

**Stretching the Envelope of Past Surface
Environments: Neoproterozoic Glacial Lakes from
Svalbard**

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Competition with neighboring corals is unlikely to have intensified during a period when coral cover has either remained similar or declined on most GBR reefs (7). Terrestrial runoff and salinity, although potentially affecting inshore reefs (20), are also unlikely causes because calcification declines at similar rates on offshore reefs away from flood plumes. Diseases can also be excluded because only visibly healthy colonies were sampled. Benthic irradiance depends on turbidity and cloud cover, but there are no data suggesting they have recently changed at GBR-wide scales. The Interdecadal Pacific Oscillation has been associated with changing currents and pH in a lagoon (21); however, these and other large-scale long-term oceanographic oscillations can be excluded because they would have affected *Porites* calcification not only after 1990 but throughout the observation period. Hence, by excluding these potential alternatives, we suggest that SST and carbonate saturation state are the two most likely factors to have affected *Porites* calcification at a GBR-wide scale.

SST is an important environmental driver of coral growth. Our data confirmed previous studies (10, 22) that coral calcification increases linearly with large-scale mean annual SST. However, studies addressing shorter time periods show declining calcification at both high and low SST (18, 23, 24) and that thermally stressed corals show reduced calcification for up to 2 years (19). In our study, calcification was likewise reduced during cooler-than-average years (negative SST-ANOM). However, during warmer years it was highly variable, suggesting increasing calcification in some warm years but declines in others. This is possibly due to the year-averaged SST-ANOM inconsistently reflecting short hot periods that reduce calcification during warm years. The recent increase in heat stress episodes (25) is likely to have contributed to declining coral calcification in the period 1990–2005.

The supersaturation of tropical sea surface waters with the calcium carbonate mineral forms calcite and aragonite is considered a prerequisite for biotic calcification, with saturation state being a function of pH and temperature. Since industrialization, global average atmospheric CO₂ has increased by ~36% (from 280 to 387 parts per thousand), the concentration of hydrogen ions in ocean surface waters has increased by ~30% (a 0.1 change in pH), and the aragonite saturation state (Ω_{arag}) has decreased by ~16% (6, 26). Studies based on meso- or microcosm experiments show that reduced Ω_{arag} , due to the doubling of CO₂ as compared with preindustrial levels, reduces the growth of reef-building corals by 9 to 56% (6), with most of these experiments suggesting a linear relationship between calcification and Ω_{arag} .

Ω_{arag} data from the GBR or adjacent waters are sparse, but estimates of a global decline in Ω_{arag} of 16% since the beginning of global industrialization are similar in magnitude to our finding of a 14.2% decline in calcification in massive *Porites*. However, the decline in calcification observed in this study began later than expected, based on the model of proportional absorption of

atmospheric CO₂ by the oceans' surface waters (26). Thus, our results may suggest that, after a period of a slight increase in extension and prolonged decline in density, a tipping point was reached in the late 20th century. The nonlinear and delayed responses may reflect synergistic effects of several forms of environmental stress, such as more frequent stress from higher temperatures and declining Ω_{arag} . Laboratory experiments have provided the first evidence documenting strong synergistic effects on corals (27), but clearly more studies are needed to better understand this key issue.

Laboratory experiments and models have predicted negative impacts of rising atmospheric CO₂ on the future of calcifying organisms (5, 6). Our data show that growth and calcification of massive *Porites* in the GBR are already declining and are doing so at a rate unprecedented in coral records reaching back 400 years. If *Porites* calcification is representative of that in other reef-building corals, then maintenance of the calcium carbonate structure that is the foundation of the GBR will be severely compromised. Verification of the causes of this decline should be made a high priority. Additionally, if temperature and carbonate saturation are responsible for the observed changes, then similar changes are likely to be detected in the growth records from other regions and from other calcifying organisms. These organisms are central to the formation and function of ecosystems and food webs, and precipitous changes in the biodiversity and productivity of the world's oceans may be imminent (28).

