The sulfur isotopic composition of Neoproterozoic seawater sulfate: implications for a snowball Earth?

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Abstract

The present study employs a method for analysis of the sulfur isotopic composition of trace sulfate extracted from carbonates collected in Namibia in order to document secular variations in the sulfur isotopic composition of Neoproterozoic oceanic sulfate and to assess variations in the sulfur cycle that may have accompanied profound climatic events that have been described as the snowball Earth hypothesis. The carbonates in the Otavi Group of Northwest Namibia contain 3–295 ppm sulfate. Positive excursions, to a high of 40 \textsuperscript{34}S (CDT), occur above the lower (Chuos Formation) and upper (Ghaub Formation) glacial intervals in the Rasthof and Maieberg cap carbonates, respectively. Positive excursions at the top of the Rasthof Formation (reaching 51 \textsuperscript{34}S) and within the overlying Gruis Formation (34 \textsuperscript{34}S) do not appear to correspond to glaciation. The \(\delta^{34}\text{S}_{\text{sulfate}}\) values within the Ombaatjie Formation exhibit shifts over relatively short stratigraphic intervals (tens of meters), varying between \(\sim 15\) and 25 \textsuperscript{34}S. Cap carbonates from Australia exhibit positive \(\delta^{34}\text{S}_{\text{pyrrhotite}}\) trends with amplitudes similar to those of Namibian \(\delta^{34}\text{S}_{\text{sulfate}}\); although, more data are necessary to firmly establish these \(\delta^{34}\text{S}\) trends as global in nature. \(\delta^{34}\text{S}_{\text{sulfate}}\) excursions found in Namibian cap carbonates are consistent with the snowball Earth hypothesis in that they appear to reflect nearly complete reduction of sulfate in an isolated, anoxic global ocean, although, there are other mechanisms that may have facilitated these large shifts in \(\delta^{34}\text{S}_{\text{sulfate}}\). Regardless, the low sulfate concentrations in Otavi carbonates, the high amplitude variability of the \(\delta^{34}\text{S}_{\text{sulfate}}\) curve, and the apparently full reduction of sulfate (as implied from \(\delta^{34}\text{S}_{\text{pyrrhotite}}\) data), even in strata low in \(C_{\text{org}}\), suggest that Neoproterozoic oceanic sulfate concentrations were much lower than modern values. Additionally, the buildup of ferrous iron and banded-iron formations during the Sturtian glacial event would indicate that Fe supply exceeded sulfide availability during the glacialis and/or that all sulfide was fixed and buried. This could be construed as further evidence in support of low oceanic sulfate (and sulfide) at this time.

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1. Introduction

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Biogeochemical processes impose significant...
and predictable isotopic fractionations on sulfur species as they are cycled between oxidized (i.e. sulfate) and reduced (i.e. sulfide) forms. Consequently, the isotopic composition of sedimentary sulfides and sulfates are sensitive indicators of environmental change. Sedimentary pyrite most commonly forms as a result of bacterial sulfate reduction and its frequent occurrence in sedimentary rocks has enabled researchers to generally reconstruct the evolution of $\delta^{34}$S$_{pyrite}$ through the Neoproterozoic [1–3]. In order to assess the true extent of fractionation and interpret variations in $\delta^{34}$S$_{pyrite}$, the contemporaneous $\delta^{34}$S of seawater sulfate must be evaluated. Previous secular $\delta^{34}$S$_{sulfate}$ trends for the Neoproterozoic have been developed using relatively rare evaporitic gypsum and barite deposits that provide only a low-resolution ‘glimpse’ of sulfate evolution (Fig. 1; [4–6]). However, $\delta^{34}$S analysis of trace sulfate in marine carbonates [7–10], which are abundant in the Neoproterozoic sedimentary record, can provide a nearly continuous record of seawater sulfate evolution assuming that primary sulfate remains associated with carbonate minerals.

The Neoproterozoic (1000–545 Ma) is of particular interest because it has been characterized as a time of dramatic environmental and biological change [11–13]. At least two distinct global glaciations may have covered most, if not all, of the world’s oceans with sea ice [14–16]. The sensitivity of $\delta^{34}$S$_{sulfate}$ to biogeochemical change makes it a candidate to evaluate aspects of the snowball Earth hypothesis, particularly whether or not the oceans were effectively isolated from air/sea exchange and riverine runoff as the result of long-term global sea-ice cover [15,16].

The present study employs a method developed by Burdett et al. [17] for analysis of the sulfur isotopic composition of trace sulfate extracted from carbonates in order to document secular variations in the sulfur isotopic composition of Neoproterozoic oceanic sulfate and to assess variations in the sulfur cycle that may have accompanied the hypothesized snowball Earth events. It should be emphasized that this is the first dataset of its kind for this time period and that more analyses from different locations/continents are needed to determine the global nature of $\delta^{34}$S$_{sulfate}$ during this interval of the Neoproterozoic.

We hypothesize that positive $\delta^{34}$S$_{sulfate}$ excursions found in Neoproterozoic cap carbonates above glacial deposits can be explained by elements of the snowball Earth hypothesis. Other mechanisms may be envisioned to explain these large shifts in $\delta^{34}$S$_{sulfate}$. Certainly, the relatively low sulfate concentrations in Neoproterozoic carbonates, the high variability in the $\delta^{34}$S$_{sulfate}$ curve, and the apparently full reduction of sulfate evidenced by $\delta^{34}$S$_{pyrite}$ values equivalent to those of sulfate suggest that Neoproterozoic oceanic sulfate concentrations were significantly lower than at present.

