

## LETTERS

# Triple oxygen isotope evidence for elevated CO<sub>2</sub> levels after a Neoproterozoic glaciation

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Understanding the composition of the atmosphere over geological time is critical to understanding the history of the Earth system, as the atmosphere is closely linked to the lithosphere, hydrosphere and biosphere. Although much of the history of the lithosphere and hydrosphere is contained in rock and mineral records, corresponding information about the atmosphere is scarce and elusive owing to the lack of direct records. Geologists have used sedimentary minerals, fossils and geochemical models to place constraints on the concentrations of carbon dioxide, oxygen or methane in the past<sup>1–4</sup>. Here we show that the triple oxygen isotope composition of sulphate from ancient evaporites and barites shows variable negative oxygen-17 isotope anomalies over the past 750 million years. We propose that these anomalies track those of atmospheric oxygen and in turn reflect the partial pressure of carbon dioxide ( $p_{\text{CO}_2}$ ) in the past through a photochemical reaction network linking stratospheric ozone to carbon dioxide and to oxygen<sup>5,6</sup>. Our results suggest that  $p_{\text{CO}_2}$  was much higher in the early Cambrian than in younger eras, agreeing with previous modelling results<sup>2</sup>. We also find that the  $\Delta^{17}\text{O}$  isotope anomalies of barites from Marinoan (~635 million years ago) cap carbonates display a distinct negative spike (around  $-0.70\text{\textperthousand}$ ), suggesting that by the time barite was precipitating in the immediate aftermath of a Neoproterozoic global glaciation, the  $p_{\text{CO}_2}$  was at its highest level in the past 750 million years. Our finding is consistent with the ‘snowball Earth’ hypothesis<sup>7,8</sup> and/or a massive methane release<sup>9</sup> after the Marinoan glaciation.

Since the discovery of widespread sulphate  $\Delta^{17}\text{O}$  anomalies in Earth’s continental deposits<sup>10</sup>, a considerable amount of triple oxygen isotope data has been gathered for sulphate of diverse origins<sup>11–14</sup>. Without exception, the  $\Delta^{17}\text{O}$  anomalies have been positive, as measured by  $\Delta^{17}\text{O}$  ( $\equiv \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ), in which  $\delta' \equiv \ln(R_{\text{sample}}/R_{\text{standard}})$  and  $R$  is the ratio of  $^{18}\text{O}/^{16}\text{O}$  or  $^{17}\text{O}/^{16}\text{O}$  (Supplementary Information 1–5). A positive anomaly indicates enrichment in  $^{17}\text{O}$  content with respect to what is expected from a terrestrial fractionation line. It is known that positive sulphate  $\Delta^{17}\text{O}$  is transferred from atmospheric ozone ( $\text{O}_3$ ) during oxidation of sulphur compounds in the atmosphere<sup>15</sup>. Overall, the  $\Delta^{17}\text{O}$  for terrestrial sulphate reaches as high as  $+5.84\text{\textperthousand}$ <sup>11</sup>.

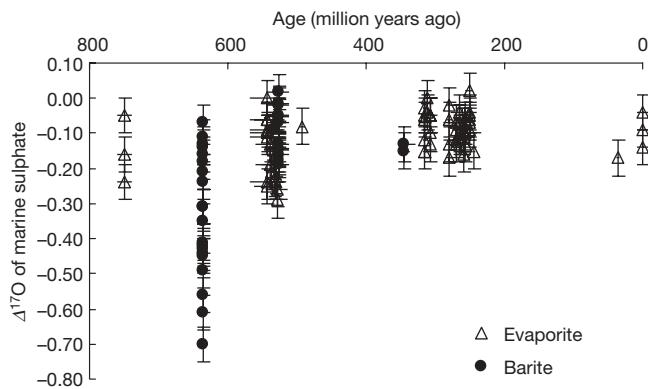
Here we report variable negative  $\Delta^{17}\text{O}$  anomalies among sulphate deposited on Earth surfaces over the past 750 million years (Fig. 1). Despite their small magnitudes, the negative  $\Delta^{17}\text{O}$  anomalies are larger than the analytical error of  $\pm 0.05\text{\textperthousand}$  and are reproducible. They were first noticed in an earlier survey of evaporite sulphate that had no direct link to atmospheric  $\text{O}_3$  chemistry<sup>16</sup>. An expanded survey revealed that marine evaporites and barites have  $\Delta^{17}\text{O}$  values ranging from  $+0.02$  to  $-0.70\text{\textperthousand}$ . Values more negative than  $-0.20\text{\textperthousand}$  are common in the Cambrian in diverse localities (for example, Siberia, Australia and India) whereas none occur in the late

