Stretching the envelope of past surface environments: Neoproterozoic glacial lakes from Svalbard

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One-sentence summaries:

Extreme multi-stable isotope compositions of sulfate and its host carbonates from Svalbard reveal an extraordinary atmosphere-biosphere condition during the deposition of a Neoproterozoic glacial diamictites.

Abstract

The oxygen isotope composition of terrestrial sulfate is affected measurably by many Earth surface processes. During the Neoproterozoic, severe “Snowball” glaciations would have had an extreme impact on the biosphere and the atmosphere. Here, we report that sulfate extracted from carbonate lenses within a Neoproterozoic glacial diamictite suite from Svalbard, with an age of ~ 635 Ma, falls well outside the currently known natural range of triple oxygen isotope compositions, and indicates that the atmosphere had either an exceptionally high atmospheric CO₂ concentrations or an utterly unfamiliar O₂ cycle during deposition of the diamictites.
Terrestrial sulfate (SO₄²⁻) has diverse origins and participates in many important physicochemical and biological processes that can be inferred from large ranges in stable sulfur and oxygen isotope compositions (1). The δ¹⁸O (2) of sulfate ranges from ~+8‰ to ~+27‰ (VSMOW) (3) for marine sulfate of different geological ages (4) and down to ~−18‰ for sulfate formed in continental Antarctica (5). In recent years, the sulfate oxygen isotope composition has been found to vary along another dimension, the Δ¹⁷O [≡ ln (δ¹⁷O+1) − 0.52ln (δ¹⁸O+1)]. The Δ¹⁷O is close to zero for most samples, but positive (up to ~+5.94‰) for those of atmospheric origin (6, 7). Most recently, small but negative Δ¹⁷O values have been reported for sulfate derived from oxidative weathering by atmospheric oxygen, with a conspicuous spike (down to −0.70‰) in the immediate aftermath of a Marinoan glaciation at ~ 635 Myrs ago (8). Here we report that these ranges are surpassed dramatically by carbonate-associated sulfate (CAS) extracted from a Neoproterozoic Marinoan (9, 10) carbonate unit from Svalbard, Arctic Ocean. This carbonate member (W2) is from the Wilsonbreen Formation (Polarisbreen Group), a formation dominated by diamictites representing a continental-scale glaciation (ref. 9, 11). W2 contains both limestones and primary dolostones with exceptionally preserved geochemistry (12). We have greatly extended the previous geochemical database, including isotope compositions of CAS (13) (Fig. S1, Table S1). Note that the “cap carbonate”, the lower Dracoinen Formation, is ~ 80 m above W2, and is not the subject of this study.

Two features of the dataset are exceptional in terms of what we know about sulfate on Earth (Fig. 1): 1) The Δ¹⁷OCAS reaches as low as −1.64‰, the most negative anomaly ever reported for terrestrial (vs. extraterrestrial) minerals; 2) The δ¹⁸OCAS reaches as high
as ~ +37.7‰, the most positive value ever reported for natural sulfate oxygen. Additional features are also intriguing. For example: 3) CAS with a distinct $^{17}$O anomaly is invariably from a limestone phase whilst CAS from the dolostone phase does not have such a distinct $^{17}$O anomaly (Fig. 1); 4) Amongst CAS from the limestones, there is a strong positive correlation in $\Delta^{17}$O–$\delta^{34}$S space and the trend line connects with CAS from the immediately pre-glacial dolostone (member E4) (Fig. 1b); 5) The positively correlated $\delta^{18}$O and $\delta^{13}$C of dolomite ranges from $\sim$−11‰ to +15‰ (VPDB) (3) and from $\sim$−2 to +5‰ (VPDB) respectively. This $\delta^{18}$O$_{\text{CO}_3}$ is the most positive value ever reported (Fig. 2a); 6) Excluding pre-glacial samples, a slope of $\sim$ 1 links two clusters of data in $\delta^{18}$O$_{\text{CAS}}$ – $\delta^{18}$O$_{\text{CO}_3}$ space (Fig. 3); and 7) those calcite samples with negative $\Delta^{17}$O$_{\text{CAS}}$ have a $\Delta^{17}$O$_{\text{CO}_3}$ value close to zero, indicating the evaporated water itself did not bear a $^{17}$O anomaly (Table S1).

