Sulphur isotopic evolution of Neoproterozoic-Cambrian seawater: new francolite-bound sulphate $\delta^{34}S$ data and a critical appraisal of the existing record

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Abstract

Francolite-bound sulphate sulphur isotope compositions from the 570 ± 20 Ma Doushantuo Formation are used to constrain seawater $\delta^{34}S$ during the late Neoproterozoic. Phosphorites of the lower ore have $\delta^{34}S$ compositions between 32.3‰ and 37.8‰, averaging 36.1‰, $\delta^{13}C$ values between ~4‰ and ~1‰, and do not exhibit anomalous cerium depletion. By contrast, phosphorites of the upper ore, which contains some of the earliest animal fossils known, have $\delta^{34}S$ between 31.6‰ and 34.5‰, averaging 33.3‰, $\delta^{13}C$ values between ~1‰ and +2‰, and exhibit a distinct negative cerium anomaly. The retention of a cerium anomaly in these upper Doushantuo phosphorites implies that oxidising conditions prevailed during early diagenetic REE scavenging, indicating that these samples are more likely to retain a seawater sulphur isotope composition. On this basis we argue that seawater $\delta^{34}S$ was 32‰ (± 2‰) during the deposition of the upper Doushantuo unit. The slightly higher values of the lower Doushantuo unit may reflect either slightly higher ambient seawater $\delta^{34}S$ or isotopic fractionation due to bacterial sulphate reduction. Almost identical constraints on seawater $\delta^{34}S$ have been reported from lowermost Cambrian phosphorites across South China, indicating that seawater $\delta^{34}S$ was similar at ~570 and ~540 Ma. A critical examination of all published data provides no firm evidence for major fluctuations in seawater sulphate $\delta^{34}S$ during the Neoproterozoic–Phanerozoic transition interval. This indicates that the onset of pervasive bioturbation had only a negligible effect on global pyritisation rates and questions recent reports of massive fluctuations in seawater sulphate $\delta^{34}S$ in response to the “Snowball Earth” glaciations. The existing $\delta^{34}S$ record is consistent with a sustained increase in seawater $\delta^{34}S$ between 750 and 570 Ma. Shorter-term fluctuations cannot be ruled out entirely, but will require more detailed study, incorporating rigorous methodologies to constrain the effects of non-marine influences.

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1. Introduction

Despite the central role of sulphur isotopes in Precambrian palaeoenvironmental interpretations (Canfield and Teske, 1996; Farquhar et al., 2000; Gorjan et al., 2000), the sulphur isotope composition of seawater sulphate during much of Precambrian time remains poorly constrained (Strauss, 1993; Strauss et al., 2001). This is due mainly to a lack of expansive evaporite sulphate deposits. Sedimentary iron sulphides are an abundant alternative, but extrapolating seawater $\delta^{34}S_{\text{sulphide}}$ from $\delta^{34}S_{\text{sulphate}}$ data is far from straightforward because of the large range of $\delta^{34}S_{\text{sulphide}}$ values found in sedimentary rocks (Strauss, 1997, 1999; Canfield and Raiswell, 1999). As a result, other methods for constraining seawater $\delta^{34}S$ must be sought. Here we use structurally substituted trace sulphate from sedimentary francolite (carbonate fluorapatite) as a proxy material for seawater sulphate $\delta^{34}S$. This approach is attractive because francolite is unlikely to form in restricted marine environments as do evaporite sulphate minerals, such as gypsum and anhydrite. However, the extent to which francolite-bound sulphate $\delta^{34}S$ has been modified by post-depositional alteration needs to be constrained (Benmore et al., 1983).

Fig. 1. Map of central Guizhou province showing the distribution of Late Proterozoic phosphorite deposits over the area and the locality from where the Weng’an phosphorite samples are derived.
High seawater $\delta^{34}S$ (~30%o or higher) during the Cambrian period was first inferred from analyses of Siberian evaporite sulphate (Pisarchik and Golubchina, 1975; Pisarchik et al., 1977; Claypool et al., 1980) and has been confirmed by isotopic studies of Neoproterozoic–Cambrian evaporites worldwide (Strauss, 1993; Strauss et al., 2001) as well as Cambrian barites and phosphorites from China and Russia (Wang and Li, 1991; Shields et al., 1999; Bliskovskiy et al., 1977). Because Proterozoic evaporite suites generally retain much lower $\delta^{34}S$ values $\leq 20\%o$ (Strauss, 1993; Gorjan et al., 2000), there appears to have been a major increase in seawater $\delta^{34}S$ sometime during the late Neoproterozoic (Holser, 1977; Clay-
pool et al., 1980; Strauss, 1993; Gorjan et al., 2000). However, only limited progress has been made towards constraining the timing of this increase since the pioneering studies of the 1970s. This contribution aims to provide a minimum age constraint on the late Neoproterozoic rise in seawater $\delta^{34}$S using francolite-bound sulphate from the $\sim 570 \pm 20$ Ma Doushan-tuo Formation, Weng’an phosphorite deposit, central Guizhou Province, South China. These new data are critically assessed in the light of published isotopic data from (i) francolite-bound sulphate, (ii) carbonate-bound sulphate, (iii) pyrite sulphide, (iv) evaporite sulphate and (v) barite sulphate.

2. Geological setting

The Doushantuo Formation represents the only world-class phosphorite resource of the Neoproterozoic era (Li, 1986). In the Weng’an district of central Guizhou Province, South China (Fig. 1), the Doushantuo Formation comprises a condensed unit of dolomite and phosphorite, which can be divided by an erosive surface into upper and lower ores (Fig. 2). Recently, the Weng’an phosphorites received considerable attention due to the discovery of algal and animal embryos preserved in francolite of the upper unit of the Doushantuo Formation (Xiao et al., 1998). Massive phosphogenesis is commonly associated with transgression (Trappe, 1998), and the two distinct units of the Doushantuo Formation are recognised across the Yangtze (or South China) Platform as being transgressive cycles separated by an exposure surface (Xiao et al., 1998). However, Zhang et al. (1998) report that only the two high stands are represented in the Weng’an region owing to it having been a topographic high during late Neoproterozoic times.