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References

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Stretching the Envelope of Past Surface Environments: Neoproterozoic Glacial Lakes from Svalbard

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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 million years ago, falls well outside the currently known natural range of triple oxygen isotope compositions and indicates that the atmosphere had either an exceptionally high atmospheric carbon dioxide concentration or an utterly unfamiliar oxygen 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 per mil (‰) [Vienna standard mean ocean water (VSMOW)] (3) for marine sulfate

of different geological ages (4) and down to $\sim 18\%$ for sulfate formed in continental Antarctica (5). In recent years, the sulfate oxygen isotope composition has been found to vary along another dimension, the $\Delta^{17}\text{O}$ [$= \ln(\delta^{17}\text{O}+1) - 0.52\ln(\delta^{18}\text{O}+1)$]. The $\Delta^{17}\text{O}$ is close to zero for most samples but positive (up to $\sim +5.94\%$) for those of atmospheric origin (6, 7). Most recently, small but negative $\Delta^{17}\text{O}$ 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 million years 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 (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 and table S1). Note that the “cap carbonate,” the lower Dracosen Formation, is ~ 80 m above W2 and is not the subject of this study.

Two features of the data set are exceptional in terms of what we know about sulfate on Earth (Fig. 1): (i) The $\Delta^{17}\text{O}_{\text{CAS}}$ reaches as low as -1.64% , the most negative anomaly ever reported for terrestrial (versus extraterrestrial) minerals, and (ii) the $\delta^{18}\text{O}_{\text{CAS}}$ reaches as high as $\sim +37.7\%$, the most positive value ever reported for natural sulfate oxygen. Additional features are also intriguing. For example, (iii) CAS with a distinct ^{17}O anomaly is invariably from a limestone phase, whereas CAS from the dolostone phase does not have such a distinct ^{17}O anomaly (Fig. 1). (iv) Among CAS from the limestones, there is a strong positive correlation in $\Delta^{17}\text{O}-\delta^{34}\text{S}$ space, and the trend line connects with CAS from the immediately preglacial dolostone (member E4) (Fig. 1B). (v) The positively correlated $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of dolomite range from ~ -11 to $+15\%$ [Vienna Pee Dee belemnite (VPDB)] (3) and from ~ -2 to $+5\%$ (VPDB), respectively. This $\delta^{18}\text{O}_{\text{CO}_3}$ is the most positive value ever reported (Fig. 2A). (vi) Excluding preglacial samples, a slope of ~ 1 links two clusters of data in $\delta^{18}\text{O}_{\text{CAS}}-\delta^{18}\text{O}_{\text{CO}_3}$ space (Fig. 3). (vii) Lastly, those calcite samples with negative $\Delta^{17}\text{O}_{\text{CAS}}$ have a $\Delta^{17}\text{O}_{\text{CO}_3}$

value close to zero, indicating that the evaporated water itself did not bear an ^{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 $\Delta^{17}\text{O}$ 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_2S 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 $\delta^{34}\text{S}_{\text{SO}_4}$ much smaller than in the corresponding $\delta^{18}\text{O}_{\text{SO}_4}$ or $\delta^{18}\text{O}_{\text{CO}_3}$ value (which should be heavily influenced by the changing $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ due to variable degrees of evaporation). No atmospheric O_2 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 in ambient solution (14–16) without direct contact between reduced sulfur species and O_2 . Such redox cycling effectively eliminated the initial sulfate ^{17}O -anomalous oxygen and replaced it with ^{17}O -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 it to retain

its ^{17}O -anomalous signature. Intensive evaporation resulted in highly positive $\delta^{18}\text{O}$ values for the remaining water in a restricted lake or basin. Therefore, carbonate formed in the water would also carry extremely positive $\delta^{18}\text{O}$ values. Both the dolomite mineralogy and the ranges of $\delta^{13}\text{C}_{\text{CO}_3}$ and $\delta^{18}\text{O}_{\text{CO}_3}$ (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 because of the intense redox cycling required to explain both the extremely high $\delta^{18}\text{O}_{\text{CAS}}$ values and the disappearance of the negative ^{17}O anomalies in these dolomites. As $\delta^{18}\text{O}_{\text{CAS}}$ increases at the same magnitude as $\delta^{18}\text{O}_{\text{CO}_3}$ (Fig. 3), this suggests that almost all of the oxygen in the sulfate was replaced by oxygen from ambient water after microbially mediated sulfur redox cycling. The highly positive $\delta^{18}\text{O}_{\text{SO}_4}$ (up to $+37.7\%$) should therefore be correlated with the highly positive $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in the lakes. The $\delta^{18}\text{O}$ of evaporated H_2O can be estimated from the highly positive $\delta^{18}\text{O}_{\text{dolomite}}$, which is unlikely to be 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 $\delta^{18}\text{O}_{\text{CAS}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ranging from ~ 20 to 30% , which is similar to the ~ 25 to 30% recently obtained from an experimental study 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 the modern hypersaline lagoons near Rio de Janeiro, Brazil, where the $\delta^{18}\text{O}_{\text{SO}_4}$ reaches $+21.3\%$

