

Superheavy pyrite ($\delta^{34}\text{S}_{\text{pyr}} > \delta^{34}\text{S}_{\text{CAS}}$) in the terminal Proterozoic Nama Group, southern Namibia: A consequence of low seawater sulfate at the dawn of animal life

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ABSTRACT

Sulfur isotope analysis ($\delta^{34}\text{S}$) of well-preserved carbonates spanning an ~10 Ma interval of the terminal Proterozoic Nama Group reveals that disseminated pyrite is consistently enriched in ^{34}S relative to coeval seawater sulfate as preserved in carbonate-associated sulfate (CAS). This observation is not consistent with the current paradigm for interpreting the geologic record of sulfur isotopes, which assumes that pyrite $\delta^{34}\text{S}$ ($\delta^{34}\text{S}_{\text{pyr}}$) will be equal to or less than co-occurring CAS $\delta^{34}\text{S}$ ($\delta^{34}\text{S}_{\text{CAS}}$) due to the kinetic isotope effect of bacterial sulfate reduction (BSR) that favors the lighter isotope of sulfur (^{32}S) during sulfur-oxygen bond breakage. Although the precise mechanism of pyrite sulfur isotope enrichment is debatable, our combined observations of extremely ^{34}S -enriched pyrite, low bulk-rock concentrations of sulfur from CAS and pyrite, and high-frequency fluctuations in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ throughout the Nama Group carbonates point to very low concentrations of sulfate in portions of the terminal Proterozoic ocean. The additional occurrence of ^{34}S -enriched pyrite in contemporaneous terminal Proterozoic sections from Poland and Canada reveal that low seawater sulfate may have been widespread in the oceans at this time. However, the absence of such extremely ^{34}S -enriched pyrite from well-preserved, coeval carbonate sections in Oman suggests that such conditions were not globally uniform. Low, geographically varied concentrations of marine sulfate in terminal Proterozoic time are consistent with elevated, geographically varied concentrations of reactive, nonpyritized iron in marine shales recently reported for this interval, suggesting that high dissolved Fe(II) and low O_2 persisted in a range of marine facies as late as 543 Ma—tens of millions of years after the origin of animals, yet prior to their major diversification in Early Cambrian time.

INTRODUCTION

The difference in $\delta^{34}\text{S}$ between coeval carbonate-associated sulfate (CAS, derived from seawater sulfate) and disseminated pyrite (derived from sedimentary sulfide) preserved in micritic limestone is widely interpreted as a proxy for the isotopic fractionation that accompanied bacterial sulfate reduction (BSR) and other sulfur redox metabolisms (e.g., disproportionation) in the paleo-ocean. Thus, this fractionation is used to infer seawater sulfate concentration (which influences sulfur isotope fractionation during BSR) and, by extension, the oxidation state of the ancient ocean (Canfield et al., 2000; Canfield and Teske, 1996; Habicht et al., 2002; Kah et al., 2004). Because BSR favors the lighter, more weakly bonded isotope of sulfur (^{32}S), pyrite is typically depleted in ^{34}S relative to coevally deposited CAS (Canfield, 2001). Here, we report on the first long-term (~10 Ma) high-resolution paired CAS-pyrite isotopic analyses that identify disseminated pyrite that

is consistently enriched, rather than depleted, in ^{34}S relative to coeval CAS. These findings have important implications for our understanding of the marine sulfur cycle and oxidation state of the ocean at the dawn of animal life.

GEOLOGIC CONTEXT

The Nama Group of southern Namibia is one of the best preserved and most continuous terminal Proterozoic limestone successions recognized in the world. The carbonate units investigated in the present study (Fig. 1) were deposited between ca. 553 and 543 Ma ago in a semidivided foreland basin of the Kalahari Craton (Grotzinger and Miller, 2008). These units were deposited in shore-associated settings ranging from upper shoreline/tidal flats to below-wave-base lower shoreface, and comprise calcisiltites, calcarenites, heterolithic interbeds, grainstones, and microbialites (Saylor et al., 1998; Grotzinger and Miller, 2008). The ubiquitous distribution of trough-bedded coarse grainstones, rip-up clasts, and wave-scoured surfaces within these units indicates that they were regularly reworked by intense storm activity (DiBenedetto and Grotzinger, 2005). See the

GSA Data Repository¹ for a detailed stratigraphic description and discussion of age constraints.