The lower Doushantuo unit at Weng’an is darker in colour than the overlying unit, which reflects the relatively high proportion of iron-rich minerals (iron oxides and pyrite) and detritus (Table 1; Fig. 3) in these samples. Lower Doushantuo samples are generally laminated, sandy, dolomitic phosphorites with alternating layers of dolomite and compacted lozenges.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height, m</th>
<th>Sample description</th>
<th>$\text{SO}_4^2-$, ppm</th>
<th>$\delta^{34}$S, 1–2 h</th>
<th>$\delta^{34}$S, 3–4 h</th>
<th>$\delta^{34}$S, 12 h</th>
<th>$\delta^{34}$S, no leach</th>
<th>$\delta^{34}$S, leach, ppm</th>
<th>REE, ppm</th>
<th>Ce anom.</th>
<th>$\delta^{13}$C</th>
<th>$\delta^{18}$O</th>
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<td>30.2</td>
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<td>34.0</td>
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<td>33.5</td>
<td>17.5</td>
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<td>-4.0</td>
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<td></td>
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<tr>
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<td>-1.15</td>
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</table>

Lam’d = laminated, m. dark = medium dark. Mineralogy is given in order of abundance; capitalised abbreviations represent major mineral components; DOL. = dolomite, FRANC. = francolite, Qtz. = quartz.
am phosphatic peloids. Upper Doushantuo samples, by comparison, are relatively poor in iron minerals and detritus, such as quartz (Fig. 3). They are relatively pure dolomitic phosphorites, showing no internal lamination. Dolomite is present largely as cement, although the base of the unit also contains silica-cemented phosphorite. Phosphate of the upper Doushantuo unit is commonly peloidal with a large size-range, up to 1 mm, while phosphatic intraclasts may reach 4 mm in diameter. Additional sedimentological and regional geological information are provided in Zhang et al. (1998) and Chen et al. (2003). Further mineralogical details can be found in Table 1.

3. Age constraints

The age of the Doushantuo Formation and whether its deposition was contemporaneous everywhere in South China have been the subject of considerable uncertainty (Evans, 2000). Recently, Pb–Pb (on clay minerals) and Lu–Hf (on francolite) age constraints of $599 \pm 4$ and $584 \pm 26$ Ma, respectively, were published from phosphorite of the upper Doushantuo ore in the Weng’an region (Barfod et al., 2002). The likelihood, discussed in that article, that there has been some influence from detrital clays means that these are unlikely to represent unambiguous minimum depositional age constraints as reported by Barfod et al. (2002) but more probably represent our best maximum age estimates for the upper Doushantuo unit at Weng’an. Such maximum ages are consistent with the commonly assumed correlation of the underlying glaciogenic Nantuo Formation with the Australian Marinoan equivalents, which is independently supported by the presence in both successions of a characteristic spiny acritarch “Pertataka” microflora (Knoll, 2000). A minimum age of $\sim 550$ Ma can be obtained for the Doushantuo Formation from its stratigraphic position below latest Neoproterozoic.
Cloudinids (*Sinotubulites*), the lowest global appearance of which has been dated in Namibia at < 549 Ma (Grotzinger et al., 1995). Sr and C isotope stratigraphy is also consistent with maximum and minimum age constraints of ~ 590 and ~ 550 Ma, respectively (Shields, 1999; Walter et al., 2000), although none of this isotopic work was carried out on the Doushantuo Formation at Weng’an. Accordingly, we tentatively assign the Doushantuo Formation at Weng’an to between ~ 590 and ~ 550 Ma (or 570 ± 20 Ma) with preference given to the older age constraint due to the newly reported radiometric ages. It is unclear how much of this time is represented in the Weng’an phosphorite deposit, but its situation on a topographic high means that it is unlikely that much of this 40-million year interval is represented (cf. Zhang et al., 1998). The condensed nature of the deposit at Weng’an suggests an extended period of deposition on the order of ≥ 10^6 years (Trappe, 1998).

### 4. Methods

Sampling was carried out throughout the Doushantuo Formation at Weng’an (Fig. 2). Sample mineralogy was determined using a light microscope and a Philips X’PERT X-ray diffractometer at the University of Ottawa. Powdered phosphorite was weighed (32–46 g), placed in beakers and rinsed thoroughly using a ~ 0.2 M ultrapure NaCl solution to remove easily soluble sulphate. The second NaCl rinse was left to stand overnight, the supernatant being retained for isotopic analysis in the case of two samples (Table 1). Subsequently, all samples were washed repeatedly using distilled water in order to remove remaining traces of NaCl or easily soluble sulphate. The maximum sulphate content deriving from the ultrapure NaCl should have been no greater than 60 μg in total according to the manufacturer, and will have been removed by the repeated rinsing. Immediately after the final rinse, samples were allowed to react with 250 ml of ultrapure 2.5 N HCl for 1–2 h each before filtration using a Millipore® filtration system. Filtration proved sluggish for four samples due to clogging of the 0.45 μm filters by fines. In those cases, incomplete filtrates were removed after 2 h, and again after 4 and 12 h, resulting in up to three separate samples for isotopic analysis (Table 1). 10 ml of 0.5M BaCl₂ solution was added to the filtrates and heated to boiling, whereupon the solutions were removed from the hotplate and left overnight to trigger BaSO₄ precipitation and then filtered. In addition, four samples were reacted with 2.5N HCl as above without any preleaching (Table 1). Isotope measurements were conducted on a VG SIRA12 mass spectrometer at the University of Ottawa. Overall uncertainties were ± 0.2‰ for δ34S and ± 5% for total sulfur content.

Rare earth element, Sr, Mn and Fe concentrations were analysed using ICP-MS on two independent sets of 2 N HNO₃ leachates at the University of Nevada at LasVegas (double focussing magnetic sector VG-Axiom) and at the Advanced Analytical Centre, James Cook University, Townsville, Australia (Varian single collector quadropole ICP-MS) with essentially the same results. Ce anomalies are calculated here as Ce/Ce* = 3CeN/(2LaN + NdN), where N refers to elemental concentrations normalised against average shale or PAAS (McLennan, 1989). For carbon and oxygen isotope analysis, organic carbon was removed by reacting samples with 5% H₂O₂. Subsamples were then reacted with orthophosphoric acid in a common acid bath linked on-line to a Micromass Optima SIRMS. Reaction was for 40 min at 90 °C, followed by a 1-h degassing of the acid bath. International NBS19 and/or internal bicarbonate standards placed every fourth sample checked for memory effect and isotopic calibration. A phosphoric acid-dolomite fractionation factor of 1.01066 (Rosenbaum and Sheppard, 1986) was used for oxygen isotope calculations (this introduces uncertainties of up to ~ 2‰ for δ18O because the evolved CO₂ is likely to derive from a mixture of dolomite, structurally substituted carbonate in the francolite lattice and minor calcite).

### 5. Results

Six lower Doushantuo samples yielded δ34S values between 35.5‰ and 37.8‰, averaging 36.9‰, while sample A-7 yielded 32.3‰. By contrast, δ34S values for upper Doushantuo samples are lower, ranging between 31.6‰ and 34.5‰, averaging 33.3‰. Our leaching experiments (Table 1) show that washing (preleaching) the samples with NaCl(aq)
has removed isotopically distinct sulphate ions from two phosphorite samples with $\delta^{34}S \approx 22-23 \%e$. Similarly, samples analysed without preleaching yielded $\delta^{34}S$ values up to 3.6\%e lower than their preleached counterparts, while two samples that took longer to filter yielded progressively lighter sulphate, by more than 6\%e in the case of sample A-1. Carbon isotopic compositions range between $1/C_0$ 3.8\%e and $1/C_0$ 1.3\%e in the lower Doushantuo unit, and between $1/C_0$ 1.1\%e and $1/C_0$ 2.2\%e in the upper Doushantuo unit.

