

## THE BIOGEOCHEMICAL AFTERMATH OF 'SNOWBALL EARTH' CONDITIONS

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### Summary

Under 'Snowball Earth' conditions the global network of oceans is thought to have been blanketed for millions of years under thick sea ice. In the darkness beneath this extended cover photosynthesizing organisms would have perished and the oceans would have quickly become anoxic. Under such conditions it is likely that sulfate-reducing bacteria would dominate microbial life, assuming utilizable substrates like acetate and lactate were available. Intense sulfate reduction would have ultimately drawn down seawater sulfate concentrations. Residual oceanic sulfate beneath the global ice cap would have been driven to positive extremes through the formation and burial of  $^{34}\text{S}$ -depleted sulfides. If true, strong sulfur isotope enrichments should be recorded in sulfates and sulfides formed in the aftermath of 'Snowball Earth' conditions. Barite crystals and fans are recognized in Neoproterozoic cap carbonates on many continents. Where these or trace sulfates in carbonate have been measured all record significantly positive ( $>+30\%$ ) sulfur isotope compositions. In some examples, sulfides isolated from cap carbonates retain values as high as  $+60\%$ . Sulfide isotopic compositions could have exceeded seawater sulfate due to the slow diffusion of sulfate into sediments and closed system fractionation, especially if seawater sulfate was previously enriched in  $^{34}\text{S}$  and concentrations were drawn down to negligible levels during global glaciation. In addition, the carbonate alkalinity necessary for rapid cap carbonate formation (with a negative carbon isotopic signature) may have been partly supplied from intense sulfate reduction during the ice age, and subsequent upwelling in the post-glacial world. Delivery of nutrients, like P and Fe, from the deep anoxic ocean in the aftermath of the 'Snowball' winter would have stimulated intense photosynthetic blooms, consistent with a marked decrease in carbon isotope fractionation in organic-rich cap carbonates worldwide.

### Introduction

One of the enduring enigmas of Neoproterozoic Earth history is the intimate association of glacial diamictites with carbonate rocks typically deposited in warm water environments. Recent studies in the Otavi Group of Namibia (Hoffman et al., 1998a, b) suggest however that this odd juxtaposition of climatic indicators is the expected consequence of a 'Snowball Earth' (cf. Kirschvink, 1992) where glaciers extended from the poles to the equator entombing the planet in ice and snow. During this ice age both the hydrologic and biological cycles would have been severely affected – photosynthesis and primary biological productivity in the oceans would have collapsed, perhaps for millions of years. Dominated by hydrothermal solutions, the oceans would have become reducing, thereby allowing soluble iron to build up in solution. This view is supported by the presence of iron-oxide cements and local iron-formation in diamictites deposited during meltback.

Termination of this deep freeze could have occurred only when levels of carbon dioxide built up from volcanic sources to levels (ca. 350x PAL) that overcame the enhanced albedo of an ice-covered planet. Assuming a modern flux of volcanic  $\text{CO}_2$  and no sink, the buildup may have taken between 4-30 Ma (Hoffman et

al., 1998b). If volcanic ash and wind-borne loess eroded from the dry centers of the continents collected on the global network of pack ice, the time required to achieve meltback would be less.

During meltback and post-glacial sea level rise, it is envisioned enhanced riverine flux of alkalinity due to intense chemical weathering of continental materials would result in the rapid global precipitation of cap carbonates in warm surface waters. An alternative view is that wind driven upwelling of deep waters (Kaufman et al., 1997) would have also provided alkalinity and nutrients to surface oceans in the aftermath of 'Snowball Earth' conditions.

The foundation of the 'Snowball Earth' hypothesis is seated in high-resolution carbon isotope stratigraphy. It has been suggested that there are at least four discrete Neoproterozoic ice ages each bracketed by extreme positive-to-negative shifts in the  $\delta^{13}\text{C}$  of seawater (Kaufman and Knoll, 1995; Fig. 1).

