduction (\( F_{MSR} \)). We evaluated this relationship by compiling \( \Delta^{34}S_{sulfate-sulfide} \) and [SO\(_4^{2-}\)]\(_{aq} \) data for 81 modern depositional systems (Supplement Table S1; cf. Habicht et al., 2002). Each system was classified (1) by salinity, as freshwater (< 10 PSU), brackish (10–30 PSU), marine (30–40 PSU), or hypersaline (> 40 PSU; note that PSU stands for practical salinity units), and (2) by redox conditions, as oxic or euxinic depending on whether the chemocline was within the sediment or the water mass, respectively.

In the interests of applying uniform criteria to the generation of this data set, we followed a specific protocol. First, we adopted a modern seawater sulfate concentration of 2775 mg L\(^{-1} \) or 28.9 mM at an average seawater density of 1025 kg m\(^{-3} \) (Millero, 2005). For brackish marine water masses, we used measured aqueous sulfate concentrations or, if unavailable, estimated dissolved sulfate concentrations from salinity data:

\[
[SO_4^{2-}] = [SO_4^{2-}]_{SW} \times S/S_{SW}. \tag{5}
\]

where [SO\(_4^{2-}\)] and S are the sulfate concentration and salinity of the water mass of interest, respectively, and S\(_{SW} \) is the salinity of average seawater (35 PSU). Second, we used only in situ water-column measurements of aqueous sulfate \( \delta^{34}S \). Third, we used sulfide \( \delta^{34}S \) values either from aqueous H\(_2\)S or from sedimentary sulfide proxies located within a few centimeters of the sediment–water interface, thus avoiding sedimentary sulfides that might be significantly \( ^{34}S \)-enriched owing to sulfate-limited burial conditions (Kaplan et al., 1963; Canfield et al., 1992). However, some variation in \( \delta^{34}S \) among syngentic early-formed sedimentary sulfides is common. Acid-volatile sulfur (AVS, consisting mainly of monosulfides; Rickard, 1975) tends to have a lighter sulfur isotopic composition, closer to that of the instantaneously generated H\(_2\)S at a given sediment depth, because it converts quickly to pyrite (Zaback and Pratt, 1992; Lyons, 1997). On the other hand, organic sulfur tends to be isotopically heavier owing to late-stage sulfurization of organic matter or, possibly, to fractionations associated with sulfur uptake (Zaback and Pratt, 1992; Werne et al., 2000, 2003, 2008). Although our data set includes a combination of pyrite, AVS, total reduced sulfur (TRS), and aqueous H\(_2\)S sulfur isotopic data owing to variations in sample analysis among published studies, it is weighted toward pyrite data (\( n = 48 \) out of a total of 81; Supplement Table S1). An analysis of \( \Delta^{34}S_{sulfate-sulfide} \) variation among the multiple sulfide sources used in our study revealed no statistically significant differences (see Appendix A3). Because pyrite \( \delta^{34}S \) is frequently analyzed in paleomarine studies, our MSR trend (Fig. 2) should be widely applicable to an analysis of paleo-seawater sulfate concentrations. One caveat in this regard is that \( \Delta^{34}SCAS-PY \) estimates for paleomarine units should be based on syngentic or early diagenetic pyrite, as determined by well-established petrographic and geochemical criteria (e.g., Wilkin et al., 1996; Lyons and Severmann, 2006).

The protocol described above produced an internally consistent data set (Table S1) that exhibits a pronounced relationship between \( \Delta^{34}S_{sulfate-sulfide} \) and [SO\(_4^{2-}\)]\(_{aq} \) (Fig. 2a). Regression of \( \Delta^{34}S_{sulfate-sulfide} \) on [SO\(_4^{2-}\)]\(_{aq} \) yields a strong positive relationship (\( r = +0.90, \ p(\alpha) < 0.01 \)). The trend represents an increase in \( \Delta^{34}S_{sulfate-sulfide} \) from \( \sim 4–6\% \) at 0.1 mM to \( \sim 30–60\% \) at 29 mM (i.e., modern seawater [SO\(_4^{2-}\)]). \( \Delta^{34}S_{sulfate-sulfide} \) appears to peak at [SO\(_4^{2-}\)]\(_{aq} \) of 15–20 mM, with a mean value \( \sim 5–10\% \) greater than for [SO\(_4^{2-}\)]\(_{aq} \) of 29 mM , but this effect is small relative to the overall relationship between \( \Delta^{34}S_{sulfate-sulfide} \) and [SO\(_4^{2-}\)]\(_{aq} \), and we did not factor it separately into the regression analysis. For hypersaline environments in which [SO\(_4^{2-}\)]\(_{aq} \) > 29 mM, \( \Delta^{34}S_{sulfate-sulfide} \) does not continue to rise but, rather, shows roughly the same range as for modern seawater (Fig. 2a). Finally, we analyzed the data by redox environment and found only minor and statistically insignificant differences between oxic and euxinic settings (note that hypersaline environments were not included in this analysis). The distributions of the oxic and euxinic data sets show broad overlap (Fig. 2a), so benthic redox conditions appear to exhibit no discernible influence on the relationship of \( \Delta^{34}S_{sulfate-sulfide} \) to [SO\(_4^{2-}\)]\(_{aq} \).

Our analysis demonstrates that a strong relationship exists between \( F_{MSR} \) and [SO\(_4^{2-}\)]\(_{aq} \) in natural aqueous systems (\( r = +0.90, \ p(\alpha) < 0.01; \) Fig. 2a). Our results are similar to, although more linear and more statistically robust than, those reported by Habicht et al. (2002) on the basis of culture experiments. We recognize that there are multiple environmental and physiological controls on fractionation by sulfate reducers (see Sect. 3), and that under certain natural and ex-
The apparent breakdown of this relationship in hypersaline environments is too small \((n = 75)\) yield a linear regression (solid line; \(y = 0.42x + 1.10\) in log units) with \(r = +0.90\) and a limited uncertainty range \((0.90 < p < 0.01)\). The MSR trend thus represents a process with an order of reaction \((n)\) of 0.42 and a rate constant \((k)\) of 1.10 (cf. Jones et al., 2007). The gray field encloses most of the data from Table S1 and highlights the overall trend. Analysis of the data set by redox environment yielded statistically indistinguishable trends for oxic \((y = 0.48x + 1.10; r = +0.88, n = 44, p(\alpha) < 0.01)\) and euxinic settings \((y = 0.40x + 1.06; r = +0.89, n = 31, p(\alpha) < 0.01)\). The Habicht et al. (2002) data set of 60 sulfate-reducing microbial (SRM) culture values is shown for comparison; these data have been converted to log–log format, and data points that are off-scale \((\text{i.e., } \Delta^{34}_{\text{S-sulfate-sulfide}} < 1\%)\) are shown by triangles on the abscissa. Neither the six hypersaline environments in our data set (red symbols) nor the Habicht et al. data (small open circles) were included in the regression analysis. (b) Use of the MSR trend to estimate paleo-seawater \([\text{SO}_4^{2-}]_{\text{sw}}\). Measured values of \(\Delta^{34}_{\text{S-sulfate-sulfide}}\) are projected from the ordinal scale to the MSR trend and then to the abscissa. Note that uncertainty in the slope of the MSR trend is accommodated by projection to the upper uncertainty limit for \(\Delta^{34}_{\text{S-sulfate-sulfide}}\) maxima and to the lower uncertainty limit for \(\Delta^{34}_{\text{S-sulfate-sulfide}}\) minima. The vertical black bar at \([\text{SO}_4^{2-}]_{\text{sw}} = 1.45\) \((\text{i.e., the modern seawater sulfate concentration of 29 mM})\) represents the range of \(F_{\text{MSR}}\) variation among modern marine SRM communities.