SUPERHEAVY PYRITE ($\delta^{34}\text{S}_{\text{PYR}} > \delta^{34}\text{S}_{\text{CAS}}$) IN THE NAMA GROUP CARBONATES

Sulfur and carbon isotope ratios and strontium concentrations obtained from well-preserved carbonate strata of the Omkyk, Hoogland, Huns, and Spitzkopf members of the Nama Group are presented in Figure 1. Of the 71 paired $\delta^{34}\text{S}_{\text{pyr}} - \delta^{34}\text{S}_{\text{CAS}}$ analyses obtained from the ~10 Ma terminal Proterozoic succession (Figs. 1B and 1C), approximately three-quarters exhibit $\delta^{34}\text{S}_{\text{pyr}}$ values (average = 36.7‰; range = 20.5‰ to 80.2‰) that are enriched in ^{34}S relative to co-deposited $\delta^{34}\text{S}_{\text{CAS}}$ (average = 27.2‰; range = 13.5‰ to 64.2‰). This “superheavy pyrite” yields anomalously negative values of $\Delta^{34}\text{S}_{\text{CAS-pyr}}$ ($\delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{pyr}}$; average = -8.2‰; range = -31.1‰ to +12.0‰). The magnitude of the ^{34}S enrichment in pyrite observed in the Nama Group carbonates is substantial, with nearly half of the ^{34}S -enriched pyrite samples exhibiting enrichment of greater than 14‰ relative to co-deposited CAS. These results are not consistent with our current view of sulfur isotopes in the geologic record (Canfield, 2001) and may have important paleoceanographic implications for this critical interval of geologic time.

Notably, both $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ fluctuate more than 20‰ over relatively short stratigraphic distances (<10 m; Fig. 1B). Assuming a constant rate of sedimentation between the dated ash beds (see the Data Repository), such fluctuations would have occurred over less than 150 ka intervals. It is also possible that the ~10 m sampling interval precluded observation of even higher-frequency fluctuations in these sulfur isotope records. Gravimetrically determined concentrations of sulfur from CAS (S_{CAS}) and sulfur from pyrite (S_{pyr}) in these carbonates were low, averaging 22.7 ppm

¹GSA Data Repository item 2009179, a table of the geochemical data, along with supplementary text, figures, and references, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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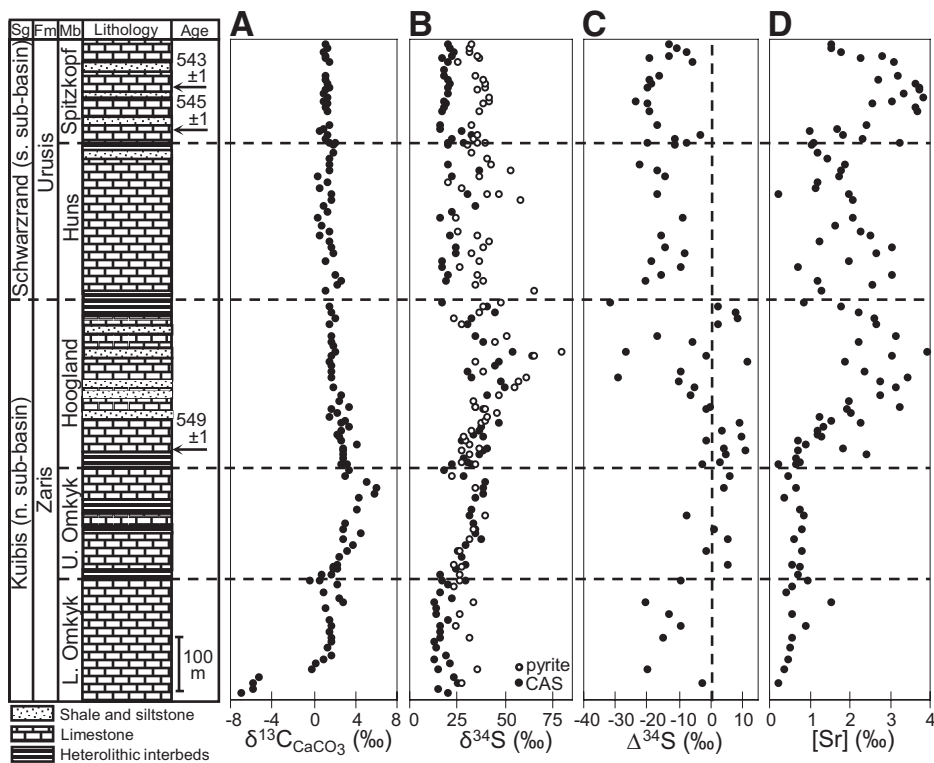


