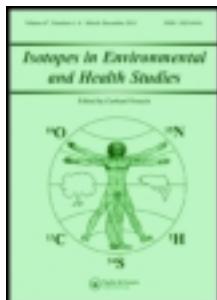


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Application of sulphur isotopes for stratigraphic correlation

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The sulphur isotopic composition of dissolved sulphate in seawater has varied considerably through time. Certain time intervals are characterised by distinct variations and a relatively high rate of change. These relatively rapid fluctuations allow for correlation of sediment sections using sulphur isotopes. Sulphur isotope reconstructions based on the analysis of carbonate associated sulphate or marine barite result in sulphur isotope records with an age resolution of 1–5 million years (Ma), and for some age intervals the resolution is <0.25 Ma. At these specific time intervals, where higher resolution records exist and excursions in the record are identified, the trends could be used for stratigraphic correlations. Such records are particularly useful in sections from deep marine sites that lack biostratigraphic controls or where biozones do not provide sufficient resolution.

Keywords: age; correlation; isotope hydrogeology; stratigraphy; sulphur-34

1. Introduction

Stable sulphur isotope ratios have been used in many geological, biological and environmental studies [1,2]. Sulphur is an important constituent of Earth's lithosphere, biosphere, hydrosphere and atmosphere and occurs as a major constituent or in trace amounts in various components of the Earth system [3]. Many of the characteristics of sulphur isotope geochemistry are analogous to those of carbon and nitrogen, as all three elements occur in reduced and oxidised forms, and undergo oxidation state changes as a result of biological processes.

Sulphur as sulphate (SO_4^{2-}) is the second most abundant anion in modern seawater with an average present day concentration of 28 mM. It has a conservative distribution with uniform SO_4 /salinity ratios in the open ocean and a very long residence time of close to 10 million years (Ma) [4,5]. In the present day ocean, seawater maintains a constant $\delta^{34}\text{S}$ value of 21 ‰ [6,7] at an analytical precision of ± 0.2 ‰ (until the salinities are brackish and well below those supportive of fully marine fauna) [6,8].

Due to the large reservoir size and long residence time of sulphate in the ocean, the isotopic composition of seawater sulphate ($\delta^{34}\text{S}_{\text{SO}_4}$) is expected to be homogeneous at any given time (at least for much of the Phanerozoic) [8], but see [9,10]. However, if the oceanic S reservoir

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has been considerably smaller in the past [11], the possibility for some small variability exists, limiting the application of the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ record for stratigraphy to intervals where the changes in the secular record are large. Fluctuations in $\delta^{34}\text{S}_{\text{SO}_4}$ have occurred over the geological record in response to changes in geological, geochemical and biological processes [12,13]. Such fluctuations result from changes in the input and output fluxes of S to the ocean and their respective isotopic signatures. Specifically, $\delta^{34}\text{S}_{\text{SO}_4}$ of seawater at any given time is controlled by the relative proportion of sulphide and sulphate input and removal from the oceans and their isotopic compositions [e.g. 14]. Sulphur is commonly present in seawater and marine sediments in one of two redox states: (i) in its oxidised state as sulphate and sulphate minerals and (ii) in its reduced form as H_2S and sulphide minerals. The oceanic $\delta^{34}\text{S}_{\text{SO}_4}$ record provides an estimate for the relative partitioning of S between the oxidised and reduced reservoirs through time.

The largest input to the oceans today is from river run-off from the continent. The $\delta^{34}\text{S}_{\text{SO}_4}$ value of this source is variable (0–10‰), but typically lower than seawater depending on the relative amount of gypsum and pyrite in the drainage basin [1,15]. Volcanism and hydrothermal activity are also small sources of S to the ocean with $\delta^{34}\text{S}_{\text{SO}_4}$ close to 0‰ [15], and hydrothermal systems can also be a small sink through the formation of anhydrite and serpentine [16,17]. The output flux is via deposition of evaporites and other sulphate-containing minerals ($\delta^{34}\text{S}_{\text{SO}_4\text{evaporite}} \cong \delta^{34}\text{S}_{\text{SO}_4\text{seawater}}$) and sulphides with $\delta^{34}\text{S}_{\text{pyrite}} \cong -15\text{‰}$ with a range of +15 to -70‰ [1,18]. The typically small isotope ratios of sulphides are a result of the strong sulphur isotope fractionation involved in bacterial sulphate reduction, the precursor for sulphide mineral formation [1,18,19]. The fractionation associated with bacterial sulphate reduction is influenced by many factors including the bacterial assemblage involved, temperature, substrate availability, whether the system behaves as a closed or open system and more (for more detail see [20]). This results in the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ being heavier than any of the input sources to the ocean. It has also been suggested that, in addition to changes in the relative rate of burial of reduced and oxidised sulphur, the marine $\delta^{34}\text{S}_{\text{SO}_4}$ record has been sensitive to the development of a significant reservoir of H_2S in ancient stratified oceans [21]. Specifically, extreme changes over very short geological time scales (such as at the Permian–Triassic boundary) along with evidence for ocean anoxia could be explained via the development of a large, relatively short-lived reservoir of H_2S in the deep oceanic water column followed by oceanic overturning and re-oxygenation of the H_2S .