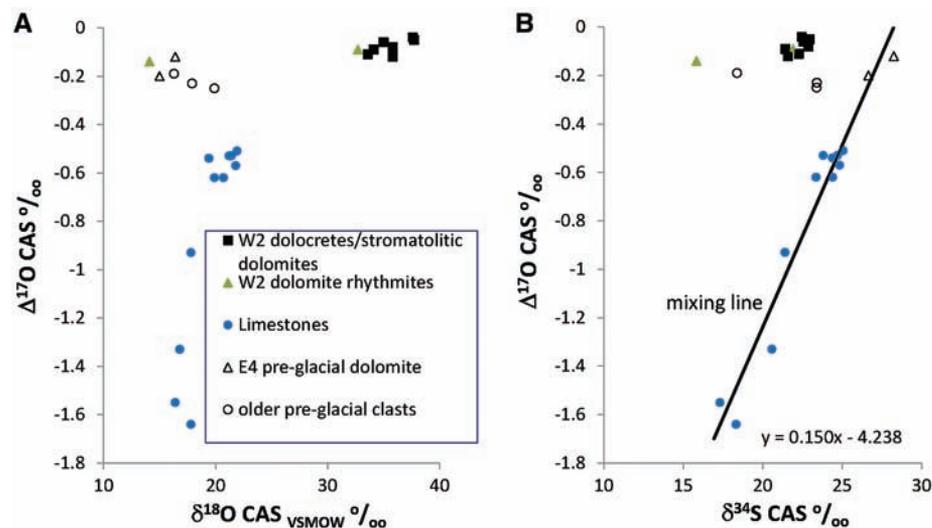


Fig. 1. (A) $\Delta^{17}\text{O}_{\text{CAS}}$ versus $\delta^{18}\text{O}_{\text{CAS}}$ and $\Delta^{17}\text{O}_{\text{CAS}}$ versus $\delta^{34}\text{S}_{\text{CAS}}$ from member W2. Dolomites with both high and low $\delta^{18}\text{O}_{\text{CAS}}$ display no $\Delta^{17}\text{O}_{\text{CAS}}$ anomaly, whereas a negative anomaly is variably developed in limestones. (B) A clear colinearity of $\Delta^{17}\text{O}_{\text{CAS}}$ versus $\delta^{34}\text{S}_{\text{CAS}}$ for limestones and immediately preglacial dolomites, interpreted as a mixing line between normal marine sulfate (high $\delta^{34}\text{S}$ and zero $\Delta^{17}\text{O}$) and sulfate from continental weathering (low $\delta^{34}\text{S}$ and negative $\Delta^{17}\text{O}$). Error bars for data are smaller than the symbols.

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in pore waters and +20.8 ‰ in surface brines with an apparent $\Delta\delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$ at $\sim+20$ ‰ (19).

The most negative value of $\Delta^{17}\text{O}_{\text{SO}_4}$ (−1.64 ‰) greatly extends the magnitude and geographic occurrence of the negative $\Delta^{17}\text{O}_{\text{SO}_4}$ associated with the Marinoan glaciation, as first reported by Bao *et al.* (8). Bao *et al.* proposed that the negative $\Delta^{17}\text{O}$ was derived from that of atmospheric O_2 involved in the oxidative weathering of sulfur compounds on the surface of Earth (8). Pre-existing ocean sulfate may not have a distinct negative $\Delta^{17}\text{O}$ 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 $\Delta^{17}\text{O}_{\text{SO}_4}$ value, where a large 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 finding is consistent with W2's setting, where much of the drainage could have been internal.

We interpret the strong correlation between $\Delta^{17}\text{O}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ 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 as 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 $\delta^{18}\text{O}$ value (from −13 to −4 ‰ VPDB) (Figs. 2B and 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 preglacial carbonates, which fall close to the $\delta^{34}\text{S}$ high end of the line (Fig. 1B). Because 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 to stabilize the position of the mixing line.