The upper and lower uncertainty limits for estimates of seawater \([\text{SO}_4^{2-}]_{\text{sw}}\) based on this relationship are

\[
\log[\text{SO}_4^{2-}] = \left(\log(\Delta^{34}_{{\text{S-CAS-PY}}}) - 1.18\right) / 0.40 \quad \text{(upper limit)},
\]

\[
\log[\text{SO}_4^{2-}] = \left(\log(\Delta^{34}_{{\text{S-CAS-PY}}}) - 1.02\right) / 0.44 \quad \text{(lower limit)}.
\]

In order to account for uncertainties in \(\Delta^{34}_{\text{S-CAS-PY}}\) as well as the MSR regression, estimates of minimum \([\text{SO}_4^{2-}]_{\text{sw}}\) should make use of minimum \(\Delta^{34}_{\text{S-CAS-PY}}\) values in combination with the upper uncertainty limit equation (Eq. 7), and estimates of maximum \([\text{SO}_4^{2-}]_{\text{sw}}\) should make use of maximum \(\Delta^{34}_{\text{S-CAS-PY}}\) values in combination with the lower uncertainty limit equation (Eq. 8; Fig. 2b).

3 Controls on fractionation by microbial sulfate reducers

The biogeochemical nature of the MSR process and its associated S-isotope fractionations have been extensively investigated in earlier studies. Sulfate reducers preferentially utilize sulfate containing \(^{32}\text{S}\) during dissimilatory reduction to hydrogen sulfide in conjunction with the anaerobic decay
of organic matter (Kaplan, 1983; Canfield, 2001; Bradley et al., 2011). The exact controls on this isotopic discrimination continue to be a topic of intense debate. The paradigmatic view is that this fractionation is mainly a kinetic effect associated with the rate-limiting step for intracellular sulfate processing, although it is known that fractionation also may accompany sulfate transport across the cell membrane (Rees, 1973; Dettmers et al., 2001; Brüchert, 2004; Bradley et al., 2011). The kinetic effect is thought to be dependent on aqueous sulfate concentrations, with substantially larger fractionations associated with \[\text{SO}_4^{2-}\]aq \(>\sim 200\mu M\) (Habicht et al., 2002; Gomes and Hurtgen, 2013; but see Canfield, 2001, for a counter example). Rees (1973) proposed a maximum discrimination of 46‰, but the theoretical basis for this value was reassessed by Brunner and Bernasconi (2005). Recent studies have documented \(F_{\text{MSR}}\) as large as 66‰ in culture experiments (Sim et al., 2011a) and 78±80‰ in natural systems (Rudnicki et al., 2001; Wortmann et al., 2001; Canfield et al., 2010). Even larger fractionations have been reported, but these are generally considered to be the result of multiple-stage disproportionation of intermediate-oxidation-state sulfur compounds (Canfield and Thamdrup, 1994).

Investigations of natural and experimental systems have documented a number of additional controls on \(F_{\text{MSR}}\). One of the most important controls is \(f_{\text{SO}_2}\), i.e., the fraction of remaining dissolved sulfate (Gomes and Hurtgen, 2013). In “open systems” containing a high concentration of dissolved sulfate (e.g., the modern ocean), \(f_{\text{SO}_4}\) does not vary measurably from 1.0 because the quantity of sulfate converted to sulfide via MSR is a small fraction of the total aqueous sulfate inventory. In this case, the produced sulfide will show the maximum degree of fractionation, which is typically \(\sim 30\) to 60‰ in modern marine systems (Fig. 2a; Table S1). In contrast, in “closed systems” in which the aqueous sulfate inventory is limited (e.g., sediment porewaters or low-sulfate freshwater systems), dissolved sulfate concentrations can be substantially reduced or completely depleted through MSR, causing \(f_{\text{SO}_2}\) to evolve toward zero. As \[\text{SO}_4^{2-}\]aq becomes smaller, sulfate reducers utilize a progressively larger fraction of the total dissolved sulfate pool, reducing the effective fractionation to small values (Habicht et al., 2002; Gomes and Hurtgen, 2013). In these settings, the aggregate δ34S composition of the produced sulfide approaches that of the original aqueous sulfate inventory, and \(\Delta^{34}S_{\text{sulfate-sulfide}}\) approaches zero (Kaplan, 1983; Habicht et al., 2002). In a macro sense, \(f_{\text{SO}_4}\) can be proxied by \[\text{SO}_4^{2-}\]aq, accounting for the strong first-order relationship between the latter parameter and \(\Delta^{34}S_{\text{sulfate-sulfide}}\) (\(r = +0.90, p(\alpha) < 0.01\); Fig. 2a). However, not all researchers agree on the importance of \(f_{\text{SO}_4}\) as a control on \(F_{\text{MSR}}\) (e.g., Leavitt et al., 2013).