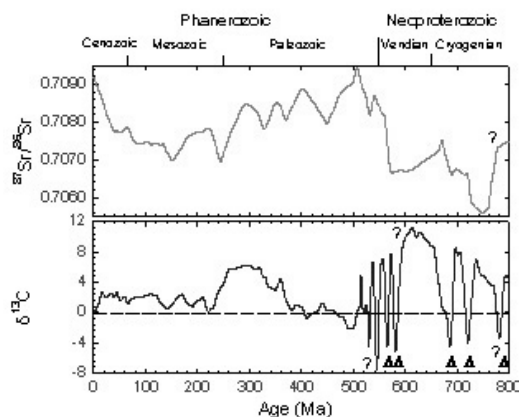


Fig. 1: Temporal variations in the Sr and C isotope composition of seawater proxies over the past 800 million years. Estimated positions of Neoproterozoic ice ages are shown as triangles. The  $\delta^{13}\text{C}$  trends for the Neoproterozoic are based on thousands of analyses of marine carbonates and co-existing organic matter from Svalbard and East Greenland, Namibia and South Africa, Arctic Canada, India and Siberia.

In the Otavi Group of Namibia, basin-wide sequence stratigraphy reveals that for the younger of two glacial events, the negative carbon-isotopic excursion begins in shallow water carbonates underlying the diamictite and continues for hundreds of meters above in the cap carbonates (Fig. 2; Hoffman et al., 1998b). Contrasting with the rest of the succession -- which contains ample evidence for sea level oscillation -- both cap carbonates shallow upward for hundreds of meters without exposure. This observation suggests that they were deposited in a single flooding event during post-glacial transgression.

Indeed, many sedimentological indicators suggest that Neoproterozoic cap carbonates worldwide were deposited rapidly. Lacking evidence of tectonic activity during deposition, the vertical space needed to accommodate the thick cap carbonate must have been created by thermal subsidence. Calculations suggest that it would take close to 9 Ma to account for 500 m of the cap carbonate in the Otavi Group (~50 m of which can be accounted for isostatically as a consequence of subglacial erosion

on the platform). The thick stratigraphic interval of negative  $\delta^{13}\text{C}$  must then have also lasted millions of years, starting in shallow water carbonates deposited before the diamictite.

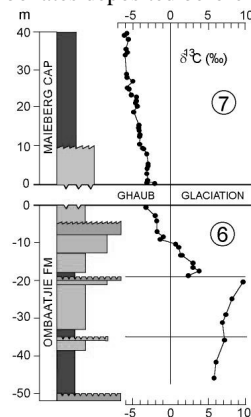


Fig. 2. Composite section across the younger glacial surface on the platform, showing high resolution  $\delta^{13}\text{C}$  data. An abrupt downturn in  $\delta^{13}\text{C}$  occurs at the base of the penultimate parasequence, and there is a postglacial descent to a nadir of  $-6\%$ ,  $\sim 40$  m above the glacial surface and  $\sim 20$  m above the maximum flooding interval. In the snowball Earth hypothesis, the glacial surface would represent  $\sim 9$  Ma, but the 500-m-thick cap carbonate would only represent thousands of years.

If the  $\delta^{13}\text{C}$  excursion is explained in terms of carbon burial fluxes, then the proportion of organic to total carbon burial changed from almost 0.5 before the glacial deposits to virtually zero immediately following. Carbonates precipitated from an ocean in which most biological productivity had ceased for time-scales greatly exceeding the carbon-residence time ( $>10^5$  yrs) would approach  $-5$  to  $-7\%$ , the isotopic composition of carbon entering the ocean. The isotopic pattern, therefore, is consistent with the hypothesis of a snowball Earth in which the base of the food chain, oceanic photosynthesis, would be severely reduced for millions of years because the ice cover would block out sunlight. Meltwater pools and bare ground, exposed through gravitational thinning and ablation of ice sheets without much rejuvenative snowfall, might provide refugia for a variety of photosynthetic bacteria and simple eukaryotes.

### Potential causes of global glaciation

Coupled energy-balance models require that atmospheric  $\text{CO}_2$  levels must have been dramatically lower ( $\sim 10^{-4}$  bar) even with lower-than-present solar luminosity. Fragmentation of the Rodinia supercontinent may have contributed to  $\text{CO}_2$  drawdown by creating new continental margins, which are major repositories for organic carbon in the modern ocean, consistent with the high  $\delta^{13}\text{C}$  values prior to the glaciation. High rates of primary productivity sustained by the bioavailability of iron (Coale et al., 1996) and phosphorous (van Cappellen and Ingall, 1994) in a largely anoxic ocean could have stimulated photosynthesis, which would facilitated glacial growth by reducing atmospheric greenhouse capacity (Kaufman et al., 1997). The downwarping of very high  $\delta^{13}\text{C}$  values likely indicates declining primary productivity and ultimate collapse of

the food chain associated with the establishment of surface refrigeration and global glaciation.

