

# Global Neoproterozoic (Sturtian) post-glacial sulfide-sulfur isotope anomaly recognised in Namibia

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## Abstract

The Neoproterozoic Earth experienced at least two, probably global, glaciations. Each glaciation was superceded by deposition of a layer of carbonate ('cap-carbonate') that has a distinctive lithology and depletion in  $^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{carbonate}} \sim -5\%$ ). The  $\sim 700$  Ma Sturtian glaciation is followed by deposition of a cap-carbonate and post-glacial succession which contain bacterially produced sulfides extremely enriched in  $^{34}\text{S}$  (average  $\delta^{34}\text{S}_{\text{sulfide}} \sim +30\%$ ) with maximum values up to  $+60\%$ . This level of  $^{34}\text{S}$  enrichment in sulfides is unique to the Sturtian post-glacial succession and recognised in Australia, Canada, and China. In the Neoproterozoic of the Nama Basin, Namibia, the Gobabis Member is the basal unit of the Court Formation, which overlies the glacial Blaubecker Formation.  $\delta^{13}\text{C}_{\text{carbonate}}$  analyses from the Gobabis Member range from  $-5.2$  to  $-2.2\%$  (average =  $-3.7\%$ ;  $n = 10$ ).  $\delta^{34}\text{S}_{\text{sulfide}}$  ranges from  $+16.1$  to  $+61.1\%$  (average =  $+37.6\%$ ;  $n = 8$ ). These results are consistent with a Sturtian age for the Blaubecker Formation and overlying Gobabis Member, which have previously been interpreted as Sturtian. The sulfur isotopic results are comparable with  $\delta^{34}\text{S}_{\text{sulfide}}$  in Sturtian post-glacial units of Australia, Canada and China. This adds to the evidence for correlation of the Blaubecker Formation with Sturtian glaciations on other continents. The cause of such elevated  $\delta^{34}\text{S}_{\text{sulfide}}$  is enigmatic. Geochemical evidence suggests the sulfide was not formed from low sulfate waters nor in euxinic conditions, which discounts any known modern analogue.  $^{34}\text{S}$  enrichment in sulfides is therefore postulated to be caused by enrichment of  $^{34}\text{S}$  in contemporaneous seawater ( $\delta^{34}\text{S}_{\text{sulfate}}$  up to  $+60\%$ ?). The rise in seawater  $\delta^{34}\text{S}_{\text{sulfate}}$  is considered to be the result of intense bacterial sulfate reduction in an anoxic ocean during the Sturtian glaciation.

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## 1. Introduction

The Neoproterozoic is characterised by at least two, probably global, glacial events. The oldest documented of these is Sturtian ( $\sim 700$  Ma; Walter et al., 2000). Neoproterozoic glacial units are frequently overlain by laminated carbonates, forming 'caps' to the glacial units (Kennedy et al., 1998). The Sturtian cap carbonates are generally dark, organic-rich dolomite; whereas the younger Marinoan glacial cap is pale (cream, pink, or tan) and organic-poor (Kennedy, 1996; Hoffman et al., 1998a; Kennedy et al., 1998).  $\delta^{13}\text{C}_{\text{carbonate}}$  values of Sturtian cap carbonates are  $\sim -5\%$  in Australia and up

to  $-6\%$  in Canada (Kaufman et al., 1997; Walter et al., 2000). Sturtian cap carbonates are typically overlain by siltstone. In Australia (Tapley Hill and Aralka Formations), China (Datangpo Formation) and Canada (Twitya Formation) these Sturtian post-glacial successions have extremely  $^{34}\text{S}$ -enriched sulfides, with a mean  $\delta^{34}\text{S}_{\text{sulfide}}$  of  $+30\%$  (Gorjan et al., 2000).

In the Nama Basin (Fig. 1) the oldest Neoproterozoic glacial horizon is the Blaubecker Formation, it is therefore interpreted to be the Sturtian glacial (Hegenberger, 1993). The Blaubecker Formation underlies the post-glacial Court Formation, of the Witvlei Group, which has the carbonate-rich Gobabis Member at its base.

