Oxygen has three naturally occurring isotopes, of mass numbers 16, 17 and 18. Their ratio in atmospheric O₂ depends primarily on the isotopic composition of photosynthetically produced O₂ from terrestrial and aquatic plants⁴–⁶, and on isotopic fractionation due to respiration⁷. These processes fractionate isotopes in a mass-dependent way, such that ¹⁷O enrichment would be approximately half of the ¹⁸O enrichment relative to ¹⁶O. But some photochemical reactions in the stratosphere give rise to a mass-independent isotope fractionation, producing approximately equal ¹⁷O and ¹⁸O enrichments in stratospheric ozone⁵ and carbon dioxide⁶, and consequently driving an atmospheric O₂ isotope anomaly. Here we present an experimentally based estimate of the size of the ¹⁷O/¹⁸O anomaly in tropospheric O₂, and argue that it largely reflects the influences of biospheric cycling and stratospheric photochemical processes. We propose that because the biosphere removes the isotopically anomalous stratospheric-derived O₂ by respiration, and replaces it with isotopically ‘normal’ oxygen by biological cycling, the magnitude of the tropospheric ¹⁷O anomaly can be used as a tracer of global biospheric productivity. We use measurements of the triple-isotope composition of O₂ trapped in bubbles in polar ice to estimate global biosphere productivity at various times over the past 82,000 years. In a second application, we use the isotopic signature of oxygen dissolved in aquatic systems to estimate gross primary production on broad time and space scales.

The magnitude of the ¹⁷O anomaly in the present atmosphere can be estimated by comparing δ¹⁷O and δ¹⁸O of ambient air O₂ (represented by the HLA standard; see Methods) with O₂ that was not affected by stratospheric processes. To make the latter, we built two airtight terrariums in which O₂ was consumed and replaced biologically. Ultraviolet radiation that could lead to mass-independent fractionation was absent. The terrariums contained Philodendron plants, soil and natural water. In both terrariums, O₂ production and consumption occurred via the higher plants as well as via bacteria and algae. Illumination was changed during the experiment with the aim of varying the ratio of photosynthesis to respiration, thereby inducing a wide range of δ¹⁷O and δ¹⁸O values.

After several turnovers, anomalous ambient air O₂ had been removed by respiration and replaced with normally fractionated O₂, and steady state was attained. Subsequent illumination changes significantly affected O₂ concentration (measured as δO₂/Ar; see Methods) and δ¹⁷O but not the ¹⁷O anomaly (Fig. 1). The δ¹⁷O versus δ¹⁸O trend for data points for which the anomaly was at steady state plot on a nearly perfect straight line (R² = 0.99999) with a slope of 0.5211 (±0.0005), as expected for mass-dependent fractionation⁴ (data not shown). The intercept of the regression line is 0.155 ± 0.008‰ or 155 ± 8 in units of per meg (see Methods). Based on this analysis, we defined the Δ¹⁷O anomaly as the deviation from normal mass-dependent fractionation (Δ¹⁷O = δ¹⁷O - 0.521δ¹⁸O); in the case of the terrarium experiment, Δ¹⁷O is equal to the intercept value of the regression line. HLA was the preferred standard for high-precision measurements in our study. However, as a reference for Δ¹⁷O it is admittedly confusing, because it has anomalous isotopic composition. An air sample with no photosynthetic O₂ added will have a Δ¹⁷O = 0 with respect to HLA, and a sample of biologically equilibrated O₂ will have a Δ¹⁷O = +155 per meg with respect to HLA. In this treatment, ocean and meteoric waters are defined as normal with Δ¹⁷O = 155 per meg. A comparison of the isotopic composition of ocean water (represented by V-SMOW) to air O₂ (δ¹⁷O = -22.960‰ and δ¹⁸O = -11.778‰), supports our conclusions that air bears a mass-independent signature. The Δ¹⁷O of V-SMOW is calculated as 184 per meg [Δ¹⁷O = (-11.778 - 0.521 × 22.961)1000]. In this calculation, the derived anomaly is very sensitive to the slope term (0.521), and thus the small difference between 184 and 155 per meg may not be significant.

