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Published in:
Biogeosciences

DOI:
10.5194/bg-12-2131-2015

Publication date:
2015

Document version
Final published version

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Citation for published version (APA):

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Download date: 03. May. 2021
Reconstruction of secular variation in seawater sulfate concentrations

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Received: 26 July 2014 – Published in Biogeosciences Discuss.: 10 September 2014
Revised: 24 January 2015 – Accepted: 18 March 2015 – Published: 10 April 2015

Abstract. Long-term secular variation in seawater sulfate concentrations ([SO₄²⁻]ₘₛₗ) 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 δ³⁴S_CAS-PY, and (2) the maximum rate of change in seawater sulfate, as proxied by ∂δ³⁴S_CAS-PY / ∂t(max). The “MSR-trend method” is based on the empirical relationship of δ³⁴S_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 [SO₄²⁻]ₘₛₗ (although results are dependent on assumptions regarding the pyrite burial flux, F_PY), and the MSR-trend method yields an estimate of mean [SO₄²⁻]ₘₛₗ. An analysis of seawater sulfate concentrations since 635 Ma suggests that [SO₄²⁻]ₘₛₗ 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 Cher muddy, 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 ($\Delta^{34}$S$_{CAS-PY}$), and (2) the maximum observed rate of variation in seawater sulfate $\delta^{34}$S ($\partial\delta^{34}$S$_{CAS}$ / $\partial t$). 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$$_{2-}$] based on an empirical relationship between $\Delta^{34}$S$_{CAS-PY}$ and aqueous sulfate concentrations (the “MSR trend”) in 81 modern depositional systems. Conceptually, the MSR-trend method is related to the fractionation relationship given in Habicht et al. (2002, their Fig. 1). Although some earlier studies have made qualitative assessments of paleo-seawater [SO$_4$$_{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.

Figure 1. The rate method. On a crossplot of aqueous sulfate concentration ([SO$_4$$_{2-}$]$_{aq}$) versus S-isotope fractionation between cogenetic sulfate and sulfide ($\Delta^{34}$S$_{sulfate-sulfide}$), the diagonal blue lines represent maximum rates of change in sulfate $\delta^{34}$S (i.e., $\partial\delta^{34}$S$_{SO_4}$/ $\partial t$(max)). For paleomarine systems, maximum seawater sulfate concentrations ([SO$_4$$_{2-}$]$_{sw}(max)$) can be estimated from the abscissa based on measured values of $\Delta^{34}$S$_{CAS-PY}$ and $\delta^{34}$S$_{CAS}$/ $\partial t$(max). The two scales on the abscissa represent [SO$_4$$_{2-}$]$_{sw}$ in oxic (O) and anoxic (A) oceans, in which pyrite burial fluxes are equal to 4 × 10$^{13}$ and 10 × 10$^{13}$ g yr$^{-1}$ (i.e., 40 and 100 % of the modern total sulfur sink flux), respectively. The typical range of $\Delta^{34}$S$_{sulfate-sulfide}$ due to MSR fractionation in modern marine systems is 30–60‰ (Habicht and Canfield, 1997). The maximum rate of seawater sulfate $\delta^{34}$S variation during the Cenozoic is ∼0.7‰ Myr$^{-1}$ (Paytan et al., 1998), yielding estimates of ∼40–80 mM for [SO$_4$$_{2-}$]$_{sw}$ through projection to the abscissa (dashed lines). These estimates exceed actual modern seawater [SO$_4$$_{2-}$], which is ∼29 mM (Millero, 2005), because the measured maximum rate of $\partial\delta^{34}$S$_{SO_4}$/ $\partial t$ (light-blue parallelogram) is less than the theoretical possible maximum rate (∼1–2‰ Myr$^{-1}$; red parallelogram).
2  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., Halevy et al., 2012). Subaerial weathering yields a riverine sulfate source flux \( F_Q \) of \( \sim 10 \times 10^{13} \text{ g yr}^{-1} \) 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 \( F_I \) of \( \sim 6 \times 10^{13} \text{ g yr}^{-1} \) with a S-isotopic composition that closely mimics that of coeval seawater \( \Delta^{34}S_{\text{SW-EVAP}} \) of \( \sim -4 \% \). The reduced sink has a flux \( F_P \) of \( \sim 4 \times 10^{13} \text{ g yr}^{-1} \) with a composition that characteristically shows a large negative fractionation relative to coeval seawater \( \Delta^{34}S_{\text{Sulfate-sulfide}} \) of \( \sim 30 \text{ to } 60 \% \); 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 \( \Delta^{34}S \) 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 rate method calculates a maximum seawater sulfate concentration \( [\text{SO}_4^{2-}]_{\text{SW(max)}} \) based on two parameters: (1) S-isotope fractionation between coenetic sedimentary sulfate and sulfide \( \Delta^{34}S_{\text{Sulfate-sulfide}} \), as proxied by \( \Delta^{34}S_{\text{CAS-PY}} \) and (2) the maximum observed rate of variation in seawater sulfate S isotopes \( \partial^{34}S_{\text{CAS-PY}}/\partial t \) (max), as proxied by \( \partial^{34}S_{\text{CAS-PY}}/\partial t \) (max) \( (\text{Fig. 1}) \). Rates of isotopic change for seawater sulfate are given by