Previous  $\delta^{13}\text{C}_{\text{Sx121.Bt1A+Bx61qq.C.C.a07q.C.q/t2G0J55AF5.1Ax61qq.C.C.Ax61qq.+q5x7AF7.5}}$

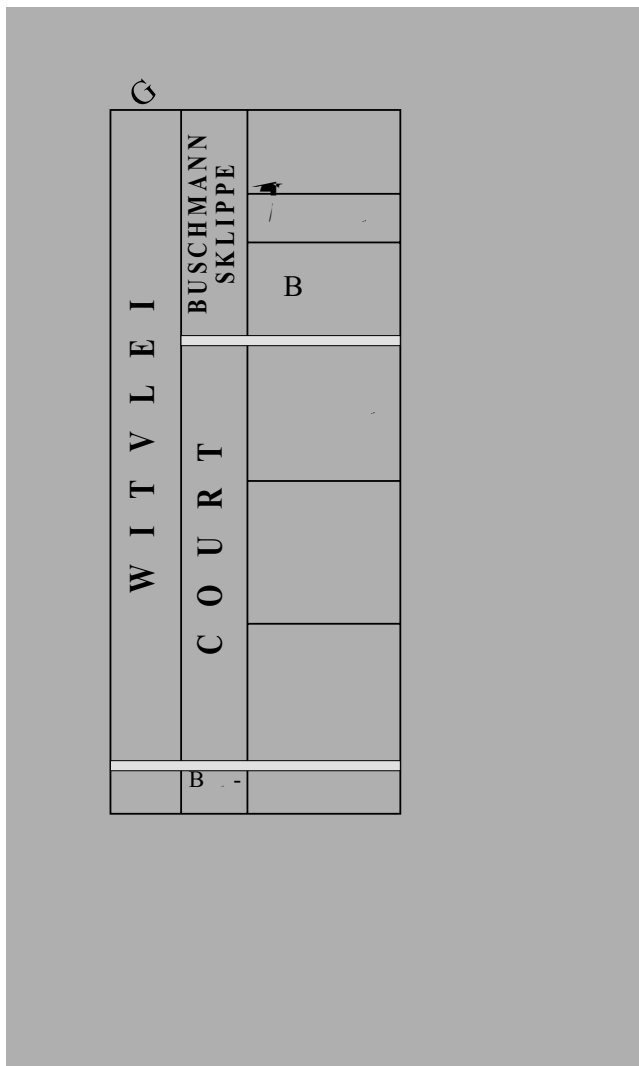
Pyrite was then removed from the previously treated sample by reaction with  $\sim 1$  M chromium(II) chloride ( $\text{CrCl}_2$ ) solution that was added to the  $\text{HCl}$ ,  $\text{SnCl}_2$ , and sample mixture. The mixture was then boiled until all  $\text{H}_2\text{S}$  was evolved from reaction of  $\text{Cr}^{2+}$  with pyrite. A flow of  $\text{N}_2$  carried the  $\text{H}_2\text{S}$  through the apparatus and it was trapped as  $\text{Ag}_2\text{S}$  as the monosulfide extraction above.  $\text{Ag}_2\text{S}$  was collected by filtration, dried, and then weighed. The  $\text{Ag}_2\text{S}$  was stored in plastic sample tubes until conversion to  $\text{SO}_2$  by reaction with copper(I) oxide ( $\text{Cu}_2\text{O}$ ) at  $1050^\circ\text{C}$ .

east of Windhoek) that are consistent with a Sturtian age for the Blaubeker Formation. We also interpret the data in terms of global correlations and discuss the origin of such  $^{34}\text{S}$ -enriched sulfides.