REE contents (Table 2) are higher in the lower Doushantuo samples, with 127–150 ppm compared with 5–60 ppm for upper Doushantuo samples. Only upper Doushantuo samples reveal any anomalous depletion in cerium when normalised against PAAS with Ce/Ce* = $\sim 0.5$. Fe and Mn concentrations (Table 2) are likewise significantly higher in lower Doushantuo samples (726–8634 and 265–337 ppm, respectively) compared with upper Doushantuo samples (334–1833 and 56–346 ppm, respectively).

### Table 2
REE and elemental concentrations of HNO$_3$-soluble fractions of Doushantuo Formation phosphorites analysed by ICP-MS

<table>
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<tr>
<th>Sample</th>
<th>Y, ppm</th>
<th>La, ppm</th>
<th>Ce, ppm</th>
<th>Pr, ppm</th>
<th>Nd, ppm</th>
<th>Sm, ppm</th>
<th>Eu, ppm</th>
<th>Gd, ppm</th>
<th>Tb, ppm</th>
<th>Dy, ppm</th>
<th>Ho, ppm</th>
<th>Er, ppm</th>
<th>Tm, ppm</th>
<th>Yb, ppm</th>
<th>Lu, ppm</th>
<th>Fe, ppm</th>
<th>Mn, ppm</th>
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### 6. Discussion

#### 6.1. Elemental composition of Doushantuo phosphorite

Iron and manganese concentrations decrease markedly from the lower unit to the upper unit. Because these multivalent metals tend to undergo post-depositional remobilisation under reducing conditions, their concentrations are generally elevated in the suboxic to anoxic parts of the sediment or water column. The relatively low concentrations in the upper unit imply that it was less influenced by the redox-related remobilisation of Fe and Mn than the lower unit. This could be due to deposition and phosphogenesis of the lower unit under more reducing conditions. Alternatively, this difference could be put down to a greater availability of free iron from detritus during early diagenesis. Good correlation between iron concentration and quartz content (Fig. 3) tends to support this latter possibility, although it is likely that the relative timing of phosphogenesis also played a role. In the upper unit, the well-preserved fossil microstructures (Xiao et al., 1998), retention of spherical forms and presence of irregularly shaped, reworked clasts all point to early phosphatisation and cementation, which would have precluded prolonged exchange with diagenetic fluids.

Rare earth element (REE) concentrations are generally high in sedimentary phosphate (francolite) because these are preferentially scavenged during diagenesis (German and Elderfield, 1990). Therefore, it is generally assumed that the REE distributions of acid-soluble leachates of phosphorites correspond to those of the francolite fraction in a carbonate-bearing phosphorite (Jarvis et al., 1994). In this case, such an assumption is further justified by published analyses of the negligible REE contents of dolomite matrix at Weng’an (Chen et al., 2003). REE contents also decrease sharply from the lower to the upper unit.
suggesting that REE scavenging was limited in the upper unit. As with Fe and Mn, the stark difference in REE content between the two Doushantuo units could reflect either more intense reducing conditions (cf. Zhang et al., 2003) in the lower unit and/or greater REE availability during early diagenesis due in part to its higher detrital content and in part to its relatively late lithification.

It was first suggested by McArthur and Walsh (1984) that the shale-normalised, REE component of phosphorites and, in particular, the presence or absence of a Ce anomaly, could be used to establish whether phosphogenesis took place under oxic or anoxic conditions. This is because shale-normalised REE patterns for seawater commonly show a negative cerium anomaly because of the reduced solubility of oxidised cerium, Ce$^{4+}$ in oxic seawater. Because phosphorites scavenge REE during early diagenesis their REE patterns will only retain the cerium-depleted signature of oxic seawater if REE scavenging takes place in the oxic parts of the sediment column, while reduction and remobilisation of metals, including the REE, within the sediment will effectively remove any initial Ce anomaly (German and Elderfield, 1990). In order to ascertain whether samples are truly depleted in cerium relative to the other REE it is inadequate to report calculated Ce anomalies because negative Ce anomalies may be created inadvertently due to positive La anomalies and highly arched REE patterns (Bau and Dulski, 1996). Upper Doushantuo REE patterns from the present study (Fig. 4) resemble typical seawater patterns, in showing relative depletion of LREE- and Ce, but also exhibit the slight MREE enrichment or arching that is characteristic of non-quantitative uptake of REE by francolite during early diagenesis (Shields and Stille, 2001). From Fig. 5 we can see that the negative Ce anomalies of upper Doushantuo samples are not artefacts of the Ce anomaly calculation because shale-normalised Ce concentrations are also depleted with respect to the general LREE trend from Pr to Gd as well as to its neighbours La and Nd. By contrast, lower Doushantou samples are not depleted in Ce and may even be slightly enriched with respect to neighbouring REE (Fig. 5).

Fig. 4. Total lanthanide or REE + Y distributions (Bau and Dulski, 1996) of HNO$_3$-soluble fractions of Doushantuo Formation phosphorites analysed at the University of Nevada at Las Vegas and normalised against shale, PAAS (McLennan, 1989). Correction for Ba concentrations on otherwise identical REE + Y distributions of the same samples analysed at James Cook University reduces, and in most cases removes the apparent positive Eu anomalies.
The retention of a marked negative Ce anomaly in the upper Doushantuo unit can be interpreted unambiguously and must imply predominantly oxic conditions in local seawater as well as during both phosphogenesis and early diagenetic REE scavenging (German and Elderfield, 1990; Shields and Stille, 2001). Therefore, the low Fe, Mn and REE concentrations of this unit can be confidently interpreted to reflect the oxidising nature of early diagenesis in this unit rather than the respective detrital contents. By contrast, the clear differences in cerium behaviour (and REE, Fe and Mn) between the lower and the upper Doushantuo ores could be attributed either to different redox conditions during early diagenesis (and possibly in seawater, cf. Chen et al., 2003) and/or to the greater availability of REE (and other redox-sensitive metals) in the lower unit after deposition. As discussed above, it is likely that a combination of three factors played a role in providing these units with their distinctly different geochemical characteristics, i.e. reducing conditions during early diagenesis of the lower unit, greater abundance of detrital minerals in the lower unit and a more extended period of phosphatisation and lithification in the lower unit.