\[
\partial^{34}S_{\text{CAS}}/\partial t = \left( (F_Q \times \Delta^{34}S_{\text{SO4-SW}}) - (F_P \times \Delta^{34}S_{\text{CAS-PY}}) \right)/M_{\text{SW}} \quad (1)
\]

where \( F_Q \times \Delta^{34}S_{\text{SO4-SW}} \) is the flux-weighted difference in the isotopic compositions of the source flux and seawater (SW), \( F_P \times \Delta^{34}S_{\text{CAS-PY}} \) is the flux-weighted difference in the isotopic compositions of the reduced-S sink flux and seawater, and \( M_{\text{SW}} \) 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:

\[
\partial^{34}S_{\text{CAS}}/\partial t \text{ (max)} = F_P \times \Delta^{34}S_{\text{CAS-PY}}/M_{\text{SW}} \quad (2)
\]

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

\[
M_{\text{SW}} = k_1 \times F_P \times \Delta^{34}S_{\text{CAS-PY}}/\partial^{34}S_{\text{CAS}}/\partial t \text{ (max)} \quad (3)
\]

[SO\(_4^{2-}\)]_{\text{SW(max)}} = k_2 \times M_{\text{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 \( 2.22 \times 10^{-26} \text{ mM g}^{-1} \). Kah et al. (2004) assumed \( F_P = 10 \times 10^{13} \text{ g yr}^{-1} \), which is the total sink flux for modern seawater sulfate, in order to model \( \partial^{34}S_{\text{CAS}}/\partial t \) (max). While this may be appropriate for intervals of widespread euxinia in the global ocean, \( F_P = 4 \times 10^{13} \text{ g yr}^{-1} \) (i.e., the modern sink flux) may better represent intervals with well-oxygenated oceans in which the sink fluxes of sulfate S and pyrite S are both substantial (Fig. 1). Assuming \( F_P = 4 \times 10^{13} \text{ g yr}^{-1} \) and values of \( \Delta^{34}S_{\text{CAS-PY}} \) and \( \partial^{34}S_{\text{CAS}}/\partial t \) (max) potentially representative of modern marine systems (e.g., 35 and 1.1 \% Myr\(^{-1} \)), Eq. 3 yields the modern seawater sulfate mass of \( M_{\text{SW}} = 1.3 \times 10^{21} \text{ g} \) and Eq. 4 yields the modern seawater sulfate concentration of \( \sim 29 \text{ mM} \).

