Revised on 11-25-2008 after "pre-edit Bao2" by editor

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

Huiming Bao[1], Ian J. Fairchild[2], Peter M. Wynn[3] & Christoph Spötl[4]

[1]Department of Geology & Geophysics, E235 Howe-Russell Complex, Louisiana State University, Baton Rouge, LA 70803, USA. [2]School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK. [3]Department of Geography, University of Lancaster, Lancaster, LA1 4YQ, UK Lancaster University, UK. [4]Institut für Geologie und Paläontologie, Leopold-Franzens-Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria

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 CO_2 concentrations or an utterly unfamiliar O_2 cycle during deposition of the diamictites.

Terrestrial sulfate (SO_4^{-2}) 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 $\delta^{18}O$ (*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 $\Delta^{17}O$ [≡ $ln\,(\delta^{17}O+1) - 0.52 ln\,(\delta^{18}O+1)$]. The $\Delta^{17}O$ 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 $\Delta^{17}O$ 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 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 Dracoisen 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 $\Delta^{17}O_{CAS}$ reaches as low as −1.64‰, the most negative anomaly ever reported for terrestrial (vs. extraterrestrial) minerals; 2) The $\delta^{18}O_{CAS}$ 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 ~−11‰ to +15‰ (VPDB) (*3*) and from ~−2 to +5‰ (VPDB) respectively. This $\delta^{18}O_{CO3}$ is the most positive value ever reported (Fig. 2a); 6) Excluding pre-glacial samples, a slope of ~ 1 links two clusters of data in $\delta^{18}O_{CAS} - \delta^{18}O_{CO3}$ space (Fig. 3); and 7) those calcite samples with negative $\Delta^{17}O_{CAS}$ have a $\Delta^{17}O_{CO3}$ 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_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 $\delta^{34}S_{SO4}$ much smaller than in the corresponding $\delta^{18}O_{SO4}$ or

$\delta^{18}O_{CO3}$ value (which should be heavily influenced by the changing $\delta^{18}O_{H2O}$ 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 them to retain their ^{17}O-anomalous signature. Intensive evaporation resulted in highly positive $\delta^{18}O$ values for the remaining water in a restricted lake or basin. Carbonate formed in the water would also therefore carry extremely positive $\delta^{18}O$ values. Both the dolomite mineralogy and the ranges of $\delta^{13}C_{CO3}$ and $\delta^{18}O_{CO3}$ (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 $\delta^{18}O_{CAS}$ values and the disappearance of the negative ^{17}O anomalies in these dolomites. As $\delta^{18}O_{CAS}$ increases at the same magnitude as $\delta^{18}O_{CO3}$ (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 $\delta^{18}O_{SO4}$ (up to +37.7‰) therefore should be correlated with the highly positive $\delta^{18}O_{H2O}$ in the lakes. The $\delta^{18}O$ of evaporated H_2O can be estimated from the highly positive $\delta^{18}O_{dolomite}$, 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 $\delta^{18}O_{CAS}$ and $\delta^{18}O_{H2O}$ ranging from ~20‰ to 30‰, which is similar to the ~ 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 $\delta^{18}O_{SO4}$ reaches +21.3‰ in pore waters and +20.8‰ in surface brines with an apparent $\Delta\delta^{18}O_{SO4-H2O}$ at ~+20‰ (*19*).

The most negative value of $\Delta^{17}O_{SO4}$ (−1.64‰) extends greatly the magnitude and geographic occurrence of the negative $\Delta^{17}O_{SO4}$ 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 $\Delta^{17}O_{SO4}$ 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 $\Delta^{17}O_{CAS}$ and $\delta^{34}S_{CAS}$ 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 $\delta^{18}O$ 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 $\delta^{34}S$-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 $\delta^{34}S$ value of ~ 0‰, the mixing line (Fig. 1b) would point to a $\Delta^{17}O$ of ~−4.2‰ for the non-marine sulfate endmember. This would imply an atmospheric $\Delta^{17}O(O_2)$ 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 $\delta^{34}S_{sulfides}$ value and the fraction of sulfate oxygen derived from atmospheric O_2 − and is likely the most negative bound. If the non-marine sulfate endmember had a $\delta^{34}S$ of ~ +18‰, as seen near the low end of the data array (Fig. 1b), the atmospheric $\Delta^{17}O(O_2)$ 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 $\Delta^{17}O(O_2)$ value probably lies somewhere between −42‰ and −6.6‰ at the time of W2 deposition. Note that the modern $\Delta^{17}O(O_2)$ is only ~ −0.10 to −0.20‰ depending on reference slope value ($\ln\alpha^{17}/\ln\alpha^{18}$) used for calculation (*22*, *23*).

There may be alternative scenarios where a large negative $\Delta^{17}O(O_2)$ could occur mathematically, although geologically there are far fewer scenarios that are viable. The magnitude of the negative $\Delta^{17}O$ value of atmospheric O_2 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 disproportionally 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

(*27*) 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 $\Delta^{17}O_{SO4}$ data on continental carbonate precipitates to ground-truth flux-balance models.