If sulfate derived from oxidative weathering of sulfides in glacial rock flour had a global average crustal $\delta^{34}\text{S}$ value of ~ 0 ‰, the mixing line (Fig. 1B) would point to a $\Delta^{17}\text{O}$ value of ~ -4.2 ‰ for the nonmarine sulfate endmember. This would imply an atmospheric $\Delta^{17}\text{O}(\text{O}_2)$ at ~ -42 ‰ if only 10% of the oxygen in sulfate came from atmospheric O_2 (8). This estimate contains two large uncertainties—the end-member $\delta^{34}\text{S}_{\text{sulfides}}$ value and the fraction of sulfate oxygen derived from atmospheric O_2 —and is probably the most negative bound. If the nonmarine sulfate endmember had a $\delta^{34}\text{S}$ value of $\sim +18$ ‰, as seen near the low end of the data array (Fig. 1B), the atmospheric $\Delta^{17}\text{O}(\text{O}_2)$ value would be ~ -6.6 ‰, assuming 1/4 of the oxygen in sulfate (a probable maximum) came from atmospheric O_2 during surface sulfide oxidation (16, 21). A realistic $\Delta^{17}\text{O}(\text{O}_2)$ value probably lies somewhere between −42 and −6.6 ‰ at the time of W2 deposition. Note that the modern $\Delta^{17}\text{O}(\text{O}_2)$ value is only ~ -0.10 to -0.20 ‰, depending on the reference slope value ($\ln\alpha^{17}/\ln\alpha^{18}$) used for calculation (22, 23).

There may be alternative scenarios where a large negative $\Delta^{17}\text{O}(\text{O}_2)$ could occur mathematically, although geologically there are far fewer scenarios that are viable. The magnitude of the negative $\Delta^{17}\text{O}$ value of atmospheric O_2 is determined by parameters such as stratosphere $\text{O}_3\text{-CO}_2\text{-O}_2$ 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 $\Delta^{17}\text{O}(\text{O}_2)$ 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 one-dimensional model in Bao *et al.* (8) would predict an atmospheric CO_2 concentration ($p\text{CO}_2$) of $\sim 12,500$ to $\sim 80,000$ parts per million during

W2 deposition, consistent with Earth having gone through a prolonged, ice-covered period (a “snowball” Earth) (24). It should be noted that a much lower $p\text{O}_2$ and a moderately high $p\text{CO}_2$ could also produce a similarly negative $\Delta^{17}\text{O}(\text{O}_2)$, but only if the corresponding O_2 residence time (i.e., $p\text{O}_2/\text{flux}$) was disproportionately long. Prolongation of the residence time while 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 $\Delta^{17}\text{O}(\text{O}_2)$ in certain time windows. These scenarios could be ex-

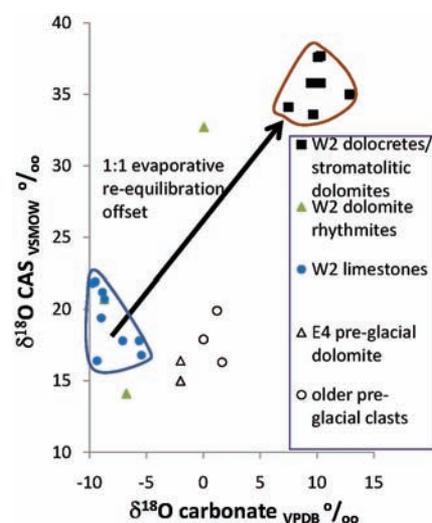
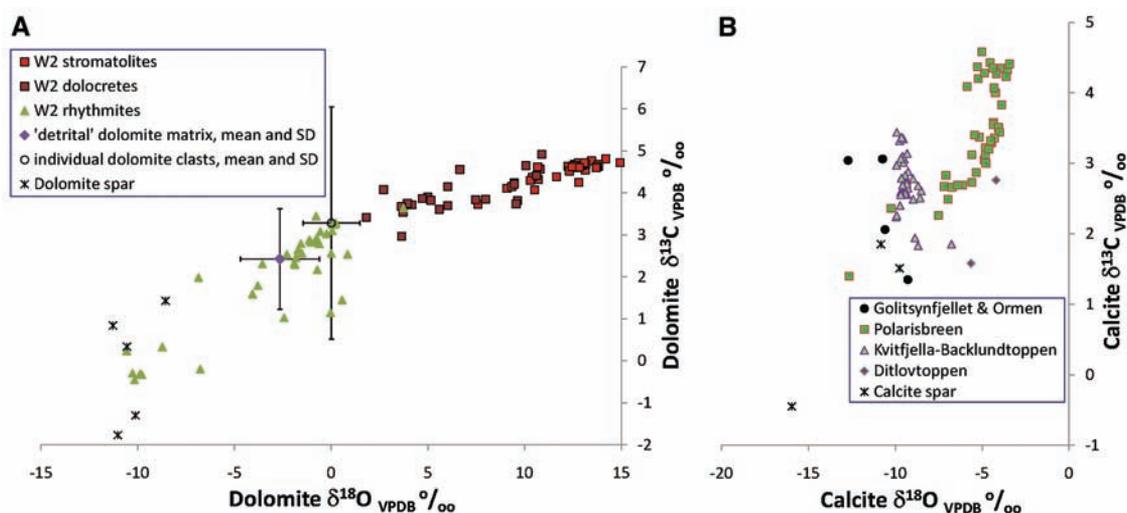