Other factors may influence \(F_{\text{MSR}}\) under certain conditions. First, different dissimilatory reduction pathways yield different isotopic discriminations. Oxidation of organic substrates to CO₂ yields larger fractionations (\(\sim 30–60\)‰) than oxidation to acetate (\(<18\)‰) (Dettmers et al., 2001; Brüchert et al., 2001; Brüchert, 2004). Incomplete oxidation of organic substrates is a feature characteristic of sulfate reducers in hypersaline environments (Habicht and Canfield, 1997; Oren, 1999; Dettmers et al., 2001; Stam et al., 2010) and may account for the somewhat smaller fractionations typically encountered in such environments (Fig. 2a). Second, the type of organic substrate also matters, as ethanol, lactate, glucose, and other compounds yield different fractionations under otherwise similar conditions (Canfield, 2001; Dettmers et al., 2001; Kleikemper et al., 2004; Sim et al., 2011b). Third, sulfate reduction rates may also influence \(F_{\text{MSR}}\), with higher rates associated with smaller isotopic discriminations (Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Rees, 1973; Chambers et al., 1975; Habicht and Canfield, 1996; Brüchert et al., 2001; Canfield, 2001; Brunner and Bernasconi, 2005). Recent experiments by Leavitt et al. (2013) showed that \(F_{\text{MSR}}\) declines rapidly with increasing sulfate reduction rates before leveling off at \(\sim 15–20\)‰ at rates >50 mmol H₂S per unit substrate per day. Habicht and Canfield (2001) hypothesized that \(F_{\text{MSR}}\) is only incidentally related to sulfate reduction rates because both are correlated with the disproportionation of intermediate-oxidation-state S compounds by sulfur-oxidizing bacteria, which have probably been present since the Archean (Johnston et al., 2005; Wacey et al., 2010). Fourth, cell external sulfide (CES) concentrations, when high, can cause back-diffusion of sulfide into cells, with subsequent oxidative recycling to sulfate (Brunner and Bernasconi, 2005; Eckert et al., 2011). Finally, temperature has been shown to affect \(F_{\text{MSR}}\) in some studies (e.g., Canfield et al., 2006) but not others (e.g., Dettmers et al., 2001). The influence of temperature on \(F_{\text{MSR}}\) may operate through the species-specific temperature dependence of enzymes.

Research to date clearly shows that controls on microbial sulfate reduction are complex and incompletely understood. This situation reflects the diverse composition of the microbial communities that process sulfur in the marine environment and the range of isotopic fractionations associated with those processes (Brüchert, 2004). Yet even though multiple environmental and physiological factors influence \(F_{\text{MSR}}\), the strength of its relationship to \[\text{SO}_4^{2-}\]aq, as documented in this study (Fig. 2a), implies that aqueous sulfate concentrations are the dominant first-order control on \(F_{\text{MSR}}\), and that other factors such as organic substrate, rates of MSR, and temperature are second-order controls whose effects may be randomized at a larger scale and do not obscure the dominant influence of \[\text{SO}_4^{2-}\]aq in most environments. Whether the quantitative form of our \(F_{\text{MSR}}-\text{SO}_4^{2-}\) relationship is unique to the present or valid for the geologic past is unclear. Microbial S-cycling processes are thought to have been conservative through time (e.g., Wacey et al., 2010), although lower atmospheric \(p\text{O}_2\) prior to \(<635\) Ma may have limited disproportionation of intermediate-oxidation-state sulfur compounds and thus the potential for large fractionations.
(Habicht and Canfield, 2001; Serensen and Canfield, 2004; Johnston et al., 2005). In the following analysis, we adopt the $F_{\text{MSR}}$–$[\text{SO}_4^{2-}]_{\text{aq}}$ relationship of Fig. 2a as a basis for evaluating the $[\text{SO}_4^{2-}]_{\text{aq}}$ of ancient seawater from 635 Ma to the present.

4 Estimation of seawater sulfate concentrations since 635 Ma

4.1 General considerations and modeling protocol

The rate and MSR-trend methods can be applied to analysis of long-term variation in seawater sulfate concentrations. Although both methods utilize measured values of $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ as a proxy for $F_{\text{MSR}}$, they are quasi-independent in having different transform functions. The transform function of the rate method (Eqs. 3 and 4) makes use of observed rates of seawater sulfate $S$-isotopic variation (i.e., $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t (\text{max})$), whereas that of the MSR-trend method (Eqs. 6–8) makes use of an empirical relationship between $F_{\text{MSR}}$ and $[\text{SO}_4^{2-}]_{\text{aq}}$. The two methods are applicable over approximately the same range of $[\text{SO}_4^{2-}]_{\text{SW}}$ concentrations ($\sim$0.1–30 mM). However, their transform functions have different sensitivities to $[\text{SO}_4^{2-}]_{\text{aq}}$, with that of the MSR-trend method being greater as reflected in its lower slope ($m=0.42$; Fig. 2) compared with that of the rate method ($m=1.0$; Fig. 1). Thus, a combination of the two methods may be the most useful approach to constraining ancient seawater $[\text{SO}_4^{2-}]_{\text{aq}}$. Because the rate method yields estimates of maximum likely $[\text{SO}_4^{2-}]_{\text{SW}}$, it should generally yield a higher estimated sulfate concentration than the MSR-trend method, which estimates the mean $[\text{SO}_4^{2-}]_{\text{SW}}$ of the time interval of interest. The pairing of these procedures is thus useful in providing both mean and maximum estimates of paleo-seawater sulfate concentrations. Combining these two methods is also useful in providing a check on the robustness of the results. For example, if the maximum estimate yielded by the rate method is less than the mean estimate yielded by the MSR-trend method, then the results should be considered unreliable.

Both the rate and MSR-trend methods require defined input variables for calculation of paleo-seawater $[\text{SO}_4^{2-}]_{\text{aq}}$. For the rate method, a record of secular variation in seawater sulfate $\Delta^{34}\text{S}$ is needed from which to calculate $\partial\Delta^{34}\text{S}_{\text{CAS}}/\partial t$. We generated a seawater sulfate $\Delta^{34}\text{S}$ record for the Phanerozoic by combining published $\Delta^{34}\text{S}_{\text{CAS}}$ data sets for the Cenozoic (Paytan et al., 1998; red circles), Cretaceous (Paytan et al., 2004; black squares), and pre-Cretaceous (Kampschulte and Strauss, 2004; blue triangles; Table S2). Secular variation in $\Delta^{34}\text{S}_{\text{SO}_4^{2-}}_{\text{SW}}$ is shown by a mean LOWESS curve (blue line for low-resolution (5 Myr) and red line for high-resolution (1 Myr) records) and a standard deviation (±1σ) range (green field for low-resolution record; Table S3). Pre-Cretaceous and Cretaceous–Cenozoic estimates of $\delta^{34}\text{S}_{\text{SO}_4^{2-}}_{\text{SW}}$ have uncertainties of ±2–7‰ and ±1‰, respectively. The labels represent four short-term (<2 Myr) intervals of high-frequency $\partial\delta^{34}\text{S}_{\text{SO}_4^{2-}}/\partial t$ variation (EMCB: early-middle Cambrian boundary; SPICE: Steptoean positive carbon isotope excursion; CTB: Cenomanian–Turonian boundary). (b) Rate of seawater $\Delta^{34}\text{S}$ variation ($\partial\Delta^{34}\text{S}_{\text{SO}_4^{2-}}/\partial t$) as calculated from the seawater sulfate $\Delta^{34}\text{S}$ LOWESS curves. The maximum Phanerozoic $\delta^{34}\text{S}_{\text{SO}_4^{2-}}/\partial t$ is <4‰ Myr$^{-1}$, although rates of 10 to >50‰ Myr$^{-1}$ have been reported from some high-resolution CAS studies. (c) $\Delta^{34}\text{S}_{\text{CAS-PY}}$ for Phanerozoic marine sediments (data from Fig. 3 of Wu et al., 2010). The continental glaciation record is adapted from Montañez et al. (2011); all ages were converted to the Gradstein et al. (2012) timescale.