6.2. Carbon isotopic composition of Doushantuo phosphorite

Our $\delta^{13}C$ data (Table 1) are similar to those of Zhou (1997) from the Weng’an phosphorite deposit, who reported a range from $-2.7\%_o$ to $+3.2\%_o$, with a switch from negative values in the lower unit to more positive values in the upper unit. Post-glacial $\delta^{13}C$ records of the late Neoproterozoic commonly show an increase from moderately negative to positive values (Kaufman and Knoll, 1995), but the Weng’an deposit does not show any of the unusually high $\delta^{13}C$ values up to $+7\%_o$ characteristic of this time, nor does it show any of the complexity of supposedly correlative $\delta^{13}C$ records from the Doushantuo Formation in Hubei Province (Lambert et al., 1987; Yang et al., 1999; Zhang et al., 2003). Widespread phosphogenesis throughout the Weng’an succession suggests that diagenetic processes (Benmore et al., 1983) may have disturbed carbon isotope systematics here (Fig. 6), but there is also the possibility that the condensed Doushantuo Formation at Weng’an covers only a portion of the time represented in other successions (cf. Zhang et al., 1998), which retain a more complex $\delta^{13}C$ profile. In this regard, we note that the positive shift observed at Weng’an matches that recorded from the phosphatic part of the much thicker Doushantuo Formation at Tianjiauanzi in Hubei Province (Zhang et al., 2003). This suggests that the Weng’an phosphorite could be time-equivalent with the upper part of member 3 and some part or all of member 4 at Tianjiauanzi (Zhang et al., 2003) and, therefore, does not retain any record of immediately post-glacial seawater chemistry.

Bulk carbonate $\delta^{13}C$ compositions from our study (Table 1) reflect a mixture of dolomite, minor calcite and francolite-bound carbonate. Upper unit samples are generally richer in dolomite than their lower unit counterparts (Table 1), and so their $\delta^{13}C$ signatures ought to be dominated by the dolomite component. This is consistent with their more positive $\delta^{18}O$ values, which range up to $-0.4\%_o$. Conversely, lower unit samples are more influenced by the minor calcite and francolite-bound component. Unfortunately, these three components cannot be separated cleanly.

![Fig. 5. Ce/Ce* vs. Pr/Pr* diagram after Bau and Dulski (1996), where Pr/Pr* = 2Pr/2/Ce + Nd). Field I: no anomaly; field IIa: positive La anomaly causes apparent negative Ce anomaly; field IIb: negative La anomaly causes apparent positive Ce anomaly; field IIIa: real positive Ce anomaly; field IIIb: real negative Ce anomaly; field IV: positive La anomaly disguises positive Ce anomaly (this field is new to this paper). Upper Doushantuo samples (filled circles) fall largely within the real negative Ce anomaly field although positive La anomalies have possibly exaggerated the extent of Ce depletion in some cases. Some Lower Doushantuo samples are similarly affected by positive La anomalies, but fail to reveal any anomalous Ce behavior and may even possess positive Ce anomalies when the La effect is taken into account.](image-url)
in this bulk carbonate dataset but it is clear that the francolite-rich and dolomite-poor samples of the lower Doushantuo unit have consistently lower $\delta^{13}$C and $\delta^{18}$O compositions (Table 1; Fig. 6). In the absence of firm information on ambient seawater $\delta^{13}$C at this time it is difficult to estimate the difference between pristine marine carbonate and francolite-bound carbonate $\delta^{13}$C, which could potentially be of use in interpreting the diagenetic environment further (Bemore et al., 1983). However, the data are consistent with a deeper locus of phosphogenesis within the sediment for the lower Doushantuo unit (Fig. 6). Planned $\delta^{13}$C analysis of the francolite-bound carbonate component should help to quantify to what extent the stratigraphic trend of increasing $\delta^{13}$C at Weng’an is due to the diagenetic incorporation of respired carbon into francolite.

### 6.3. Sulphur isotopic composition of trace sulphate in Doushantuo phosphorite

The simplest interpretation of our $\delta^{34}$S data is that they present a faithful record of contemporaneous seawater S-isotopic composition (cf. Shen et al., 2000). However, this interpretation requires supporting evidence because four complicating factors may influence the measured $\delta^{34}$S values of sedimentary francolite-bound sulphate: (i) Deviation of S-isotopic composition of local seawater from the global ocean $\delta^{34}$S value; (ii) S-isotopic fractionation of pore water sulphate caused by bacterial sulphate reduction and/or upward diffusion of hydrogen sulphide; (iii) Inadvertent incorporation of non-francolite sulphate during sample preparation; and (iv) Postdepositional S-isotopic exchange. We treat these issues separately below.

#### 6.3.1. How representative is francolite-bound sulphate of seawater sulphate?

Because massive phosphogenesis is a marine process, which occurs as a result of vigorous ocean circulation and nutrient replenishment (Trappe, 1998), phosphorites ought to incorporate sulphate that is isotopically representative of the global ocean. Phosphorites form in areas of low sedimentation rate (Trappe, 1998), and thus integrate the isotopic signature of seawater over a prolonged interval. These considerations make marine phosphorite potentially more useful for the reconstruction of seawater sulphate $\delta^{34}$S evolution than evaporite sulphate minerals, which are commonly affected by non-marine waters. The Doushantuo phosphorite is no exception to this, being a condensed, marine deposit, which ought to have incorporated marine sulphate at deposition provided that the oceans were isotopically homogeneous as

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Fig. 6. Crossplot showing bulk carbonate $\delta^{13}$C against francolite bound $\delta^{13}$C for Doushantou phosphorites from this study. Higher $\delta^{34}$S values may reflect sulphate reduction during early diagenesis (see inset with data from Goldhaber and Kaplan, 1980), which may also be reflected in a lowering of carbonate $\delta^{13}$C values due to the incorporation of respired carbon.
today. The present-day ocean residence time for sulphate is on the order of 7 million years, however, it could have been shorter during parts of the Precambrian due to lower sulphate concentrations (e.g. Hurtgen et al., 2002). The depositional context of the Weng’an site on a topographic high during a marine transgression further maximises the potential for retaining a global ocean δ34S signature.

6.3.2. Effect of diagenetic bacterial sulphate reduction on francolite δ34S

Modern sediments exhibit increasing sulphate δ34S and decreasing sulphate concentration with depth (Goldhaber and Kaplan, 1980; McArthur et al., 1986) due to bacterial sulphate reduction and its associated isotopic fractionation (Fig. 6: inset). Sulphate reduction causes a large isotopic fractionation that leaves the sulphate reservoir enriched in the heavier isotope 34S, and thus leads to higher δ34S values in francolite-bound sulphate. As outlined above, distinct Ce depletion in our upper Doushantuo samples implies oxic conditions during deposition and early diagenetic phosphogenesis (German and Elderfield, 1990; Shields and Stille, 2001). The preservation of a primary oxic seawater signature, together with the general absence of pyrite in these samples, should therefore exclude the possibility that sulphate reduction affected the S-isotope composition of the ambient sulphate reservoir. Consequently, the δ34S values from those samples (31–34 ‰) ought to represent a close approximation to contemporaneous seawater sulphate δ34S taking into account a slight, ≤ +1 ‰, fractionation from seawater sulphate δ34S (Jarvis et al., 1994). Conversely, the lack of a Ce anomaly in our lower Doushantuo samples is consistent with, but not proof of, suboxic to anoxic conditions during early diagenetic phosphogenesis and REE scavenging. Nevertheless, the higher concentrations of certain metals (Fe, Mn and REE) and the visible presence of pyrite imply considerable metal recycling under reducing (suboxic to anoxic) conditions. Therefore, the higher francolite-bound sulphate δ34S values of the lower Doushantuo unit are more likely to reflect active sulphate reduction rather than any ~ 5 ‰ change in ambient seawater δ34S. Either interpretation would be consistent with the existence of high seawater δ34S (≥30 ‰) during the period of deposition of the Doushantuo Formation at Weng’an.