References and Notes

1. H. M. Bao, D. Rumble, D. R. Lowe, *Geochimica et Cosmochimica Acta* 71, 4868 (2007).
2. $\delta^{18}O$ or $\delta^{17}O \equiv R^x_{sample}/R^x_{standard} - 1$ and $R^x = {}^{18}O/{}^{16}O$ or ${}^{17}O/{}^{16}O$; the same δ 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 $\delta^{34}S$.
4. G. E. Claypool, W. T. Holser, I. R. Kaplan, H. Sakai, I. Zak, *Chemical Geology* 28, 199 (1980).
5. R. A. Socki, R. P. Harvey, D. L. Bish, E. Tonui, H. Bao, in *Lunar and Planetary Science Conference*. (NASA, Houston, 2008), vol. XXXIX, pp. 1964.
6. H. M. Bao, *Chemical Geology* 214, 127 (2005).
7. H. M. Bao, M. H. Thiemens, D. B. Loope, X. L. Yuan, *Geophysical Research Letters* 30, 1843; 10.1029/2003GL016869 (2003).
8. H. M. Bao, J. R. Lyons, C. M. Zhou, *Nature* 453, 504 (2008).
9. G. P. Halverson, A. C. Maloof, P. F. Hoffman, *Basin Research* 16, 297 (2004).
10. G. P. Halverson, in *Neoproterozoic Geobiology and Paleobiology* S. Xiao, A. J. Kaufman, Eds. (Springer, New York, 2006) pp. 231-271.
11. I. J. Fairchild, M. J. Hambrey, *Precambrian Research* 73, 217 (1995).
12. I. J. Fairchild, M. J. Hambrey, B. Spiro, T. H. Jefferson, *Geological Magazine* 126, 469 (1989).

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

14. G. W. Luther, *Geochimica et Cosmochimica Acta* 51, 3193 (1987).

15. C. O. Moses, J. S. Herman, *Geochimica et Cosmochimica Acta* 55, 471 (1991).

16. N. Balci, W. C. Shanks, B. Mayer, K. W. Mandernack, *Geochimica et Cosmochimica Acta* 71, 3796 (2007).

17. M. R. Talbot, *Chemical Geology* 80, 261 (1990).

18. J. Farquhar, D. E. Canfield, A. Masterson, H. Bao, D. Johnston, *Geochimica et Cosmochimica Acta* 72, 2805 (2008).

19. N. F. Moreira, L. M. Walter, C. Vasconcelos, J. A. McKenzie, P. J. McCall, *Geology* 32, 701 (2004).

20. I. J. Fairchild, M. J. Hambrey, *Precambrian Research* 26, 111 (1984).

21. B. J. Reedy, J. K. Beattie, R. T. Lowson, *Applied Spectroscopy* 48, 691 (1994).

22. A. Angert, S. Rachmilevitch, E. Barkan, B. Luz, *Global Biogeochemical Cycles* 17, #1030 (2003).

23. B. Luz, E. Barkan, *Geochimica et Cosmochimica Acta* 69, 1099 (2005).

24. R. T. Pierrehumbert, *Journal of Geophysical Research-Atmospheres* 110 (2005).

25. I. J. Fairchild, M. J. Kennedy, *Journal of the Geological Society* 164, 895 (2007).

26. D. A. D. Evans, *American Journal of Science* 300, 347 (2000).

27. P. F. Hoffman, D. P. Schrag, *Terra Nova* 14, 129 (2002).

28. T. J. Crowley, W. T. Hyde, W. R. Peltier, *Geophysical Research Letters* 28, 283 (2001).

29. 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 $\delta^{34}S_{CAS}$ analysis; C.S. carried out $\delta^{13}C$ and $\delta^{18}O$ 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.

Correspondence should be addressed to H.B. (bao@lsu.edu).

Figures;