### Consequences for ocean chemistry

The fantastic consequences of a snowball Earth would include enhanced albedo, as well as the near shut down of photosynthetic life and the hydrologic cycle. With the development of a global network of thick sea ice, evaporation of ocean water would nearly have ceased. Continental glaciers that formed in the early stages of surface refrigeration would thin gravitationally lacking rejuvenative snowfall, and may have ablated completely in some regions. Thus sea level drawdown may not have been significant under snowball Earth conditions (Hoffman et al., 1998b). The buildup of volcanic ash and dust blown from the dry interior of continents onto the pack ice may, however, have reduced snowball albedo.

While the continental flux of elements to seawater would have ceased during snowball Earth conditions, the hydrothermal flux would not. Iron, manganese, and other reduced elements should have built up, and the Ca/Mg ratio would have increased. Over the postulated millions of years of Snowball Earth conditions, the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of seawater should approach the hydrothermal source, unless seawater strontium concentrations were otherwise buffered.

In strong contrast, available data from well-preserved limestone ( $\text{Sr} > 1000$  ppm) above and below each of the two Otavi glacial horizons shows little to no change in  $^{87}\text{Sr}/^{86}\text{Sr}$  across the ice ages (Kaufman et al., 1997; Jacobsen and Kaufman, 1999). This discrepancy may be explained if -- during 'Snowball Earth' conditions -- the oceans trapped beneath the global ice pack became increasingly acidic. The acid source would come from hydrothermal emanation of  $\text{CO}_2$  and  $\text{SO}_2$ . Without the input of alkalinity from rivers, carbonates would dissolve in the deep sea and the CCD would rise, perhaps up to the thick pack ice. Assuming a higher heat flow in the Neoproterozoic, the hydrothermal flux of  $\text{CO}_2$  would likely be greater than the modern flux [ $\sim 0.83 \times 10^{12}$  mol/year; Des Marais and Moore, 1984], and gas exchange through cracks in the ice would accentuate carbonate dissolution. The diagenetic flux of strontium to seawater, which at present is relatively insignificant, would experience a dramatic rise. Increasing this small flux by an order of magnitude would buffer hydrothermal inputs over the proposed multi-million year time scale, by delivering abundant Sr to seawater (hence increasing residence time of that element) with  $^{87}\text{Sr}/^{86}\text{Sr}$  approximated by pre-glacial carbonates (Fig. 3.).

### The biogeochemical aftermath

Without the photosynthetic delivery of oxygen, the glacial oceans would soon have become totally anoxic. Under such conditions it is proposed that a consortium of heterotrophs including sulfate-reducing bacteria would likely have dominated microbial life, assuming that low molecular carbon substrates like acetate and lactate, as well as sulfate, were readily available. Similar to the Black Sea today, intense sulfate reduction in the water column for millions of years would have built up deep ocean alkalinity, and likely drawn sulfate (the second most abundant anion in modern seawater at 28 mM concentration) down to negligible levels.

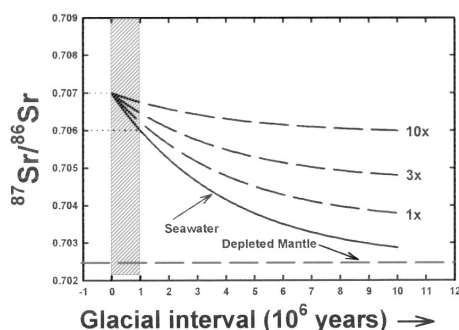


Fig. 3. Evolution curves of seawater Sr as a consequence of shutting off all continental sources under varying proportion of modern diagenetic fluxes during the proposed length of global glaciation (from Jacobsen and Kaufman, 1999).

As sulfide concentrations increased,  $^{34}\text{S}$ -depleted pyrite should have formed – assuming ferrous iron from hydrothermal sources was readily available – and accumulated in deep ocean sediments beneath the thick pack ice. Unabated this biologically mediated reaction would have driven residual sulfate to positive  $\delta^{34}\text{S}$  extremes.

In the aftermath of global glaciation any sulfate minerals or trace sulfate incorporated into the carbonate lattice of cap carbonate facies should reflect the  $^{34}\text{S}$  enrichment. However, following meltback, the photosynthetic production of oxygen would have likely driven sulfate reducers back into the sediments. Due to the diffusive limitation of sulfate into sediments, these heterotrophs would have been cut off from oceanic sulfate and  $\delta^{34}\text{S}$  of newly formed sulfides could have risen to values higher than contemporaneous seawater by closed system fractionation.