Palaeozoic or modern settings. Most remarkably, barite cements from the Marinoan cap carbonate sequences deposited ~635 million years ago possess extremely negative  $\Delta^{17}\text{O}$  values both in West Africa (down to  $-0.40\text{\textperthousand}$ ) and in South China (down to  $-0.70\text{\textperthousand}$ ) (Supplementary Information 1).

We propose that the triple oxygen isotope compositions of sulphate carry a portion of the tropospheric O<sub>2</sub> signal, which has had variable negative  $\Delta^{17}\text{O}$  values that are determined largely by stratospheric O<sub>3</sub>–CO<sub>2</sub>–O<sub>2</sub> chemistry, and consequently the  $p_{\text{CO}_2}$ , in the past (Fig. 2). We describe the connection between  $p_{\text{CO}_2}$  and sulphate  $\Delta^{17}\text{O}$  in three steps.

First, sulphate derived from oxidative weathering carries an atmospheric O<sub>2</sub> signal. Sulphate oxygen ultimately comes from water and oxidants such as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> or atmospheric O<sub>2</sub>. When atmospheric O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> is the oxidant, the product sulphate bears a positive  $\Delta^{17}\text{O}$  value<sup>10,15</sup>. The contribution of this atmospheric sulphate to ocean sulphate, however, is negligible compared with the influx from oxidative weathering. Early studies on sulphate derived from surface sulphur oxidations showed that, depending on reaction conditions and pathways, 0% to ~50% of the sulphate oxygen carries an O<sub>2</sub> signal<sup>17</sup>. More recent laboratory experiments show that 8 to 15% of the oxygen in product sulphate came from O<sub>2</sub> when O<sub>2</sub> is involved in pyrite oxidation<sup>18</sup>.

Second, modern atmospheric O<sub>2</sub> is known to have a small negative  $\Delta^{17}\text{O}$  anomaly, as first suggested by Bender *et al.*<sup>19</sup> and later documented by terrarium experiments<sup>20</sup>. The key chemical processes that bring a negative  $\Delta^{17}\text{O}$  anomaly to atmospheric O<sub>2</sub> are the reactions of O<sub>3</sub>–CO<sub>2</sub>–O<sub>2</sub> in the stratosphere<sup>5,6</sup>. The Chapman reactions produce O<sub>3</sub> that is highly positive in both its  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values. Photolysis of O<sub>3</sub> yields O (<sup>1</sup>D) which transfers the oxygen isotope



**Figure 1 | The  $\Delta^{17}\text{O}$  of evaporite and barite sulphate over the past 750 million years.**

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signature of  $O_3$  to  $CO_2$  via the exchange reaction  $O(^1D) + CO_2 \rightarrow CO_3^* \rightarrow O(^3P) + CO_2$ . The net result is the generation of  $\delta^{18}O$ -high and  $\Delta^{17}O$ -positive  $CO_2$  and  $\delta^{18}O$ -low and  $\Delta^{17}O$ -negative  $O_2$ . The stratospheric  $O_2$  mixes with  $O_2$  in the troposphere but does not exchange oxygen with surface water. The exact magnitude of the non-mass-dependent  $^{17}O$  anomaly for current atmospheric  $O_2$  is debated, because of an uncertainty in kinetic fractionation slope<sup>21–23</sup>. Subtracting the effect of a newly calibrated slope<sup>23</sup> that is slightly different from the defined slope of 0.52, we calculated that tropospheric  $O_2$  has ~83% of its  $\Delta^{17}O$  signal (around -0.19‰) inherited from a stratospheric photochemical process (Supplementary Information 2 and 3.1). In fact,  $O_2$  is the only known atmospheric oxidant that has a negative  $^{17}O$  anomaly or a negative  $\Delta^{17}O$  ( $O_2$ ) value.