Figure 1. Lithologic, temporal, and chemostratigraphic constraints of the studied Nama Group sections. Data plotted are $\delta^{13}\text{C}_{\text{CaCO}_3}$ (A), $\delta^{34}\text{S}_{\text{pyr}}$ (open circles) and $\delta^{34}\text{S}_{\text{CAS}}$ (closed circles) (B), $\Delta^{34}\text{S} = \delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{pyr}}$ (dashed line = 0‰) (C), and bulk-rock [Sr] (D). U-Pb dates were obtained from zircons in ash beds (Grotzinger et al., 1995) within the Hoogland (549 ± 1 Ma; northern subbasin) and Spitzkopf members (545 ± 1 Ma and 543 ± 1 Ma; southern subbasin). Carbon isotope stratigraphy and U-Pb zircon dates were used to integrate the sampled Nama Group sections into a temporally continuous composite stratigraphic section that maximizes representation of CAS-hosting carbonate units (Saylor et al., 1998). Full data set available in the Data Repository (see footnote 1).

(range: 0.2–117.7 ppm) and 33.8 ppm (range: 1.5–212.0 ppm), respectively.

QUALITY OF PRESERVATION

Low Mn/Sr ratios (99% of samples < 2), high concentrations of Sr (average [Sr] = 1805 ppm), relatively enriched $\delta^{18}\text{O}$ (87% of samples > -10‰), and $\delta^{13}\text{C}$ data that track coeval terminal Proterozoic sequences throughout the world (see Fig. DR1 in the Data Repository) suggest that the sampled Nama Group carbonates, including their associated sulfate and pyrite, are well preserved and were derived from seawater connected to the global ocean (Grotzinger et al., 1995; Saylor et al., 1995). Furthermore, neither of the anomalous trends observed in the Nama Group carbonates, enriched $\delta^{34}\text{S}_{\text{pyr}}$ and depleted $\delta^{34}\text{S}_{\text{CAS}}$, show significant ($p < 0.05$) positive correlation with conventional geochemical indicators of diagenesis (light $\delta^{18}\text{O}$ and elevated Mn/Sr; see the Data Repository for discussion).

OTHER OCCURRENCES OF HEAVY PYRITE IN TERMINAL PROTEROZOIC TIME

Heavy pyrite in the terminal Proterozoic has also been reported for the Random Formation

in Canada (23.4‰; Strauss et al., 1992) and for the Mazowze (23.6‰), Wlodowa (27.6‰), and Lublin (26.8‰) Formations in Poland (Bottomley et al., 1992). However, a high-resolution paired analysis of $\delta^{34}\text{S}_{\text{pyr}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ in the Ara

Group of Oman (Fike and Grotzinger, 2008), which straddles the Precambrian-Cambrian boundary, does not exhibit such extremely ^{34}S -enriched pyrite with respect to CAS. Thus, the occurrence of ^{34}S -enriched pyrite in coeval formations from Namibia (this study), Poland (Bottomley et al., 1992), and Canada (Strauss et al., 1992) appears to reflect widespread, but not global, ^{34}S enrichment of pyrite-forming sedimentary sulfide relative to marine sulfate in terminal Proterozoic time.