6.3.3. Contamination during sample preparation

Most of the extracted sulphate is derived from structurally substituted sulphate in the francolite, as francolite abundance correlates well with sulphate recovery, at least for the upper Doushantuo unit (Fig. 3). However, there are three major sources of contamination that need to be constrained: loosely bound sulphate, organic sulphur and oxidised pyrite sulphur, which may become inadvertently incorporated into the analysed fraction. It is important that attempts are made to limit, and, if possible, eliminate contamination from these sources because they would all possess non-seawater S-isotopic compositions. Loosely bound sulphate or weathered sulphide may be removed by washing in a solution of pure NaCl (see Methods), but sulphate produced by oxidation during sample preparation can only be totally eliminated by preparing samples in an anaerobic environment. This is especially important when pyrite or organic matter is abundant (e.g. Mallinson and Compston, 1998; Poulton et al., 1998) as is the case with our lower Doushantuo samples.

Our experiments allow us to quantify the effects of such contamination on the measured δ34S values at less than −2 ‰ for most samples. Leaching experiments (Table 1) show that washing (preleaching) with NaCl(aq) has removed isotopically distinct (depleted) sulphate from two phosphorite samples of the lower Doushantuo unit with δ34S = ~22–23 ‰. These same samples as well as an additional sample from the same unit were analysed for δ34S with and without preleaching with the outcome that preleached samples are enriched in δ34S relative to non-preleached samples. Clearly, the measured δ34S values of non-preleached samples do not correspond to the δ34S composition of the francolite sulphate fraction only, but are instead strongly influenced by a source of isotopically depleted sulphate, most probably oxidised pyrite sulphur. Isotopically similar pyrite δ34S values, i.e. ~22–23 ‰, have been reported from the Doushantuo Formation in other parts of the South China Platform (e.g. Lambert et al., 1987). The same two lower Doushantuo samples were also allowed to stand for up to 12 h after francolite dissolution had ceased, resulting in progressively lighter yields of sulphate δ34S, by as much as 6.1 ‰ in the case of sample A-1. This indicates that isotopically distinct sulphate contributed to measured δ34S even after all francolite and
carbonate had been dissolved, implying that sulphate continued to form during the experiment (cf. Mallinson and Compton, 1998). Because all samples were preleached and reaction was swift, the real $\delta^{34}S$ values of most lower Doushantuo phosphorites are likely to be only a maximum of about 1–2‰ higher than measured, while it is unlikely that similar corrections need to be applied to upper Doushantou data because neither preleaching nor lengthy exposure to the atmosphere seems to have significantly changed the isotopic composition of two samples from the upper Doushantuo unit (Table 1).

These effects can be further constrained by examining the relationship between francolite abundance and sulphate concentration in the Doushantuo samples (Fig. 3). In cases where francolite is the dominant source of sulphate there ought to be an approximately linear relationship between these two parameters. Upper Doushantuo samples clearly exhibit such a relationship and display a restricted isotopic range, averaging 33.3‰. However, the lower Doushantuo samples fall into two groups, which are both isotopically distinct. Those samples that follow the same linear relationship depicted by the upper Doushantuo samples average 37.7‰ (from the arguments above this is most likely a slight underestimate of the true francolite value), while those that exhibit anomalously high sulphate contents yield lower $\delta^{34}S$ values, averaging 34.9‰. The most plausible explanation for this would be that the measured $\delta^{34}S$ values of the more depleted samples have been significantly affected by pyrite oxidation, which renders suspect their $\delta^{34}S$ values. However, it is unlikely to reflect a shift in seawater $\delta^{34}S$, but instead could result from inadvertent incorporation of pyrite sulphur in the isotopic analysis of that sample.

In sum, the above arguments show that unravelling the effects of sample preparation on measured $\delta^{34}S$ results in an enhancement of the difference between the two Doushantuo units to at least 6‰, which could correspond either to a decrease in seawater $\delta^{34}S$ across the lower–upper Doushantuo boundary and/or to a change in the diageneric conditions of sulphate uptake. In the light of these units’ contrasting elemental compositions and diageneric histories as outlined above, and the clear evidence for sulphate reduction in the form of pyrite in the lower unit, we favour the second option. This interpretation is still consistent with the existence of high seawater $\delta^{34}S$ (>30‰) during the entire period of deposition of the Doushantuo Formation at Weng’an.

6.3.4. Post-diagenetic isotopic exchange

The Doushantuo Formation at Weng’an shows no signs of metamorphism, while the samples derive from a freshly exposed quarry face and are not obviously weathered. Little research has been carried out on the effects of late- or post-diagenetic S-isotopic exchange, however, the effects of surface weathering are likely to be minor because francolite is thought to lose sulphate from its lattice during post-depositional alteration rather than undergo isotopic exchange (cf. McArthur et al., 1986; Jarvis et al., 1994). The rare earth element patterns of the Doushantuo phosphorites (Fig. 4) show no indication of preferential REE loss that might have resulted from surface weathering (cf. Chen et al., 2003).

7. Neoproterozoic-Cambrian seawater $\delta^{34}S$ evolution

Neoproterozoic marine sulphate $\delta^{34}S$ data have been compiled by Strauss (1993) and Walter et al. (2000). Those data, although sparse and sometimes stratigraphically ambiguous, are consistent with an increasing trend in seawater $\delta^{34}S$ during the late Neoproterozoic either between ~750 and ~600 Ma (Strauss, 1993), or alternatively between ~650 and ~540 Ma (Gorjan et al., 2000). Because of the high seawater $\delta^{34}S$ constraints from the Doushantuo Formation presented here, only the former hypothesis appears to be consistent with our data, however, shorter-term fluctuations in seawater $\delta^{34}S$ cannot be ruled out. Recently, the reemergence of the “Snowball Earth” hypothesis (Hoffman et al., 1998; Hoffman and Schrag, 2002) has fuelled speculation about possible massive and reversible changes to the S biogeochemical cycle during the late Neoproterozoic (e.g. Hurtgen et al., 2002; Gorjan et al., 2003; Zhang et al., 2003). However, the use of a wide range of proxy materials, such as phosphorite (Shen et al., 2000), carbonate (Hurtgen et al., 2002; Zhang et al., 2003), pyrite (Ross et al., 1995; Gorjan et al., 2003),
The necessity for any changes in global seawater (e.g., Hall et al., 1991) to trace seawater sulphate $\delta^{34}S$ has resulted in considerable divergence of opinion concerning the true course of seawater sulphate $\delta^{34}S$ evolution. Here we outline the case for Neoproterozoic–Cambrian seawater $\delta^{34}S$ evolution using each of these approaches individually.