## 2. Methods

In sedimentary rocks sulfur can exist as pyrite ( $\text{FeS}_2$ ), iron monosulfide ( $\text{FeS}$  as mackinawite, pyrrhotite or an amorphous phase), elemental sulfur ( $\text{S}^0$ ), sulfate ( $\text{SO}_4^{2-}$ ), or organically-bound sulfur. In this study iron monosulfide and pyrite were extracted from 1 to 5 g of crushed sample. Only the  $\delta^{34}\text{S}$  of pyrite was analysed because it was overwhelmingly the most abundant form. The sulfur extraction procedure is based on the method presented in Canfield et al. (1986).

Firstly, monosulfide compounds (acid-volatile-sulfur, AVS) were removed from the crushed sample by reaction with 6 M hydrochloric acid ( $\text{HCl}$ ) and tin(II) chloride ( $\text{SnCl}_2$ ). The crushed sample was boiled for 5 min with reagents under flow of  $\text{N}_2$ . This converts AVS to hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas which is reacted with silver nitrate ( $\text{AgNO}_3$ ) to form the extremely insoluble silver sulfide ( $\text{Ag}_2\text{S}$ ).



with abundant kerogenous and pyritic laminae, and kerogenous silty dolomite. The dolomite is anhedral with a grain size of 5–25  $\mu\text{m}$ . Dolomite laminae are 50–1000  $\mu\text{m}$  thick, separated by wispy silty and kerogenous laminae 10–100  $\mu\text{m}$  thick. Pyrite occurs as grains and framboids 5–40  $\mu\text{m}$  wide. There are small nodules and veins (parallel to cleavage) of a later generation of carbonate. There are some millimetre-scale lenses of fine-grained quartz sandstone, and one example of a carbonate-cemented carbonate sand with intraclasts of acicular carbonate crusts.

#### 4. Results

Eight analyses of  $\delta^{34}\text{S}_{\text{pyrite}}$  are shown in Fig. 3 and Table 1. It ranges from +16.1‰ to +61.1‰ (average = +37.6‰). The pyrite of the Gobabis Member is mostly framboidal and 5–40  $\mu\text{m}$  diameter. Ten analyses of  $\delta^{13}\text{C}_{\text{carbonate}}$  are shown in Fig. 2 and Table 2. Values

range from -5.2‰ to -2.2‰ (average = -3.7‰).  $\delta^{18}\text{O}_{\text{carbonate}}$  values ranged from -9.3 to -5.2‰ (average = -7.5‰). Fig. 2 shows no apparent trend in  $\delta^{13}\text{C}_{\text{carbonate}}$ , while  $\delta^{34}\text{S}_{\text{pyrite}}$  apparently increases with decreasing age, although the trend is weak.

#### 5. Discussion

##### 5.1. Controls on seawater $\delta^{34}\text{S}_{\text{sulfate}}$

The  $\delta^{34}\text{S}_{\text{sulfate}}$  of seawater is determined by the magnitude and  $\delta^{34}\text{S}$  of fluxes in and out of the ocean. In the modern environment the major sulfur flux into the ocean comes from the weathering of the continents into riverine sulfate ( $\delta^{34}\text{S}_{\text{sulfate}} \sim +7\text{‰}$ ). A lesser amount comes from hydrothermal sources ( $\delta^{34}\text{S}_{\text{sulfate}} \sim +3\text{‰}$ ) (Charleson et al., 1992; Alt, 1995). The major fluxes of sulfur out of the ocean are the deposition of sulfate evaporites and sedimentary sulfides. Sulfate evaporites are deposited with minimal fractionation. But sulfide deposition, mediated by sulfate-reducing bacteria, involves a large fractionation. Laboratory experiments with sulfate-reducing bacteria report fractionation of upto 46‰ from the starting sulfate values, but fractionations upto 70‰ are noted in the natural environment (Nielsen, 1978). This bacterially mediated fractionation is the main reason for the positive  $\delta^{34}\text{S}_{\text{sulfate}}$  value of seawater.