The evidence that seawater $\delta^{34}\text{S}_{\text{SO}_4}$ has fluctuated considerably over time, until relatively recently, was based on comprehensive, though not continuous, isotope data sets obtained from marine evaporitic sulphate deposits and pyrite. More recently, marine barite has been used to construct a continuous high-resolution seawater $\delta^{34}\text{S}_{\text{SO}_4}$ curve for the Cenozoic and Cretaceous [22,23]. Methods to analyse sulphate that is associated with marine carbonate deposits (Carbonate Associated Sulphate, CAS) have also been developed and new data sets using these methods are becoming available. Specifically, CAS has been used to reconstruct global change in the sulphur cycle on both long [24,25] and short [26,27] time scales. The new data from barite and from CAS show considerably more detail and fill significant gaps in the former data set, revealing previously unrecognised structures.

The seawater $\delta^{34}\text{S}_{\text{SO}_4}$ record has been used extensively to shed light on global biogeochemical cycles on Earth [2,5]. However, this isotope system has so far not been used extensively as a tool for stratigraphic correlation or dating. Detailed relatively high-resolution seawater $\delta^{34}\text{S}_{\text{SO}_4}$ data reveal certain intervals where the rate of change and the unique features of the record may yield a reliable numerical age and could be used for correlation between stratigraphic sections and sequences (Figure 1). These fluctuations likely resulted from rapid perturbations in the sulphur cycle that induce such changes. Notably the sensitivity of the oceanic S reservoir to change also depends on the size of the reservoir, thus the concentration of S in seawater [11,28,29].

Application of sulphur isotopes for stratigraphy is particularly important for sequences dominated by evaporites or deep-sea sediments, where fossils are not abundant or have a restricted