SUPERHEAVY PYRITE THROUGHOUT THE GEOLOGIC PAST

A compilation of prior studies investigating $\delta^{34}\text{S}_{\text{pyr}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ of roughly coeval samples throughout the geologic past reveals that superheavy pyrite—despite its absence from the Phanerozoic record—has occurred several times throughout Precambrian time (Fig. 2). Ten previous studies, investigating 16 different lithologic formations (537–1850 Ma old) from around the world, report average $\delta^{34}\text{S}_{\text{pyr}}$ values that are equal to or greater than average $\delta^{34}\text{S}_{\text{CAS}}$ values obtained from approximately coeval formations (see the Data Repository for references and details). Many of these occurrences are clustered in Late Neoproterozoic time (Fig. 2), which may indicate something important about sulfur cycling and redox conditions in the atmosphere and ocean at the dawn of metazoan life. Next, we explore a few potential explanations for the occurrence of this phenomenon in the Nama Group carbonates.

POTENTIAL CAUSES OF SUPERHEAVY PYRITE IN THE NAMA GROUP CARBONATES

Ocean Stratification

Recent reports of superheavy pyrite in Neoproterozoic carbonates from the Liantuo For-

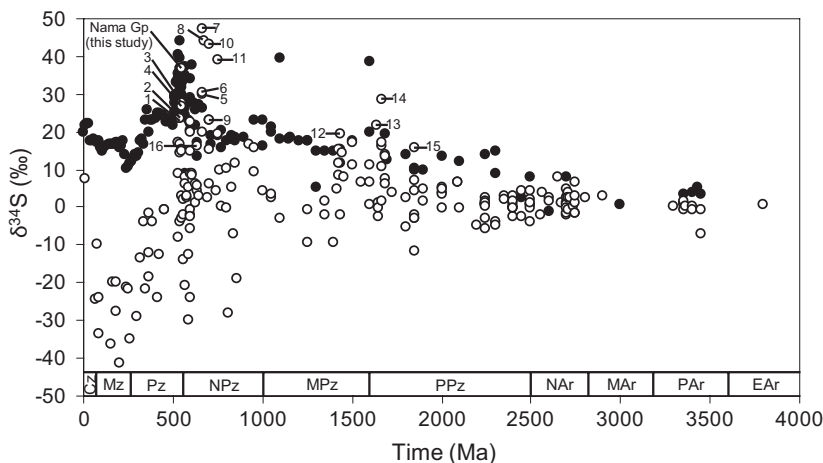


Figure 2. Compilation of previously published investigations of $\delta^{34}\text{S}_{\text{pyr}}$ (open circles) and $\delta^{34}\text{S}_{\text{CAS}}$ (closed circles) in the geological record. Numerals 1–16 correspond to reports of average $\delta^{34}\text{S}_{\text{pyr}}$ values that are equal to or greater than average $\delta^{34}\text{S}_{\text{CAS}}$ values obtained from penecontemporaneous formations. Data are averaged across formations. Details and references are provided in the Data Repository (see footnote 1).

mation in south China (Tie-bing et al., 2006) and the Zhamoketi Formation in northwest China (Shen et al., 2008) attribute this extreme ^{34}S enrichment of pyrite to decoupling of the surface- and bottom-water sulfur reservoirs through glacially induced ocean stratification, which led to pyrite-forming, bottom-water sulfur reservoirs that generated enriched $\delta^{34}\text{S}_{\text{pyr}}$ via closed-system Rayleigh distillation, while the CAS-forming surface waters recorded normal (undistilled) $\delta^{34}\text{S}_{\text{CAS}}$. Such an ocean stratification model, however, is not applicable to the Nama Group carbonates because sedimentological evidence indicates that these carbonates were deposited in a shallow, storm-dominated ramp environment (Saylor et al., 1998; DiBenedetto and Grotzinger, 2005), which would have been well mixed.