Third, the magnitude of  $\Delta^{17}O$  ( $O_2$ ) should have changed over time. This is because its controlling factors, such as  $p_{CO_2}$ ,  $p_{O_2}$ ,  $p_{O_3}$ , and the rates of photolysis, photosynthesis or respiration<sup>5,6,24</sup>, have not remained constant over geological time. For tropospheric  $O_2$ , the negative  $\Delta^{17}O$  signal is in a steady state, with influx from the stratosphere and photosynthesis, and outflux from respiration and oxidative weathering<sup>20</sup>. In the current atmosphere, the  $O_2$  flux from photosynthesis or respiration/weathering is only 1/300 of that from troposphere–stratosphere exchange<sup>20</sup>. Thus, the  $\Delta^{17}O$  of tropospheric  $O_2$  is determined by stratospheric  $O_2$  transferred into the troposphere during stratosphere–troposphere exchange, and the lifetime of tropospheric  $O_2$  with respect to photosynthesis and respiration. Higher  $p_{CO_2}$  implies a greater reservoir of  $\Delta^{17}O$ -positive  $CO_2$ , and a corresponding more negative  $\Delta^{17}O$  for  $O_2$ .

We ran a one-dimensional photochemical model of the modern atmosphere for a variety of  $p_{CO_2}$  conditions and for present-day  $p_{O_2}$  (see Methods Summary). The resulting  $\Delta^{17}O$  ( $O_2$ ) varies linearly with  $p_{CO_2}$  for small increases in  $p_{CO_2}$ , confirming the linear scaling assumption of Luz *et al.*<sup>20</sup>. The linear relationship is also confirmed by examining actual measurements of  $p_{CO_2}$  and  $\Delta^{17}O$  ( $O_2$ ) from two ice cores (GISP2 and Siple Dome) by two separate research groups<sup>20,24</sup>. According to the model the scaling becomes weaker than linear at high  $p_{CO_2}$  (Supplementary Information 6). An increase in the photosynthesis flux will reduce the magnitude of  $\Delta^{17}O$  ( $O_2$ ) by

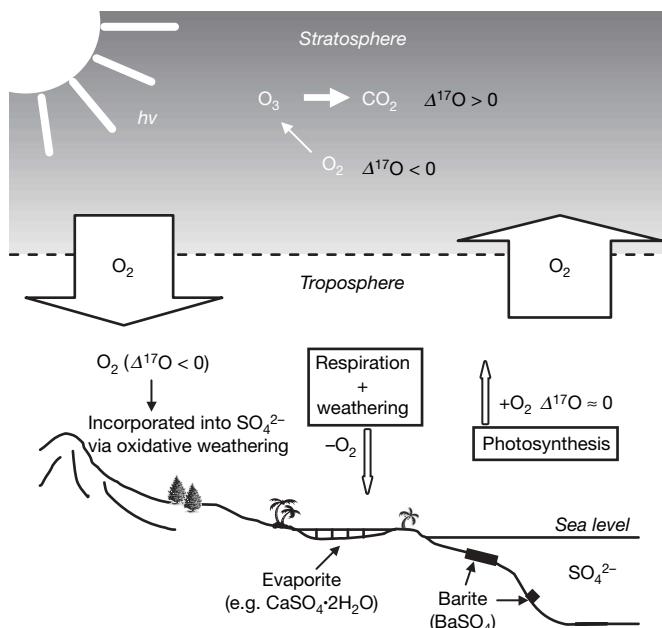
decreasing the atmospheric lifetime of  $O_2$  for a given  $O_2$  reservoir mass. To first order, a doubling of the photosynthesis flux will result in a halving of  $\Delta^{17}O$  ( $O_2$ ), assuming photosynthesis and respiration are in steady state.