2. Geologic setting

Carbonate samples were collected from two sections on the western Congo Craton of Namibia: the Entrance (13°58.07’E, 19°11.01’S) and the Khowarib (14°00.26’E, 19°15.30’S) sections in 1998. Together, the sections provide a relatively
continuous succession of carbonate rocks that include the Rasthof, Gruis, Ombaatjie and Maieberg Formations within the Otavi Group [18,19]. Two diamictites, the Chuos and Ghaub Formations, are intercalated within these carbonate strata. The Chuos Formation (Sturtian) occurs directly below the Rasthof Formation and overlies volcanic strata from which a U-Pb date of 746 ± 4 Ma [20] was obtained. The Ghaub Formation was not present in our sections but occurs stratigraphically between the Ombaatjie Formation and the Keilberg Member of the Maieberg Formation elsewhere in Namibia [19]. Kaufman et al. [13] and Hoffman et al. [16] argue that the Ghaub Formation is also Sturtian (~720 Ma) in age. However, Kennedy et al. [21] suggest a Marinoan age (~600 Ma) based on lithologic and Sr-isotope correlations to radiometrically dated sections in Australia. Paleomagnetic data suggests that deposition of the Otavi Group occurred at ~12° paleolatitude at 743 ± 30 Ma and ~39°S at 547 ± 4 Ma [22].

Light-colored (organic-carbon-poor), micritic dolostones and limestones devoid of visible pyrite were collected (~10-m intervals where possible) in order to preclude any obvious secondary alteration in the S-isotopic composition of the trace sulfate that may have resulted from sulfate reduction and/or subsequent pyrite oxidation.

3. Analytical methods

The method for extraction of trace sulfate from carbonates used in this study is modified slightly from that described by Burdett et al. [17]. Carbonate rock samples ranging in mass from 30 to 150 g were ground and soaked in a 5.25% sodium hypochlorite (NaOCl) solution for ~24 h to eliminate any non-carbonate-associated sulfates, organic sulfur compounds and metastable sulfides. After the sediment was rinsed with deionized water, it was dissolved in 3 N HCl and brought to an near boil (~90°C) for 1 h. Insoluble residues were removed using 0.5-μm filters.

The pH of the filtrate was brought to between 3 and 5 using 6 N NaOH and 10 to 15 ml of saturated bromine water (strong oxidant) was added in order to facilitate the precipitation of iron oxyhydroxides. This oxidation and precipitation step was necessary because iron oxyhydroxides were apt to precipitate simultaneously with BaSO4. This oxidation and precipitation process was allowed to proceed for ~4 h and the iron oxyhydroxides were removed by a second filtration (Whatman No. 40).

Approximately 25–30 ml of saturated BaCl2 (100 g BaCl2/100 ml H2O) was added to the filtrate and brought to a near boil (~90°C) for greater than 4 h. After cooling, precipitated barium sulfate was filtered through Whatman No. 42 ashless filter papers. The filter and precipitate were placed in a crucible and carefully ashed with a torch on low flame. This step eliminates possible loss due to flash burning of the filter paper. After the filter was ashed, it was placed in a combustion furnace for 2 h at ~900°C.

The preparation of sulfate minerals for isotopic analysis was slightly modified from Yanagisawa and Sakai [23]. Approximately 10 mg of BaSO4 sample was mixed with V2O5 (100 mg) and SiO2 (100 mg) and combusted in the presence of copper turnings (100–150 mg) under vacuum for a quantitative conversion to sulfur dioxide (SO2). The V2O5-SiO2 mixture is utilized to lower the decomposition temperature of BaSO4 so that it is completed after 15 min at 1000–1050°C [23]. Additionally, the ratio of (V2O5+SiO2)/BaSO4 of 20:1 is used to buffer the 18O/16O ratio of SO2 by isotope exchange. The ratio of 34S/32S is affected by overlap of ion currents due to 32S16O18O+ and 34S16O16O+. Therefore, a constant ratio of 18O/16O of SO2 must be accomplished among samples in order to apply a consistent correction factor [23]. The 20:1 ratio of (V2O5+SiO2)/BaSO4 satisfies this requirement. The copper turnings are used to reduce any SO3 to SO2 during the combustion process.

Sulfate concentrations were determined on the extraction line during the combustion of the BaSO4 precipitate. Because the chemically precipitated BaSO4 contained various amounts of impurities, the isolated SO2 pressure was measured and BaSO4 concentrations were assessed by calibration with known amounts of the National Bureau of Standards (NBS) 127 barite. Sulfate concentra-
tions are given in ppm. The purified SO₂ was sealed within pyrex tubing and analyzed on a VG Prism Series II isotope ratio mass spectrometer. Sulfur isotope ratios are expressed as per mil (‰) deviations from the S isotope composition of the Cañon Diablo Troilite using the conventional delta (δ³⁴S) notation. Sulfur isotopic results were generally reproducible within ± 0.2 ‰.

For stable carbon and oxygen isotope ratios, powdered bulk carbonates were roasted at 350°C under vacuum to remove any organic carbon present. The carbonates were then reacted at 90°C in phosphoric acid in an automated carbonate device (common acid bath) attached to a Finnegan-MAT 252 mass spectrometer. Isotopic ratios are expressed as per mil deviations from the Vienna Peedee belemnite marine-carbonate standard calibrated with NBS 19 carbonate using the conventional delta (δ¹³C and δ¹⁸O) notation. Isotopic results were reproducible within ± 0.1 ‰.