Bacterial Sulfate Reduction (BSR) under Low Seawater $[\text{SO}_4^{2-}]$

Microbial culture experiments have shown that the degree of sulfur isotope fractionation ($\delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$) that accompanies bacterial sulfate reduction (BSR) in seawater will decrease proportionally with the concentration of seawater sulfate when $[\text{SO}_4^{2-}]$ is less than 2 mM (Fig. 3A; Habicht et al., 2002, 2005; Canfield, 2001; Harrison and Thode, 1958). Thus, the extreme ^{34}S enrichment of pyrite relative to CAS in the Nama Group carbonates may partly reflect low seawater $[\text{SO}_4^{2-}]$ in terminal Proterozoic time. This explanation is consistent with the low concentrations of S_{CAS} (avg = 22.7 ppm) and S_{pyr} (avg = 33.8 ppm) and the high-frequency fluctuations in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ in the Nama Group carbonates, which are indicative of a short residence time for SO_4^{2-} in the ocean due to a small reservoir and/or rapid flux. However, low seawater $[\text{SO}_4^{2-}]$ —by itself—is not sufficient to explain the anomalously negative $\Delta^{34}\text{S}_{\text{CAS-pyr}}$ values (average = -8.2‰) observed in the Nama Group carbonates, as microbial culture studies (Harrison and Thode, 1958; Canfield, 2001; Habicht et al., 2002, 2005) indicate that sulfur isotope fractionation during BSR will approach zero but not invert as seawater $[\text{SO}_4^{2-}]$ declines. An additional mechanism is required to generate the negative $\Delta^{34}\text{S}_{\text{CAS-pyr}}$ values observed in the Nama Group carbonates.

Intense Aerobic Reoxidation of Sedimentary Sulfide

Laboratory experiments have shown that the aerobic oxidation of H_2S yields SO_4^{2-} and other oxidized species of sulfur that are depleted in ^{34}S (relative to the parent H_2S) by 4‰ – 5‰ for abiotic oxidation (Fry et al., 1988) and up to 18‰ for bacterial oxidation (Kaplan and Rittenberg, 1964). If mass-dependent fractionation during BSR was minimal due to low seawater $[\text{SO}_4^{2-}]$ (Harrison and Thode, 1958; Canfield,