Importantly, the terrarium experiment cannot represent all Earth-surface processes affecting Δ¹⁷O. For example, the range of isotopic variations in global meteoric waters is much greater than in

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References
the experiment, and a recent study\(^\text{a}\) indicates that in these waters the \(\delta^{17}\text{O}/\delta^{18}\text{O}\) slope is slightly different than in respiration. Furthermore, the humidity in the terrariums was at saturation and important isotope fractionation due to evapo-transpiration from leaves\(^\text{b}\) was not reflected in our experiment. In addition, the \(\delta^{17}\text{O}/\delta^{18}\text{O}\) slopes in the various processes consuming oxygen (dark respiration, cyanide resistant respiration, photorespiration and the Mehler reaction) may vary slightly from 0.521. Because the relative rates of these processes in our experiment are not expected to be the same as in the global biosphere, the intercept of the regression line in natural systems may differ from the value we measured. Thus, while the 155 per meg estimate clearly demonstrates the anomalous isotopic signature of atmospheric O\(_2\), further study is needed in order to better constrain the magnitude of the anomaly.

Our experimental determination of the mass-independent anomaly in O\(_2\) can be compared with estimates of its stratospheric production. Bender \textit{et al.}\(^\text{a}\) first suggested that photochemical mass-independent fractionation processes in the stratosphere involving ozone and CO\(_2\) species could result in anomalous O\(_2\). In the stratosphere, the ozone recombination reaction, \(O + O_2 \rightarrow O_3\), causes O\(_3\) to be mass-independently fractionated. The anomalous fractionation is well documented, although its cause is debated\(^\text{11-13}\). Theory\(^\text{14}\) and laboratory experiments\(^\text{15}\) suggest that the anomalous ozone enrichment is transferred to CO\(_2\). Ultraviolet photolysis of ozone in the stratosphere generates an electronically excited oxygen atom which can undergo isotope exchange with CO\(_2\):

\[
O_3 + h\nu \rightarrow O(1D) + O_2
\]

\[
O(1D) + CO_2 \rightarrow CO_2^* + O(3P)
\]

Thus, because the ultimate source of the oxygen in O\(_3\) and O(1D) in the stratosphere is the O\(_2\) reservoir, O\(_2\) becomes anomalously depleted as CO\(_2\) becomes anomalously enriched. We note that there is no stratospheric loss term for the enrichment in CO\(_2\), and the net stratospheric enrichments are lost only at the Earth’s surface by isotope exchange with liquid water in leaves and in the oceans\(^\text{14,16}\) (Fig. 2). In contrast, O\(_2\) does not exchange isotopes with water\(^\text{17}\), and the depletion disappears only through the consumption of O\(_2\) by respiration and its replacement by photosynthesis. The respiratory and photosynthetic fluxes are relatively small (Fig. 2) compared with the stratospheric production, and thus the \(\Delta^{17}\text{O}\) anomaly accumulates to a measurable level of 155 per meg over the residence time of atmospheric O\(_2\) (~1,200 yr; ref. 10).

To test the hypothesis that stratospheric processes can generate the 155 per meg anomaly in atmospheric O\(_2\), we estimate the production rate of anomalous O\(_2\) from stratospheric photochemistry. We use observations of mass-independently fractionated CO\(_2\) and its correlation with N\(_2\)O (a long-lived tracer that is photolysed in the stratosphere), coupled with calculations of the annual mass flux of air from the stratosphere to the troposphere. We frame the calculations in terms of N\(_2\)O for two reasons. First, observations of \(\Delta^{17}\text{O}\) of CO\(_2\) (\(\Delta^{17}\text{O}_{\text{CO}_2}\)) are extremely sparse, so their tight correlation with N\(_2\)O—a species that has been extensively measured in the stratosphere—serves as a proxy for the distribution of \(\Delta^{17}\text{O}_{\text{CO}_2}\) in the stratosphere. Second, we can use knowledge of either the stratospheric loss rate for N\(_2\)O (ref. 18) or the age of stratospheric air as a function of N\(_2\)O (ref. 19) in order to calculate the N\(_2\)O mixing ratio, and therefore \(\Delta^{17}\text{O}_{\text{CO}_2}\), in air returning to the troposphere. Table 1 shows annual production rates of \(\Delta^{17}\text{O}_{\text{CO}_2}\) estimated from two different mass-flux calculations\(^\text{20,21}\), coupled with the two means of estimating N\(_2\)O returning to the troposphere. In order to estimate the anomalous O\(_2\) transferred to the troposphere each year, we assume that stratospheric CO\(_2\) is the only species that can sequester a mass-independent enrichment that leaves the O\(_2\) reservoir anomalously depleted. We also assume that photochemical transfer of the mass-independent fractionation from O\(_3\) to CO\(_2\) via O(1D) scales with both CO\(_2\) and O\(_3\) abundances. Because the O\(_2\) anomaly accumulates over 1,200 years, knowledge of CO\(_2\) and O\(_2\) levels back to pre-industrial times are required. While CO\(_2\) levels are well constrained from ice-core data, we must rely on photochemical—dynamical atmospheric models for pre-industrial ozone levels. Crutzen and Brühl\(^\text{22}\) and Martiniere \textit{et al.}\(^\text{23}\) predict pre-industrial stratospheric ozone levels greater than the present-day atmospheric ozone by up to 30–40% over significant regions of the stratosphere. The annual production rate (P) of anomalous O\(_2\) (\(\Delta^{17}\text{O}_{\text{O}_2}\)) is then calculated from:

\[
P[\Delta^{17}\text{O}_{\text{O}_2}] \text{(per meg yr}^{-1}\text{)} = -fP[\Delta^{17}\text{O}_{\text{CO}_2}] \text{(per meg yr}^{-1}\text{)} \quad (1)
\]

The factor \(f\) allows scaling for the pre-industrial ratio of CO\(_2/O_2\) (280/210,000), for the increase of CO\(_2\) to its present level (358 p.p.m.) and for a ~30% decrease in O\(_3\) since pre-industrial times. Thus, \(f = (280/210,000)(280/358)\). The estimated 1,200-

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**Figure 2** Simplified O\(_2\), CO\(_2\) and \(\Delta^{17}\text{O}\) cycle. The values of \(\Delta^{17}\text{O}_{\text{O}_2}\) and \(\Delta^{17}\text{O}_{\text{CO}_2}\) (in units of per meg with respect to HLA) are indicated for the stratosphere and the troposphere. The fluxes shown are in units of \(10^{15} \text{mol yr}^{-1}\) and the values in parenthesis are \(\Delta^{17}\text{O}_{\text{O}_2}\) and \(\Delta^{17}\text{O}_{\text{CO}_2}\). The tropospheric value of \(\Delta^{17}\text{O}_{\text{CO}_2}\) is taken as equal to \(\Delta^{17}\text{O}\) of ocean and leaf water (155 per meg, see text). Note that the net positive anomaly flux in CO\(_2\) (1280 ± 0.408 – 155 ± 0.408) from stratosphere to the troposphere is of the same absolute magnitude as the negative anomaly flux in O\(_2\) (–1.50 ± 306). This negative anomaly flux from the stratosphere is balanced by the positive anomaly flux in O\(_2\) from the biosphere (155 ± 2.97).
year accumulation of anomalous O₂ from stratospheric photochemical fractionation from these production rates ranges from 104 to 131 per meg (Table 1), consistent with the measured anomaly of 155 per meg. Carrying the known uncertainties through these calculations yields an error estimate of ±25%, and the true uncertainty may be higher given our present state of knowledge of mass-independent fractionation processes in the stratosphere and of rates of stratosphere–troposphere exchange over the past 1,200 years.

Additional confirmation of the stratospheric origin of the atmospheric anomaly comes from isotope mass balance in the troposphere (Fig. 2). Anomalous CO₂ with excess ¹⁷O enters the troposphere and brings a net anomaly flux ([(1.280 × 0.408 – 155 × 0.408)] × 10¹⁶ per meg mol yr⁻¹). A parallel negative anomaly flux of the same absolute magnitude is carried by O₂ (–1.5 × 306 × 10¹⁶ per meg mol yr⁻¹). The anomaly in the CO₂ flux is removed by hydration–dehydration reaction with water, and the negative flux in O₂ is balanced by a positive anomaly flux from the biosphere (155 × 2.97 × 10¹⁶ per meg mol yr⁻¹). The value of Δ¹⁷O₂O₂ in air returning from the stratosphere was calculated as 1.280 per meg (–Δ¹⁷O₂O₂/f + 155, with f as in equation (1)). This estimate is in good agreement with the corresponding values in Table 1. Thus, the two independent mass-balance calculations strongly suggest that the magnitude of the atmospheric Δ¹⁷O₂ anomaly reflects the ratio between two important global processes—biospheric O₂ production and stratospheric photochemistry involving O₂, O₃, and CO₂.