LOWESS curves were then used to calculate rates of change in seawater sulfate concentrations ($\partial\delta^{34}\text{S}_{\text{SO}_4^{2-}}/\partial t$) through the Phanerozoic (Fig. 3b). For both the rate and MSR-trend methods, $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$ is a defined input variable. As a proxy, we utilized the Phanerozoic $\Delta^{34}\text{S}_{\text{CAS-PY}}$ record of Wu et al. (2010). According to this record, $\Delta^{34}\text{S}_{\text{CAS-PY}}$ averaged
Our composite record shows that seawater sulfate $\delta^{34}S$ was heavy ($\sim 30-40 \%e$) during the Ediacaran to middle Cambrian, declined steeply during the late Cambrian to Early Ordovician, and stabilized at intermediate values ($\sim 20-30 \%e$) during the Middle Ordovician to Early Devonian (Table S3; Fig. 3a). Sulfate $\delta^{34}S$ declined further during the Middle Devonian to Early Mississippian, reaching a minimum of $\sim 12-16 \%e$ during the mid-Mississippian to the end of the Permian. Sulfate $\delta^{34}S$ then rose sharply to $\sim 20 \%e$ during the Early Triassic, before declining slightly to a local minimum of $\sim 15 \%e$ around the Jurassic–Cretaceous boundary. Sulfate $\delta^{34}S$ rose slowly during the Cretaceous and early Cenozoic, increased rapidly from 17 to 22 \%e at 40–50 Ma, and then stabilized at 21–23 \%e during the mid- to late Cenozoic (Fig. 3a). The low-frequency LOWESS curve exhibits low rates of $\delta^{34}S$ variation, with a mean of 0.25(±0.17) \%e Myr$^{-1}$ and a maximum of $\sim 0.8 \%e$ Myr$^{-1}$ (Fig. 3b). The high-frequency LOWESS curve exhibits somewhat higher rates of $\delta^{34}S$ variation, with a mean of 0.40(±0.45) \%e Myr$^{-1}$ and a maximum of $\sim 2.5 \%e$ Myr$^{-1}$ (Fig. 3b). Both curves show exceptionally low rates of seawater sulfate $\delta^{34}S$ variation during the Late Cretaceous and Cenozoic (the “Cenozoic minimum”) and the mid-Mississippian to mid-Permian (the “Late Paleozoic minimum”).

Our reconstructions of mean and maximum seawater sulfate concentrations through the Phanerozoic, based respectively on the MSR-trend and rate methods, are shown in Fig. 4. The mean curve suggests that [SO$_4^{2-}$]$_{SW}$ was low in the late Ediacaran ($\sim 1–4$ mM) but rose sharply in the early Cambrian (to $\sim 3–15$ mM) and remained in that range until the Permian. A long, slow rise in [SO$_4^{2-}$]$_{SW}$ began in the Early Permian and culminated at $\sim 12–38$ mM in the Middle Triassic. Subsequently, [SO$_4^{2-}$]$_{SW}$ declined slightly by the mid-Cretaceous (to $\sim 7–25$ mM) and then rose slightly during the Late Cretaceous to early Cenozoic (to $11–35$ mM). The standard deviation range for the mean curve (blue band) suggests an uncertainty of plus or minus a factor of $\sim 2\sigma$ in the mean estimate, with the magnitude of the uncertainty shrinking modestly from the Cambrian to the present. The modern seawater sulfate concentration of 29 mM falls within the standard deviation range of the mean trend (Fig. 4).

A maximum [SO$_4^{2-}$]$_{SW}$ curve can be calculated for both the low- and high-frequency Phanerozoic $\delta^{34}S$ records of Fig. 3a. The low- and high-frequency maximum [SO$_4^{2-}$]$_{SW}$ curves (shown as black and red lines, respectively, in Fig. 4) mirror the upward trend through the Phanerozoic seen in the mean curve and thus are consistent with a factor of $\sim 4\sigma$ increase in seawater sulfate concentrations since the early Cambrian. Although the maximum [SO$_4^{2-}$]$_{SW}$ curves exhibit values that are mostly unrealistically large, it is worth noting that (1) these curves represent the maximum possible, not the most likely, concentrations of seawater sulfate and that (2) the smallest values on the maximum curves are more robust constraints on [SO$_4^{2-}$]$_{SW}$ than the largest values. The second observation is based on the fact that the smallest values derive from the largest measured rates of $\delta^{34}S_{CAS}$ variation (Fig. 3b), i.e., those rates that most closely approach the theoretical maximum, whereas the largest values are associated with intervals of little or no $\delta^{34}S_{CAS}$ variation. Thus, the lower envelope of maximum [SO$_4^{2-}$]$_{SW}$ values (dashed line, Fig. 4) provides a more useful constraint on seawater sulfate concentrations than the full curve. We also suggest that, although the upper limits on [SO$_4^{2-}$]$_{SW}$ imposed by the rate method may have limited utility for assessment of Phanerozoic seawater sulfate, this method may be of greater value in analyzing Archean and Proterozoic seawater sulfate concentrations, which are thought to have been quite low (< 1 mM; Kah et al., 2004; Canfield et al., 2007; Planavsky et al., 2012).

The results of the rate method are dependent on several factors that influence the estimation of rates of seawater sulfate $\delta^{34}S$ variation, $\partial\delta^{34}S_{SO_4} / \partial t$ (max) may be overestimated if there is an increase in $\delta^{34}S_{CAS}$ variance due to diagenesis or procedural artifacts during CAS extrac-
Figure 5. Comparison of Phanerozoic seawater sulfate $[\text{SO}_4^{2-}]$ records. The mean trend of the present study is shown by a thick blue line, with the ±1σ uncertainty range shown as a blue band. Estimates are based either on fluid-inclusion studies (Horita et al., 2002; Brennan et al., 2004; Lowenstein et al., 2005) or C–S-cycle modeling (Holser et al., 1989; Berner, 2004; Gill et al., 2007; Wortmann and Chernyavsky, 2007; Wortmann and Paytan, 2012; Haley et al., 2012). Arrows indicate unconstrained minimum or maximum values.