Relationships among the rate-method parameters are illustrated in Fig. 1 for \( \Delta^{34}S_{\text{CAS-PY}} \) from 1 to 100 \% (or-dinal scale) and for discrete values of \( \partial^{34}S_{\text{CAS}}/\partial t \) (max) ranging from 1 to 100 \% Myr\(^{-1} \) (diagonal lines). [SO\(_4^{2-}\)]_{\text{SW}} increases linearly with increasing \( \Delta^{34}S_{\text{CAS-PY}} \) (at constant \( \partial^{34}S_{\text{CAS}}/\partial t \) (max)) and decreases linearly with increasing \( \partial^{34}S_{\text{CAS}}/\partial t \) (max) (at constant \( \Delta^{34}S_{\text{CAS-PY}} \)). The measured maximum \( \partial^{34}S_{\text{CAS}}/\partial t \) for a paleomarine unit is generally smaller than the theoretical maximum \( \partial^{34}S_{\text{SO4}}/\partial t \) 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 [SO\(_4^{2-}\)]_{\text{SW}} are generally larger than actual seawater sulfate concentrations, so Eq. 4 yields the maximum likely [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 \( \partial^{34}S_{\text{CAS}}/\partial t \) (max) of \( \sim 0.7 \% \text{ Myr}^{-1} \) (based on the Cenozoic seawater sulfate \( \Delta^{34}S \) record; Paytan et al., 1998). These inputs yield [SO\(_4^{2-}\)]_{\text{SW(max)}} values between \( \sim 40 \text{ and } 80 \text{ mM} \), which is modestly larger than the actual modern [SO\(_4^{2-}\)]_{\text{SW}} of \( \sim 29 \text{ mM} \) (Fig. 1). Overestimation of modern [SO\(_4^{2-}\)]_{\text{SW}} is due to measured \( \partial^{34}S_{\text{CAS}}/\partial t \) values for the Cenozoic (\( \leq 0.7 \% \text{ Myr}^{-1} \)) being lower than the theoretical maximum for modern seawater (\( \sim 1–2 \% \text{ Myr}^{-1} \)). This situation is probably typical of marine units of all ages – measured rates of \( \partial^{34}S_{\text{CAS}} \) 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 \( F_P \). This method is likely to yield an accurate estimate of seawater sulfate concentrations only if \( F_P \) is inversely proportional to the residence time of sulfate in seawater \( (t_{\text{SO4}}) \), which basically requires the ma-
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 $\left[SO_{4}^{2-}\right]_{sw}$-dependent pyrite burial flux relationship of Wortmann and Chernyavsky (2007). This procedure yielded Phanerozoic $\left[SO_{4}^{2-}\right]_{sw}$ estimates that are close ($\pm 10\%$) 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 $\left[SO_{4}^{2-}\right]_{aq}$ 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:

$$[SO_{4}^{2-}] = [SO_{4}^{2-}]_{sw} \times S/S_{sw}.$$  

(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 sulfate 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 cogenetic 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 $\Delta^{34}S_{CAS-PY}$ estimates for paleomarine units should be based on syngenetic 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. However, 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 (Fig. 2a) needs further testing; our data set for the possibly near-ubiquitous influence of $\text{SO}_4^{2-}$ to hold for a wide range of natural environments, reflecting the pattern of covariation between $F_{\text{MSR}}$ and $\Delta^{34}S_{\text{CAS-PY}}$ from the ordinal scale to the MSR trend and then to the abscissa (Fig. 2b), or by using the following empirical equation:

$$\log[\text{SO}_4^{2-}] = \left(\log(\Delta^{34}S_{\text{CAS-PY}}) - 1.10\right)/0.42.$$  