In an attempt to learn about past variations in global biosphere production, we have analysed isotope-core samples from Summit, Greenland (GISP2 ice core, Table 2). Here we make a preliminary and provisional interpretation of the results using the following equation:

$$\Delta^{17}O_{O_2} = k(CO_2)/P$$ (2)

where \(\Delta^{17}O_{O_2} = \Delta^{17}O_{O_2} - 155\) per meg, \([CO_2]\) is the atmospheric CO₂ concentration, \(k\) is a proportionality constant relating the rate of anomalous O₂ production to \([CO_2]\), and \(P\) is gross production by the global biosphere. In writing this equation, we assume that the production rate of anomalously depleted O₂ in the stratosphere is proportional to the CO₂ mixing ratio, and that \(k\) is constant between glacial and interglacial times. Of course, \(k\) enforces contributions from both the stratospheric circulation and isotope photochemistry involving ultraviolet flux, O₃ and CO₂, and there are significant uncertainties in predicting these aspects of past atmospheres. Crutzen and Brühl22 and Martiniere et al.23 predict that perturbations to stratospheric ozone from changes in temperature and chemistry (for example, due to changes in \([N_2O]\) and \([CH_4]\)) between the pre-industrial interglacial and glacial times largely cancel, with modelled ozone changes at all stratospheric altitudes of 10% or less. Changes in the stratospheric circulation due to dynamical feedbacks as climate has changed appear to be more uncertain24. However, it is not unreasonable to expect that the effect of changes in the circulation on the global \(k\) could largely cancel out. If the circulation slowed down, the Δ¹⁷O₂ anomalies of air returning from the stratosphere would be larger but with a smaller mass flux, whereas if the circulation strengthened, the anomalies would be smaller but with a larger mass flux into the troposphere. More complicated chemical/dynamical/biological ozone feedbacks might also have occurred; these include changes in tropopause height which might alter stratospheric water vapour, or changes in the ocean biospheric production of OCS which is oxidized to sulphuric acid in the stratosphere, producing aerosol. Until further modelling studies of stratospheric chemistry and dynamics in past atmospheres are made, we assume that \(k\) is constant. We then calculate ‘normalized gross biosphere production’, \(P/P_m\), as follows, where the subscript \(t\) denotes time before present and subscript 0 denotes present:

$$P/P_m = k/k_0([CO_2]/[CO_2]_0) \times (\Delta^{17}O_{O_2}/\Delta^{17}O_{O_2})$$ (3)

Table 1 Calculation of the Δ¹⁷O of atmospheric O₂

<table>
<thead>
<tr>
<th>Mass flux of air from the stratosphere (10¹⁷ kg yr⁻¹)</th>
<th>Stratospheric turnover time (yr)</th>
<th>[N₂O] returning to troposphere (p.p.b.v.)</th>
<th>Δ¹⁷O_CO₂ (per meg)</th>
<th>P(Δ¹⁷O_CO₂) (per meg yr⁻¹)</th>
<th>P(Δ¹⁷O_O₂) (per meg yr⁻¹)</th>
<th>Estimated 1200-yr accumulation of Δ¹⁷O_O₂ (per meg)††</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0†‡</td>
<td>-</td>
<td>2461</td>
<td>1550</td>
<td>67⁰</td>
<td>-0.091</td>
<td>-109</td>
</tr>
<tr>
<td>6.4‡</td>
<td>-</td>
<td>2921</td>
<td>530</td>
<td>80⁰</td>
<td>-0.09</td>
<td>-131</td>
</tr>
<tr>
<td>-</td>
<td>2.64</td>
<td>250†‡</td>
<td>1460</td>
<td>63⁰</td>
<td>-0.086</td>
<td>-104</td>
</tr>
<tr>
<td>-</td>
<td>1.06</td>
<td>294†‡</td>
<td>500</td>
<td>76⁰</td>
<td>-0.103</td>
<td>-124</td>
</tr>
</tbody>
</table>