### 7.1. Structurally substituted sulphate in francolite

$\delta^{34}S$ data from francolite-bound sulphate of the Doushantuo Formation have also been reported by Shen et al. (2000) for two locations in central Guizhou Province, with values between 34 %e and 42 %e, and a mean of 37 %e. These values match our lower Doushantuo data, which is confirmed by their identical Ce anomalies, averaging 0.9 ($n = 29$) (Feng, 1993, cited in Shen et al., 2000). Shen et al. (2000) conclude that the lowest $\delta^{34}S$ values from their study, about 34 %e, best represent seawater $\delta^{34}S$, which is in broad agreement with this study. However, Shen et al. (2000) argue further on the basis of significantly lower francolite-bound sulphate $\delta^{34}S$ from Lower Cambrian phosphorites of South China (Shen et al., 1998) that there was a major decrease in seawater sulphate $\delta^{34}S$ across the Neoproterozoic–Cambrian transition in China followed by a major increase during the Early Cambrian. We find ourselves in conflict with this interpretation because of our published study of francolite $\delta^{34}S$ from Lower Cambrian phosphorites across South China (Shields et al., 1999), in which we reported identical constraints on Cambrian seawater $\delta^{34}S$ to those from the Neoproterozoic Doushantuo Formation. The methods employed by Shen et al. (1998, 2000) do not enable them to establish the extent to which measured $\delta^{34}S$ values have been affected by sulphide reoxidation during sample preparation or weathering or whether sulphate reduction during phosphogenesis has influenced francolite $\delta^{34}S$. The inadvertent incorporation of non-seawater sulphate may explain the apparent negative shift in $\delta^{34}S$ across the Neoproterozoic–Phanerozoic transition (Shen et al., 2000) as well as the positive shift recorded in phosphorite nodules from the Lower Cambrian of South China (Shen et al., 1998) without the necessity for any changes in global seawater $\delta^{34}S$. As outlined in this paper, there are many potential pitfalls when utilising francolite-bound sulphate $\delta^{34}S$ to trace seawater $\delta^{34}S$ evolution that must be dealt with systematically in each study. If the constraints outlined in this paper and our previous study (Shields et al., 1999) are valid, existing francolite-bound $\delta^{34}S$ data do not support the presence of major fluctuations in seawater $\delta^{34}S$ across the Neoproterozoic–Cambrian transition interval or during the Early Cambrian.

### 7.2. Carbonate-associated sulphate

A promising alternative approach to determine seawater $\delta^{34}S$ has been pioneered by H. Strauss and A. Kampschulte (Kampschulte, 2001; Kampschulte et al., 2001), which utilises structurally substituted, carbonate-bound sulphate. Encouraging results have been obtained from skeletal calcite and bulk limestone from the Phanerozoic carbonate record as well as modern shells (Kampschulte et al., 2001). From those data it can be seen that modern structurally substituted sulphate is isotopically similar to ambient seawater (21 ± 1 %e) right across the marine realm, while deviations from this are only found in restricted basins, such as the Black Sea, or in extreme environments, such as the Arctic Ocean (Kampschulte, 2001).

Recently, this approach has been applied to Neoproterozoic carbonate rocks in Namibia, China and Brazil. Hurtgen et al. (2002) have published carbonate-bound sulphate $\delta^{34}S$ data from the Otavi Group of northwestern Namibia, spanning the glaciogenic Ghaub Formation, which, according to isotope stratigraphy-based correlation schemes, probably represents an equivalent glacial interval to that recorded by the pre-Doushantuo Nantuo Formation (Shields, 1999; Walter et al., 2000). The Hurtgen et al. study reveals considerable variation in measured $\delta^{34}S$ after each glacial episode recorded in Namibia (Chuos and Ghaub), ranging between 10 %e and 51 %e, which, although abrupt in the stratigraphic succession, are interpreted to reflect changes in seawater sulphate $\delta^{34}S$. If contemporaneous with the Doushantuo Formation at Weng’an, such unprecedented $\delta^{34}S$ swings would clearly be in conflict with the francolite-based $\delta^{34}S$ constraints presented here. The tendency of sulphate reduction to fractionate the $\delta^{34}S$ signatures of ambient dissolved sulphate represents a problem for carbonate rocks as well as for phosphorites because limestones commonly undergo diagenetic recrystallisation, while dolomite, in particular, tends
to form as a secondary mineral phase under conditions of active sulphate reduction (Burns et al., 2000). This could explain the restriction of the most extreme swings of up to 30% to dolomitic strata in the study of Hurtgen et al. as well as the equally abrupt fluctuations between 13% and 28% in the relatively more consistent 34S data from limestones of the pre-glacial Ombaatje Formation.

Carbonate-associated sulphate 34S data have also been reported from the Doushantuo Formation at the Tianjiauanzi section in Hubei Province (Zhang et al., 2003). These authors report considerable variation in measured 34S of −10‰ to 46‰, and also interpret their results as recording massive fluctuations in ambient seawater sulphate 34S. In our discussion above we tentatively suggested correlation of the Weng’an section phosphorite with the top of member three and with some or all of member four at Tianjiauanzi based on C-isotope stratigraphy. Francolite 34S data from the present study would then be contemporaneous with consistently lower, carbonate-associated sulphate 34S values at Tianjiauanzi of between 27.1‰ and 35.5‰ (n = 5) in the upper part of member three and variable 34S between 10.8‰ and 31.3‰ (n = 10) in member 4. The techniques used in the Zhang et al. study do not permit the authors to constrain the isotopic fractionation effects of early diagenetic, sulphate reduction, especially important considering the dolomitic nature of these strata, nor to distinguish between carbonate-derived sulphate and sulphate from oxidised pyrite. In our opinion, the wild fluctuations reported from carbonate-associated sulphate 34S studies from the Neoproterozoic (Varni et al., 2001; Zhang et al., 2003; Hurtgen et al., 2002) are unlikely to reflect equivalent changes in seawater sulphate 34S. Before carbonate-associated sulphate can be used more widely to reconstruct Proterozoic seawater 34S, sample preparation techniques and diagenetic assessments should be developed that are at least as rigorous as those now standard in francolite S-isotope studies (Benmore et al., 1983; Jarvis et al., 1994; Poulton et al., 1998; this paper).