Fig. 3. $\delta^{18}\text{O}$ of CAS versus $\delta^{18}\text{O}$ of host carbonate from member W2. The offset of evaporative dolomites from less evaporative limestones has a 1:1 trend pointing to an isotopic steady state between sulfate and water permitted by intense redox recycling.

Fig. 2. (A) $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ for different types of dolomites for different locations of member W2. Dolomite rhythmite precipitates have mostly similar compositions to detritus but define a clear evaporative trend to high- $\delta^{18}\text{O}$ samples. (B) $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ for limestones from different locations of member W2. Limestones show variation in $\delta^{18}\text{O}$ value that may be primary or reflect variable timing of stabilization from Mg-calcite. For all data points, the error bars are smaller than the symbols, except for those displayed.



plored by combining models and further empirical data, but geology offers a stronger constraint because 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 the Marinoan phase ending ~635 million years ago is supported by evidence of low palaeomagnetic latitudes (26). The snowball Earth model (27) predicts a progressive accumulation of volcanic volatiles in the atmosphere that are not removed by weathering until the rapid demise of the ice age as the ice-albedo feedback reverses. If sulfate with large negative $\Delta^{17}\text{O}$ signals derived from oxidative weathering could only be generated in a large 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 $\Delta^{17}\text{O}_{\text{SO}_4}$ data on continental carbonate precipitates to ground-truth flux-balance models.

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- Reference units for stable isotope compositions: VSMOW for sulfate $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$; VPDB for carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$; and Vienna Canyon Diablo Troilite for sulfate $\delta^{34}\text{S}$.
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- 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; and C.S. carried out $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis of host carbonates. We thank G. Halverson for discussion and Y. Peng for analytical assistance. Financial and facility supports were provided by Louisiana State University, NSF, and Chinese Academy of Science (H.B.), Natural Environment Research Council (NERC) standard grant (GR3/C511805/1) and NERC inductively coupled plasma mass spectrometry facilities (I.J.F.), and Austrian Science Funds (C.S.). The authors declare no competing financial interests.

Supporting Online Material

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Materials and Methods

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Figs. S1 and S2

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Why Peer Discussion Improves Student Performance on In-Class Concept Questions

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When students answer an in-class conceptual question individually using clickers, discuss it with their neighbors, and then revote on the same question, the percentage of correct answers typically increases. This outcome could result from gains in understanding during discussion, or simply from peer influence of knowledgeable students on their neighbors. To distinguish between these alternatives in an undergraduate genetics course, we followed the above exercise with a second, similar (isomorphic) question on the same concept that students answered individually. Our results indicate that peer discussion enhances understanding, even when none of the students in a discussion group originally knows the correct answer.

In undergraduate science courses, conceptual questions that students answer using personal response systems or “clickers” are promoted as a means to increase student learning [e.g. (1, 2)], often through peer instruction (PI) (3). Instructors using this approach break up their lectures with multiple-choice questions to test understanding of the concepts being presented. When PI is used, students are first asked to answer a question in-

dividually, and then a histogram of their responses may be displayed to the class. If there is substantial disagreement among responses, students are invited to discuss questions briefly with their neighbors and then revote before the correct answer is revealed. The instructor then displays the new histogram and explains the reasoning behind the correct answer. Most instructors report that the percentage of correct answers, as well as

students’ confidence in their answers, almost always increases after peer discussion (2–4).

It is generally assumed that active engagement of students during discussion with peers, some of whom know the correct answer, leads to increased conceptual understanding, resulting in improved performance after PI. However, there is an alternative explanation: that students do not in fact learn from the discussion, but simply choose the answer most strongly supported by neighbors they perceive to be knowledgeable. We sought to distinguish between these alternatives, using an additional, similar clicker question that students answered individually to test for gains in understanding. Our results indicate that peer discussion enhances understanding, even when none of the students in a discussion group originally knows the correct answer.

In an undergraduate introductory genetics course for biology majors at the University of Colorado–Boulder (additional demographic in-

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