* Mass flux across the 100-mbar surface (based on ref. 20).
† Mass flux across the 380-K potential-temperature surface (based on ref. 21).
‡ Stratosphere defined as mass of atmosphere above 100 mb (5.2 x 10¹⁷ kg), based on ref. 20.
§ Stratosphere defined as mass of atmosphere above 380 K (6.8 x 10¹⁷ kg), based on ref. 21.
¶ Calculated using an N₂O loss rate of 12.5 Mt N yr⁻¹ and a growth rate of 0.3 M N yr⁻¹ (ref. 18), and mass fluxes of air into and out of the stratosphere in column 1: flux out = flux in – loss rate – growth rate.
¶ [N₂O] for stratospheric air with a mean age equivalent to the turnover time in column 2, derived from simultaneous observations of stratospheric CO₂ and N₂O mixing ratios⁶. Excluding extrapolations from observations⁴ of the correlation of Δ¹⁷O_O₂ with N₂O mixing ratios (or CH₄ and the relation between stratospheric CH₄ and N₂O) to the values of N₂O in column 3.
** Annual production rate of Δ¹⁷O_CO₂ in the troposphere by transport from the stratosphere, including dilution factors (mass flux from stratosphere/mass of the troposphere) of 0.043 and 0.152, respectively, for the mass fluxes in column 1.
†† Annual production rate of Δ¹⁷O_CO₂ in the troposphere by transport from the stratosphere given by Δ¹⁷O_CO₂ in column 4 divided by the turnover time and including a dilution factor (annually averaged mass of the atmosphere above 100 mb or 380 K/mass of the atmosphere below) of 0.13 and 0.152, respectively.
† Note that using a more realistic mixing CO₂ time series over the past 1,200 years, and integrating CO₂ rather than using a constant f in equation (1), alters these estimates by <2%. Note also that a value of 1.3 was used (included in f) to scale [O₂] back to pre-industrial times, a number that may represent an upper limit based on model predictions in ref. 23 for which changes in this magnitude were predicted above 28 km and below 26 km.

Table 2 Isotope data and normalized productivity in the GISP2 ice core

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Gas age (kyr)</th>
<th>Climate</th>
<th>δ¹⁵N (%)</th>
<th>δ¹⁷O (%)</th>
<th>δ¹⁷O (per meg)</th>
<th>[CO₂] (p.p.m.v.)†</th>
<th>P/P_m‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,007</td>
<td>18.67</td>
<td>Interglacial</td>
<td>0.41</td>
<td>1.050</td>
<td>0.584</td>
<td>37</td>
<td>190</td>
</tr>
<tr>
<td>2,059</td>
<td>25.78</td>
<td>Glacial</td>
<td>0.38</td>
<td>0.822</td>
<td>0.467</td>
<td>39</td>
<td>190</td>
</tr>
<tr>
<td>2,212</td>
<td>36.67</td>
<td>Interstadial</td>
<td>0.39</td>
<td>0.413</td>
<td>0.236</td>
<td>21</td>
<td>210</td>
</tr>
<tr>
<td>2,492</td>
<td>56.17</td>
<td>Interstadial</td>
<td>0.42</td>
<td>0.365</td>
<td>0.226</td>
<td>35</td>
<td>210</td>
</tr>
<tr>
<td>2,668</td>
<td>82.03</td>
<td>Interglacial</td>
<td>0.32</td>
<td>0.236</td>
<td>0.135</td>
<td>12</td>
<td>235</td>
</tr>
</tbody>
</table>

* The oxygen isotope data shown were corrected for gravitational fractionation by subtraction of the δ¹⁷O value from the measured δ¹⁷O and by subtraction of 2(δ¹⁷O) from the measured δ¹⁷O.† From ref. 28.
‡ Normalized productivity.
Normalized gross-production values, calculated for 5 times during the past 82 kyr, range from 0.87 to 0.97, not greatly different from the values today. Meyer25 estimated that net gross-production, which today accounts for ~40% of global photosynthesis, would then have been slightly higher than today’s value.

In a similar way to the application of δ17O as a tracer of global biospheric production, δ18O of dissolved O2 (δ18O\textsubscript{dis}O\textsubscript{2}) can be used for inferring the rate of O2 production by aquatic organisms. The δ17O\textsubscript{dis}O\textsubscript{2} in the photic zone of oceans and lakes depends on the relative rates of air–water gas exchange (which is strongly modulated by the stratospheric anomaly) to dissolved O2 and biological-O2 cycling (which removes this anomaly). Our measurements of δ18O\textsubscript{dis}O\textsubscript{2} over a range of biological productivity demonstrate this point. In the Dead Sea, where at present photosynthesis is zero, δ18O\textsubscript{dis}O\textsubscript{2} with respect to HLA is ~7 per mil. This value, as expected, is identical within the analytical error to atmospheric O2. In the Red Sea (Station A near Eilat, 10 m depth, May 1998), δ18O\textsubscript{dis}O\textsubscript{2} was 51 per mil, indicating moderate production. In the highly productive Sea of Galilee (3 m depth; February–April 1998), δ18O\textsubscript{dis}O\textsubscript{2} values ranged from 114 to 136 per mil and clearly demonstrate the effect of rapid biological production. Infinitely rapid production would completely eliminate the anomaly, and δ18O\textsubscript{dis}O\textsubscript{2} would equal δ18O of H2O (taken as 155 per mil).

