

LETTERS

Triple oxygen isotope evidence for elevated CO₂ 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^{1–4}. 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_{CO_2}) in the past through a photochemical reaction network linking stratospheric ozone to carbon dioxide and to oxygen^{5,6}. Our results suggest that p_{CO_2} was much higher in the early Cambrian than in younger eras, agreeing with previous modelling results². We also find that the ¹⁷O isotope anomalies of barites from Marinoan (~635 million years ago) cap carbonates display a distinct negative spike (around -0.70‰), suggesting that by the time barite was precipitating in the immediate aftermath of a Neoproterozoic global glaciation, the p_{CO_2} was at its highest level in the past 750 million years. Our finding is consistent with the ‘snowball Earth’ hypothesis^{7,8} and/or a massive methane release⁹ after the Marinoan glaciation.

Since the discovery of widespread sulphate ¹⁷O anomalies in Earth’s continental deposits¹⁰, a considerable amount of triple oxygen isotope data has been gathered for sulphate of diverse origins^{11–14}. Without exception, the ¹⁷O 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 ¹⁸O/¹⁶O or ¹⁷O/¹⁶O (Supplementary Information 1–5). A positive anomaly indicates enrichment in ¹⁷O 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 (O₃) during oxidation of sulphur compounds in the atmosphere¹⁵. Overall, the $\Delta^{17}\text{O}$ for terrestrial sulphate reaches as high as +5.84‰¹¹.

Here we report variable negative ¹⁷O anomalies among sulphate deposited on Earth surfaces over the past 750 million years (Fig. 1). Despite their small magnitudes, the negative ¹⁷O anomalies are larger than the analytical error of $\pm 0.05\text{‰}$ and are reproducible. They were first noticed in an earlier survey of evaporite sulphate that had no direct link to atmospheric O₃ chemistry¹⁶. An expanded survey revealed that marine evaporites and barites have $\Delta^{17}\text{O}$ values ranging from +0.02 to -0.70‰. Values more negative than -0.20‰ 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‰) and in South China (down to -0.70‰) (Supplementary Information 1).

We propose that the triple oxygen isotope compositions of sulphate carry a portion of the tropospheric O₂ signal, which has had variable negative $\Delta^{17}\text{O}$ values that are determined largely by stratospheric O₃–CO₂–O₂ chemistry, and consequently the p_{CO_2} , in the past (Fig. 2). We describe the connection between p_{CO_2} and sulphate $\Delta^{17}\text{O}$ in three steps.

First, sulphate derived from oxidative weathering carries an atmospheric O₂ signal. Sulphate oxygen ultimately comes from water and oxidants such as O₃, H₂O₂ or atmospheric O₂. When atmospheric O₃ or H₂O₂ is the oxidant, the product sulphate bears a positive $\Delta^{17}\text{O}$ value^{10,15}. 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 O₂ signal¹⁷. More recent laboratory experiments show that 8 to 15% of the oxygen in product sulphate came from O₂ when O₂ is involved in pyrite oxidation¹⁸.

Second, modern atmospheric O₂ is known to have a small negative ¹⁷O anomaly, as first suggested by Bender *et al.*¹⁹ and later documented by terrarium experiments²⁰. The key chemical processes that bring a negative ¹⁷O anomaly to atmospheric O₂ are the reactions of O₃–CO₂–O₂ in the stratosphere^{5,6}. The Chapman reactions produce O₃ that is highly positive in both its $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values. Photolysis of O₃ yields O (¹D) which transfers the oxygen isotope

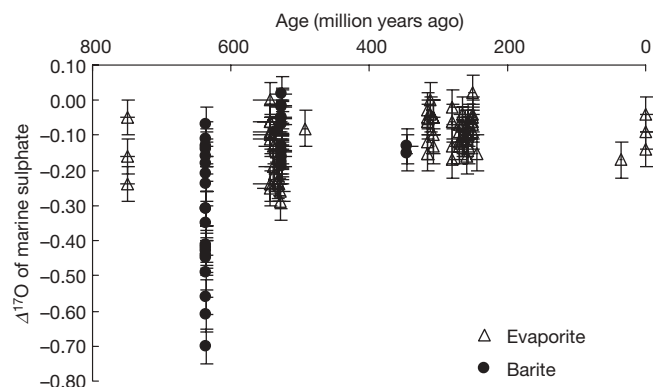


Figure 1 | The $\Delta^{17}\text{O}$ of evaporite and barite sulphate over the past 750 million years.

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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^{21–23}. Subtracting the effect of a newly calibrated slope²³ that is slightly different from the defined slope of 0.52, we calculated that tropospheric O_2 has $\sim 83\%$ 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^{5,6,24}, 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 weathering²⁰. In the current atmosphere, the O_2 flux from photosynthesis or respiration/weathering is only 1/300 of that from troposphere–stratosphere exchange²⁰. 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.*²⁰. 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^{20,24}. 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