7.3. Pyrite sulphide

Although the isotopic discrimination between seawater sulphate and bacterially mediated sulphide can be highly variable, some studies have utilised the S isotopic composition of sedimentary pyrite to constrain seawater 34S. Phanerozoic and late Neoproterozoic sedimentary rocks show a range of isotopic discriminations from seawater 34S, averaging 51‰ (Strauss, 1999). Such high discriminations can be explained by the influence of disproportionating bacteria on S-isotope fractionation following sulphate reduction (Canfield and Thamdrup, 1994), and could be related to the increased complexity of microbially mediated, sulphide redox systematics within the sediment after about 0.8 ± 0.2 Ga (Canfield and Teske, 1996). By contrast, early Neoproterozoic and earlier sedimentary rocks exhibit lower discriminations, which are characteristic of unidirectional bacterial sulphate reduction (Canfield and Teske, 1996). The oldest sedimentary rocks to show a modern isotopic range are from the ~800 Ma Bitter Springs Formation (Gorjan et al., 2000) The ~600 Ma Isaac Formation and underlying Kaza Group of the Windermere Supergroup, Canada also display the characteristic Phanerozoic range of 34S values of about 50‰, while mean values undergo a positive shift from the Kaza Group to the Isaac Formation of 8‰ (Ross et al., 1995). This positive shift is interpreted to reflect an increase in ambient seawater sulphate 34S, at ~600 Ma, reflected in the highest pyrite 34S values, which increase from 20‰ to 35‰. In the absence of supporting data from the sulphate 34S record it is difficult at present to confirm or deny this apparently plausible hypothesis.

Applying the pyrite 34S approach in cases where the full range of isotopic fractionation is not recorded represents even more of a challenge. For example, it has been recognised that many late Neoproterozoic pyrites are isotopically very heavy. Pre-Marinoan (also pre-Doushantuo) pyrite 34S averages 30‰ and may reach as high as 60‰ in Australia, Canada, China and Namibia (Gorjan et al., 2003; Fig. 5). Although this phenomenon is not entirely understood (Strauss, 1999), the highest of these values have been interpreted to mean that ambient seawater 34S was as high as 60‰ at this time (Gorjan et al., 2003), which, if true, makes it difficult to explain the much lower 20–30‰ isotopic signatures of approximately contemporaneous sulphate minerals (e.g. Gorjan et al., 2000; Misi and Kyle, 1994) without invoking massive fluctuations in seawater 34S. However, 34S-enriched
pyrite is common throughout the lower Palaeozoic, too, even during times when seawater $\delta^{34}S$ is known to have been much lower (e.g. Strauss, 1999). For example, average pyrite $\delta^{34}S$ values from Precambrian–Cambrian sections in Poland can be as high as 32.6%o (Strauss, 1997), while pyrite $\delta^{34}S$ from the Precambrian–Cambrian boundary type-section in Newfoundland (Strauss et al., 1992) reaches as high as 53%o, at the same time that seawater $\delta^{34}S$ is known to have been no higher than 30–35%o (Shields et al., 1999; Strauss et al., 2001). In the Newfoundland study, seawater sulphate $\delta^{34}S$ is approximately 50%o more enriched than the most depleted pyrite ($\sim 20$%o), which is consistent with late Neoproterozoic and Phanerozoic sulphate-sulphide $\delta^{34}S$ discrimination (Canfield and Teske, 1996; Strauss, 1999). The Newfoundland study indicates that for pyrite to be at all useful in constraining seawater $\delta^{34}S$ many data are required from any given succession so that the full range of pyrite $\delta^{34}S$ can be revealed.

### 7.4. Evaporite sulphate

Although expansive evaporite deposits from Australia and Canada constrain seawater $\delta^{34}S$ to $\leq 20$%o at 800 ± 50 Ma (Strauss, 1993; Walter et al., 2000; Fig. 7), there are only sparse evaporite $\delta^{34}S$ data for the succeeding interval until ~545 Ma. High $\delta^{34}S$ values, averaging between 28%o and 33%o, are typical of the Neoproterozoic–Cambrian transition (Walter et al., 2000; Strauss et al., 2001) but older samples are dogged by uncertainties of stratigraphic correlation, age and signal integrity. The only indisputably Neoproterozoic III evaporite $\delta^{34}S$ data come from Australia and range between 20%o and 29%o (Calver, 1995; in Walter et al., 2000). Some of these $\delta^{34}S$ data derive from isolated samples of anhydrite or gypsum and so are of questionable quality for the purpose of tracing global seawater $\delta^{34}S$. Nevertheless, 10 samples from post-Marinoan strata of the Georgina Basin (Walter et al., 2000: Table 9) yield a tight grouping around 27%o ($\pm 2$%o), which is 5% lower than the approximately contemporaneous constraints from our study. Pre-Marinoan evaporites are also scarce but five samples from the Tapley Hill Formation yield an average $\delta^{34}S$ value of 26%o (Gorjan et al., 2000). Sedimentary barite and gypsum have also been analysed from a thin stromatolitic, most probably pre-Marinoan horizon in Brazil with an average $\delta^{34}S$ value of 27.7%o, (Misi and Kyle, 1994; Misi and Veizer, 1998). In the absence of large, expansive evaporites during this entire interval, data from such isolated evaporite occurrences, which do not derive from regionally expansive units, must be considered ambiguous due to the possible effects of basin restriction, which could cause either enrichment or depletion in basin sulphate $\delta^{34}S$ with respect to global seawater (e.g. Pisarchik et al., 1977). Nevertheless available evaporite $\delta^{34}S$ values are consistent with quite muted variation, and do not support major fluctuations in seawater $\delta^{34}S$ during the Neoproterozoic.

### 7.5. Barite sulphate

Stratiform or bedded barite frequently retains the S-isotopic signature of ambient seawater (Jewell, 1999) and so can potentially be used to constrain seawater sulphate $\delta^{34}S$. For example, Late Cambrian (~500 Ma) barites from western Canada yield an average $\delta^{34}S$ of 30.4%o ($n = 29$) (Shanks et al., 1987), while late Early Cambrian (~515 Ma) barites from Sardinia yield an average $\delta^{34}S$ of 33.2%o ($n = 6$) (Boni et al., 1988), indistinguishable from many Cambrian evaporite and phosphorite $\delta^{34}S$ data. Mineralised stratiform barite is found right across the South China Platform and exhibits the characteristically high $\delta^{34}S$ values of other Cambrian sulphate minerals, and presumably coeval seawater, averaging 35%o ($n = 18$), and ranging between 32%o and 40%o (Wang and Li, 1991). Strontium isotope compositions of these barites (Wang and Chu, 1994) are 0.7084–5 ($n = 12$), which is indistinguishable from contemporaneous seawater $^{87}$Sr/$^{86}$Sr at ~540 Ma (Shields, 1999).