Our reconstruction of long-term secular variation in seawater sulfate concentrations shows a strong relationship to first-order Phanerozoic climate cycles (cf. Algeo et al., 2014). In particular, the interval of the Late Paleozoic Ice Age, which lasted from the mid-Mississippian through the mid-Permian, was characterized by a major change in the oceanic sulfate reservoir. At that time, minimum values developed for both seawater sulfate $\Delta^{34}\text{S}_{\text{CAS}}$ and rates (Fig. 3a) and rates of $\Delta^{34}\text{SO}_4$ variation (<1%Myr$^{-1}$; Fig. 3b), accompanied by a concurrent increase in sulfate–sulfide fractionation (from <30 to >40%$^{16}\text{S}$; Fig. 3c). Whether these are general features of seawater sulfate during icehouse climate modes is not entirely certain. A second interval of global climatic cooling and continental glaciation during the Late Cretaceous and Cenozoic also shows low rates of $\Delta^{34}\text{SO}_4$ variation and an increase in sulfate–sulfide fractionation but, in contrast to the Late Paleozoic, 34S-enriched and relatively stable seawater sulfate $\Delta^{34}\text{S}$ values (Fig. 3). The greater stability of seawater sulfate during the Cenozoic relative to the Late Paleozoic may be due to a long-term increase in total seawater sulfate mass (Figs. 4–5). We hypothesize that the Late Paleozoic was characterized by low rates of pyrite burial (hence, lower $\Delta^{34}\text{SO}_4$) and a consequent increase in the mass of seawater sulfate (hence, lower $\Delta^{34}\text{SO}_4 / \partial t$) (cf. Haley et al., 2012). Low rates of pyrite burial at that time may have been due to a combination of lower sea-level elevations (reducing the total shelf area available for sulfate reduction; cf. Haley et al., 2012; Algeo et al., 2014), enhanced oceanic
ventilation (increasing aerobic decay of organic matter), and increased burial of organic matter in low-sulfate freshwater settings, which was linked to the spread of terrestrial floras (DiMichele and Hook, 1992).

4.3 High-frequency variation in seawater sulfate during the Neoproterozoic and Phanerozoic

We applied the rate and MSR-trend methods to an analysis of short-term variation in $[\text{SO}_4^{2-}]_{SW}$ during selected intervals of the Neoproterozoic and Phanerozoic for which high-resolution $\delta^{34}\text{S}_{\text{CAS-PY}}$ studies are available. For the Neoproterozoic, recent studies have provided S-isotope records from a number of sites globally as well as improved radiometric geochronologic constraints that are needed for the rate method. Based on these studies, we have estimated $\partial\delta^{34}\text{S}_{\text{SO}_4}/\partial t(\text{max})$ for 10 late Neoproterozoic units (Table S4; Fig. 6). Radiometric studies of the Doushantu Formation in South China (Halverson et al., 2005; Zhang et al., 2005, 2008) provided key ages from which we calculated $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ of 5‰ Myr$^{-1}$ at $\sim636–633$ Ma and 1.3‰ Myr$^{-1}$ at $\sim568–551$ Ma (McFadden et al., 2008; Li et al., 2010). The Neoproterozoic succession of Sonora, Mexico, yielded $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ estimates of 6 and 4‰ Myr$^{-1}$ (Loyd et al., 2012, 2013). The latest Neoproterozoic Zars Formation (Nama Group) in Namibia and upper Huqf Supergroup in Oman yielded $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ estimates of 20‰ Myr$^{-1}$ and 40‰ Myr$^{-1}$, respectively, at 549–547 Ma (Fike and Grotzinger, 2008; Ries et al., 2009). The rate method yielded $[\text{SO}_4^{2-}]_{SW}$ estimates ranging from <0.1 to >100 mM, with most between ~1 and 10 mM (Table S4). The MSR-trend method yielded $[\text{SO}_4^{2-}]_{SW}$ estimates ranging from <0.1 to 70 mM, with most between ~1 and 16 mM. Many units exhibit combinations of $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ and $\Delta^{34}\text{S}_{\text{CAS-PY}}$ values that plot close to or slightly below the MSR trend (Fig. 6), yielding $[\text{SO}_4^{2-}]_{SW}$ estimates for the MSR-trend method that are equal to or somewhat smaller than the rate-based estimates. This pattern conforms to our expectation that the rate method yields maximum estimates of $[\text{SO}_4^{2-}]_{SW}$. The only potentially anomalous result is for the upper Huqf Supergroup, which yielded a MSR-trend estimate (12–45 mM) that is larger than the rate-method estimate (1.5–8 mM; Table S4).

We also analyzed $[\text{SO}_4^{2-}]_{SW}$ for a set of eight units of Cambrian age. These units yielded $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ of 7 to 23‰ Myr$^{-1}$ for the early Cambrian, 9 to 20‰ Myr$^{-1}$ for the early–middle Cambrian boundary (EMCB), and 8 to 20‰ Myr$^{-1}$ for the late Cambrian SPICE (Table S4; Fig. 7). These ranges are sufficiently similar that they suggest a limited range of seawater $[\text{SO}_4^{2-}]_{SW}$ variation during the Cambrian. The rate method yielded $[\text{SO}_4^{2-}]_{SW}$ estimates ranging from <0.1 to 18 mM, with most between ~1 and 6 mM. The MSR-trend method yielded $[\text{SO}_4^{2-}]_{SW}$ estimates ranging from <0.1 to 40 mM, with most between ~1 and 8 mM. The two methods thus yielded similar estimates of seawater
Figure 8. Analysis of seawater sulfate concentrations for eight Mesozoic–Cenozoic marine units. The parallelogram for each unit was generated using the rate method. The red field represents the long-term average $\Delta^{34}S_{\text{CAS-PY}}$ for the Mesozoic–Cenozoic based on data in Wu et al. (2010). A summary of results and data sources is given in Table S4; other details as in Figs. 1–2.

sulfate concentrations, implying that the results are reasonably robust and that the rate method is not yielding unrealistically large values. All Cambrian units show sulfate–sulfide fractionations smaller than the Paleozoic mean of $30 \pm 5 \%$ (Wu et al., 2010), resulting in lower $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates than for the long-term record (Fig. 4). Once again, most units exhibit combinations of $\frac{\delta^{34}S_{\text{CAS}}}{\delta t(\text{max})}$ and $\Delta^{34}S_{\text{CAS-PY}}$ values that plot close to or slightly below the MSR trend (Fig. 7). However, two units (the SPICE events in Australia and Nevada) yield MSR-trend estimates that are larger than their rate-method estimates. The reasons for these potentially anomalous results will be considered below.

Finally, we analyzed a set of eight Mesozoic units, ranging in age from the Early Triassic to the late Middle Cretaceous (Table S4; Fig. 8). These units show $\frac{\delta^{34}S_{\text{CAS}}}{\delta t(\text{max})}$ of 6 to $60 \% \text{ Myr}^{-1}$, with the highest rates during the Early Triassic and Early Jurassic. The rate method yielded $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from 1.1 to 120 mM, with most between $\sim 3$ and 20 mM. The MSR-trend method yielded $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from 1 to 110 mM, with most between $\sim 30$ and 100 mM (Table S4). In contrast to the late Neoproterozoic and Cambrian, many Mesozoic units exhibit a narrow spread of $\Delta^{34}S_{\text{CAS-PY}}$ values that conform with the mean sulfate–sulfide fractionation for the Mesozoic–Cenozoic (Wu et al., 2010; Fig. 8) and that are within the range for modern marine systems ($\sim 30–60 \%$; Table S1). As a consequence, many Mesozoic units exhibit the anomalous pattern of having MSR-trend estimates that are larger than their rate-method estimates.