4. Carbonate-associated sulfate

Natural and synthetic carbonates contain trace amounts of sulfur. Using X-ray absorption near-edge structure, Pingitore et al. [24] determined that the S species incorporated in a variety of carbonates (e.g. fossil corals of aragonite, corals diagenetically altered to calcite, inorganic aragonite and dolomites) were sulfate. Additionally, analytical techniques including infrared and Raman spectra as well as X-ray absorption spectroscopy have revealed that the sulfate ion substitutes for the carbonate ion in natural and synthetic carbonates [24-26].

In laboratory experiments designed to assess controls on sulfate incorporation into synthetic calcites and aragonites, Busenberg and Plummer [25] found that the amount of trace sulfate substituting for the carbonate ion was primarily dictated by the sulfate concentration in the original solution and the rate of crystal growth. They determined that the amount of sulfate incorporated into calcite is proportional to the log of sulfate concentration in solution and the log rate of crystal growth (e.g. carbonate ion concentration). Thus, the faster the carbonate crystal precipitates and the more sulfate available for carbonate ion substitution, the more sulfate is substituted into the calcite and aragonite. Several studies have documented the amount of trace sulfate included in both natural (biogenic and inorganic) and synthetic carbonates. Table 1 is a summary of non-biogenic findings as well as results from the present study. Because Neoproterozoic carbonates do not contain carbonate skeletal material, our analytical effort focuses on analysis of micritic, probably inorganic precipitates. Precipitation of this material, probably as low-Mg calcite, could have been biologically induced in surface waters. The analysis of micritic carbonates also avoids diagenetic overprints associated with processes causing recrystallization and microspar to sparry calcite and/or dolomite.

Although trace sulfate substitutes for the carbonate ion, an important question is whether or not isotopic fractionation occurs during the incorporation process. Burdett et al. [17] analyzed the δ³⁴S of trace sulfate extracted from modern foraminifera and compared the values to the δ³⁴S of measured seawater sulfate. They found that the average δ³⁴S of the modern foraminifera (20.64 ± 0.39%) were on average 0.25% more depleted in ³⁴S than the average seawater values (20.80 ± 0.36%). Because this deviation was within the standard error, they determined that the δ³⁴S of trace sulfate found in biogenic carbonate directly reflects the δ³⁴S of oceanic sulfate from which it precipitated. Additionally, Kampschulte et al. [10] analyzed the δ³⁴S of trace sulfate extracted from a variety of modern biogenic carbonates in various environments and determined the average value to be 21.2 ± 0.8 ‰. This value is consistent with their analyses of contemporaneous seawater sulfate (20.9 ± 0.5 ‰). Finally, Kampschulte et al. [10] compared the δ³⁴S values of trace sulfate in Carboniferous brachiopods to contemporaneous whole rock carbonates. Their results indicate that the whole rock carbonates are only slightly enriched in ³⁴S (0.5 ‰ on average) compared to the brachiopods. Thus, barring subsequent diagenetic alteration, the δ³⁴S of trace sulfate in Neoproterozoic micritic limestones and dolostones is assumed to represent the δ³⁴S of seawater sulfate at the time of precipitation.
5. Results

5.1. Sulfur isotopes

Analytical results for the Namibian carbonates are summarized in Table 2 and Fig. 2. A positive sulfur isotope excursion, reaching 41% from a value of 30% just above the glacial deposits, occurs stratigraphically above the lower glacial interval (Chuos Formation) in the Rasthof Formation. Carbonates of the Ombombo Subgroup are present below the Chuos Formation in some sections in Namibia; however, a significant unconformity exists between the Ombombo and Chous Formations [27] making it difficult to assess the full magnitude of the excursion for the event. The average δ³⁴S_{sulfate} value for evaporitic deposits of the Redstone River Formation in Northwest Canada, a unit older than the Chuos Formation, is ~18% [5]. Therefore, a crude estimate for the full magnitude of the δ³⁴S_{sulfate} excursion for this event is 20%, assuming the δ³⁴S values from both the Redstone River and Rasthof Formations represent the global sulfur isotopic composition of seawater sulfate.

δ³⁴S_{sulfate} values drop in the middle Rasthof Formation to ~20%. A ~33% excursion, to 52%, occurs within the upper portion of the Rasthof Formation (Fig. 2). This excursion does not correspond with any glacial deposits or significant negative carbon isotope excursions in Namibia. A further ~20% positive sulfur isotope excursion, reaching 34%, occurs within the Gruis Formation. This excursion does not occur with any glacial deposits in Namibia but does correspond to a negative carbon isotope excursion of ~5% (Fig. 2).

The δ³⁴S_{sulfate} values within the Ombaatjie Formation exhibit significant shifts over relatively short stratigraphic intervals, varying between ~15 and 25% (Fig. 2). Another positive excursion, reaching 39%, appears stratigraphically above the upper glacial interval (Ghaub Formation) in the Maieberg Formation. The δ³⁴S_{sulfate} values from

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Table 1

<table>
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<tr>
<th>Location</th>
<th>Formation age</th>
<th>Rock type</th>
<th>Range of sulfate conc. (ppm)</th>
<th>Ave. sulfate conc. (ppm)</th>
<th>No. of samples</th>
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value for sample KH 9 near the base of the Maieberg Formation is 11 $\%_{\text{o}}$. However, because KH 9 represents a single sample excursion and other values at the base of the Maieberg Formation are $\sim 24 \%_{\text{o}}$, a conservative estimate of the magnitude of the excursion within the Maieberg Formation is 15 $\%_{\text{o}}$.