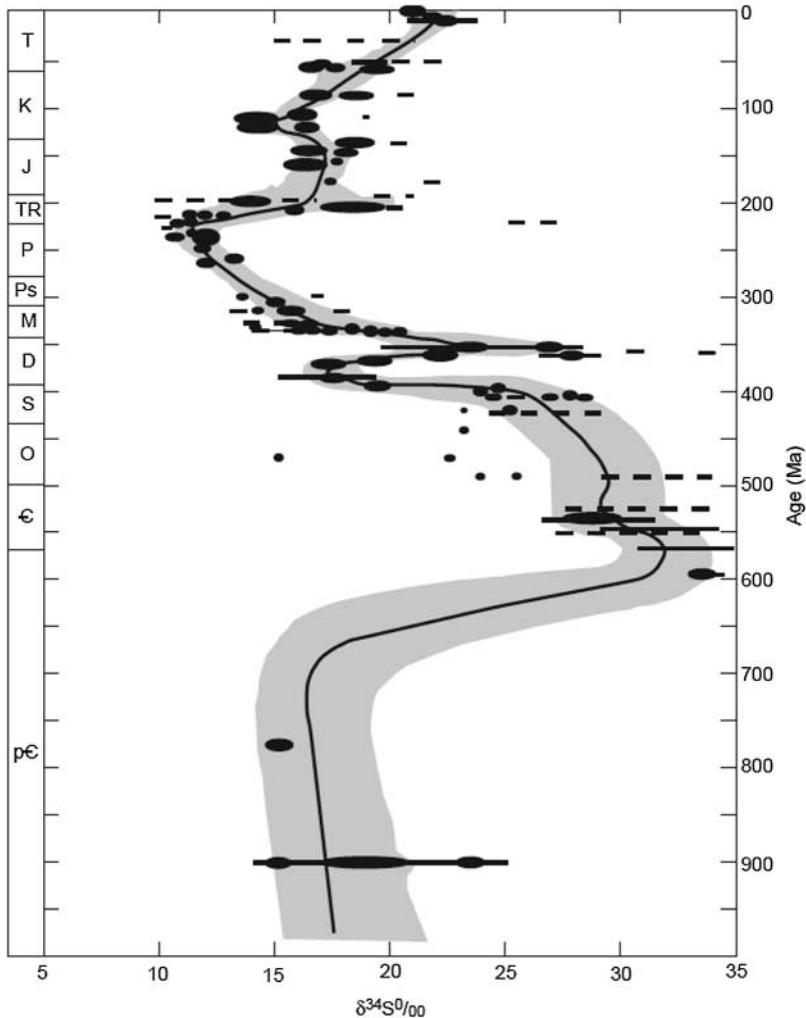


Figure 1. Sulphur isotope curve based on the evaporite record of Claypool *et al.* [36]. Solid lines represent data from Claypool and data he compiled from the literature plotted at their most probable age. Dashed lines show the range of all available few analyses for each time interval. The heavy line is the best estimate of $\delta^{34}\text{S}$ of the ocean. The shaded area is the uncertainty related to the curve.

distribution range, paramagnetic minerals are rare, and other stratigraphic tools (e.g. oxygen isotopes in carbonates) cannot be utilised. It is important to note that the use of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ for stratigraphic applications works only for marine minerals containing sulphate. Moreover, it is crucial to confirm the integrity of the record to ensure its pristine nature and the lack of post-depositional alteration [24,25]; such alterations are common as summarised in [30,31].

While the potential for the utility of sulphur isotope stratigraphy exists, this system has not been broadly applied. The examples for the application of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ for stratigraphic correlations predominantly focus on the Neoproterozoic and often employ other methods of correlation, such as $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ as well [32–34]. The main limitation for broader application of this isotope system for stratigraphy and correlation is the lack of reliable, high-resolution, globally representative isotope records that could be assigned a numerical age scale. As such records become available, the utility of this system can expand considerably.

In this manuscript we provide a few examples for the use of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ data for stratigraphic correlations and discuss the utility, limitations and future needs for application of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ for stratigraphy.

2. Sulphur isotope records

Age resolution of the S isotope curve varies with the type of data comprising the record and the specific objectives for the various studies producing the data. The older sections compiled from evaporite and CAS data have a lower resolution because of the scarcity of evaporites and because CAS depends on the integrity of the carbonates and fossils used for reconstruction, which, in many locations, are subjected to extensive post-depositional alteration [30,31] or may record local effects [35]. In addition, large temporal gaps between samples make it difficult to correlate between sites and thus make exact age determinations challenging. Despite these limitations, robust CAS records exist for specific time periods and the confidence within each such time interval is considerably improved from the earlier evaporite records. Age resolution of records based on barite is much better, but so far barite has been recovered predominantly from pelagic sediments, limiting the applicability to the last 130 Ma.

3. Suitability of long-term seawater S isotope records for stratigraphy

The Phanerozoic evaporite record compiled by Claypool *et al.* [36] with further work done by Strauss [12] has several characteristics that make it difficult to use it for S isotope stratigraphy. First, the record has large gaps that leave long periods of time unaccounted for. In [36], a best-estimate curve was visually approximated to combine and extrapolate between disparate data sets; however, this smoothes over finer fluctuations that may be present. Second, the absolute seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values recorded at each time point range considerably confounding the issue. The range of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values within each time interval is approximately 5‰ for most of the data sets used which makes pinpointing an age from a stratigraphic perspective difficult since, in many cases, the broad fluctuations that occur over time are within $\pm 5\%$ (Figure 1). Third, the ages used for each sample are approximate due to the scarcity of fossils in sections used to compile the isotope curves. Even in the evaporite record from Strauss [37] that derives its ages after Harland *et al.* [38], the age uncertainty spans more than 10 Ma depending on the segment (or specific time range), which makes it difficult to use these data for stratigraphic correlation.