Ideally, the rate and MSR-trend methods will yield similar $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates, providing support for the correctness of the results, and the majority of the paleomarine units considered in this study follow this pattern. However, a subset of the study units show differences that fall into two categories: (1) type I deviation – rate-method estimates $\gg$ MSR-trend estimates (lower right field, Fig. 9); (2) type II deviation – MSR-trend estimates $\gg$ rate-method estimates (upper left field, Fig. 9). Such deviations may provide insights into underlying controls on seawater sulfate concentrations. The most likely explanation for the type I deviations is that the measured $\frac{\delta^{34}S_{\text{CAS}}}{\delta t(\text{max})}$ for a given unit is much less than its theoretical maximum. This situation can develop whenever the marine sulfur cycle is in equilibrium (i.e., source and sink fluxes in balance), reflecting persistently stable environmental conditions. In this case, $\Delta^{34}S_{\text{CAS-PY}}$ will be controlled by $[\text{SO}_4^{2-}]_{\text{SW}}$, which may be equal or close to that of the global ocean, but $\frac{\delta^{34}S_{\text{CAS}}}{\delta t(\text{max})}$ will be controlled by the mass of aqueous sulfate within the restricted basin, which will be a function of basin volume.
A possible environmental explanation for type II deviations is sulfate reduction within a restricted marine basin. In this case, \( \Delta^{34}\delta_{\text{CAS-PY}} \) is controlled by seawater \( [\text{SO}_4^{2-}] \), which may be identical (or nearly so) to that in the global ocean. However, the total mass of sulfate in the restricted marine basin will be much less than that in the global ocean, allowing a more rapid evolution of seawater sulfate \( ^{34}\delta\text{S} \) in response to oceanographic perturbations. We hypothesize that most of the type II deviations in our study units are the product of MSR within semi-restricted marine basins. For example, the Neoproterozoic Ara Group (Huqf Supergroup) of Oman was deposited in a fault-bounded basin in which massive evaporite deposits accumulated (Fike and Grotzinger, 2008). Also, most of the Mesozoic units showing type II deviations are known to have been deposited in basins that were subject to a degree of water mass restriction. The Triassic–Jurassic European epicontinental sea was broad, shallow, and laced with local tectonic grabens with restricted deepwater circulation (Röhl et al., 2001; Berra et al., 2010). The Early Cretaceous South Atlantic was only weakly connected to the global ocean during deposition of Aptian sediments (Wortmann and Chernyavsky, 2007), and restriction of the Atlantic Ocean continued at least through deposition of organic-rich facies at the Cenomanian–Turonian boundary (Owens et al., 2013). The Cretaceous Western Interior Seaway was almost certainly semi-restricted throughout its existence (Adams et al., 2010). The only Mesozoic unit not to show a type II deviation, the Middle Triassic Bravaisberget Formation of Spitsbergen (Karcz, 2010; Fig. 8), was deposited in the largely unrestricted Boreal Ocean. These examples serve to illustrate the need to understand the hydrography of paleomarine basins in applying the rate method of estimating paleoseawater sulfate concentrations.

Comparison of the \( [\text{SO}_4^{2-}]_{\text{SW}} \) estimates for individual Neoproterozoic and Phanerozoic units shown in Figs. 6–8 with the long-term \( [\text{SO}_4^{2-}]_{\text{SW}} \) curve in Fig. 4 provides additional insights regarding secular variation in seawater sulfate inventories. With the exception of the Middle Triassic Bravaisberget Formation, all Mesozoic units exhibit MSR-trend estimates that overlap the long-term trend but rate estimates that fall below it (Fig. 10). As discussed above, we infer that this pattern reflects anomalously high measured \( \partial^{34}\delta_{\text{CAS}} / \partial t(\text{max}) \) values as a consequence of rapid evolution of seawater sulfate \( ^{34}\delta\text{S} \) within semi-restricted marine basins of the proto-Atlantic and western Tethys oceans. Cambrian units exhibit a wide range of \( [\text{SO}_4^{2-}]_{\text{SW}} \) estimates, although a cluster of results falls just below the long-term trend, with many estimates between 1 and 5 mM (Fig. 10). We infer that either our long-term record (Fig. 4) overestimates \( [\text{SO}_4^{2-}]_{\text{SW}} \) for the Cambrian, or the studied units are biased toward low \( [\text{SO}_4^{2-}]_{\text{SW}} \). Late Neoproterozoic units exhibit an even wider range of \( [\text{SO}_4^{2-}]_{\text{SW}} \) estimates than Cambrian units and lack any apparent clustering (Fig. 10). However, all but one of these units yield similar \( [\text{SO}_4^{2-}]_{\text{SW}} \) est-

![Figure 10. Seawater sulfate concentrations for late Neoproterozoic and Phanerozoic marine units (Figs. 6–8) compared with long-term \([\text{SO}_4^{2-}]_{\text{SW}}\) curve (Fig. 4). Estimates of \([\text{SO}_4^{2-}]_{\text{SW}}\) are based on (1) the rate method (calculated as per Eqs. 3 and 4; shown as open boxes) and (2) the MSR-trend method (calculated as per Eqs. 6–8; shown as solid boxes); note that unit symbols and colors are keyed to Table S4 and Figs. 6–8. See text for discussion. Other details as in Fig. 4.](image)
estimates for the MSR-trend and rate methods (Fig. 6), suggesting that the estimates are robust. We infer that the late Neoproterozoic (635–542 Ma) was characterized by a highly unstable marine sulfur cycle, as a consequence of which seawater sulfate concentrations varied tremendously. This inference is supported by some earlier studies (Li et al., 2010; Loyd et al., 2012, 2013), although other studies have inferred low (Hurtgen et al., 2002, 2005, 2006; Ries et al., 2009) or monotonically rising sulfate concentrations (Halverson and Hurtgen, 2007) during this interval.