Nonetheless, if the $\sim 33 \%_{\text{o}}$ positive excursion reaching 52 $\%_{\text{o}}$ in the upper Rasthof Formation represents the global isotopic composition of seawater sulfate at that time, then it is among the largest recorded for any time in Earth history. For comparison, the magnitude of the largest $\delta^{34}S_{\text{Sulfate}}$ excursion recorded in Phanerozoic evaporites is $\sim 15 \%_{\text{o}}$ (mid to late Devonian; [4]).

5.2. Carbon and oxygen isotopes

Similar to what other authors have found [13,16], our low-resolution records indicate that $\delta^{13}C_{\text{Carbonate}}$ values increase through the Rasthof, Gruis and mid-Ombaatjie Formations and then decrease by $\sim 12 \%_{\text{o}}$ in the upper Ombaatjie Formation, immediately below the stratigraphic equivalent to the Ghaub diamictite (Fig. 2; Table 2). $\delta^{13}C_{\text{Carbonate}}$ values hover between $-2$ to $-3 \%_{\text{o}}$ in the Maieberg Formation above the Ghaub Formation. As mentioned previously, there is a negative $\delta^{13}C_{\text{Carbonate}}$ excursion associated with the Rasthof/Gruis transition with values falling from $\sim 6 \%_{\text{o}}$ (sample EN 6; Table 2) to $\sim 1 \%_{\text{o}}$ (sample KH 23; Table 2) over 71 m. The $\delta^{18}O_{\text{Carbonate}}$ values have a trend similar to that of the $\delta^{13}C_{\text{Carbonate}}$ values.

5.3. Sulfate concentrations

The carbonates in the Otavi Group contain 3 to
295 ppm sulfate (Fig. 2; see Table 1 for comparison to other published results). Sulfate concentrations in the cap carbonates are initially low (25 ppm in the Maieberg Formation and 38 ppm in the Rasthof Formation), then rise to ~200 ppm, and finally decrease again to values as low as 3 ppm. A similar pattern is observed for the upper Rasthof/Gruis Formations (coincident with the 20% δ34S sulfate excursion). Furthermore, sulfate concentrations in the Ombaatjie Formation are initially low (33 ppm) and then increase to values as high as 295 ppm below the Ghaub Formation. Fig. 3 illustrates that there is no correlation between trace sulfate concentrations and the δ34S sulfate values of the Otavi carbonates. This lack of correlation is important because an inverse correlation between sulfate concentrations and δ34S sulfate might suggest that microbial sulfate reduction was responsible for decreasing sulfate concentrations in pore waters and enriching any residual sulfate with respect to 34S which might be incorporated in diagenetic calcite.

6. Discussion

6.1. Controls on the δ34S of seawater sulfate

A brief discussion of the sulfur cycle and controls on the δ34S of oceanic sulfate is necessary to interpret the mechanisms that may have induced the large positive excursions in δ34S sulfate that occur in Namibian cap carbonates (Fig. 2). The primary source of seawater sulfate is riverine delivery resulting from the weathering of pyrite and calcium sulfate minerals under an O2-bearing atmosphere. Sulfur is also delivered to the ocean via hydrothermal inputs (e.g. mantle sulfur). Sulfate is removed from the oceans by primarily two mechanisms: (1) calcium sulfate (gypsum) precipitation and (2) bacterial sulfate reduction and the formation of sedimentary pyrite. Sulfur removed during calcium sulfate precipitation involves minimal isotopic fractionation (0–2.4%; [28,29]). By contrast, a significant kinetic isotope effect (4–46%; [30–33]) occurs during bacterial sulfate reduction as obligate anaerobes preferentially dissimilate the lighter 32S in the production of H2S and pyrite. Consequently, sedimentary pyrite is commonly depleted in 34S relative to contemporaneous sulfate.

Secular variations in the sulfur isotopic composition of seawater sulfate have typically been attributed to changes in the burial ratio of reduced versus oxidized sulfur. Positive excursions in δ34S sulfate represent the preferential removal of 32S from the oceans via an increase in the fraction of total sulfur buried as pyrite. By contrast, negative excursions in δ34S sulfate are expressed when the fraction of total sulfur buried as calcium sulfate (oxidized S) increases generally because the δ34S of riverine sulfate is ~6% (assuming that one third of riverine sulfate derives from pyrite-oxidation and two thirds from evaporites and other sulfate sources, e.g. [34]) and seawater sulfate δ34S approaches the riverine value as the fraction of sulfide buried decreases. However, the magnitude of and time represented by the δ34S sulfate excursion, as well as the oceanic residence time of sulfate, need to be considered when assessing possible processes responsible for sulfur isotopic excursions.

Holser [35] identified positive δ34S sulfate excursions, ranging in amplitude from 5 to 15%, that occurred over short time intervals (<5 Myr) in the late Neoproterozoic, late Devonian and early Triassic. Holser [35] argued that it would be extremely difficult to modify the sulfur isotopic composition of seawater sulfate by 15%
in less than 5 Myr assuming that the oceanic residence time of sulfate was 20 Myr. He suggested that anoxia in isolated stratified basins allowed bacterial sulfate reduction to occur within the isolated subsurface and caused the $\delta^{34}$S of sulfate to increase within those basins. Subsequent oceanic mixing forced a rapid (<5 Myr) increase in $\delta^{34}$S sulfate recorded in evaporites that formed from surface seawater. More recent work indicates that the residence time of oceanic sulfate today is $\approx$ 10 Myr [34].