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

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

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

In order to account for uncertainties in $\Delta^{34}S_{\text{CAS-PY}}$ as well as the $F_{\text{MSR}}$ regression, estimates of minimum $[\text{SO}_4^{2-}]_{\text{sw}}$ should make use of minimum $\Delta^{34}S_{\text{CAS-PY}}$ 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 $\Delta^{34}S_{\text{CAS-PY}}$ 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 $^{32}$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; Detmers 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 \([\text{SO}_4^{2-}]_{\text{aq}} > \sim 200 \mu\text{M} \) (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 70–80\% 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 multistage 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 \(f_{\text{SO}_4}\), 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 \(\sim 30 \text{ to } 60\%\) 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 \(f_{\text{SO}_4}\) to evolve toward zero. As \([\text{SO}_4^{2-}]_{\text{aq}}\) 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 \(\delta^{34}\text{S}\) composition of the produced sulfide approaches that of the original aqueous sulfate inventory, and \(\Delta^{34}\text{S}_{\text{sulfate-sulfide}}\) approaches zero (Kaplan, 1983; Habicht et al., 2002). In a macro sense, \(f_{\text{SO}_4}\) can be probed by \([\text{SO}_4^{2-}]_{\text{aq}}\), accounting for the strong first-order relationship between the latter parameter and \(\Delta^{34}\text{S}_{\text{sulfate-sulfide}}\) (\(r = +0.90, p(\alpha) < 0.01\); 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 CO\(_2\) yields larger fractionations (\(\sim 30\text{–}60\%\)) than oxidation to acetate (\(< 18\%\)) (Detmers 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; Detmers 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; Detmers 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 \(\sim 15\text{–}20\%\) at rates > 50 mmol H\(_2\)S 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., Detmers 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 \([\text{SO}_4^{2-}]_{\text{aq}}\), 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 \([\text{SO}_4^{2-}]_{\text{aq}}\) in most environments. Whether the quantitative form of our \(F_{\text{MSR}}-[\text{SO}_4^{2-}]_{\text{aq}}\) 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 \(\sim 635\text{ Ma}\) may have limited disproportionation of intermediate-oxidation-state sulfur compounds and thus the potential for large fractionations.
(Habicht and Canfield, 2001; Sørensen and Canfield, 2004; Johnston et al., 2005). In the following analysis, we adopt the $F_{\text{MSR}}-\left[\text{SO}_4^{2-}\right]_{\text{aq}}$ relationship of Fig. 2a as a basis for evaluating the $\left[\text{SO}_4^{2-}\right]_{\text{aq}}$ 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., $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t$), whereas that of the MSR-trend method (Eqs. 6–8) makes use of an empirical relationship between $F_{\text{MSR}}$ and $\left[\text{SO}_4^{2-}\right]_{\text{aq}}$. The two methods are applicable over approximately the same range of $\left[\text{SO}_4^{2-}\right]_{\text{SW}}$ concentrations ($\sim 0.1$–$30$ mM). However, their transform functions have different sensitivities to $[\text{SO}_4^{2-}]_{\text{SW}}$, 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 $[\text{SO}_4^{2-}]$. 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 $[\text{SO}_4^{2-}]$. 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 $\delta^{34}\text{S}_{\text{SO4}}-\text{SW}$ 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 ($\pm1\sigma$) range (green field for low-resolution record; Table S3). Pre-Cretaceous and Cretaceous–Cenozoic estimates of $\delta^{34}\text{S}_{\text{SO4}}-\text{SW}$ have uncertainties of $\pm2$–$7\%$ and $\pm1\%$, respectively. The labels represent four short-term (<2 Myr) intervals of high-frequency $\partial\delta^{34}\text{S}_{\text{SO4}}/\partial t$ 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 ($\partial\delta^{34}\text{S}_{\text{SO4}}/\partial t$) as calculated from the seawater sulfate $\delta^{34}\text{S}$ LOWESS curves. The maximum Phanerozoic $\partial\delta^{34}\text{S}_{\text{SO4}}/\partial t$ is $<4\%\text{Myr}^{-1}$, although rates of 10 to $>50\%\text{Myr}^{-1}$ 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 ($\partial\delta^{34}\text{S}_{\text{SO4}}/\partial t$) 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...
30 ± 3% from 540 to 300 Ma, increased gradually from 30 to 45% between 300 and 270 Ma, and then fluctuated around 42 ± 5% from 270 to 0 Ma (Fig. 3c).

4.2 Long-term variation in seawater sulfate concentrations

Our composite record shows that seawater sulfate δ34S was heavy (~30–40‰) during the Ediacaran to middle Cambrian, declined steeply during the late Cambrian to Early Ordovician, and stabilized at intermediate values (~20–30‰) during the Middle Ordovician to Early Devonian (Table S3; Fig. 3a). Sulfate δ34S declined further during the Middle Devonian to Early Mississippian, reaching a minimum of ~12–16‰ during the mid-Mississippian to the end of the Permian. Sulfate δ34S then rose sharply to ~20‰ during the Early Triassic, before declining slightly to a local minimum of ~15‰ around the Jurassic–Cretaceous boundary. Sulfate δ34S rose slowly during the Cretaceous and early Cenozoic, increased rapidly from 17 to 22‰ at 40–50 Ma, and then stabilized at 21–23‰ during the mid- to late Cenozoic (Fig. 3a). The low-frequency LOWESS curve exhibits low rates of δ34S variation, with a mean of 0.25(± 0.17)%Myr−1 and a maximum of ~0.8‰Myr−1 (Fig. 3b). The high-frequency LOWESS curve exhibits somewhat higher rates of δ34S variation, with a mean of 0.40(± 0.45)%Myr−1 and a maximum of ~2.5‰Myr−1 (Fig. 3b). Both curves show exceptionally low rates of seawater sulfate δ34S 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 Phanerzoic, based respectively on the MSR-trend and rate methods, are shown in Fig. 4. The mean curve suggests that [SO42−]SW was low in the late Ediacaran (~1–4 mM) but rose sharply in the early Cambrian (to ~3–15 mM) and remained in that range until the Permian. A long, slow rise in [SO42−]SW began in the Early Permian and culminated at ~12–38 mM in the Middle Triassic. Subsequently, [SO42−]SW declined slightly by the mid-Cretaceous (to ~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 ~2 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 [SO42−]SW curve can be calculated for both the low- and high-frequency Phanerzoic δ34S records of Fig. 3a. The low- and high-frequency maximum [SO42−]SW curves (shown as black and red lines, respectively, in Fig. 4) mirror the upward trend through the Phanerzoic seen in the mean curve and thus are consistent with a factor of ~4 increase in seawater sulfate concentrations since the early Cambrian. Although the maximum [SO42−]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 [SO42−]SW than the largest values. The second observation is based on the fact that the smallest values derive from the largest measured rates of δ34SCAS 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 δ34SCAS variation. Thus, the lower envelope of maximum [SO42−]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 [SO42−]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 δ34S variation. δ34SO4/∂t(max) may be overestimated if there is an increase in δ34SCAS variance due to diagenesis or procedural artifacts during CAS extrac-
Figure 5. Comparison of Phanerozoic seawater sulfate [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; Halevy et al., 2012). Arrows indicate unconstrained minimum or maximum values.