A key attribute of sulphate is that it does not exchange oxygen with ambient water in most Earth surface environments<sup>25</sup>. Therefore, evaporite and barite sulphates from a given geological period would have a range of  $\Delta^{17}O$  values owing to initial variable sulphide oxidation pathways, subsequent redox cycling, or mixing of freshwater or atmospheric sulphate. However, the minimum  $\Delta^{17}O$  value for that period has to be set by the  $\Delta^{17}O$  ( $O_2$ ) at that time.

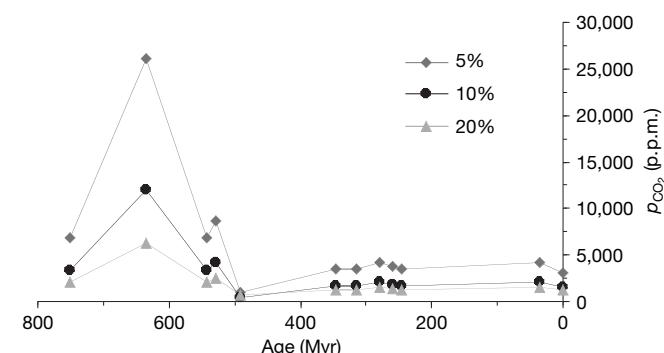
There are still temporal blanks to be filled in Fig. 1, but the low  $\Delta^{17}O$  cluster in the early Cambrian stands out as a distinct feature. The lowest sulphate  $\Delta^{17}O$  value, -0.29‰, is around three times more negative than those in the late Palaeozoic or modern evaporite and barite sulphates, suggesting a more negative  $\Delta^{17}O$  ( $O_2$ ) and thus a much higher atmospheric  $p_{CO_2}$  in Early Cambrian. This is consistent with the GEOCARBSULF modelling result on the  $p_{CO_2}$  and  $p_{O_2}$  history in the Phanerozoic<sup>2</sup>, in which  $p_{CO_2}$  was ~20 times higher in the early Cambrian Period than in the late Palaeozoic or modern era. The most extraordinary feature in Fig. 1 is the barite cements from several ~635-Myr-old cap carbonate sequences in South China<sup>26</sup> and West Africa, occurring in dolostone matrices within a few metres above the Marinoan glacial diamictites. The  $\Delta^{17}O$  spike for these barites is around seven times more negative than that of the modern marine sulphate, implying that the atmosphere in the immediate aftermath of Marinoan deglaciation had the highest  $p_{CO_2}$  ratio ever for the past 750 million years.

Converting the record of marine sulphate  $\Delta^{17}O$  into a record of atmospheric  $p_{CO_2}$  requires us to know the fraction of sulphate oxygen contributed from atmospheric  $O_2$ . Comparing the average  $\Delta^{17}O$  for modern marine sulphate with  $\Delta^{17}O$  for modern  $O_2$  and considering the many uncertainties involved (Supplementary Information 5),  $\sim 10\% \pm 10\%$  of the marine sulphate oxygen  $\Delta^{17}O$  signal is estimated to have come from atmospheric  $O_2$ . Although consistent with a recent estimate<sup>18</sup>, this number is provisional and should be further calibrated both in the laboratory and in nature. Applying this value, we obtain a  $\Delta^{17}O$  ( $O_2$ ) value of -2.4‰ and -6.5‰ for the early Cambrian and at ~635 Myr ago, respectively. According to our one-dimensional model, these  $\Delta^{17}O$  ( $O_2$ ) values imply  $p_{CO_2}$  of ~4,200 p.p.m. in the early Cambrian and ~12,000 p.p.m. at the time of barite precipitation in the Marinoan cap carbonate sequences. The estimated  $p_{CO_2}$  value is sensitive to the presumed  $O_2$  fraction in sulphate oxygen (Fig. 3).