It is difficult to assign durations to the $\delta^{34}$S sulfate excursions in Namibia due to the lack of radiometric age dates. However, using thermal subsidence models, Halverson et al. [27] suggested that the Ombaatjie Formation was deposited in less than 3 Myr and Hoffman et al. [36] suggested that the average shallow-water carbonate accumulation rate for the entire Otavi Group was $\geq$ 52 m/Myr. Therefore, the $> 15\%$ shifts in $\delta^{34}$S sulfate that take place over short stratigraphic distances (< 50 m) within Namibia may have occurred over less than 1 Myr. If we assume the $> 15\%$ shifts found in Namibian carbonates represent global excursions and that the residence time of seawater sulfate was $\approx$ 10 Myr in the Neoproterozoic, then $> 15\%$ shifts in $\delta^{34}$S sulfate would be extremely difficult to produce in 1 Myr or less (without proposing highly unusual conditions).

A way to develop $\delta^{34}$S sulfate excursions without necessarily modifying the fraction of sulfide burial is to change the degree of fractionation between sulfide and sulfate. Laboratory results indicate that pure cultures of sulfate-reducing bacteria produce sulfide depleted in $^{34}$S by 4–46‰ compared with the initial sulfate [30,31,37]. Habicht and Canfield [33] determined that natural populations of sulfate-reducing bacteria from several coastal marine environments produced sulfide depleted in $^{34}$S by 19–43‰. However, sulfides in marine sediments and euxinic (anoxic–sulfidic) waters are commonly depleted in $^{34}$S by 45–70‰ relative to seawater sulfate [31,2]. It should be noted that Woortman et al. [38] documented sulfate-reducing bacteria in carbonates buried 10–180 m below the seafloor that produced sulfide depleted in $^{34}$S by 65–72‰ in association with methane in pore waters. Nonetheless, bacterial sulfate reduction alone cannot explain the $\delta^{34}$S values of sulfides in modern, coastal-marine environments.

Canfield and Teske [2] have proposed that this additional depletion in $\delta^{34}$S sulfide is a result of the oxidative part of the sulfur cycle. The very depleted $\delta^{34}$S sulfide values are thought to reflect an initial fractionation by sulfate-reducing bacteria followed by an additional fractionation (7–11‰) that results from the disproportionation of intermediate sulfur species such as S0 and S2O32– (thiosulfate) [31,39]. Through repeated cycles of sulfide oxidation to S0 and subsequent disproportionation, sulfides become depleted in $^{34}$S to a greater degree than the initial sulfate reduction. These processes may be responsible for the depletion of $^{34}$S values from 45 to 70‰ as recorded in natural environments such as the Black Sea water column [40,41] and surface sediments of the Peru margin [42] and thereby increase $\Delta^{34}$S.

Canfield and Teske [2] have argued that an increase in the variability of the sulfur isotopic composition of pyrite at a $\approx$ 800 Ma represents a rise in atmospheric oxygen. This increase in oxygen would have forced the oxic–anoxic interface from surface to deeper waters, increasing the oxidation state of coastal sediments below the photic zone. They proposed that this oxygenation event was coincident with the proliferation of non-photosynthetic sulfur-oxidizing bacteria. The rise of these bacteria would have promoted the oxidative part of the sulfur cycle facilitating an increase in the sulfur isotope fractionation between seawater sulfate and pyrite from $\approx$ 35‰ before 800 Ma to 55‰ after 800 Ma. Canfield and Teske [2] proposed that before 800 Ma, sulfide oxidation occurred mainly by phototrophic bacteria, resulting in a more direct oxidation of sulfide to sulfate, with less formation of sulfur intermediates.

This shift represents a change in microbial evolution. It seems unlikely that bacteria would switch the magnitude of fractionation for a period of time and then return to the earlier one unless there were substantial variation in the volume of anoxic marine waters and accompanying changes in the depth of oxygenation within the photic zone. In short, it is very difficult to generate a $> 15\%$ excursion, either by simply changing the
magnitude of fractionation or by increasing the burial ratio of sulfides to sulfates (assuming an oceanic residence time of 10 Myr for sulfate) and therefore other mechanisms or combination of mechanisms must be considered.

6.2. Implications for a Neoproterozoic snowball Earth

Researchers have suggested that global glaciations have occurred at least twice in the Neoproterozoic [14–16]. The evidence for this hypothesis comes from paleomagnetic data from several continents that indicates that glacial strata were deposited near the paleoequator. Many of the glacial deposits are capped by carbonate rocks [43] characterized by large negative $\delta^{13}C_{\text{carbonate}}$ anomalies (Fig. 2; [44,16]) that have been interpreted to signify a collapse in oceanic biological productivity induced by global glaciation ([16]; see Kennedy et al. [45] for an opposing view). Kirschvink [15] suggested that if the entire ocean were covered with ice, the hydrologic cycle would have essentially been disabled and continental glaciers would have been sparse. Additionally, he proposed that oceanic anoxia would have developed as a result of sea-ice cover, encouraging the build up of ferrous iron and the return of banded iron formations (BIFs). The Chuos Formation in Namibia is an iron-rich diamictite with interbedded ironstones [18]. Considering Earth’s evolution, this reflects the deposition of such deposits following a time interval of ca. 1 Ga devoid of BIFs. Nonetheless, with a greatly reduced or absent hydrologic cycle, CO$_2$ consumption via weathering and photosynthesis would have dropped off dramatically. Hoffman et al. [16] argued that global icehouse conditions would have persisted until subaerial volcanism had pumped enough CO$_2$ into the atmosphere to provoke an extreme greenhouse effect sufficient to overcome the extreme ice-albedo effect. As a consequence of rapid warming, ice meltback and reestablishment of the hydrologic cycle, the high concentrations of CO$_2$ in the atmosphere would have been transferred to the oceans perhaps stimulating the rapid precipitation of postglacial carbonate sediments (cap carbonates).