... or it may be underestimated if there is a decrease in δ$^{34}$S$_{CAS}$ variance due to diagenesis or procedural smoothing. Data smoothing is inherent in the calculation of LOWESS curves (cf. Song et al., 2014), and underestimation of δ$^{34}$S$_{SO_4}$/∂t(max) is thus almost certain when smoothed δ$^{34}$S$_{SO_4}$ data sets are used as inputs. It may be responsible for the absence of short-term excursions in our Phanerozoic [SO$_4^{2-}$]$_{SW}$ curve (Fig. 3a), since a number of short (<2 Myr) intervals of strongly elevated δ$^{34}$S$_{SO_4}$/∂t rates have been documented for the Phanerozoic (Wortmann and Chernyavsky, 2007; Adams et al., 2010; Gill et al., 2011a,b; Newton et al., 2011; Wotte et al., 2012; Owens et al., 2013; Song et al., 2014; see Sect. 4.3). During these intervals, δ$^{34}$S$_{SO_4}$/∂t ranged from 10 to >50‰ Myr$^{-1}$ (Table S4), rates that are considerably higher than peak rates for the long-term δ$^{34}$S$_{CAS}$ curve (ca. 2–4‰ Myr$^{-1}$; Fig. 3b). Because lower values for δ$^{34}$S$_{SO_4}$/∂t(max) yield higher maximum estimates of [SO$_4^{2-}$]$_{SW}$ for ancient seawater (Eqs. 3 and 4), smoothing may account for some of the divergence between the mean and maximum trends in Fig. 4. The existence of such short-term episodes of seawater sulfate drawdown during the Phanerozoic has been attributed to several causes, including episodic massive evaporite deposition (Wortmann and Paytan, 2012) and reduced ventilation of marine sediments and a consequent increase in MSR in the aftermath of mass extinction events (Canfield and Farquhar, 2009).

Comparison of our Phanerozoic seawater sulfate concentration curve with previously published estimates reveals similarities and differences (Fig. 5). Most of these records exhibit a local minimum during the Jurassic or Cretaceous, although the absolute estimates of [SO$_4^{2-}$] for this minimum vary widely (~2 to 25 mM). Our higher estimates (~13-16 mM) compared to those of Wortmann and Paytan (2012) (uniformly <7 mM) may be a consequence of our choice of input data set, i.e., the Phanerozoic δ$^{34}$S$_{CAS-PY}$ record of Wu et al. (2010). The latter is based on a large compilative data set that yielded a strongly time-averaged trend, which is likely to have dampened variation in our [SO$_4^{2-}$]$_{SW}$ estimates. The various records are also in agreement that seawater sulfate was elevated during the Permian–Triassic, with concentrations of ~15–30 mM. The records diverge prior to the Permian, however, with one model (Holser et al., 1989) suggesting high values (30–50 mM) and another model (Berner, 2004) low values (<2 mM) through the mid-Paleozoic. Our model indicates intermediate sulfate concentrations (5–10 mM) at that time (Fig. 5). The various records also show dissimilar patterns across the Ediacaran–Cambrian boundary, with uniformly high values in the Holser et al. (1989) model and steeply falling values in the Berner (2004) model. The results of the present study favor a steep rise in seawater sulfate at this boundary. Our Phanerozoic seawater sulfate concentration record, along with that of Halevy et al. (2012), is in good agreement with the available fluid-inclusion data (Fig. 5) and thus appears generally robust, although it probably does not capture short-term episodes of seawater sulfate drawdown (see Sect. 4.3).

