J. Chem. Phys. **108**, 5888–5897 (1998).

26. MacGorman, D. R. & Rust, W. D. *The Electrical Nature of Storms* 32 (Oxford Univ. Press, New York, 1998).
27. Pruppacher, H. R. & Klett, J. D. *Microphysics of Clouds and Precipitation* 813–814 (Kluwer Academic, Dordrecht, 1996).
28. Di Palma, T. M., Latini, A., Satta, M. & Giardini Guidoni, A. Molecular beam studies of ammonia clustered with metals produced by pulsed laser reactive ablation. *Int. J. Mass Spectrom.* **179/180**, 319–326 (1998).

Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity

Boaz Luz*, Eugeni Barkan*, Michael L. Bender†, Mark H. Thiemens‡ & Kristie A. Boering§

* *The Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
† *Department of Geosciences, Princeton University, Princeton, New Jersey 08544, USA*
‡ *Department of Chemistry, University of California, San Diego, La Jolla, California 92093, USA*
§ *Departments of Chemistry and of Geology and Geophysics, University of California, Berkeley, California 94720-1460, USA*

....

Oxygen has three naturally occurring isotopes, of mass numbers 16, 17 and 18. Their ratio in atmospheric O_2 depends primarily on the isotopic composition of photosynthetically produced O_2 from terrestrial and aquatic plants[1–3], and on isotopic fractionation due to respiration[4]. These processes fractionate isotopes in a mass-dependent way, such that ^{17}O enrichment would be approximately half of the ^{18}O enrichment relative to ^{16}O. But some photochemical reactions in the stratosphere give rise to a mass-independent isotope fractionation, producing approximately equal ^{17}O and ^{18}O enrichments in stratospheric ozone[5] and carbon dioxide[6,7], and consequently driving an atmospheric O_2 isotope anomaly. Here we present an experimentally based estimate of the size of the $^{17}O/^{16}O$ anomaly in tropospheric O_2, 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 stratosphere-derived O_2 by respiration, and replaces it with isotopically 'normal' oxygen by photosynthesis, the magnitude of the tropospheric ^{17}O anomaly can be used as a tracer of global biosphere production. We use measurements of the triple-isotope composition of O_2 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 ^{17}O anomaly in the present atmosphere can be estimated by comparing $\delta^{17}O$ and $\delta^{18}O$ of ambient air O_2 (represented by the HLA standard; see Methods) with O_2 that was not affected by stratospheric processes. To make the latter, we built two airtight terrariums in which O_2 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, O_2 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
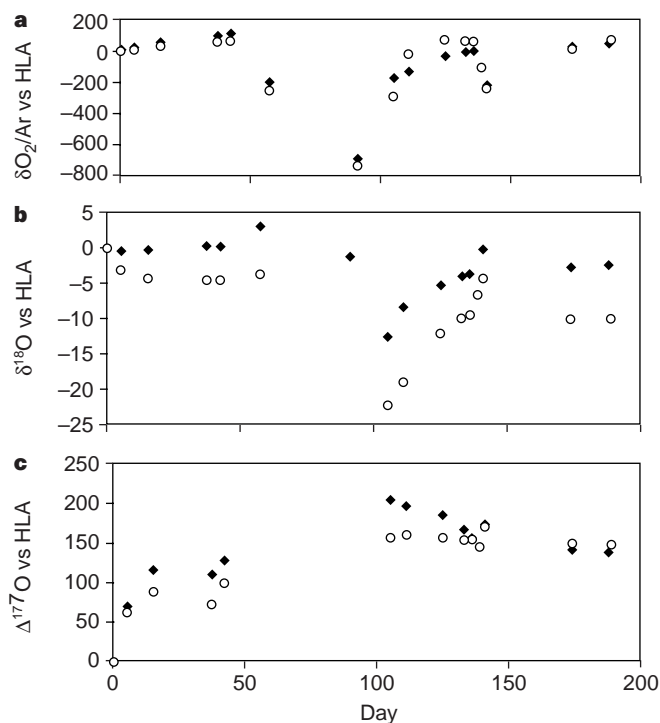
Figure 1 Removal of the atmospheric ^{17}O anomaly by biological cycling. Shown are variations of $\delta O_2/Ar$ (**a**) $\delta^{18}O$ (**b**) and $\Delta^{17}O$ (**c**) in the terrarium experiment. Data points: diamonds, terrarium PK; circles, terrarium PDS. Horizontal scale: days from the beginning of the experiment. Light: continuous illumination, days 1–42; room light, days 43–90; 10 h light, 14 h dark, days 91–136 and days 142–198; dark, days 137–141.

respiration, thereby inducing a wide range of $\delta^{18}O$ and $\delta^{17}O$ values.