We propose the following model to account for this unusual carbonate paragenesis. The environment consisted of lacustrine oases within a continental ice sheet. The lakes were dominantly suboxic and, where local meltwater inflow was low, they and their near-surface porewaters were driven to high salinities by extreme evaporation, accompanied by intense microbial sulfate redox reactions. Sulfate with negative $\Delta^{17}$O values was produced by oxidative weathering involving atmospheric O$_2$ on the land surface, and was washed into the lakes, along with pre-existing sulfate in rocks undergoing weathering. This mixed sulfate was reduced to sulfides (H$_2$S or HS$^-$) by bacteria and subsequently reoxidized to sulfate by a different microbial community in an oxic to suboxic condition. The re-oxidation was highly efficient, thus causing sulfur isotope mass-balance and resulting in a change in the $\delta^{34}$S$_{\text{SO}_4}$ much smaller than in the corresponding $\delta^{18}$O$_{\text{SO}_4}$ or
\[ \delta^{18}O_{CO_3} \text{ value (which should be heavily influenced by the changing } \delta^{18}O_{H_2O} \text{ due to variable degrees of evaporation). No atmospheric } O_2 \text{ signal was incorporated into the newly regenerated sulfate in the water column, as abundant Mn and Fe (Table S1) would shuttle electrons between sulfite and dissolved } O_2 \text{ in ambient solution (14-16) without direct contact between reduced sulfur species and } O_2. \text{ Such redox cycling effectively eliminated the initial sulfate }^{17}O-\text{anomalous oxygen and replaced it with }^{17}O-\text{normal oxygen from the ambient water during the precipitation of dolostones. The sulfate in limestones however appears not to have been subjected to such intense redox cycling, thus enabling them to retain their }^{17}O-\text{anomalous signature. Intensive evaporation resulted in highly positive } \delta^{18}O \text{ values for the remaining water in a restricted lake or basin. Carbonate formed in the water would also therefore carry extremely positive } \delta^{18}O \text{ values. Both the dolomite mineralogy and the ranges of } \delta^{13}C_{CO_3} \text{ and } \delta^{18}O_{CO_3} \text{ (displaying heavier-than-marine values) are characteristic of restricted evaporitic settings (17).}

The evaporative dolomite-precipitating environments are evidence of microbial activity because they contain microbial laminites (12) and due to the intense redox cycling required to explain both the extremely high } \delta^{18}O_{CAS} \text{ values and the disappearance of the negative }^{17}O \text{ anomalies in these dolomites. As } \delta^{18}O_{CAS} \text{ increases at the same magnitude as } \delta^{18}O_{CO_3} \text{ (Fig. 3), this suggests that almost all the oxygen in the sulfate was replaced by oxygen from ambient water after microbially-mediated sulfur redox cycling. The highly positive } \delta^{18}O_{SO_4} \text{ (up to }^{+37.7}\%\text{) therefore should be correlated with the highly positive } \delta^{18}O_{H_2O} \text{ in the lakes. The } \delta^{18}O \text{ of evaporated } H_2O \text{ can be estimated from the highly positive } \delta^{18}O_{dolomite}, \text{ which is unlikely the result of late alteration. Taking into account the uncertainties in precipitation temperature, precipitation kinetics, and}
diagenetic imprint, we estimate (from Fig. 3) a difference between $\delta^{18}O_{\text{CAS}}$ and $\delta^{18}O_{\text{H}_2\text{O}}$ ranging from $\sim 20\%$ to $30\%$, which is similar to the $\sim 25\%$ to $30\%$ recently obtained from an experimental studies of sulfate reduction (18). We know of no other environments where the microbial sulfate redox cycling has reached a complete steady state with highly evaporitic ambient water. The closest analog is modern hypersaline lagoons near Rio de Janeiro, Brazil, where the $\delta^{18}O_{\text{SO}_4}$ reaches $+21.3\%$ in pore waters and $+20.8\%$ in surface brines with an apparent $\Delta\delta^{18}O_{\text{SO}_4-H_2O}$ at $\sim +20\%$ (19).