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 δ$^{34}$S (~12–16‰; Fig. 3a) and rates of δ$^{34}$S$_{SO_4}$ variation (<1‰ Myr$^{-1}$; Fig. 3b), accompanied by a concurrent increase in sulfate–sulfide fractionation (from <30 to >40‰; 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 δ$^{34}$S$_{SO_4}$ variation and an increase in sulfate–sulfide fractionation but, in contrast to the Late Paleozoic, 34S-enriched and relatively stable seawater sulfate δ$^{34}$S values (Fig. 3). The greater stability of seawater sulfate δ$^{34}$S 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 δ$^{34}$S$_{SO_4}$) and a consequent increase in the mass of seawater sulfate (hence, lower δ$^{34}$S$_{SO_4}$/∂t) (cf. Halevy 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. Halevy 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 $[\text{SO}_4^{2-}]_{\text{SW}}$ during selected intervals of the Neoproterozoic and Phanerozoic for which high-resolution $\delta^{34}S_{\text{CAS}}$ 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 $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ for 10 late Neoproterozoic units (Table S4; Fig. 6). Radiometric studies of the Doushantuo Formation in South China (Halverson et al., 2005; Zhang et al., 2005, 2008) provided key ages from which we calculated $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ of 5 ‰ Myr$^{-1}$ at 636–633 Ma and 1.3 ‰ Myr$^{-1}$ at 568–551 Ma (McFadden et al., 2008; Li et al., 2010). The Neoproterozoic succession of Sonora, Mexico, yielded $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ estimates of 6 and 4 ‰ Myr$^{-1}$ (Loyd et al., 2012, 2013). The latest Neoproterozoic Zaris Formation (Nama Group) in Namibia and upper Huqf Supergroup in Oman yielded $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ 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 $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from < 0.1 to > 100 mM, with most between ~ 1 and 10 mM (Table S4). The MSR-trend method yielded $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from < 0.1 to 70 mM, with most between ~ 1 and 16 mM. Many units exhibit combinations of $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ and $\Delta^{34}S_{\text{CAS-PY}}$ values that plot close to or slightly below the MSR trend (Fig. 6), yielding $[\text{SO}_4^{2-}]_{\text{SW}}$ 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 $[\text{SO}_4^{2-}]_{\text{SW}}$. 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 $[\text{SO}_4^{2-}]_{\text{SW}}$ for a set of eight units of Cambrian age. These units yielded $\frac{\partial \delta^{34}S_{\text{CAS}}}{\partial t}(\text{max})$ 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 $[\text{SO}_4^{2-}]$ variation during the Cambrian. The rate method yielded $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from < 0.1 to 18 mM, with most between ~ 1 and 6 mM. The MSR-trend method yielded $[\text{SO}_4^{2-}]_{\text{SW}}$ estimates ranging from < 0.1 to 40 mM, with most between ~ 1 and 8 mM. The two methods thus yielded similar estimates of seawater...
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 ± 5 ‰ (Wu et al., 2010), resulting in lower [SO\textsubscript{4}\textsuperscript{2−}]\textsubscript{SW} estimates than for the long-term record (Fig. 4). Once again, most units exhibit combinations of \(\frac{\Delta \delta^{34}S_{CAS}}{\partial t} \) (max) and \(\Delta^{34}S_{CAS-PY} \) 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 \(\Delta^{34}S_{CAS} / \partial t\) (max) of 6 to 60 ‰ Myr\textsuperscript{-1}, with the highest rates during the Early Triassic and Early Jurassic. The rate method yielded [SO\textsubscript{4}\textsuperscript{2−}]\textsubscript{SW} estimates ranging from 1.1 to 120 mM, with most between ~3 and 20 mM. The MSR-trend method yielded [SO\textsubscript{4}\textsuperscript{2−}]\textsubscript{SW} estimates ranging from 1 to 110 mM, with most between ~30 and 100 mM (Table S4). In contrast to the late Neoproterozoic and Cambrian, many Mesozoic units exhibit a narrow spread of \(\Delta^{34}S_{CAS-PY} \) 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 (~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 [SO\textsubscript{4}\textsuperscript{2−}]\textsubscript{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 \(\Delta^{34}S_{CAS} / \partial t\) (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, \(\Delta^{34}S_{CAS-PY} \) will be controlled by [SO\textsubscript{4}\textsuperscript{2−}]\textsubscript{SW}, which may be equal or close to that of the global ocean, but \(\Delta^{34}S_{CAS} / \partial t\) (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, $\Delta^{34}\text{CAS-PY}$ is controlled by seawater [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 $^{34}\text{S}$ 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 [SO$_4^{2-}$]$_{SW}$ estimates for individual Neoproterozoic and Phanerozoic units shown in Figs. 6–8 with the long-term [SO$_4^{2-}$]$_{SW}$ 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 $\partial\delta^{34}\text{CAS} / \partial t$ values as a consequence of rapid evolution of seawater sulfate $^{34}\text{S}$ within semi-restricted marine basins of the proto-Atlantic and western Tethys oceans. Cambrian units exhibit a wide range of [SO$_4^{2-}$]$_{SW}$ 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 [SO$_4^{2-}$]$_{SW}$ for the Cambrian, or the studied units are biased toward low [SO$_4^{2-}$]$_{SW}$. Late Neoproterozoic units exhibit an even wider range of [SO$_4^{2-}$]$_{SW}$ estimates than Cambrian units and lack any apparent clustering (Fig. 10). However, all but one of these units yield similar [SO$_4^{2-}$]$_{SW}$ estimates...