This post-snowball scenario is consistent with the known record of  $\delta^{34}\text{S}$  measurements of stratiform barite and gypsum, as well as finely disseminated pyrite -- in carbonate or organic-rich shale above Neoproterozoic glacial strata (Fig. 4).

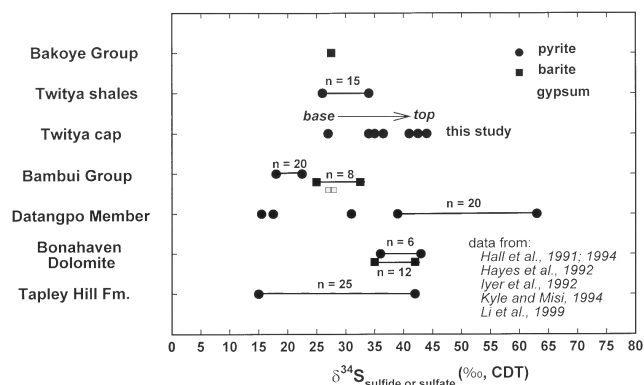


Fig. 4: Range of  $\delta^{34}\text{S}$  measurements of barite, gypsum, and pyrite in post-glacial Neoproterozoic units. Data are reported from the literature and new  $\delta^{34}\text{S}$  analyses of pyrite separates from an organic-rich cap carbonate atop Rapitan glacial deposits in the Mackenzie Mountains (see Kaufman et al., 1997).

In some cases the measurements were from samples in fine-grained and finely laminated dolomites, classically termed cap carbonates while others are part of a thick parasequence immediately above diamictites of glacial origin. In this

hypothesis, Ba concentrations may have risen in the anoxic Snowball ocean, sourced from hydrothermal vents. As oxidants, including sulfate, increased in concentration in post-Snowball oceans, relatively insoluble barite would necessarily precipitate.

The extreme sulfide  $\delta^{34}\text{S}$  values in the cap carbonates are possible if seawater sulfate was already  $^{34}\text{S}$  enriched and present in low concentrations -- the expected consequence of a 'Snowball Earth' whose deep oceans were dominated by sulfate-reducing bacteria. Sustaining bacterial sulfate reduction for millions of years would be difficult without a source of low molecular weight carbon compounds, typically generated by a consortium of other heterotrophs including methanogens. It is plausible that a sustainable flux of organic matter might have come from carbonate sediments dissolving under increasingly acidic ocean conditions.

### Bacterial sulfate reduction and post-'Snowball' lithologies

Worldwide, the classically defined cap carbonates are most typically composed of extremely fine-grained and finely laminated dolomicrite (Kennedy, 1996; Kaufman et al., 1997). These lithologies are also commonly enriched in both iron and manganese relative to carbonates in other parts of the sedimentary succession. Given that the kinetic barriers to dolomite precipitation from seawater may be overcome through 1.) dilution, 2.) an increase in temperature, and/or 3.) a decrease in sulfate content, it is possible to speculate that the post-'Snowball' cap dolomites were primary precipitates.

Diluting seawater overcomes the problem of high ion strength by increasing the Mg/Ca ratio. This would theoretically allow for dolomite formation given that  $\text{Mg}^{2+}$  was readily available. The normal source of magnesium would be seawater, but this ion would be sequestered in mid-ocean ridge basalts during hydrothermal circulation during the long 'Snowball' winter. While both  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  would be delivered to seawater from rivers following intense chemical weathering, like Sr, the concentrations of these ions in seawater may have been buffered by carbonate dissolution. There would have been an additional flux of these elements to seawater if abundant wind-blown loess dissolved in acidic waters following meltback.

Further enhancing the potential to precipitate dolomite, ocean temperatures would have necessarily increased in the post-Snowball world. Estimates suggest that surface temperatures rose as high as 35-40°C under a dense atmosphere of  $\text{CO}_2$  and water vapor.

Finally, as sulfate ion is considered to be an inhibitor of dolomite crystallization, prolonged bacterial sulfate reduction during global glaciation may have ultimately removed this last kinetic barrier to primary dolomite formation.