The seawater $\delta^{34}\text{S}_{\text{SO}_4}$ isotope record derived from CAS is more robust (Figure 2). The record is consistent with the evaporite data in the broad strokes, but a better constraint on the ages of the samples is possible. The data set presented in [24] and references therein show a record for the Phanerozoic that reduces the uncertainty in age and seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values considerably from those associated with evaporites. The CAS samples were taken from stratigraphically well-constrained biogenic calcites (using the time scale of Harland *et al.* [38]) with a resolution of 1-5 Ma within data sets. However, the data sets analysed are not continuous, leaving gaps, which, while not as glaring as those in the evaporite record, still limit the accuracy of a smooth curve and may miss finer details. The CAS data that represent older ages have a wider range of S isotope values than that of more recent (younger) samples, e.g. a ‘scatter’ of $\pm 10\%$ and even up to 20‰ in the Cambrian and Ordovician for samples with similar ages. More recent samples have narrower ranges, from 5 to 10‰, and would thus be more useful for stratigraphy, although in some places, the low temporal resolution still makes it difficult to distinguish noise from trend [24]. The data compiled and presented in [24] is based on a moving average to create a continuous

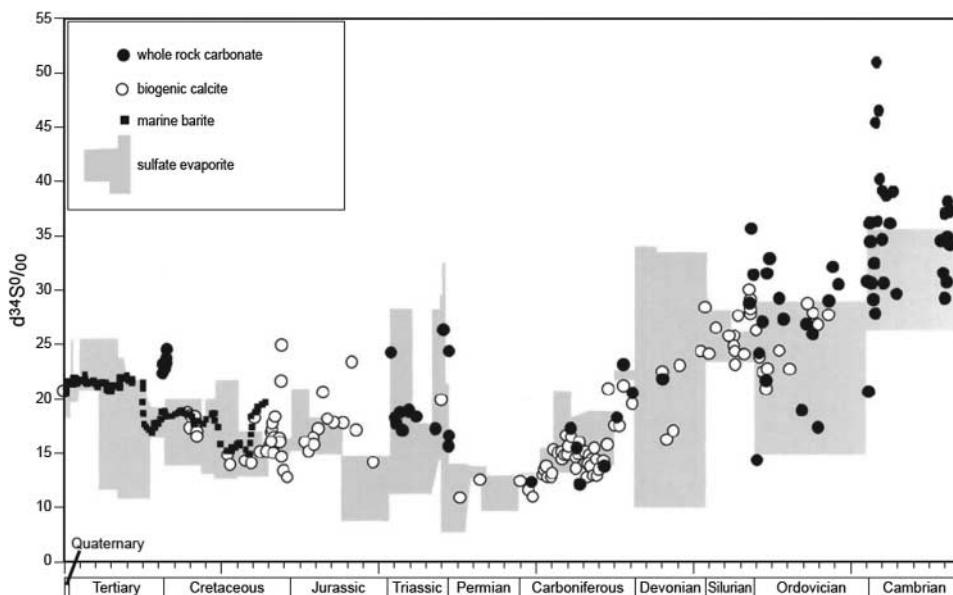


Figure 2. The carbonate associated sulphate record from Kampschulte and Strauss [24], evaporite data from Strauss [12] and barite data from Paytan *et al.* [7,22].

curve (Figure 2). The effect is to smooth out the observed variation which then makes it difficult to assess the error associated with both the isotope data set (e.g. seawater $\delta^{34}\text{S}_{\text{SO}_4}$) and the age resolution. This makes it difficult to resolve trends and compare the data with other records or to use the curve for precise sample age determination. The barite-based seawater $\delta^{34}\text{S}_{\text{SO}_4}$ curve covering the past 130 Ma provides a record with a resolution of less than 1 Ma with very few gaps (Figure 3). The age of the samples is constrained by biostratigraphy and Sr isotopes and typically