Figure 10. Seawater sulfate concentrations for late Neoproterozoic and Phanerozoic marine units (Figs. 6–8) compared with long-term [SO$_4^{2-}$]$_{SW}$ curve (Fig. 4). Estimates of [SO$_4^{2-}$]$_{SW}$ 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.

cause the most heavily scrutinized ancient geologic epochs are those with unstable environments.

**Type II deviations**, in which $\partial\delta^{34}\text{CAS} / \partial t$ (max) is anomalously high, are more common, being present in three units of late Neoproterozoic and Cambrian age (Figs. 6–7) and seven out of eight units of Mesozoic age (Fig. 8). Several factors might potentially produce this pattern. First, $\partial\delta^{34}\text{CAS} / \partial t$(max) may have been overestimated owing to inadequate geochronologic constraints, diagenetic artifacts, or analytical uncertainties in measuring $^{34}\text{S}$CAS. However, the fact that type II deviations are more common among Mesozoic units (Fig. 8), which are generally better dated and less diagenetically altered than older units (Figs. 6–7), suggests that such problems are relatively uncommon and unlikely to be responsible for most such anomalies. Second, the measured $\Delta^{34}\text{CAS-PY}$ for a given paleomarine unit may be unrepresentative, perhaps because of unusually large MSR fractionation (cf. Habicht et al., 2002; Canfield et al., 2010). This explanation may be applicable, for example, to Pleistocene Mediterranean sapropels (Scheiderich et al., 2010), which exhibit unusually large $\Delta^{34}\text{CAS-PY}$ values (60±5‰; Fig. 8). However, none of the anomalous units of late Neoproterozoic, Cambrian, or Mesozoic age exhibits a $\Delta^{34}\text{CAS-PY}$ larger than the typical modern range of ~30–60‰, so elevated sulfate–sulfide fractionation is unlikely as a general explanation. We are therefore inclined to regard most type II deviations as products of local depositional conditions and to seek an environmentally based mechanism to account for them.
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 [SO$_2^{−}$$_{4}$]$_{SW}$, respectively, for a paleomarine unit of interest. Both techniques make use of $\Delta^{34}$S$_{CAS-PY}$, i.e., the isotopic fractionation associated with microbial sulfate reduction (MSR). The rate method evaluates [SO$_2^{−}$$_{4}$]$_{SW}$ as a function of $\partial\delta^{34}$S$_{CAS} / \partial t$ (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 [SO$_2^{−}$$_{4}$] can be derived from two readily measurable sedimentary parameters: $\Delta^{34}$S$_{CAS-PY}$ and $\partial\delta^{34}$S$_{CAS} / \partial t$ (max). Based on these methods, an analysis of long-term variation since 635 Ma suggests that [SO$_2^{−}$$_{4}$]$_{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 $\delta^{34}$S$_{CAS}$ 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 [SO$_2^{−}$$_{4}$] 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 $\delta^{34}$S$_{CAS}$ 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 δ34S (i.e., δ34Sosm / δτ(max)) is inversely proportional to the residence time of sulfate in seawater (τ). The exact quantitative form of this relationship can be derived from Eq. (2) of Algeo et al. (2014), reorganization of which yields

\[ M_{SW} / F_{PY} = k_1 \times \Delta^{34}S_{CAS-PY} / \delta^{34}S_{CAS} / \delta\tau (max). \]  

(A1)

The residence time of sulfur in seawater is equal to the mass of seawater sulfate divided by the total sink flux, i.e., the reduced sulfur flux (F_{PY}) plus the oxidized sulfur flux (F_{EVAP}):

\[ \tau = M_{SW} / (F_{PY} + F_{EVAP}). \]  

(A2)

If we let \( \varphi_{PY} \) be the fraction of the total S flux represented by pyrite burial (i.e., \( F_{PY} / (F_{PY} + F_{EVAP}) \)), then

\[ \tau \times \varphi_{PY}^{-1} = M_{SW} / F_{PY}, \]  

(A3)

and substitution into Eq. (A1) yields

\[ \tau \times \varphi_{PY}^{-1} = k_1 \times \Delta^{34}S_{CAS-PY} / \delta^{34}S_{CAS} / \delta\tau (max). \]  

(A4)

This equation quantifies the inverse proportionality between the maximum rate of change of seawater sulfate δ34S and the residence time of sulfur in seawater.