##### 5.2. Fractionation of sulfur isotopes

Sulfate-reducing bacteria reduce sulfate to hydrogen sulfide (Goldhaber and Kaplan, 1974). The bacterially formed hydrogen sulfide reacts with sedimentary iron to form iron sulfides. Pyrite is the most stable iron-sulfide under normal conditions and therefore the most abundant form (Berner et al., 1979). Organic matter is the fuel for sulfate-reducing bacteria, which oxidise it to carbon dioxide, with concomitant reduction of sulfate to hydrogen sulfide (sulfate being the ultimate electron acceptor, as oxygen is in animal respiration).

Bacterial reduction of sulfate fractionates sulfur isotopes because the  $^{32}\text{S}$  isotope is preferentially metabolised by the bacteria. This results in the sulfide being enriched in  $^{32}\text{S}$  compared to the starting sulfate. In the Phanerozoic, sedimentary sulfides are typically enriched in  $^{32}\text{S}$  between 0‰ and 70‰, with the bulk around 50‰, compared to the seawater sulfate (Nriagu et al., 1991; see also Fig. 2 in Canfield, 1998). Phanerozoic seawater  $\delta^{34}\text{S}_{\text{sulfate}}$  values vary between  $\sim +12$  (at Permian–Triassic boundary) and  $\sim +33\text{‰}$  (at Proterozoic–Cambrian boundary) (Claypool et al., 1980; Holser, 1992). This means that sedimentary sulfides typically have a  $\delta^{34}\text{S}$  value less than 0‰.

Neoproterozoic seawater  $\delta^{34}\text{S}_{\text{sulfate}}$  values appear to be similar to those of the Phanerozoic, but the variation

mation consists of unsorted boulders and pebbles in an unstratified fine-sandy to shaly matrix. Boulders are faceted and striated indicating a glacial origin. The Gobabis Member is a dark carbonate, consisting of two main facies, a third has only minor distribution. The older is a laminite of alternating light and dark carbonate with sub-millimeter laminae. Organic content is 0.1–0.2%. The younger facies is a well-bedded to massive carbonate. The change in facies reflects a movement from deep to shallow-water environment. The older facies is very similar to that of Sturtian post-glacial successions in Australia (Tapley Hill and Aralka Formations) and Canada (Twitya Formation). The Marinoan cap carbonates are distinctly different. The Marinoan Bildah Member of the Witvlei Group is a thickly bedded to massive light-gray to pink dolomite, similar to Marinoan cap carbonates in other parts of Namibia (e.g., Maieberg Formation of the Otavi Group in *vi Bildissof suc-*

(Thode, 1991). An euxinic environment would have  $\delta^{34}\text{S}_{\text{organic}}$  equal to  $\delta^{34}\text{S}_{\text{pyrite}}$  because of the supply of  $\text{H}_2\text{S}$  with a constant  $\delta^{34}$

2. Although the ocean-upwelling model explains the sudden rise of  $\delta^{34}\text{S}_{\text{sulfide}}$  it has difficulty in explaining the sudden decline at the close of post-glacial silt deposition (Tapley Hill Formation and global equivalents; see Fig. 4). If there was a single upwelling of  $^{34}\text{S}$ -enriched sulfate (as the cause of  $^{34}\text{S}$ -enriched sulfide) at the close of the Sturtian glaciation then we would expect that this would

was caused by the massive burial of organic matter.

### Conclusion

The Gobabi... of the Court... nation, intercepted... has extremely positive  $\delta^{34}\text{S}_{\text{pyrite}}$ ... +6.1 to +61.1‰ (average = ...  $\text{C}_{\text{carbonate}}$ ... range from -5.2 to -2.8‰ (average = -3.7‰).

of lithology... stratigraphic setting, and... we correlate the Gobabi... post-glacial successions in... comparable units elsewhere... Ho man et al... 1998;... Frimmel... 2001) are...

The... of this... sulfides is at present best explained... in  $\delta^{34}\text{S}_{\text{sulfate}}$ ... of contemporaneous... up to +60‰). This rise in...  $\delta^{34}\text{S}_{\text{sulfate}}$ ... considered to be the result of intense bacterial reduction of sulfate in an anoxic... Sturtian... weathering of continental sulfides...  $^{34}\text{S}$ -enriched sulfides, formed during... sulfate.

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