5 Conclusions

The rate and MSR-trend methods developed in this study for quantifying paleo-seawater sulfate concentrations are complementary and quasi-independent, providing estimates of maximum and mean \([\text{SO}_4^{2-}]_{\text{SW}}\), respectively, for a paleomarine unit of interest. Both techniques make use of \(\Delta^{34}\text{S}_{\text{CAS-PY}}\), i.e., the isotopic fractionation associated with microbial sulfate reduction (MSR). The rate method evaluates \([\text{SO}_4^{2-}]_{\text{SW}}\) as a function of \(\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})\), i.e., the maximum observed rate of change in seawater sulfate, whereas the MSR-trend method makes use of an empirical relationship between MSR fractionation and aqueous sulfate concentrations. The significance of our quantitative approach is that estimates of paleo-seawater \([\text{SO}_4^{2-}]_{\text{SW}}\) can be derived from two readily measurable sedimentary parameters: \(\Delta^{34}\text{S}_{\text{CAS-PY}}\) and \(\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})\). Based on these methods, an analysis of long-term variation since 635 Ma suggests that \([\text{SO}_4^{2-}]_{\text{SW}}\) was low during the late Neoproterozoic (<5 mM), rose sharply across the Ediacaran–Cambrian boundary (to ~5–10 mM), and rose again during the Permian to near-modern levels (~10–30 mM). However, high-resolution \(\delta^{34}\text{S}_{\text{CAS}}\) studies provide evidence of episodic high-frequency (~<2 Myr) events during which seawater sulfate concentrations were drawn down in response to massive evaporite deposition, reduced sediment ventilation and increased pyrite burial in the aftermath of mass extinctions, or other factors. The techniques developed in this study for quantitative analysis of paleo-seawater \([\text{SO}_4^{2-}]_{\text{SW}}\) should be applicable to marine units of any age provided that (1) MSR fractionation has been a conservative process through time (i.e., the dominant pathways of sulfur metabolism have not changed greatly) and (2) sufficient time control exists for estimation of rates of \(\delta^{34}\text{S}_{\text{CAS}}\) variation. As more S-isotopic studies of cogenetic sulfate and sulfide become available, it should ultimately be possible to reconstruct variation in seawater sulfate concentrations throughout Earth history.
Appendix A: Extended discussion

A1 Relationship of rate of seawater sulfate change to sulfate residence time

The maximum possible rate of change in seawater sulfate $\delta^{34}$S (i.e., $\Delta \delta^{34}$S$_{SW}$/$\partial t$) is inversely proportional to the residence time of sulfate in seawater ($\tau$). The exact quantitative form of this relationship can be derived from Eq. (2) of Algeo et al. (2014), reorganization of which yields

$$M_{SW}/F_{PY} = k_1 \times \Delta^{34}S_{CAS-PY}/\Delta \delta^{34}S_{CAS}/\partial t (\text{max}).$$  \hspace{1cm} (A1)

The residence time of sulfur in seawater is equal to the mass of seawater divided by the total sink flux, i.e., the reduced sulfate flux ($F_{PY}$) plus the oxidized sulfur flux ($F_{EVAP}$): $\tau = M_{SW}/(F_{PY} + F_{EVAP})$.  \hspace{1cm} (A2)

The dashed horizontal lines represent the pyrite burial flux ($F_{PY}$) with $\Delta^{34}S_{CAS-PY}$ (their Fig. 4). We explored the effects of varying pyrite burial fluxes on seawater sulfate concentration estimates as follows. Equations (2–3) have four variables: $\Delta^{34}S_{CAS}$ (or $M_{SW}$, since these are interconvertible via Eq. 4), $F_{PY}$, $\Delta^{34}S_{CAS-PY}$, and $\Delta \delta^{34}S_{CAS}/\partial t$. However, $\Delta^{34}S_{CAS-PY}$ can be modeled as a function of $\Delta^{34}S_{CAS}$ (i.e., the MSR trend of Fig. 2 and Eq. 6), reducing the number of potentially independent variables to three (we state “potentially independent” as there may in fact be some dependency among these variables). Now it is possible to explore the effects of simultaneous variations in $\Delta^{34}S_{CAS}$ and $F_{PY}$ on $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ via a modified form of Eq. (2):

$$\Delta \delta^{34}S_{CAS}/\partial t (\text{max}) = k_1 \times k_2 \times F_{PY} \times \exp(\log(SO_4^{2-})_{SW} \times 0.20 + 1.10)/[SO_4^{2-}]_{SW} .$$  \hspace{1cm} (A5)

The three modeled parameters exhibit log-linear relationships, with larger $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ associated with larger $[SO_4^{2-}]_{SW}$ and $F_{PY}$ (Fig. A1). $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ scales linearly with $F_{PY}$, so uncertainty in the latter parameter is directly mirrored in the former parameter. The range of $F_{PY}$ used in our study (i.e., $4 \times 10^{13}$ g yr$^{-1}$) is consistent with variation in $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ from $\sim 1$ to 100% Myr$^{-1}$. The $F_{PY}$–$[SO_4^{2-}]_{SW}$ relationship of Wortmann and Chernyavsky (2007, their Fig. 4; red curve, Fig. A1), if correct, indicates that variation in $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ cannot exceed $\sim 3%$ Myr$^{-1}$ under any set of conditions.

We tested the influence of sulfate-dependent pyrite burial fluxes on seawater sulfate concentration estimates by applying the relationship of Wortmann and Chernyavsky (2007) to our rate-method calculations. Their relationship can be re-

### Table A1. Regression statistics for reduced sulfur phases (0–40 PSU only; see Fig. A3).

<table>
<thead>
<tr>
<th>Sulfur phase</th>
<th>n</th>
<th>r</th>
<th>m</th>
<th>b</th>
<th>p(α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>48</td>
<td>0.92</td>
<td>0.46</td>
<td>−0.35</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sediment AVS</td>
<td>6</td>
<td>0.81</td>
<td>0.42</td>
<td>−0.06</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Sediment TRS</td>
<td>11</td>
<td>0.98</td>
<td>0.33</td>
<td>0.20</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Aqueous H$_2$S</td>
<td>16</td>
<td>0.84</td>
<td>0.44</td>
<td>−0.20</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Figure A1. Relationship of $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ to $F_{PY}$ and $[SO_4^{2-}]_{SW}$ with $\Delta^{34}S_{CAS-PY}$ estimated as a function of $[SO_4^{2-}]_{SW}$ (Fig. 2, Eq. 6). The dashed horizontal lines represent the pyrite burial fluxes used in this study for anoxic and anoxic paleoarctic systems, i.e., $4 \times 10^{13}$ and $10 \times 10^{13} g$ yr$^{-1}$, respectively. The red line represents the $[SO_4^{2-}]_{SW}$ dependency of the pyrite burial flux as given by Wortmann and Chernyavsky (2007, their Fig. 4). Note that, according to the latter relationship, $\Delta \delta^{34}S_{CAS}/\partial t (\text{max})$ values cannot exceed $\sim 3%$ Myr$^{-1}$ under any set of conditions.
Although Eq. (A7) has two unknowns, i.e., $[\text{SO}_4^{2-}]_{\text{SW}}(\text{max})$ and $F_{\text{PY}}$, it can be solved because $F_{\text{PY}}$ is a function of $[\text{SO}_4^{2-}]_{\text{SW}}$ in Fig. 4 of Wortmann and Chernyavsky (2007). The empirical relationship between $[\text{SO}_4^{2-}]_{\text{SW}}$ and $\partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})$ can be represented as follows:

$$[\text{SO}_4^{2-}]_{\text{SW}}(\text{max}) / F_{\text{PY}} = k_1 \times k_2 \times \Delta^{34}\text{S}_{\text{CAS-PY}} / \partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max}).$$  \hspace{1cm} (A7)

This second-order polynomial equation can now be solved for $[\text{SO}_4^{2-}]_{\text{SW}}$ using the quadratic solution, after which $F_{\text{PY}}$ can be calculated from Eq. (A6).