It should be noted that the ~12,000 p.p.m.  $p_{CO_2}$  may be a snapshot of a dynamic transition of atmospheric conditions immediately after the deglaciation<sup>27</sup>. The high  $p_{CO_2}$  could be the consequence of two causes, which are not mutually exclusive. First, the Neoproterozoic ‘snowball’ Earth hypothesis predicted a long-term build-up of



**Figure 2 | How evaporite or barite sulphate records the negative  $^{17}O$  anomaly of tropospheric  $O_2$  that originated in the stratosphere.** The  $O_2$ – $O_3$ – $CO_2$  reaction network refers to those depicted in Supplementary Information 6, Supplementary Fig. 2. Sizes of the solid white arrows indicate relative fluxes (not to scale).



**Figure 3 | Model-calculated partial pressures of  $CO_2$  based on the lowest sulphate  $\Delta^{17}O$  value for a given period in geological history.** The diamonds, circles and triangles are for  $O_2$  signatures of 5, 10 and 20 mol% in sulphate oxygen, respectively.

volcanic CO<sub>2</sub> in the atmosphere, up to ~350 times the modern level, that finally offset the albedo effect and brought the Earth out of an otherwise perpetual snowball state<sup>7,8</sup>. Therefore, the high  $p_{CO_2}$  at the time of barite precipitation could be a relic of the high  $p_{CO_2}$  during the ‘snowball’ Earth. A second cause could be a catastrophic release of methane hydrates just after a global deglaciation, which, on the oxidation of methane, gave rise to a high  $p_{CO_2}$  level<sup>9</sup>. Whatever the cause, consistently more negative  $\Delta^{17}O$  values for the lower barite bed than for the upper one at multiple sites at Baizhu, Hubei Province, South China (Supplementary Information 7 and Supplementary Fig. 5) probably attest to a rapid CO<sub>2</sub> drawdown. The level of  $p_{CO_2}$  and the rate of CO<sub>2</sub> drawdown in the immediate aftermath of the Marinoan glaciation should ultimately be constructed with improved knowledge of seawater mixing and stratification in the post-glacial oceans and the exact fraction of O<sub>2</sub> being incorporated in marine sulphate.

Sulphate’s negative  $\Delta^{17}O$  value is so far the only known mineral-isotope proxy that directly records the  $^{17}O$  anomaly of past atmospheric O<sub>2</sub>. Although the sulphate  $\Delta^{17}O$  record does not have the sensitivity to detect atmospheric  $p_{CO_2}$  changes between glacial and interglacial times, it can be particularly useful in evaluating extreme levels of atmospheric CO<sub>2</sub> or O<sub>2</sub> that have occurred throughout the Earth’s history.

## METHODS SUMMARY

Sulphate was extracted from evaporites using Millipore water (18 MΩ) and 1 M HCl, and precipitated as barite (BaSO<sub>4</sub>). Pure BaSO<sub>4</sub> was obtained from sedimentary barite via a modified DTPA (diethylenetriaminepentaacetic acid)-dissolution and re-precipitation (DDARP) method<sup>28</sup>. We extracted O<sub>2</sub> by using a CO<sub>2</sub>-laser fluorination system<sup>29</sup> and measured for the  $\delta^{17}O$  and  $\delta^{18}O$  on a Finnigan MAT 253 in a dual-inlet mode. The average O<sub>2</sub> sample size is ~25 micromoles, and is ~25% to 35% of the total barite oxygen yield. The standard deviation associated with the  $\Delta^{17}O$  is ±0.03‰ for multiple (N ≈ 3) runs of the same O<sub>2</sub> gas on the MAT 253, and ±0.05‰ for replicates of the same BaSO<sub>4</sub> via laser-fluorination. The reported  $\delta^{18}O$  was +9.4‰ (a kinetic effect) plus the raw value obtained from the laser-fluorination method. The error is ±0.7‰ for pure and fine-grained barite samples. Some  $\delta^{18}O$  values were obtained from the temperature-conversion elemental analyser with errors within ±0.5‰. No effort is made to distinguish them because an accurate  $\delta^{18}O$  value is not important to this study and errors in the  $\delta^{18}O$  and the  $\delta^{17}O$  cancel out during the  $\Delta^{17}O$  calculation. The sample was run only when the  $\Delta^{17}O$  zero enrichment was checked to be less than ±0.05‰. We have found that N<sub>2</sub> contamination can result in an erroneous, negative, but small  $\Delta^{17}O$  value when N<sub>2</sub>/O<sub>2</sub> is >2% in our MAT 253. Most of our samples have N<sub>2</sub>/O<sub>2</sub> < 0.3% and none of the reported data had N<sub>2</sub>/O<sub>2</sub> > 1%.