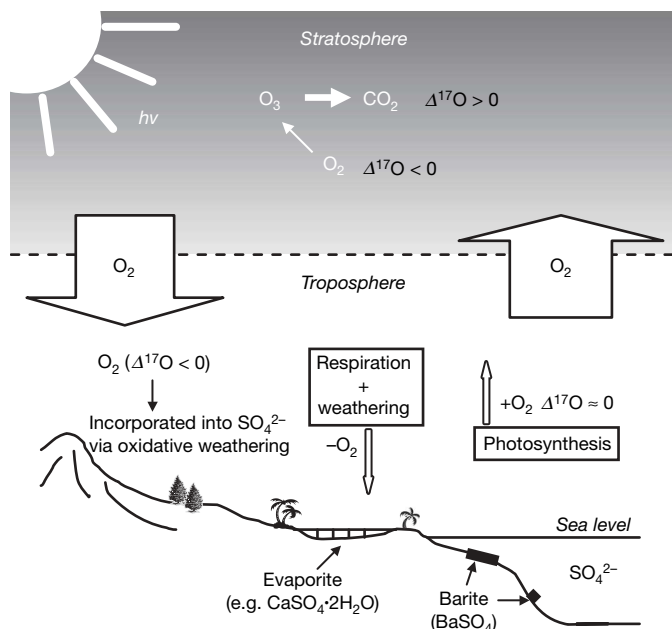


Figure 2 | How evaporite or barite sulphate records the negative ^{17}O anomaly of tropospheric O_2 that originated in the stratosphere. The O_2 – O_3 – CO_2 reaction network refers to those depicted in Supplementary Information 6, Supplementary Fig. 2. Sizes of the solid white arrows indicate relative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

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 environments²⁵. 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 Phanerozoic², 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 China²⁶ 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 estimate¹⁸, 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 $\sim 4,200$ p.p.m. in the early Cambrian and $\sim 12,000$ 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 $\sim 12,000$ p.p.m. p_{CO_2} may be a snapshot of a dynamic transition of atmospheric conditions immediately after the deglaciation²⁷. 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

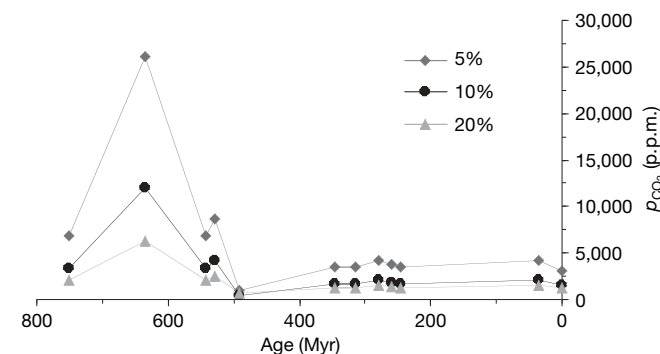


Figure 3 | Model-calculated partial pressures of CO_2 based on the lowest sulphate $\Delta^{17}O$ value for a given period in geological history. The diamonds, circles and triangles are for O_2 signatures of 5, 10 and 20 mol% in sulphate oxygen, respectively.

volcanic CO₂ 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^{7,8}. 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} level⁹. Whatever the cause, consistently more negative $\Delta^{17}\text{O}$ 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 CO₂ drawdown. The level of p_{CO_2} and the rate of CO₂ 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 O₂ being incorporated in marine sulphate.

Sulphate's negative $\Delta^{17}\text{O}$ value is so far the only known mineral-isotope proxy that directly records the ¹⁷O anomaly of past atmospheric O₂. Although the sulphate $\Delta^{17}\text{O}$ 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 CO₂ or O₂ that have occurred throughout the Earth's history.

METHODS SUMMARY

Sulphate was extracted from evaporites using Millipore water (18 M Ω) and 1 M HCl, and precipitated as barite (BaSO₄). Pure BaSO₄ was obtained from sedimentary barite via a modified DTPA (diethylenetriaminepentaacetic acid)-dissolution and re-precipitation (DDARP) method²⁸. We extracted O₂ by using a CO₂-laser fluorination system²⁹ and measured for the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ on a Finnigan MAT 253 in a dual-inlet mode. The average O₂ sample size is ~25 micromoles, and is ~25% to 35% of the total barite oxygen yield. The standard deviation associated with the $\Delta^{17}\text{O}$ is $\pm 0.03\text{‰}$ for multiple ($N \approx 3$) runs of the same O₂ gas on the MAT 253, and $\pm 0.05\text{‰}$ for replicates of the same BaSO₄ via laser-fluorination. The reported $\delta^{18}\text{O}$ was +9.4‰ (a kinetic effect) plus the raw value obtained from the laser-fluorination method. The error is $\pm 0.7\text{‰}$ for pure and fine-grained barite samples. Some $\delta^{18}\text{O}$ values were obtained from the temperature-conversion elemental analyser with errors within $\pm 0.5\text{‰}$. No effort is made to distinguish them because an accurate $\delta^{18}\text{O}$ value is not important to this study and errors in the $\delta^{18}\text{O}$ and the $\delta^{17}\text{O}$ cancel out during the $\Delta^{17}\text{O}$ calculation. The sample was run only when the $\Delta^{17}\text{O}$ zero enrichment was checked to be less than $\pm 0.05\text{‰}$. We have found that N₂ contamination can result in an erroneous, negative, but small $\Delta^{17}\text{O}$ value when N₂/O₂ is >2% in our MAT 253. Most of our samples have N₂/O₂ < 0.3% and none of the reported data had N₂/O₂ > 1%.

In our one-dimensional photochemical model, temperature-dependent isotopomer-specific rate coefficients for O₃ formation³⁰ are used. Solar ultraviolet flux, vertical eddy mixing, temperature profiles, and atmospheric composition other than CO₂ are assumed to be unchanged relative to the present-day atmosphere. An O₂ atmospheric residence time of 1,200 yr³⁰ is used for all cases.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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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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