What effect would a snowball Earth have on the sulfur cycle? A schematic model of the snowball Earth and how it relates to the sulfur cycle is presented in Fig. 4A. If the Earth’s oceans were blanketed with ice and the hydrologic cycle shutdown, riverine delivery of relatively depleted $\delta^{34}S_{\text{sulfate}}$ (ca. 6 $\%_e$) from the continents via pyrite weathering and/or evaporite dissolution would essentially cease. Assuming that sufficient organic substrates existed to allow sulfate-reducing bacteria to continue to preferentially dissiplate $^{32}S$ and that the sulfide was precipitated as pyrite (available Fe), the isolated oceanic reservoir of sulfate would become progressively enriched in $^{34}S$. Hoffman et al. [16] have suggested that the duration of the snowball event may have been 8 Myr. During this time, the oceanic sulfate reservoir would decrease significantly while bicarbonate (HCO$_3^-$) concentration would rise. During deglaciation (Fig. 4B), deepwater overturn would supply $^{34}S$-enriched sulfate (but at low concentrations) to surface waters and, as a result, trace sul-

Fig. 4. Schematic diagrams illustrating processes operating during model simulation of (A) the snowball earth episode and (B) the cap carbonate period.
fate incorporated in postglacial carbonates would reflect the enriched $\delta^{34}$S. Additionally, $^{13}$C-depleted HCO$_3^-$ that formed as a result of sulfate reduction (2 mol of HCO$_3^-$ is produced for every 1 mol of SO$_4^{2-}$ that is reduced) would be delivered to surface waters during deepwater overturn. This excess HCO$_3^-$ would encourage the precipitation of $^{13}$C-depleted cap carbonates. As the hydrologic cycle resumed and perhaps rapid input of sulfate was reestablished, the $\delta^{34}$S$_{\text{sulfate}}$ of oceans would gradually or perhaps rapidly return to more typical values of 20‰ over tens of millions of years.

Gorjan et al. [3] proposed a similar scenario to that described above for the Sturtian glacial event based on Neoproterozoic $\delta^{34}$S$_{\text{pyrite}}$ values from Australia. By contrast, they argued that the paucity of enriched $\delta^{34}$S$_{\text{sulfate}}$ values associated with the Marinoan glacial deposits indicate that the second ‘snowball’ event was more severe than the Sturtian event. In their model, as a result of the greater intensity of the Marinoan snowball event, primary production during the glacial event was significantly decreased resulting in an oxic ocean and very little bacterial sulfate reduction.

The assessment of possible changes in $\delta^{34}$S$_{\text{sulfate}}$ resulting from a snowball Earth episode through a simple numerical model of the sulfur cycle elucidates the significance of changes and provides an idea of the sensitivity of $\delta^{34}$S$_{\text{sulfate}}$ to assumptions made.

6.3. Results of numerical modeling

Our simulation of the ‘snowball’ sulfur cycle requires that most of the world ocean becomes anoxic. This could occur easily under prolonged global ice cover (e.g. [46]), and would probably occur if air/sea exchange were largely inhibited, even if areas of open water existed in the tropics as produced in some AGCM studies [47,48]. We assume that this open water would not be sufficient to ventilate the oceans. As in the previous discussion, the model also assumes that the oceanic sulfate reservoir is isolated from main sulfur inputs (weathering flux, subaerial volcanism), but the model does allow input of hydrothermal sulfide at the mid-ocean ridge (Fig. 4A). Thus, even with open water, the rate of weathering and river fluxes to the ocean must be very small to nonexistent.

In the model, sulfate reduction and pyrite formation continues at the assumed rate for marine environments today, for 5 Myr – a duration at the low end of those proposed by Hoffman et al. [16] for a snowball Earth episode. One important question is whether organic compounds would become limiting to bacterial sulfate reduction over this timescale. We assume that it would not because we might expect a chemosynthetic anaerobic bacterial ecosystem and/or production of organic matter by photosynthesis under thin ice [49] and/or in areas of open ocean in the tropics that may have existed (e.g. [47]). Occurrence of BIFs associated with Sturtian ‘snowball’ glacial deposits indicates that iron availability does not limit pyrite formation (e.g. [15,16]).

Fig. 5 shows the results of one simulation for which the initial oceanic sulfate mass is about half of that for the present. Fig. 6 demonstrates the sensitivity of the amplitude of the sulfur isotope excursion to initial sulfate reservoir mass. The only way to produce a 20‰ positive excursion over 5 Myr using reasonable assumptions is to have a relatively small initial sulfate reservoir mass. At any rate, over 5 Myr or so, the $\delta^{34}$S$_{\text{sulfate}}$ continues to rise.

In the model simulation shown in Fig. 5, $1.8 \times 10^{19}$ mol of sulfate is reduced over the 5 Myr snowball event. This equates to the production of $3.5 \times 10^{19}$ mol of HCO$_3^-$. Kennedy et al. [45] estimate that $8 \times 10^{17}$ mol of carbonate is required to deposit a 1-m-thick layer of cap carbonate on carbonate shelves equivalent to the modern aerial extent. The amount of HCO$_3^-$ produced in our snowball simulation via sulfate reduction is 44 times that of the above estimate.