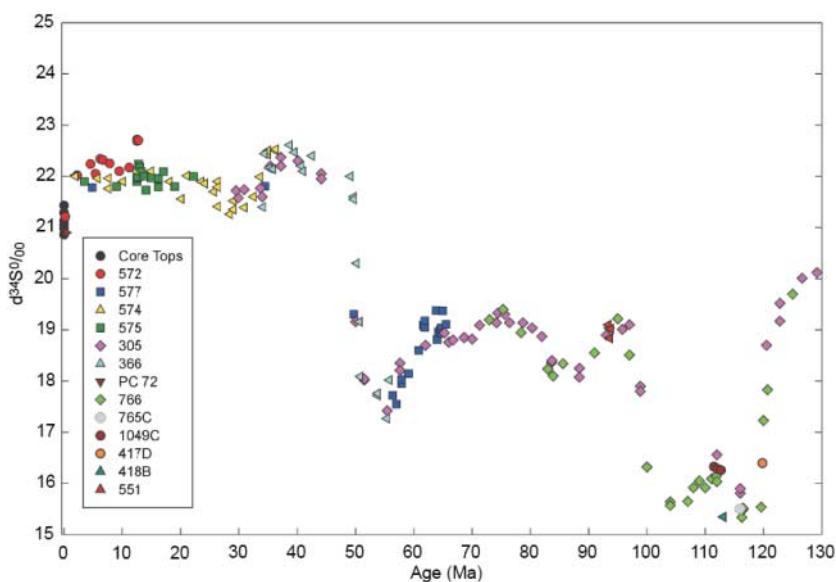


Figure 3. Seawater sulphate S isotope curve from marine barite for 130 Ma to present [22].

has an error of less than 100,000 years. The continuous and secular (based on data from multiple sites for each time interval) nature and the high resolution of this record illuminate finer features that are missed in the lower resolution records. The record also has a narrower range of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values for each time point ($<0.5\%$), further constraining the curve.

Despite the limitations noted above, some general trends in the available records are observed. The current compilation of sulphur isotope records includes data sets from the Cambrian to the present. In the Cambrian, the average seawater $\delta^{34}\text{S}_{\text{SO}_4}$ value is in the range of around 30‰ [12,24,36], and these relatively high values are sustained through the Cambrian, ending with anomalously high seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values at the Cambrian/Ordovician boundary. After this point, the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ decreases steadily through the remainder of the Paleozoic, reaching a minimum at the Permian/Triassic boundary with an average value of $13.2 \pm 2.5\%$. Through the Mesozoic, the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values are generally lower than in the Paleozoic, ranging between 14 and 20‰. The seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values increase quite rapidly from $13.2 \pm 2.5\%$ at the Permian/Triassic boundary to 17‰ in the Jurassic and decreases again to about 15‰ in the early Cretaceous [12,24,36]. The average value in the Cretaceous is about 19‰, but two distinct excursions towards lower values are seen: one at ~ 120 Ma and the second at ~ 90 Ma [22]. A decrease in seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values from ~ 20 to 16‰ is seen in the Paleocene before climbing sharply in the Early to Middle Eocene to the near modern value of 21‰ where it remains steady for the remainder of the Cenozoic [7] with a small drop in the value over the past million years.

The general trends for the record throughout the Phanerozoic can be used for broad age assignments (e.g. typically only at the epoch scale) and correlations at distinct intervals with defined excursions (e.g. the Permian–Triassic Boundary).

4. Geological boundaries and specific age intervals

Strauss [12] reviewed secular variations in $\delta^{34}\text{S}_{\text{sulphide}}$ across time boundaries characterised by profound biological or geological changes. These time boundary studies have used data obtained from sedimentary sulphides. The premise behind the study of isotope excursions at age boundaries is based on the expected perturbations in the biosphere which may impact sulphate reduction rates. During a catastrophic event, where productivity plunges, the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values of the oceans are expected to decrease because of a reduction in organic matter availability, leading to lower sulphate reduction and less burial of products such as pyrite that are characterised by low isotope ratios. The subsequent biological radiations should have the opposite effect. Accordingly, the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values in the open ocean should first decrease across a time boundary associated with a catastrophic extinction or major ecosystem reorganisation, and then increase during the period of recovery. The magnitude of the effect is likely related to the intensity of the extinction event, the rate of recovery and the size of the oceanic sulphur reservoir. Four extinction events have been studied [12]: the Precambrian–Cambrian, the Frasnian–Famennian, the Permian–Triassic and the Cretaceous–Tertiary boundaries. Of these, only the Permian–Triassic event shows the expected trend. Fluctuations occur at the other boundaries, but no secular (globally concurrent) variations during geological time boundaries have been observed (see also [21]). In part the reason for the inconsistent results between sections and between extinction events may be related to the inherent problems of analysing sulphides instead of sulphates to reconstruct seawater $\delta^{34}\text{S}_{\text{SO}_4}$ and the multitude of controls impacting the isotopic composition of sulphides [19,20]. Therefore, local effects may mask any global sulphur variations when using sulphide sulphur to reconstruct seawater $\delta^{34}\text{S}$.