At the time of our sampling in the Sea of Galilee, the rate of air–lake gas exchange was about 0.15 mol m\textsuperscript{-2} d\textsuperscript{-1} (based on the dependence of gas exchange in lakes on wind speed26). In April 1998, δ18O\textsubscript{dis}O\textsubscript{2} was 136 per mil and the lake thus lost 136 × 0.15 per mil mol d\textsuperscript{-1} to the atmosphere. Assuming for simplicity that the lake was at steady state, this loss was balanced by gross production (P) anomaly flux of 155P per mil mol d\textsuperscript{-1}, and P can be calculated as 0.13 mol d\textsuperscript{-1} (136/155 × 0.15). This example shows that if the rate of air–water gas exchange is known, δ18O\textsubscript{dis}O\textsubscript{2} can be used to constrain gross production. Constraining production in this way has the advantage that it reflects a spatially and temporally integrated value, and can be easily applied over wide regions in lakes and seas.

### Methods

In the terrarium experiment, water was introduced to the bottom of the chambers through tubing connected to an outside reservoir made of flexible Teflar in order to compensate for gas gains and losses and to keep constant ambient pressure. The light sources were fluorescent lamps (about 100 μE m\textsuperscript{-2} s\textsuperscript{-1} with negligible ultraviolet flux). Terrarium PK contained water from the Sea of Galilee (δ18O = −0.5‰ vs V-SMOW), and terrarium PDS contained Dan River water (δ18O = −6.6‰ vs V-SMOW). About 1.5 ml of dissolved gases were extracted from water samples, and about 3 ml air were extracted from ice-core samples. Most mass spectrometric analyses were carried out at the Hebrew University of Jerusalem. Dried and CO\textsubscript{2}-free air was passed with a high purity He carrier (30 ml min\textsuperscript{-1}) through a chromatographic column (5 m × 2 mm inside diameter stainless-steel tube packed with 45/60 mesh 5Å molecular sieve and held at 0°C). O2 and Ar eluted completely in 15 min, and were collected by passing the carrier gas through a trap containing coarse 5Å molecular sieve held at −196°C. The remaining He carrier was pumped out, the purified O2 and Ar were transferred to stainless-steel tubes7 and admitted to a multi-collector mass spectrometer (Finnigan Delta-Plus). The δ18O and δ15N of O2 and δ17O\textsubscript{dis}O\textsubscript{2}/Ar were measured against a reference O2/Ar mixture that was calibrated against air standard HLA. This standard was prepared by cryogenic drying (−80°C) of 4 litres of outside air and is stored in a stainless-steel container. Because atmospheric mixing is rapid compared to the processes altering its isotopic composition, HLA is representative of all atmospheric oxygen. In all analyses samples in duplicate. Corrections were applied in order to account for the sensitivity of ionization efficiencies of the three isotopic species of oxygen to variations in the O2/Ar ratio. Isotopic and O2/Ar ratios are given as: δ18O/Ar(‰) = (δ18O/Ar\textsubscript{sample})/(δ18O/Ar\textsubscript{air}) − 110×; δ15N(‰) = (δ15N/Ar\textsubscript{sample})/(δ15N/Ar\textsubscript{air}) − 110× where δO denotes 18O or 16O; and δ15N(per meg) = (δ15N - 0.5218‰)×10\textsuperscript{-3}. The analytical precision (standard error) of δ18O, δ15N and δ17O measurements were 0.003‰, 0.009‰ and 9 per meg, respectively. For the purpose of cross calibration, standards and duplicates of ice-core samples were run also at UCSD. The average inter-laboratory differences for δ18O, δ15N and δ17O were 0.044‰, 0.029‰ and 7 per meg, respectively.