Where barite $\delta^{34}S$ data cannot be supported by approximately contemporaneous evaporite data, interpretations may be rather more ambiguous (Cecile et al., 1983) as in the case of published barite data from the Neoproterozoic. In an exhaustive study, barite from the ~620 (~50) Ma Ben Eagach Schist of the Dalradian Supergroup of Scotland (Willan and Coleman, 1983; Hall et al., 1991) yielded consistent $\delta^{34}S$ values of 35–40%o (Hall et al., 1991). These results were interpreted by the authors to correspond
to ambient seawater, but they could equally represent maximum estimates (cf. Cecile et al., 1983), which would be consistent with the locally abundant sulphide mineralisation. If valid, these constraints could have important implications for pre-Marinoan seawater $\delta^{34}$S and for the timing of the Neoproterozoic rise in seawater sulphate $\delta^{34}$S.

An opportunity for determining seawater sulphate $\delta^{34}$S directly after the late Neoproterozoic (Marinoan) glaciation has presented itself in the form of barite precipitates in post-glacial “cap carbonates” from NW Africa, Australia and Canada (Hoffman and Schrag, 2002). Strontium isotope analyses (Strauss, 1993; Shields et al., 1997) confirm that the NW African barites formed under the influence of seawater. However, reported $\delta^{34}$S values are highly variable even within one outcrop with $\delta^{34}$S of 21–46‰ ($n=7$) (Shields et al., 1997). Such stratiform, synsedimentary, unmineralised barite deposits have been reported for other times in Earth history, too, and are thought to be the result of euxinic conditions, which allow barium to become concentrated in anoxic seawater, with barite precipitation at the redox front (Jewell, 1983). Because of the apparent necessity for sulphate reducing conditions in sedimentary basins with primary marine barite, interpretations of barite

![Fig. 7. Temporal evolution of sedimentary sulphate $\delta^{34}$S during the Neoproterozoic and early Palaeozoic.](image-url)

Fig. 7. Temporal evolution of sedimentary sulphate $\delta^{34}$S during the Neoproterozoic and early Palaeozoic. (1) Bitter Springs Formation, Australia; (2) Redstone River, Canada; (3) Tapley Hill Formation, Australia; (4) Irecê Basin, Brazil; (5) Georgina Basin, Australia; (6) Siberia (unnamed uppermost Precambrian/lowest Cambrian); (7) Hansean Formation, India; (8) Hormuz Formation, Iran; (9) Siberia (lower Cambrian); (10) Desu Series, Iran; (11) Siberia (upper lower Cambrian); (12) Siberia (lower Middle Cambrian); (13) Northwest Territories, Canada; (14) Williston Basin, USA and other Upper Ordovician evaporites; (15) Michigan, USA; M = lowermost Cambrian (Meishucunian) phosphorites, China; D = Doushantuo Formation phosphorites, China. Data from Calver (1995); Gorjan et al. (2000); Claypool et al. (1980); Vinogradov et al. (1994); Fox and Videtich (1997); Holser and Kaplan (1966); Houghton (1980); Misi and Veizer (1998); Shields et al. (1999); Strauss (1993); Strauss and Deb (unpublished data); Strauss et al. (2001) and this study. Vertical lines show age-uncertainty of $\delta^{34}$S data around mean values shown as circles. Phosphorite data (M and D) are shown in black with mean values of estimated “best-preserved” data from each study shown in white at 33‰ (Shields et al., 1999; this paper). Omitted from this figure are barite data and isolated evaporite sulphate data points.
δ34S in terms of seawater δ34S need to be cautious. More work is needed on other cap carbonate barite from around the world before any firm conclusions can be drawn regarding immediately post-glacial seawater δ34S.

7.6. Implications for the Neoproterozoic–Cambrian sulphur biogeochemical cycle

Barring massive and exactly reversible shifts in the isotopic composition of the ocean sulphate reservoir, francolite-bound sulphate δ34S data from South China indicate that seawater sulphate δ34S was >30‰ during all of the interval from 570 to 540 Ma. Evaporite sulphate data extend this period of high δ34S to cover much of the Neoproterozoic III to end-Cambrian interval, although evaporite δ34S values are found to be consistently lower and more variable than francolite-bound δ34S values, which could indicate a non-seawater contribution to most evaporite basins. Barite data complete this picture for the Cambrian Period, invariably providing high constraints on seawater δ34S, while more poorly constrained barite from Scotland and Brazil tentatively suggest that seawater δ34S was high even during the pre-Marinoan (>600 Ma) Neoproterozoic.

The lack of a shift in seawater δ34S across the Neoproterozoic–Cambrian transition interval is intriguing. One predictable consequence of the introduction of pervasive bioturbation at this transition would have been an increase in sulphide loss due to sulphide reoxidation (Canfield and Raiswell, 1999), which has the potential to cause a fall in global pyritisation rates, thus lowering seawater δ34S. However, the absence of any such change at the Proterozoic–Phanerozoic transition implies that the effect of sulphide reoxidation on increased sulphide loss might have been balanced by, for example, enhanced preservation of reactive iron (cf. Canfield and Raiswell, 1999: p. 712).

The results reported in this paper require that the root cause or causes for high seawater δ34S be sought in rocks older than about 570 Ma. The current δ34S record appears to be equally compatible with a two-stage rise in seawater δ34S, possibly associated with the late Neoproterozoic glaciations, or with a more gradual increase through the interval ~750 to ~570 Ma. The first possibility is supported by the pyrite-based study of Ross et al. (1995), however, evaporite data from Brazil and Australia do not lend support for any major shift in seawater δ34S across the Marinoan glaciation interval. Alternatively, some aspects of the sulphur cycle would be more consistent with a sustained, long-term change in the S-isotopic budget of the late Neoproterozoic ocean. Firstly, the observed increase in sulphate-pyrite isotopic discrimination, associated with an increase in sulphate concentrations in the ocean, which took place sometime after about 800 Ma (Canfield and Teske, 1996), would have caused seawater δ34S to increase after this time, assuming the same rates of sedimentary sulphate reduction. Secondly, assuming that the observed positive correlation between Phanerozoic seawater 87Sr/86Sr and δ34S (Strauss, 1993) continues into the Neoproterozoic would imply a role for a tectonic driver to increasing seawater δ34S. The availability of metabolisable organic matter may also have exerted some degree of control on the exogenic sulphur isotope biogeochemical cycle. The prolonged nature of high seawater δ34S, once reached indicates that such large-scale, evolutionary processes were the major drivers in determining seawater sulphate isotope systematics during the late Neoproterozoic rather than relatively short-term environmental perturbations.

8. Conclusions

This study confirms the usefulness of francolite-bound sulphate for constraining the sulphur isotopic evolution of seawater sulphate. However, our work also underlines the importance of first constraining the impact of early diagenesis and sample preparation on measured δ34S values. Phosphorites from the upper Doushantuo Formation, South China formed under oxic conditions and are likely to have retained near-seawater δ34S compositions. These data, together with published data, allow us to postulate that seawater δ34S did not change significantly during the Terminal Proterozoic to Cambrian interval. The major rise to high seawater δ34S at the end of the Proterozoic occurred before the onset of Neoproterozoic III, at least partly driven by a long-term shift in the nature of the sulphur biogeochemical cycle.
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