In our one-dimensional photochemical model, temperature-dependent isotopomer-specific rate coefficients for O<sub>3</sub> formation<sup>30</sup> are used. Solar ultraviolet flux, vertical eddy mixing, temperature profiles, and atmospheric composition other than CO<sub>2</sub> are assumed to be unchanged relative to the present-day atmosphere. An O<sub>2</sub> atmospheric residence time of 1,200 yr<sup>20</sup> is used for all cases.

Received 7 September 2007; accepted 31 March 2008.

- Rye, R., Kuo, P. H. & Holland, H. D. Atmospheric carbon dioxide concentrations before 2.2 billion years ago. *Nature* **378**, 603–605 (1995).
- Berner, R. A. GEOCARBSULF: A combined model for Phanerozoic atmospheric O<sub>2</sub> and CO<sub>2</sub>. *Geochim. Cosmochim. Acta* **70**, 5653–5664 (2006).
- Ekart, D. D., Cerling, T. E., Montanez, I. P. & Tabor, N. J. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* **299**, 805–827 (1999).
- Royer, D. L. et al. Paleobotanical evidence for near present-day levels of atmospheric CO<sub>2</sub> during part of the Tertiary. *Science* **292**, 2310–2313 (2001).
- Yung, Y. L., DeMore, W. B. & Pinto, J. P. Isotopic exchange between carbon dioxide and ozone via O(<sup>1</sup>D) in the stratosphere. *Geophys. Res. Lett.* **18**, 13–16 (1991).
- Yung, Y. L. et al. Carbon dioxide in the atmosphere: Isotopic exchange with ozone and its use as a tracer in the middle atmosphere. *J. Geophys. Res.* **102** (D9), 10857–10866 (1997).
- Hoffman, P. F., Kaufman, A. J., Halverson, G. P. & Schrag, D. P. A Neoproterozoic snowball Earth. *Science* **281**, 1342–1346 (1998).
- Pierrehumbert, R. T. High levels of atmospheric carbon dioxide necessary for the termination of global glaciation. *Nature* **429**, 646–649 (2004).
- Jiang, G. Q., Kennedy, M. J. & Christie-Blick, N. Stable isotopic evidence for methane seeps in Neoproterozoic postglacial cap carbonates. *Nature* **426**, 822–826 (2003).
- Bao, H. M. et al. Anomalous  $^{17}O$  compositions in massive sulphate deposits on the Earth. *Nature* **406**, 176–178 (2000).
- Bao, H. M., Thiemens, M. H., Loope, D. B. & Yuan, X. L. Sulfate oxygen-17 anomaly in an Oligocene ash bed in mid-North America: Was it the dry fogs? *Geophys. Res. Lett.* **30** (16), 1843, doi:10.1029/2003GL016869 (2003).
- Howell, K. J. & Bao, H. M. Caliche as a geological repository for atmospheric sulfate. *Geophys. Res. Lett.* **33**, L13816, doi:10.1029/2006GL026518 (2006).
- Alexander, B. et al. Climate driven changes in the oxidation pathways of atmospheric sulfur. *Geophys. Res. Lett.* **29** (14), 1685, doi:10.1029/2002GL014879 (2002).
- Bao, H. M. & Merchant, D. R. Quantifying sulfate components and their variations in soils of the McMurdo Dry Valleys, Antarctica. *J. Geophys. Res.* **111** (D16301), doi:10.1029/2005JD006669 (2006).
- Savarino, J., Lee, C. C. W. & Thiemens, M. H. Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth. *J. Geophys. Res.* **105** (D23), 29079–29088 (2000).
- Bao, H. M. Sulfate in modern playas settings and in ash beds in hyperarid deserts: Implication on the origin of  $^{17}O$ -anomalous sulfate in an Oligocene ash bed. *Chem. Geol.* **214**, 127–134 (2005).
- van Stempvoort, D. R. & Krouse, H. R. in *Environmental Geochemistry of Sulfide Oxidation* Vol. 550 (eds Alpers, C. N. & Blowes, D. W.) 446–480 (American Chemical Society, Washington DC, 1994).