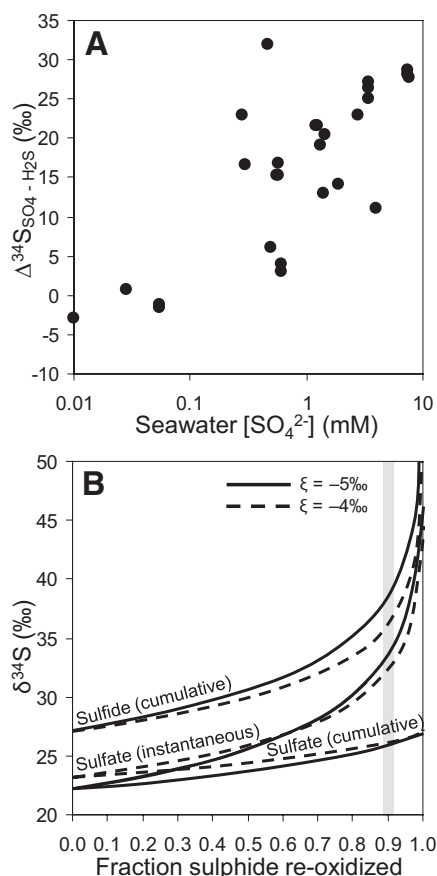


Figure 3. A: Experimentally derived correlation between seawater sulfate concentration ($[\text{SO}_4^{2-}]$) and sulfur isotope fractionation ($\Delta^{34}\text{S}_{\text{SO}_4 - \text{H}_2\text{S}}$) for marine sulfate-reducing bacteria (Harrison and Thode, 1958; Canfield, 2001; Habicht et al., 2002, 2005). Mass-dependent fractionation declines for $[\text{SO}_4^{2-}]$ less than 2 mM and effectively ceases for sulfate concentrations less than 0.2 mM. B: Evolution of the sulfide and sulfate reservoirs in response to storm-driven, aerobic reoxidation of sedimentary sulfide. Model assumes an instantaneous oxidative isotope fractionation ($\xi = \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$) between -4‰ (dashed curves) and -5‰ (solid curves; Fry et al., 1988), 90% reoxidation of sedimentary sulfide (gray vertical bar; typical of coastal, storm-associated sediments; Canfield and Teske, 1996; Berner and Westrich, 1985; Jorgensen, 1982), and no mass-dependent fractionation during bacterial sulfate reduction due to low seawater $[\text{SO}_4^{2-}]$ (A; Habicht et al., 2002). Coupling minimal mass-dependent fractionation during bacterial sulfate reduction (A; driven by low seawater $[\text{SO}_4^{2-}]$) with ^{34}S enrichment of sedimentary sulfide via storm-driven aerobic oxidation (B) would generate superheavy pyrite and negative $\Delta^{34}\text{S}_{\text{CAS-pyr}}$ values comparable to those observed in the studied Nama Group carbonates. Model terms and formulae are provided in the Data Repository (see footnote 1).

2001; Habicht et al., 2002, 2005), as is reported for the latter Proterozoic (see discussion below), then such oxidative fractionation of sulfur isotopes could significantly enrich $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ relative to $\delta^{34}\text{S}_{\text{SO}_4}$ via Rayleigh-type distillation.

The ubiquitous distribution of storm deposits in the studied Nama Group carbonates (DiBenedetto and Grotzinger, 2005) indicates that the Nama basin sediments were regularly reworked and ventilated by storm activity, which likely resulted in intense aerobic reoxidation of dissolved sulfide within these sediments. In modern coastal marine sediments that are regularly ventilated by storm activity, up to 90% of reduced sulfide is believed to be reoxidized before being buried as pyrite (Jorgensen, 1982; Berner and Westrich, 1985; Canfield and Teske, 1996). However, in modern marine systems, the oxidative 4‰ – 5‰ ^{34}S enrichment of sedimentary sulfide resulting from such storm-driven ventilation is masked by the 20‰ – 40‰ ^{34}S depletion of sulfide (Canfield, 2001) that accompanies BSR under the relatively high $[\text{SO}_4^{2-}]$ of modern seawater.

We have generated a simple closed-system Rayleigh distillation model (Fig. 3B) to explore the potential isotopic effects of such extreme reoxidation of dissolved sedimentary sulfide amidst the backdrop of very low concentrations of seawater sulfate. Assuming no mass-dependent fractionation during sulfate reduction (due to low seawater $[\text{SO}_4^{2-}]$), an initial $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ of 27.2‰ (average $\delta^{34}\text{S}_{\text{CAS}}$ of the studied Nama Group carbonates), instantaneous oxidative fractionation factors ($\xi = \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$) of -4‰ and -5‰ (Fry et al., 1988), and a sulfide reoxidation rate of 90% (Jorgensen, 1982; Berner and Westrich, 1985; Canfield and Teske, 1996), the model predicts $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ ranging from 36.4‰ to 38.7‰ , cumulative $\delta^{34}\text{S}_{\text{SO}_4}$ ranging from 26.2‰ to 25.9‰ , and $\Delta^{34}\text{S}_{\text{SO}_4 - \text{H}_2\text{S}}$ ranging from -10.3‰ to -12.8‰ , which are consistent with the average $\delta^{34}\text{S}_{\text{pyr}}$ (36.7‰), $\delta^{34}\text{S}_{\text{CAS}}$ (27.2‰), and $\Delta^{34}\text{S}_{\text{SO}_4 - \text{H}_2\text{S}}$ (-8.2‰) observed in the Nama Group carbonates deposited between 553 and 543 Ma ago. Although disproportionation reactions, which were not included in the model, could dampen these Rayleigh effects, storm-driven reworking of sediments with highly oxygenated surface waters would likely favor the oxidation of sulfide directly to sulfate.