### Evidence for post-Snowball productivity blooms

Prolonged sulfate reduction beneath the Snowball ice pack would have additional consequences for ocean chemistry. Specifically, reactions that result in the degradation of organic matter by SRB cause both calcite and aragonite supersaturation by increasing alkalinity. This effect is compounded if sulfide produced in the reaction is removed by precipitation as pyrite and/or if sulfate reduction is linked to methane oxidation. Alkalinity formed by this biogenic process would be necessarily depleted in  $^{13}\text{C}$ . As a sudden increase in ocean alkalinity is required for the rapid precipitation of the cap carbonate, it seems

likely that -- in addition to the flux of alkalinity from riverine inputs following meltback and intense weathering of continental rocks -- the deep ocean was also a major repository of  $^{13}\text{C}$ -depleted carbonate ion). Hydrothermal emanations would also have resulted in the buildup of Ba, as noted above, and Fe in ocean waters, both micronutrients necessary for photoautotrophic carbon fixation.

On meltback of the global ice pack it is envisioned that wind driven upwelling would have commenced resulting in the rapid delivery of alkalinity and nutrients to surface waters. This view is consistent with the observation of 1.) significant Fe enrichment in the uppermost laminated facies of many Neoproterozoic diamictites, 2.) generally higher concentrations of Mn and Fe in cap carbonate facies, and 3.) the presence of thin cap carbonates in deep slope settings. Gas exchange between the surface ocean and the high carbon dioxide atmosphere would initially result in a further lowering of pH. However, this must have been followed by a pH increase as cold deep waters with high concentrations of calcium and alkalinity mixed with warm tropical surface waters, allowing for the rapid deposition of the cap carbonates. Drawdown of  $\text{CO}_2$  and pH increase would also be accomplished through intense microbial activity promoted by an abundance of micronutrients and phosphorous.

Causally related to renewed primary productivity in post-glacial oceans may be the observation that in the Otavi succession  $\Delta\delta$  is lowest in the cap carbonates. In the organic-rich cap (Rasthof) above the older of two diamictites (Chuoss) in northern Namibia,  $\Delta\delta$  goes as remarkably low as 12-15‰, while the organic poor cap above the younger (Ghaub) diamictite has a  $\Delta\delta$  value nearer to 20‰.

The hypothesis that the anoxic, glacial oceans were saturated with biolimiting nutrients like phosphorous and iron may provide a clue to the reduced  $\Delta\delta$  values. In much younger sediments an equivalent to this measure has been used to determine temporal variations in the abundance of the greenhouse gas  $\text{CO}_2$  (Hayes, 1993), assuming that a lowering of atmospheric  $\text{pCO}_2$  would limit the availability of this key nutrient for biosynthesis. Since carbon limitation in seawater can result in an increase of biomass  $\delta^{13}\text{C}$  (Rau et al., 1989) a smaller  $\Delta\delta\text{C}$  between organic and inorganic phases should be observed under a lower atmospheric  $\text{CO}_2$ .

However, following Snowball Earth conditions,  $\text{CO}_2$  concentrations are considered to have been phenomenally high. Instead, in post-glacial times carbon limitation would be the result of the extreme growth rate of photoautotrophs, rather than low atmospheric  $\text{CO}_2$  concentrations. Under conditions where nutrients are readily available, the rate of carbon fixation within cells can be faster than the rate of diffusion of dissolved  $\text{CO}_2$  into the cells (Bidigare et al., 1997), which in part may be related to cell geometry. This would result in less isotopic discrimination and enrichment of  $^{13}\text{C}$  in biomass.

## Conclusions

The hypothesis of post-Snowball upwelling of deep anoxic and alkaline seawater, saturated with biolimiting nutrients like iron (Coale et al., 1996) and phosphorous (van Cappellen and Ingall, 1994) is consistent with enhanced growth rates and concomitant reduction of  $\Delta\delta$  in the organic-rich cap carbonates.

This view is strongly supported by recent experiments conducted during the IronEx II iron fertilization of the low productivity equatorial Pacific Ocean (Bidigare et al., 1999).

These authors report up to a 7‰ carbon isotopic enrichment in algal biomass, which is largely the result of elevated growth rates. In addition, the carbon isotopic enrichment (also recorded as a significantly reduced  $\Delta\delta\text{C}$ ) and stimulation of growth rate were accompanied by a seven-fold increase in the export of particulate organic carbon to sediments. These studies of thus provide a means to test for iron-stimulated changes in growth rates in sedimentary records during 'Snowball Earths' and other intervals of Earth history.

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