Although consistent global trends across extinction boundaries were not uniformly observed, periods of large and rapid fluctuations are detected both in high-resolution CAS studies that focus

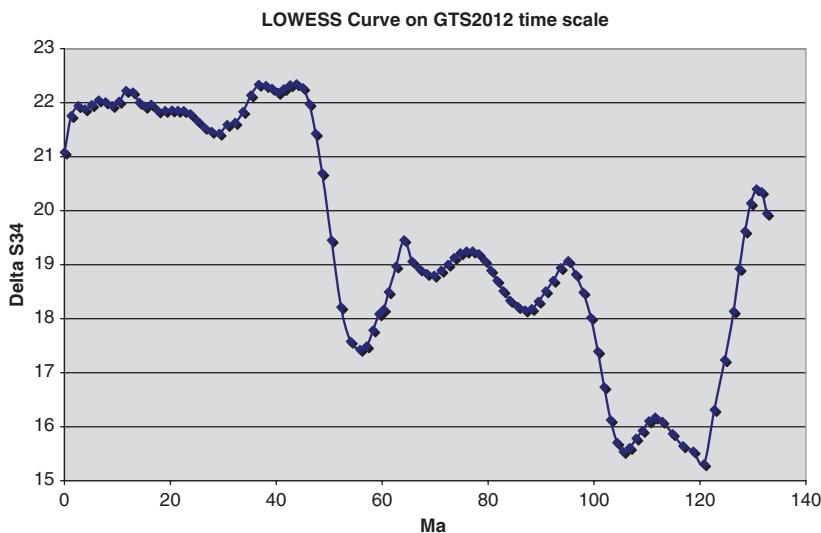


Figure 4. LOWESS curve for the last 130 Ma years generated from marine barite data [22] age model is based on the GTS 2012 time scale.

on specific time intervals and in a relatively high-resolution record for the past 130 Ma using marine barite [7,22]. The time periods best suited for dating are those that are distinguished by rapid changes in seawater $\delta^{34}\text{S}_{\text{SO}_4}$. The features that appear in the barite high-resolution curve show five time periods with relatively abrupt changes in seawater $\delta^{34}\text{S}_{\text{SO}_4}$ that could lead to precise dating: 130–116, 107–96, 96–86, 83–75 and 65–45 Ma. Resolving ages during periods of smaller fluctuations is possible but would likely necessitate a much larger data set and finer resolution in order to match multiple points and avoid offsets between data from distinct sites [23]. The plateaus, notably from ~ 30 to about 2 Ma, where seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values do not significantly change, are not useful because there are few features that can be teased out and distinguished from sampling and analytical error. The trends in seawater $\delta^{34}\text{S}_{\text{SO}_4}$ can be illustrated using LOWESS regression for the marine barite data set over the Cretaceous and Cenozoic (Figure 4). The seawater $\delta^{34}\text{S}_{\text{SO}_4}$ data sets used for producing the LOWESS regression are from Paytan *et al.* [7,22]. The time scales used for the curve as reported in [7,22] are based on 0–6.4 [39], 6.4–70 Ma [40], 70–98.5 [41,42] and 98.5–206 Ma [43]. All ages were adjusted to the GTS 2012 time scale. Based on the LOWESS curve we calculated the age resolution associated with four age intervals that exhibit abrupt changes in seawater $\delta^{34}\text{S}_{\text{SO}_4}$, 130–120, 105–95, 64–55 and 55–46 Ma. In addition, smaller but resolved shifts are also observed at 95–87 and 87–78 Ma. Age resolutions are 0.5, 0.7, 1.2 and 1.5 Ma, respectively, for the four age sections and 2.1 Ma, for the smaller shifts between 96 and 78 Ma, based on the data and an analytical error of 0.2‰.

Below we present a few examples for which published seawater $\delta^{34}\text{S}_{\text{SO}_4}$ data either from CAS or barite is of relatively high temporal resolution and thus could be used for stratigraphic applications. We note that some potential exists for applying this tool for samples spanning the Paleozoic, as could be seen from the examples below. At present with the currently available data sets, no such applications are recommended.

4.1. Cambrian

The seawater $\delta^{34}\text{S}_{\text{SO}_4}$ data from the Cambrian based on CAS is characterised by relatively high values ($>30\%$) and can be used to identify samples of Cambrian age; however, distinguishing

between older and younger samples within the Cambrian may be difficult. These values are based on only two data sets and thus, it is important to verify the global nature of these isotope values using data from other distinct sites such that post-deposition alteration of the isotope values can be ruled out.