We recognize that such a simplified, closed-system Rayleigh distillation model is not representative of the sedimentary sulfide reservoir. However, an open steady-state model would behave comparably if the production of sedimentary sulfide via BSR was sufficiently slow (Valley, 1986; Zaback et al., 1993; Canfield, 2001), as this would prevent the ^{34}S -depleted signal of the newly reduced sulfide from overwhelming the ^{34}S -enriched signal of the Rayleigh-distilled sulfide reservoir. Such a slow rate of sulfide production is consistent with a low concentration of seawater sulfate.

SEAWATER $[\text{SO}_4^{2-}]$ IN TERMINAL PROTEROZOIC TIME

The mechanisms proposed here to explain the formation and frequency of superheavy pyrite

in the Nama Group carbonates each require low concentrations of seawater sulfate in terminal Proterozoic time. Otherwise, the normal mass-dependent fractionation of sulfur isotopes during BSR would have likely offset whatever mechanism led to the formation of the super-heavy pyrite. Low seawater sulfate is independently supported by the low concentrations of S_{CAS} (avg = 22.7 ppm) and S_{pyr} (avg = 33.8 ppm) and the high-frequency fluctuations in both $\delta^{34}S_{CAS}$ and $\delta^{34}S_{pyr}$ ($\pm 20\%$ over 150 ka) observed in the Nama Group carbonates (Fig. 1B).

Multiple studies have invoked low seawater $[SO_4^{2-}]$ throughout the latter Proterozoic to explain the relatively enriched $\delta^{34}S_{pyr}$ and/or reduced $\Delta^{34}S_{CAS-pyr}$ observed in deposits from this interval (Canfield, 2004; Kah et al., 2004; Fike et al., 2006; Hurtgen et al., 2006; Lyons et al., 2006; Tie-bing et al., 2006; Shen et al., 2008). A recent report of enrichments in reactive Fe (relative to total Fe) with correspondingly low degrees of pyritization in terminal Proterozoic marine shales also points to anoxic, ferruginous and, therefore, low-sulfur conditions in the ocean at this time (Canfield et al., 2008). Likewise, a high-resolution sulfur isotope analysis of contemporaneous, shallow-water carbonates from the Ara Group in Oman reveals enrichment in both $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ in terminal Proterozoic time, which is consistent with relatively low seawater $[SO_4^{2-}]$ over this interval (Fike and Grotzinger, 2008). Unlike the Nama Group, however, the Ara Group contains $\delta^{34}S_{CAS}$ that is consistently heavier than $\delta^{34}S_{pyr}$, suggesting that seawater $[SO_4^{2-}]$ in the Oman basin was not as low as that in the Nama basin. Additional discussion of seawater $[SO_4^{2-}]$ in terminal Proterozoic time is provided in the Data Repository.

CONCLUSIONS

Our discovery that $\delta^{34}S_{pyr}$ was substantially heavier than co-deposited $\delta^{34}S_{CAS}$ over an ~10 Ma interval of terminal Proterozoic time reveals that the difference between $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ is not necessarily a straightforward proxy for the isotope fractionation imparted by BSR and, by extension, seawater $[SO_4^{2-}]$ and atmospheric pO_2 . This shortcoming likely arises from the fact that the sulfur isotope system continues to evolve within sedimentary pore waters isolated from the water column, before it is recorded in the geologic record. The occurrences of super-heavy pyrite in coeval formations from Poland and Canada suggest that ^{34}S enrichment of sedimentary sulfide was widespread in terminal Proterozoic time, yet differences in $\delta^{34}S_{pyr}$ between well-preserved coeval carbonate sections from Namibia (this study) and Oman (Fike and Grotzinger, 2008) indicate that this may not have been a global phenomenon. Although the mechanisms responsible for the extreme enrichment of pyrite observed in the Nama Group carbonates are debatable, our observations of nega-

tive $\Delta^{34}S_{CAS-pyr}$, low concentrations of CAS and pyrite, and high-frequency fluctuations in $\delta^{34}S_{CAS}$ and $\delta^{34}S_{pyr}$ throughout the studied section all support the assertion that, at the dawn of animal life, sulfate concentrations in at least portions of the oceans were much lower than they are today.

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