Some time during deglaciation the ocean must convect, and we suggest that the eventual mixing of the ocean brings the ‘late’ enriched $\delta^{34}$S signal incorporated into cap carbonates augmented by continued pyrite formation that accompanies high productivity (high nutrient flux to surface waters) following deglaciation (Fig. 4B). This may explain the positive excursion in $\delta^{34}$S$_{\text{sulfate}}$ that occurs within but not at the base of the
younger cap carbonate (e.g. Maieberg Formation, Fig. 2).

At this point, pyrite formation associated with highly productive surface oceans and cap carbonate formation exhausts sulfate in the sulfate-depleted ocean and the $\delta^{34}$S$_{\text{sulfate}}$ is essentially zero. The abrupt large decrease in $\delta^{34}$S$_{\text{sulfate}}$ at about 6 Myr in the model progression results from rapid influx of riverine sulfate (meltwater, volcanic, etc.) for 1 Myr at an assumed rate of about $5 \times$ that at present (and $\delta^{34}$S of 6‰) as suggested by Hoffman and Schrag [46], who actually suggested much higher river fluxes than that. The abrupt decrease results from the high input flux and low concentration of oceanic sulfate. Following the runoff event, the sulfate concentration and sulfur isotopic compositions approach a new steady state, with the $\delta^{34}$S$_{\text{sulfate}}$ near 22‰.

Certainly, the assumption that organic substrates would be available to sulfate-reducing bacteria throughout a snowball Earth event is questionable. Organic compounds may have only been available for the first million years or throughout the snowball event at much lower concentrations. However, it is possible that oceanic sulfate concentrations may have been lower than prescribed in our model. If this were the case, less organic carbon and bacterial sulfate reduction would be necessary to deplete oceanic sulfate concentrations and enrich $\delta^{34}$S$_{\text{sulfate}}$. Additionally, bacterial sulfate reduction rates (and $\Delta^{34}$S) would be expected to change as a function of sulfate and organic carbon availability.

In any event, the sulfur isotope trends produced in the model described above are similar to those observed in our Namibian data (Fig. 2), and we suggest that the above scenario best accounts for the patterns observed, although differences may exist between the two episodes (see discussion below). Dramatic positive excursions, reaching $\sim 40\%$, appear stratigraphically above the glacial intervals (Chuos and Ghaub Formations) in the Rasthof and Maieberg cap carbonates (Fig. 2). Additionally, Neoproterozoic $\delta^{34}$S$_{\text{pyrite}}$ records from Australia (Fig. 7; [3]) appear to parallel the Namibian $\delta^{34}$S$_{\text{sulfate}}$ records. Gorjan et al. [3] examined two Neoproterozoic sequences within Australia: the Adelaide Rift Complex and the Amadeus Basin. These sections each contain two diamicites (Fig. 7). The Adelaide Rift Complex contains the Sturt/Apila (Sturtian) and Elatina (Marinoan) Formations and the Amadeus Basin contains the Areyonga (Sturtian) and Olympic/Boord (Marinoan) Formations. $\delta^{34}$S$_{\text{pyrite}}$ values within the cap carbonates overlying these diamicites begin with values as low as $-35\%$ and increase sharply to $\sim 40\%$. These maximum $\delta^{34}$S$_{\text{pyrite}}$ values are very similar to our maximum $\delta^{34}$S$_{\text{sulfate}}$ values and seem to indicate diminished $\Delta^{34}$S$_{\text{sulfate}}$--pyrite values that suggest reduction of sulfate by bacteria was complete at these sites.
Possible correlations between Namibia (present study) and Australia [3] using lithologic (glacial) events and $\delta^{34}\text{S}$ trends are illustrated in Fig. 7.

6.4. Sturtian versus Marinoan and oceanic sulfate concentrations

As previously discussed, Gorjan et al. [3] suggested that the lack of enriched $\delta^{34}\text{S}_{\text{sulfate}}$ values associated with the Elatina Formation in the Adelaide Rift Complex indicate that the second ‘snowball’ event was more severe than the Sturtian event resulting in a substantial decrease in primary productivity and bacterial sulfate reduction. However, they admit that the only sulfate sample they analyzed was likely secondary. The enriched $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ values from the Maieberg Formation in Namibia and the Marinoan cap carbonate in the Amadeus Basin (Fig. 7; [3]), respectively, suggests that bacterial sulfate reduction was operating either during and/or after the glacial event. In both of these cap carbonates, $\delta^{34}\text{S}$ values begin low and increase up section. This suggests that the enriched $\delta^{34}\text{S}$ values may in part represent intense bacterial sulfate reduction in the aftermath of a glacial event. However, the lack of BIFs associated with the Marinoan event (both in Namibia and Australia) indicates that sulfide supply exceeded iron availability and therefore bacterial sulfate reduction must have been operating during the glacial event itself. Elevated trace sulfate concentrations in the Ombaatjie Formation relative to the postglacial Maieberg Formation also suggest sulfate-reducing bacteria were active during the glacial episode. The more depleted $\delta^{34}\text{S}$ values at the base of the Marinoan
Cap carbonates may have resulted from periods of intense weathering supplying relatively depleted $^{34}\text{S}$ to the oceans.