A2 Effects of [SO4^{2-}]SW-dependent pyrite burial fluxes on [SO4^{2-}]SW estimates

Although we made use of fixed estimates of the pyrite burial flux (F_{PY}), i.e., \( 4 \times 10^{13} \) g yr\(^{-1} \) for oxic oceans and \( 10 \times 10^{13} \) g yr\(^{-1} \) for anoxic oceans, it is possible that F_{PY} is dependent on [SO4^{2-}]SW. Wortmann and Chernyavsky (2007) inferred a nonlinear positive relationship of F_{PY} with [SO4^{2-}]SW (their Fig. 4). We explored the effects of varying pyrite burial fluxes on seawater sulfate estimates as follows. Equations (2–3) have four variables: [SO4^{2-}]SW (or M_{SW}, since these are interconvertible via Eq. 4), F_{PY}, \( \Delta^{34}S_{CAS-PY} \), and δ34Sosm / δτ. However, \( \Delta^{34}S_{CAS-PY} \) can be modeled as a function of [SO4^{2-}]SW (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 [SO4^{2-}]SW and F_{PY} on δ34Sosm / δτ(max) via a modified form of Eq. (2):

\[ \delta^{34}S_{CAS} / \delta\tau (max) = k_1 \times k_2 \times F_{PY} \times \exp(\log([SO4^{2-}]_{SW} \times 0.42 + 1.10) / [SO4^{2-}]_{SW}). \]  

(A5)

The three modeled parameters exhibit log-linear relationships, with larger δ34Sosm / δτ(max) associated with larger [SO4^{2-}]SW and F_{PY} (Fig. A1). δ34Sosm / δτ(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., \( 4–10 \times 10^{13} \) g yr\(^{-1} \)) is consistent with variation in δ34Sosm / δτ(max) from \(~1\) to 100% Myr\(^{-1} \). The F_{PY}–[SO4^{2-}]SW relationship of Wortmann and Chernyavsky (2007, their Fig. 4; red curve, Fig. A1), if correct, indicates that variation in δ34Sosm / δτ(max) cannot exceed \(~3\)% 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-

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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 $F_{\text{PY}}$ is given by the polynomial equation

$$[\text{SO}_4^{2-}]_{\text{SW}}(\text{max}) / F_{\text{PY}} = -0.0018([\text{SO}_4^{2-}]_{\text{SW}})^2 + 0.2842([\text{SO}_4^{2-}]_{\text{SW}}) + 0.4651. \quad (A8)$$

With substitution and reorganization, Eqs. (A7) and (A8) yield

$$0 = -0.0018([\text{SO}_4^{2-}]_{\text{SW}})^2 + 0.2842([\text{SO}_4^{2-}]_{\text{SW}}) + \left(0.4651 - k_1 \times k_2 \times \Delta^{34}\text{S}_{\text{CAS-PY}} / \partial\delta^{34}\text{S}_{\text{CAS}} / \partial t(\text{max})\right). \quad (A9)$$

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 for oxic 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
To fully reconstruct the secular change in seawater sulfate concentrations during the Phaner-
The Supplement related to this article is available online at doi:10.5194/bg-12-2131-2015-supplement.

Author contributions. T. J. Algeo developed the project concept and modeling methodology; G. M. Luo, H. Y. Song, T. W. Lyons, and D. E. Canfield provided isotopic data; and all authors assisted in drafting the manuscript.

Acknowledgements. We thank U. G. Wortmann and an anonymous reviewer for constructive reviews and C. P. Slomp for editorial handling of the manuscript. Research by T. J. Algeo and T. W. Lyons is supported by the Sedimentary Geology and Paleobiology program of the US National Science Foundation and the NASA Exobiology program. T. J. Algeo also gratefully acknowledges support from the China University of Geosciences, Wuhan (SKL-GPMR program GPMR201301, and SKL-BGEG program BGL21407).

Edited by: C. P. Slomp

References


Hurtgen, M. T., Arthur, M. A., and Halverson, G. P.: Neoproterozoic sulfur isotopes, the evolution of microbial sulfur species, and the