- Balci, N., Shanks, W. C., Mayer, B. & Mandernack, K. W. Oxygen and sulfur isotope systematics of sulfate produced by bacterial and abiotic oxidation of pyrite. *Geochim. Cosmochim. Acta* **71**, 3796–3811 (2007).
- Bender, M., Sowers, T. & Labeyrie, L. The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core. *Glob. Biogeochem. Cycles* **8**, 363–376 (1994).
- Luz, B. et al. Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity. *Nature* **400**, 547–550 (1999).
- Young, E. D., Galy, A. & Nagahara, H. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* **66**, 1095–1104 (2002).
- Miller, M. F. Isotopic fractionation and the quantification of  $^{17}O$  anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* **66**, 1881–1889 (2002).
- Luz, B. & Barkan, E. The isotopic ratios  $^{17}O/^{16}O$  and  $^{18}O/^{16}O$  in molecular oxygen and their significance in biogeochemistry. *Geochim. Cosmochim. Acta* **69**, 1099–1110 (2005).
- Blunier, T., Barnett, B., Bender, M. L. & Hendricks, M. B. Biological oxygen productivity during the last 60,000 years from triple oxygen isotope measurements. *Glob. Biogeochem. Cycles* **16** (3), 1029, doi:10.1029/2001GB001460 (2002).
- Gamsjäger, H. & Murmann, R. K. in *Advances in Inorganic and Bioinorganic Mechanisms* Vol. 2 (ed. Sykes, A. G.) 317–381 (Academic, London, 1983).
- Jiang, G. Q. et al. Stratigraphy, sedimentary structures, and textures of the late Neoproterozoic Doushantuo cap carbonate in South China. *J. Sediment. Res.* **76**, 978–995 (2006).
- Kasemann, S. A. et al. Boron and calcium isotope composition in Neoproterozoic carbonate rocks from Namibia: evidence for extreme environmental change. *Earth Planet. Sci. Lett.* **231**, 73–86 (2005).
- Bao, H. M. Purifying synthetic barite for oxygen isotope measurement by dissolution and reprecipitation in a chelating solution. *Anal. Chem.* **78**, 304–309 (2006).
- Bao, H. M. & Thiemens, M. H. Generation of O<sub>2</sub> from BaSO<sub>4</sub> using a CO<sub>2</sub>-laser fluorination system for simultaneous analysis of  $\delta^{18}O$  and  $\delta^{17}O$ . *Anal. Chem.* **72**, 4029–4032 (2000).
- Mauersberger, K., Krankowsky, D., Janssen, C. & Schinke, R. in *Advances in Atomic, Molecular, and Optical Physics* Vol. 50 1–54 (Elsevier Academic, San Diego, 2005).

**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

**Acknowledgements** We thank numerous colleagues who have contributed evaporite and barite samples over the years, including W. T. Holser, M. Tucker, C. Spötl, R. Denison, C. Laughrey, S. C. Morris, S. P. Das Gupta, K. Benison, B.-H. Fu, S. Xiao, G. Retallack, W.-L. Zang, J. Hanor, B. Ellwood, D. Henry, B. Dutrow and A. J. Kaufman. One important barite sample, collected by G. P. Halverson, P. F. Hoffman and A. C. Maloof in Mauritania, West Africa, was obtained from M. H. Thiemens and D. P. Schrag. We thank Huifeng Bao for field assistance, M. Khachaturyan for laboratory assistance, and NSF, LSU, NASA (Planetary Atmospheres), the NNSF of China, the Chinese Academy of Sciences and the Chinese Ministry of Science and Technology for financial support.

**Author Contributions** H.B. designed the research, developed analytical procedures and performed measurements. J.R.L. did one-dimensional photochemical modelling and C.M.Z. directed fieldwork in South China. H.B. and J.R.L. wrote the manuscript.

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