Figure 1

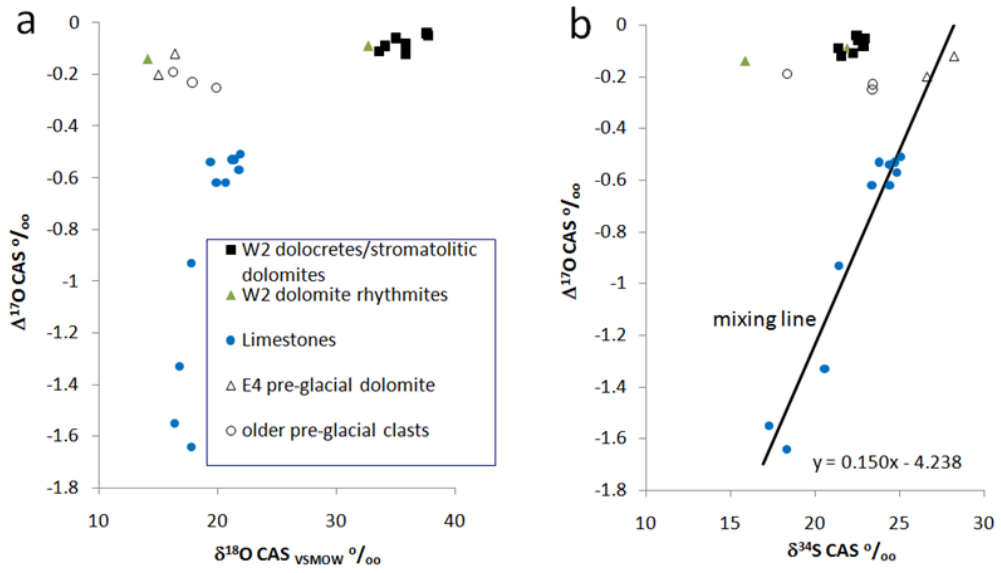


Figure 2

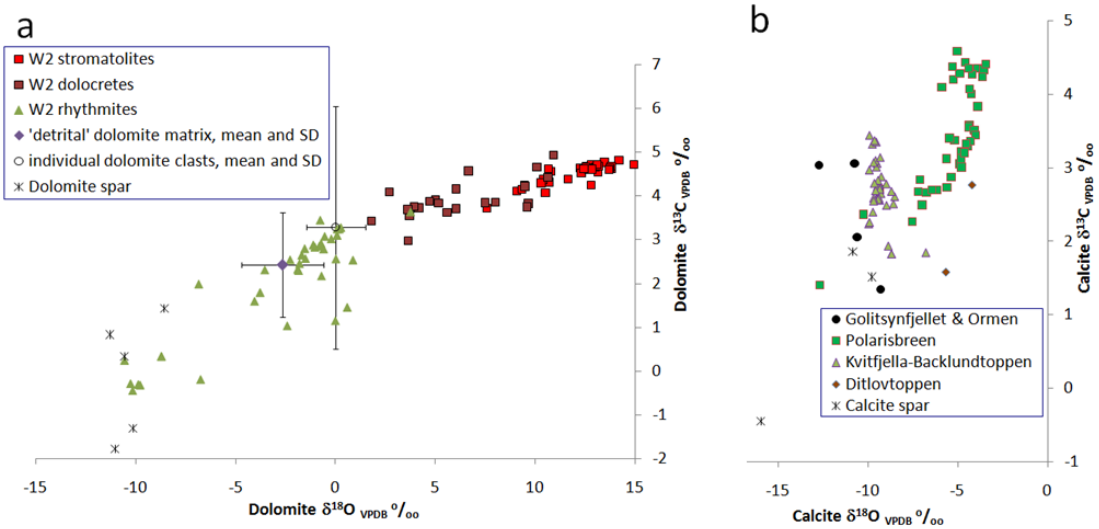
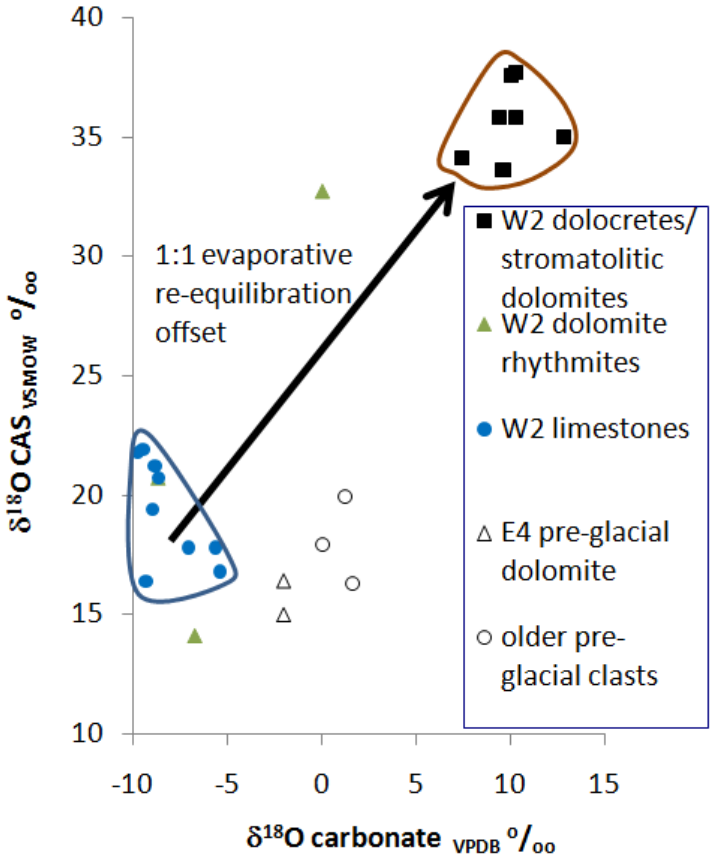


Figure 3


40
35
30
25
20
15
10
-10
-5
0
5
10
15
δ18O CAS VSMOW °/oo
δ18O carbonate VPDB °/oo
1:1 evaporative re-equilibration offset
W2 dolocretes/ stromatolitic dolomites
W2 dolomite rhythmites
W2 limestones
E4 pre-glacial dolomite
older pre-glacial clasts

Supporting Online Material