Additionally, the absence of BIFs associated with the Marinoan glacial event may suggest oceanic sulfate concentrations were higher prior to the Marinoan relative to the Sturtian event. Elevated oceanic sulfate concentrations would allow for more bacterial sulfate reduction thereby increasing the availability of sulfide (for Fe-sulfide deposition) and precluding BIF formation. Also, a larger reservoir of oceanic sulfate would require increased amounts of bacterial sulfate reduction to increase $^{34}\text{S}$. Therefore, the Marinoan glacial event may have supported bacterial sulfate reduction but not enough to significantly alter the oceanic sulfate reservoir.

By contrast, Sturtian $^{34}\text{S}_{\text{pyrite}}$ values within the glacial event become progressively enriched up section and continue to increase without interruption through the base of the cap carbonates. Similarly, $^{34}\text{S}_{\text{sulfate}}$ values at the base of the Rasthof Formation in Namibia begin enriched (30\%) and reach a maximum of 41\%. This suggests that sulfate reduction operated through the snowball Earth event, decreasing oceanic sulfate concentrations and enriching $^{34}\text{S}$. Furthermore, the continuous enrichment of $^{34}\text{S}$ within the cap carbonates suggests that oceanic sulfate concentrations remained low and were further affected by bacterial sulfate reduction in the aftermath of the glacial event.

Nevertheless, assuming the $^{34}\text{S}_{\text{sulfate}}$ data from Otavi carbonates are representative of global seawater sulfate during the Neoproterozoic, we contend that the high variability in the $^{34}\text{S}_{\text{sulfate}}$ curve, the low concentrations of sulfate within the Namibian carbonates (relative to other carbonates; see Table 2 for comparison) and the apparently nearly full reduction of sulfate as inter-
Interpreted from $\delta^{34}\text{S}_{\text{pyrite}}$ data all indicate that Neoproterozoic oceanic sulfate concentrations were significantly lower than at present. Additionally, the buildup of ferrous iron and BIFs during the Sturtian glacial event would indicate that Fe supply exceeded sulfide availability during the glacial period and/or that all sulfide was fixed and buried. This could be construed as further evidence in support of low oceanic sulfate (and sulfide) at this time.

6.5. Alternatives

As mentioned previously, large $\delta^{34}\text{S}_{\text{sulfate}}$ excursions also occur in the upper Rasthof and Gruis Formations in Namibia (Fig. 2). Gorjan et al. [3] present $\delta^{34}\text{S}_{\text{pyrite}}$ values reaching $50+\%\text{e}$ in Australia (Fig. 7). These excursions do not correspond with any glacial deposits in either Namibia or Australia. Therefore, additional mechanisms that may facilitate the large $\delta^{34}\text{S}_{\text{sulfate}}$ excursions must be considered. As discussed previously, our data suggest that Neoproterozoic oceanic sulfate concentrations were lower than they are today. This decrease in sulfate concentration reduces the residence time of oceanic sulfate and increases its susceptibility to isotopic shifts. For example, a highly productive ocean may increase the amount of organic carbon delivered to the water column and sediments, thereby encouraging sulfate reduction in an already sulfate-poor ocean. With continued sulfate reduction and sedimentary pyrite formation, the residual oceanic sulfate becomes enriched in $^{34}\text{S}$ and as the oceanic sulfate reservoir is exhausted the $\Delta^{34}\text{S}_{\text{sulfate-pyrite}}$ becomes zero. This scenario is also consistent with our data (Fig. 7).

7. Conclusion

We suggest that the large positive $\delta^{34}\text{S}_{\text{sulfate}}$ excursions found in Neoproterozoic cap carbonates are consistent with the snowball Earth events outlined by Hoffman et al. [16] and Kirschvink [15]. For example, if the Earth’s oceans were covered with ice for millions of years, the source of riverine sulfate with $\delta^{34}\text{S}$ values of ca. 6%e from the continents via pyrite weathering would have disappeared. Assuming that sulfate-reducing bacteria continued to operate sufficiently, even with a reduced availability of organic substrate, the oceanic sulfate pool would have been driven to more enriched $\delta^{34}\text{S}$ values, while the sulfate concentration decreased. Following a prolonged period, ocean stratification would have broken down and promoted deepwater overturn. The upwelled deepwater would have had very low sulfate substantially enriched in $^{34}\text{S}$. As a result, the trace sulfate associated with postglacial carbonates was lower in concentration and enriched in $^{34}\text{S}$. As the delivery of riverine sulfate was re-established, the $\delta^{34}\text{S}_{\text{sulfate}}$ returned to more typical values of 20%e over perhaps millions of years. The records of Neoproterozoic $\delta^{34}\text{S}_{\text{pyrite}}$ values from western Canada and Australia parallel our $\delta^{34}\text{S}_{\text{sulfate}}$ results. The generally small $\Delta^{34}\text{S}_{\text{sulfate-pyrite}}$ values suggest that reduction of sulfate by bacteria was complete at these sites even though the sediments are low in organic carbon. The low sulfate concentrations in Neoproterozoic carbonates, the high amplitude variability of the $\delta^{34}\text{S}_{\text{sulfate}}$ curve and the apparently full reduction of sulfate suggest that Neoproterozoic oceanic sulfate concentrations were much lower than modern values and, therefore, the residence time was much shorter. Though the snowball Earth hypothesis provides a reasonable explanation for two of four large positive $\delta^{34}\text{S}$ excursions observed in the Neoproterozoic of Namibia, two large excursions are not clearly associated with glacial events. It is possible that multiple large-scale episodes of ocean stratification and anoxia occurred during this period with or without development of full glacial conditions.

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