The most negative value of $\Delta^{17}O_{\text{SO}_4}$ ($-1.64\%$) extends greatly the magnitude and geographic occurrence of the negative $\Delta^{17}O_{\text{SO}_4}$ following the Marinoan glaciation as first reported in Bao et al. (8). Bao et al proposed the negative $\Delta^{17}O$ was derived from that of atmospheric $O_2$ involved in the oxidative weathering of sulfur compounds on the surface of the Earth (8). Pre-existing ocean sulfate may not have a distinct negative $\Delta^{17}O$ value because continuous microbial sulfur redox cycling tends to replace sulfate oxygen with a water oxygen signal. Thus, sulfate in a restricted continental basin could have the most negative $\Delta^{17}O_{\text{SO}_4}$ where a significant portion of the sulfate was derived from non-marine sources. The value $-1.64\%$ is more than twice the magnitude of the $-0.70\%$ reported for barites from Marinoan cap carbonates from South China (8). This is consistent with W2’s setting, where much if not all the drainage could have been internal.

We interpret the strong correlation between $\Delta^{17}O_{\text{CAS}}$ and $\delta^{34}S_{\text{CAS}}$ in limestones (data feature 4, Fig. 1b) as a mixing line between two sulfate endmembers: a pre-existing marine sulfate and a sulfate newly supplied from continental weathering, rather than an evaporative trend for an already mixed sulfate in the lakes. This can be justified because of the absence of evaporative characteristics in the limestones and their much narrower
scatter of δ¹⁸O value (from −13‰ to −4‰ VPDB) (Fig. 2b, Fig. 3) compared with that of
the evaporative dolomites (from −11‰ to +15‰ VPDB) (Fig. 2a). The “mixing” scenario
is also supported by the isotope compositions of CAS in the pre-glacial carbonates, which
fall close to the δ³⁴S-high end of the line (Fig. 1b). Since sulfate evaporite relics are
known to occur in the underlying E4 tidal-flat carbonates (20) it is likely that weathering
of coeval nodular or bedded sulfate from lateral equivalents of E4 helped stabilize the
position of the mixing line.

If sulfate derived from oxidative weathering of sulfides in glacial rock flour had a
global average crustal δ³⁴S value of ~ 0‰, the mixing line (Fig. 1b) would point to a
Δ¹⁷O of ~−4.2‰ for the non-marine sulfate endmember. This would imply an
atmospheric Δ¹⁷O(O₂) at ~ −42‰ if only 10% of the oxygen in sulfate came from
atmospheric O₂ (8). This estimate contains two large uncertainties – the end-member
δ³⁴S_sulfides value and the fraction of sulfate oxygen derived from atmospheric O₂ – and is
likely the most negative bound. If the non-marine sulfate endmember had a δ³⁴S of ~
+18‰, as seen near the low end of the data array (Fig. 1b), the atmospheric Δ¹⁷O(O₂)
would be ~ −6.6‰ assuming 1/4 of the oxygen in sulfate (a probable maximum) came
from atmospheric O₂ during surface sulfide oxidation (16, 21). A realistic Δ¹⁷O(O₂) value
probably lies somewhere between −42‰ and −6.6‰ at the time of W2 deposition. Note
that the modern Δ¹⁷O(O₂) is only ~ −0.10 to −0.20‰ depending on reference slope value
(ln₂¹⁷/O₂/ln₂¹⁸/O₂) used for calculation (22, 23).

There may be alternative scenarios where a large negative Δ¹⁷O(O₂) could occur
mathematically, although geologically there are far fewer scenarios that are viable. The
magnitude of the negative Δ¹⁷O value of atmospheric O₂ is determined by parameters
such as stratosphere O$_3$-CO$_2$-O$_2$ reactions, the size of the atmospheric O$_2$ and CO$_2$
reservoirs, stratosphere-troposphere flux, and troposphere O$_2$ fluxes (8). The controlling
parameters are often hard to determine, especially for an unfamiliar Earth system, but
some constraints exist. Other things being equal, higher CO$_2$ concentrations lead to a
more negative $\Delta^{17}$O(O$_2$) value as the CO$_2$ develops a positive anomaly by exchange with
oxygen. Assuming a steady-state O$_2$ reservoir and modern gas fluxes, the 1-D model in
Bao et al (8) would predict a pCO$_2$ level of ~12,500 to ~ 80,000 ppm during W2
deposition, consistent with the Earth having gone through a prolonged, ice-covered
period, i.e. a ‘snowball’ Earth (24). It should be noted that a much lower pO$_2$ and a
moderately high pCO$_2$ also could produce a similarly negative $\Delta^{17}$O(O$_2$), but only if the
corresponding O$_2$ residence time (i.e. pO$_2$/flux) were disproportionately long. Prolongation
of the residence time whilst keeping oxygen concentrations low implies much lower rates
of both O$_2$ removal by respiration/decomposition and input by photosynthesis, a balance
that is consistent with near-global glaciations. Other non-steady-state scenarios can also
be imagined where bizarre combinations of changes in reservoirs and fluxes of
atmospheric O$_2$ and CO$_2$ could have resulted in the observed large negative $\Delta^{17}$O(O$_2$) in
certain time windows. These scenarios could be explored by combining models and
further empirical data, but geology offers a stronger constraint since circumstances under
which sulfate can be preserved in terrestrial sedimentary records are uncommon.