Using Eq. (A9), we calculated $[\text{SO}_4^{2-}]_{\text{SW}}$ on the basis of $\partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})$ and $\Delta^{34}\text{S}_{\text{CAS-PY}}$. These relationships are plotted as variation in $\partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})$ as a function of $[\text{SO}_4^{2-}]_{\text{SW}}$ and $\Delta^{34}\text{S}_{\text{CAS-PY}}$ (Fig. A2; cf. Fig. 1). At high $[\text{SO}_4^{2-}]_{\text{SW}}$, the two sets of $\partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})$ curves are nearly colinear, which is because the value of $F_{\text{PY}}$ in Fig. 4 of Wortmann and Chernyavsky (2007) for $[\text{SO}_4^{2-}]_{\text{SW}} > 10 \text{mM}$ is nearly invariant and similar to the flux that we used foroxic marine environments (i.e., $4 \times 10^{13} \text{g yr}^{-1}$). In contrast, the two sets of curves diverge sharply at $[\text{SO}_4^{2-}]_{\text{SW}} < 1 \text{mM}$, which is a consequence of the much lower $F_{\text{PY}}$ values associated with low seawater sulfate concentrations in the Wortmann and Chernyavsky curve.

The $\partial \delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})$ curves based on the sulfate-dependent pyrite fluxes of Wortmann and
Chernyavsky (2007) require comment. First, the MSR trend (Fig. 2) corresponds almost entirely to a limited range of $\partial \delta^{34}S_{\text{CAS}} / \partial t(\text{max})$ values (i.e., 2 to 4\% Myr$^{-1}$; Fig. A2). This suggests that there ought to be quite limited variation in $\partial \delta^{34}S_{\text{CAS}} / \partial t(\text{max})$ over a wide range of seawater sulfate concentrations in nature. Second, many combinations of the two sediment parameters that can be measured (i.e., $\Delta^{34}S_{\text{CAS-PY}}$ and $\partial \delta^{34}S_{\text{CAS}} / \partial t(\text{max})$) cannot yield a $[SO_4^{2-}]_{\text{SW}}$ estimate. For example, no $[SO_4^{2-}]_{\text{SW}}$ estimate is possible for $\Delta^{34}S_{\text{CAS-PY}}$ of 7\% in combination with any $\partial \delta^{34}S_{\text{CAS}} / \partial t(\text{max})$ value that is larger than $\sim$4\% Myr$^{-1}$ (Fig. B2). This situation exists because high rates of variation in seawater sulfate $\delta^{34}S$ are not possible where the pyrite burial flux is sharply curtailed by $[SO_4^{2-}]_{\text{SW}}$ dependency (as in Fig. 4 of Wortmann and Chernyavsky, 2007). However, many paleomarine units exhibit $\partial \delta^{34}S_{\text{CAS}} / \partial t(\text{max})$ values outside the narrow range permitted by the Wortmann and Chernyavsky (2007) relationship (see Table S4 and Figs. 6–8). If the Wortmann and Chernyavsky (2007) parameterization of the $F_{\text{PY}}$–$[SO_4^{2-}]_{\text{SW}}$ relationship is correct, then one must conclude that all of these published higher rates are products of uncertain geochronologic dating, diagenetic artifacts, or sample processing and analytical problems. On the other hand, the use of fixed values for $F_{\text{PY}}$ in our rate-method calculations (Eqs. 2–4) yields estimates of $[SO_4^{2-}]_{\text{SW}}$ that are – for the most part – consistent with estimates of $[SO_4^{2-}]_{\text{SW}}$ based on the MSR-trend method (Sect. 2.2; see Figs. 6–8 for examples). We acknowledge that some form of sulfate dependency of pyrite burial fluxes may exist but suggest that it may differ from the relationship given by Wortmann and Chernyavsky (2007).

### A3 Sources of sulfide $\delta^{34}S$ data

Although all sulfate $\delta^{34}S$ data used in the calculation of $\Delta^{34}S_{\text{sulfate-sulfide}}$ values in Fig. 2 are based on aqueous $SO_4^{2-}$ measurements, we used sulfide $\delta^{34}S$ data from multiple sources: pyrite, sediment acid-volatile sulfur (AVS), sediment total reduced sulfur (TRS), and aqueous $H_2S$ (Table S1). We have constructed a version of Fig. 2 that shows the different sulfide phases, and we calculated separate regressions for each phase (Fig. A3). The following points should be noted about this figure. First, each of the four phases yields a statistically significant regression ($r = 0.81$–0.92; $p(\alpha) < 0.05$; Table A1). Second, the four phases have similar regression slopes although slightly variable y intercepts. For this reason, TRS and AVS yield $\Delta^{34}S_{\text{CAS-PY}}$ values that are, on average, slightly larger for a given $[SO_4^{2-}]_{\text{SW}}$ than pyrite and aqueous $H_2S$. Third, the four regression lines generally converge at higher $[SO_4^{2-}]_{\text{SW}}$, and the largest differences occur at low $[SO_4^{2-}]_{\text{SW}}$, where data are sparser.

One point that bears reflection is that estimates of paleoseawater $[SO_4^{2-}]_{\text{SW}}$ are based not on aqueous sulfide $\delta^{34}S$, which cannot be measured for paleomarine systems, but on mineral sulfide (generally pyrite) $\delta^{34}S$. Therefore, the critical relationship for establishing a viable MSR-trend proxy for $[SO_4^{2-}]_{\text{SW}}$ is that between sulfate $\delta^{34}S$ and pyrite $\delta^{34}S$. Although we could have used the pyrite $\delta^{34}S$ data alone, we opted to include other sulfide phases to produce a larger sulfide $\delta^{34}S$ data set, especially one containing more data at low $[SO_4^{2-}]_{\text{SW}}$, with the goal of generating a stable relationship over a wider range of $[SO_4^{2-}]_{\text{SW}}$ values. Whether there are real differences in the regression relationships among these four sulfide phases is an issue that will require further inquiry. These sulfide phases yield similar relationships between $\Delta^{34}S_{\text{sulfate-sulfide}}$ and $[SO_4^{2-}]_{\text{SW}}$ that, based on the available data, are statistically indistinguishable (Fig. A3).
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