4.2. Devonian

Seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values in the Devonian show a downward trend decreasing from $\sim 25\%$ in the Late Silurian to $\sim 19\%$ in the lower middle Devonian. A steep slope from 408–395 Ma with a 6% change over 13 Ma can potentially be used for correlations, although as noted above, the age uncertainty for this time interval is rather large, which may limit accurate dating. Moreover, as for the Cambrian, the record is based on only a small number of data points from one locality.

4.3. Carboniferous

The Carboniferous is also characterised by a decrease in the CAS data from $\sim 20\%$ in the Early Carboniferous (Mississippian) to $\sim 15\%$ at 334 Ma where it remains until decreasing to around 12% in the Late Carboniferous (Pennsylvanian; [26,24]). Thus, there is a potential for stratigraphic applications for the Early and Late Carboniferous, provided the available data are indeed representative of global trends.

4.4. Permian/Triassic

The Permian record seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values are around 12% . This value is seen in the 16 samples analysed for the Permian [24]. This overall seawater $\delta^{34}\text{S}_{\text{SO}_4}$ value is distinctive for the period and is useful for dating the period as a whole but the plateau in the record does not lend itself to more precise correlation within the Permian.

The Permian/Triassic boundary has been sampled at higher resolution of 1 Ma [21,44–47] and shows distinct fluctuations that are more useful for correlations. Specifically, the transition from the Paleozoic to the Mesozoic is marked by an abrupt shift in sulphur isotope values from the low 12% value of the Late Permian to 29.7% in the lower Triassic. The excursion of at least 10% over only a few million years or even less allows for age resolution of less than 100,000 years and robust correlation to be made. Another potential period suitable for correlation is in the uppermost Triassic where short-term fluctuations between 11.1 and 24.3% occur [24].

Many studies focused on the Permian/Triassic boundary [21,44–54] use $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, biostratigraphy, paleomagnetism and other methods to correlate the S isotope records and use the S data to investigate the causes and consequences of various biogeochemical cycles across the boundary. The generally similar trends reported for sections throughout the world indicate that the trends are primary and, most importantly, global. Accordingly, the secular and defined trend in the S isotope record at this time interval could be used for correlation even if other data are not available. Indeed, Cortecchi *et al.* [48] used the S isotope record to correlate among sections representing this age interval despite relatively low-resolution data available at that time. At present, a relatively high-resolution record showing much finer trends reported by Luo *et al.* [54] exists and is particularly useful for correlation applications as seen in Figure 5(a).

4.5. Jurassic

The Jurassic seawater $\delta^{34}\text{S}_{\text{SO}_4}$ values range from 14.2 to 18.0% with two exceptional excursions. The first occurs in the lower middle Jurassic with a seawater $\delta^{34}\text{S}_{\text{SO}_4}$ value of 23.4% . The second