Although various aspects of Neoproterozoic glaciations are intensely disputed (25),
our results confirm a profound difference from Phanerozoic ice ages. A near-global
distribution of glaciated continents during a ‘Marinoan’ phase ending 635-630 Myr ago is
supported by evidence of low palaeomagnetic latitudes (26). The ‘snowball’ Earth model
predicts a progressive accumulation of volcanic volatiles in the atmosphere which are not removed by weathering until the rapid demise of the ice age as the ice-albedo feedback reverses. If sulfate with large negative $\Delta^{17}O$ signals derived from oxidative weathering could only be generated in significant quantity after melting of the “snowball” and exposure of continents, then the diamictites above W2 had to be deposited during final glacial retreat, a hypothesis that should prompt a re-examination of their sedimentology. The alternative “slushball” model, in which parts of the ocean area are ice-free (28), would also permit accumulation of sulfate from prolonged oxidative weathering in certain continental “oases” where arid but cold conditions prevailed. This study provides an effective way to study the dynamics of sedimentation and atmospheric-hydrosphere-biosphere interactions during a global glaciation and highlights the need for further stratigraphically constrained $\Delta^{17}O_{SO_4}$ data on continental carbonate precipitates to ground-truth flux-balance models.
References and Notes


2. $\delta^{18}O$ or $\delta^{17}O = R_{\text{sample}}^{x}/R_{\text{standard}}^{x} - 1$ and $R^{x} = {^{18}}O/{^{16}}O$ or $^{17}O^{16}O$; the same $\delta$ notation applies to $\delta^{13}C$ or $\delta^{34}S$ in this paper.

3. Reference units for stable isotope compositions: Vienna Standard Mean Ocean Water (VSMOW) for sulfate $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$, Vienna PeeDee Belemnite (VPDB) for carbonate $\delta^{13}C$ and $\delta^{18}O$, and Vienna Canyon Diablo Troilite (VCDT) for sulfate $\delta^{34}S$.


13. Materials and methods are available as supporting material on *Science Online*.


H.B. and I.J.F. designed research and led the writing of the manuscript. H.B. performed CAS extraction and triple oxygen isotope measurements. I.J.F secured samples from field expeditions, and conducted sedimentological, petrographic, mineralogical and elemental studies. P.M.W. conducted preliminary CAS extraction and performed $\delta^{34}\text{S}_{\text{CAS}}$ analysis; C.S. carried out $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis of host carbonates. We thank Galen Halverson for discussion and Yongbo Peng for analytical assistance. Financial and facility supports are provided by LSU, NSF, and Chinese Academy of Science (H.B.), NERC standard grant (GR3/C511805/1) and NERC ICP-MS facilities (I.J.F.), and Austrian Science Funds (C.S.).

**Author Information**

The authors declare no competing financial interests.

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**Figures;**
Figure 3

[Graph showing 
\[ \delta^{18}O_{\text{CAS,SMOW}} \text{ vs. } \delta^{18}O_{\text{carbonate,VPDB}} \] with various data points and labels for different geological samples: W2 dolocretes, stromatolitic dolomites, W2 dolomite rhythmites, W2 limestones, E4 pre-glacial dolomite, and older pre-glacial clasts. An arrow indicates 1:1 evaporative re-equilibration offset.]
Supporting Online Material

1. Methods

2. The Middle Carbonate Member (W2) the Wilsonbreen Formation, Neoproterozoic

Svalbard

Table S1

Table S2