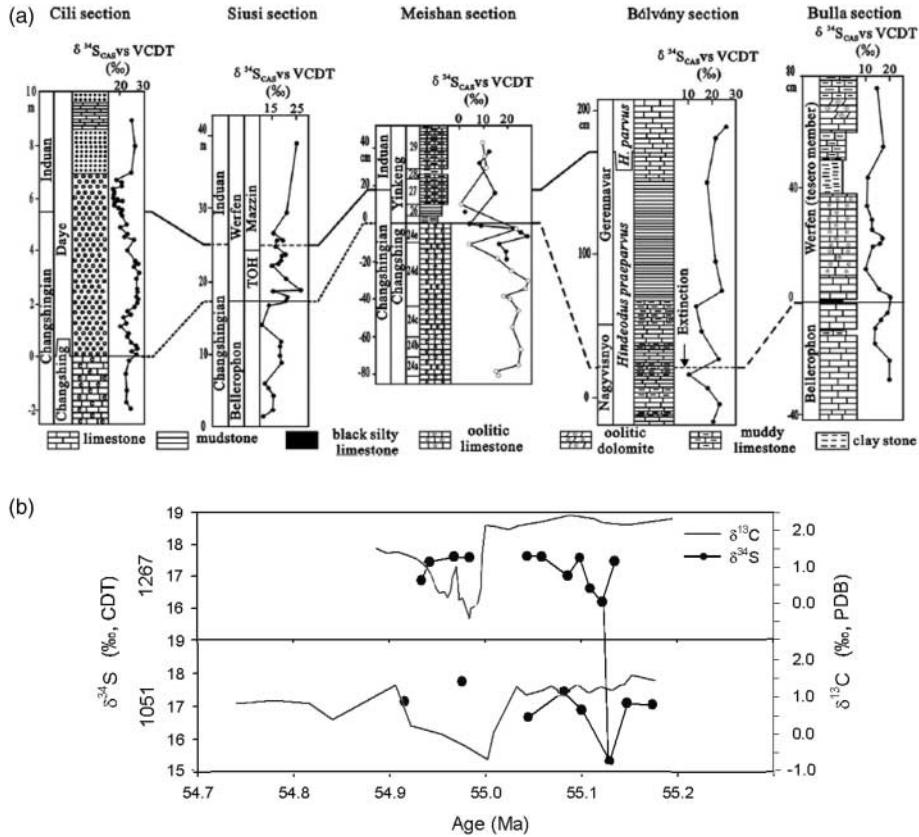


Figure 5. (a) Global comparison of the sulphate sulphur isotope compositions during the Perm-Triassic transition among different sections, figure reproduced from Luo *et al.* [54]; (b) $\delta^{13}\text{C}$ and seawater $\delta^{34}\text{S}$ isotope records over the Paleocene Eocene Thermal Maximum in the Atlantic Ocean. Site 1051 is in the North Atlantic and Site 1267 is in the South Atlantic. The S isotope record was used to correlate the two sites when the $\delta^{13}\text{C}$ record was insufficient. Ages were determined by biostratigraphy [55].

occurs in the upper middle Jurassic with a $\delta^{34}\text{S}$ value of 20.7‰ [24]. The potential for correlation exists; however, the majority of the data, 18 samples, are poorly constrained with an error of ± 31.2 Ma that needs to be resolved before these samples can be used for stratigraphy [24].

4.6. Cretaceous

The Cretaceous record which is based on data from barite is characterised by a negative shift from ~ 20 to 15 ‰ between 130 and 120 Ma, remaining low until 104 Ma when it rises to ~ 19 ‰ over 10 Ma. There is also a small minimum at 87 Ma with a value of 18.0‰, returning to values of 19‰ at ~ 80 Ma for the remainder of the period (Figure 3). It is possible that higher resolution sampling will reveal even finer trends that could be used to better refine correlations (see [23]). These excursions can be used for correlations.

4.7. Cenozoic

For the Cenozoic (Figure 3), the age resolution of the record is < 1 Ma. Following the Cretaceous/Tertiary boundary, the value drops precipitously from ~ 19 to ~ 16 ‰. Following

this minimum, a relatively rapid rise to $\sim 22\text{‰}$ in the Early to Mid Eocene is observed, and this value is maintained until the Pleistocene with little change. The decrease and increase observed between 65 and 47 Ma are distinctive and could be used for correlation. A possible decrease of about 1‰ over the last 2 Ma is also evident but is defined by relatively few samples.

The utility of using S isotopes for correlation between sites for Cenozoic sections is illustrated in Figure 5(b) from Gray [55]. Ocean Drilling Program Site 1051 is located in the North Atlantic and does not have such a distinct record of the carbon isotope excursion in the $\delta^{13}\text{C}$ record that is typically used for correlation purposes during the Paleocene Eocene Thermal Maximum (PETM ~ 55 Ma) making it difficult to correlate to other sites such as Site 1267 in the South Atlantic. At both sites, however, a minimum in the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ record was recorded and used to align the two records. Ages were determined by biostratigraphy. This record serves to illustrate the potential use of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ for correlation and as more such detailed high-resolution secular records (e.g. based on coherent data from multiple locations and settings) become available for different geological periods, seawater $\delta^{34}\text{S}_{\text{SO}_4}$ stratigraphy can be more widely utilised.

5. Summary

S isotope data from archives that accurately represent the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ (CAS and barite) are becoming more widely available for many study locations and as illustrated above, have the potential to become a more useful tool for stratigraphy and correlation as we refine the global S isotope record. While high-quality data from sulphides are also available, sulphur isotopes from sulphates are better suitable than sulphides as a stratigraphy tool, as sulphides typically do not reflect seawater values because $\delta^{34}\text{S}$ in sulphides is impacted by many local parameters, confounding the data. The challenge in the next few years is to expand the data available to produce reliable, high-resolution, secular data of seawater S isotope values such that a high-resolution curve which can resolve fine short-term fluctuations can be used for correlations. When such records become available, the utility of this system can expand considerably.

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