After several turnovers, anomalous ambient air O_2 had been removed by respiration and replaced with normally fractionated O_2, and steady state was attained. Subsequent illumination changes significantly affected O_2 concentration (measured as $\delta O_2/Ar$; see Methods) and $\delta^{18}O$ but not the ^{17}O anomaly (Fig. 1). The $\delta^{18}O$ versus $\delta^{17}O$ trend for data points for which the anomaly was at steady state plot on a nearly perfect straight line ($R^2 = 0.99999$) with a slope of 0.5211 (± 0.0005), as expected for mass-dependent fractionation[8]. 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 $\Delta^{17}O$ anomaly as the deviation from normal mass-dependent fractionation ($\Delta^{17}O = \delta^{17}O - 0.521\delta^{18}O$); in the case of the terrarium experiment, $\Delta^{17}O$ 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 $\Delta^{17}O$ it is admittedly confusing, because it has anomalous isotopic composition. An air sample with no photosynthetic O_2 added will have a $\Delta^{17}O = 0$ with respect to HLA, and a sample of biologically equilibrated O_2 will have a $\Delta^{17}O = +155$ per meg with respect to HLA. In this treatment, ocean and meteoric waters are defined as normal with $\Delta^{17}O = 155$ per meg. A comparison of the isotopic composition of ocean water (represented by V-SMOW) to air O_2 ($\delta^{18}O = -22.960$‰ and $\delta^{17}O = -11.778$‰)[6], supports our conclusions that air bears a mass-independent signature. The $\Delta^{17}O$ of V-SMOW is calculated as 184 per meg [$\Delta^{17}O = (-11.778 - 0.521 \times 22.96) \, 1,000$]. 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 $\Delta^{17}O$. For example, the range of isotopic variations in global meteoric waters is much greater than in

547

the experiment, and a recent study[9] indicates that in these waters the $\delta^{17}O/\delta^{18}O$ 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[2,3] was not reflected in our experiment. In addition, the $\delta^{17}O/\delta^{18}O$ 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 et al.[10] 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[11–13]. Theory[14] and laboratory experiments[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:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + CO_2 \rightarrow CO_3^*$$

$$CO_3^* \rightarrow CO_2 + O(^3P)$$
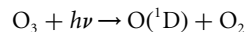
Thus, because the ultimate source of the oxygen in O_3 and $O(^1D)$ in the stratosphere is the O_2 reservoir, O_2 becomes anomalously depleted as CO_2 becomes anomalously enriched. We note that there is no stratospheric loss term for the enrichment in CO_2, and the net stratospheric enrichments are lost only at the Earth's surface by isotope exchange with liquid water in leaves and in the ocean[3,14,16] (Fig. 2). In contrast, O_2 does not exchange isotopes with water[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 $\Delta^{17}O$ 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_2O (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_2O for two reasons. First, observations of $\Delta^{17}O$ of CO_2 ($\Delta^{17}O_{CO_2}$) are extremely sparse, so their tight correlation with N_2O—a species that has been extensively measured in the stratosphere—serves as a proxy for the distribution of $\Delta^{17}O_{CO_2}$ in the stratosphere. Second, we can use knowledge of either the stratospheric loss rate for N_2O (ref. 18) or the age of stratospheric air as a function of N_2O (ref. 19) in order to calculate the N_2O mixing ratio, and therefore $\Delta^{17}O_{CO_2}$, in air returning to the troposphere from the stratosphere. Table 1 shows annual production rates of $\Delta^{17}O_{CO_2}$ estimated from two different mass-flux calculations[20,21] coupled with the two means of estimating N_2O 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_3 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 Bruhl[22] and Martiniere et al.[23] predict pre-industrial stratospheric ozone levels greater than the present-day atmosphere by up to 30–40% over significant regions of the stratosphere. The annual production rate (P) of anomalous O_2 ($\Delta^{17}O_{O_2}$) is then calculated from:

$$P[\Delta^{17}O_{O_2}](\text{per meg yr}^{-1}) = -fP[\Delta^{17}O_{CO_2}](\text{per meg yr}^{-1}) \quad (1)$$

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, $f = (280/210,000)(280/358)1.3$. The estimated 1,200-
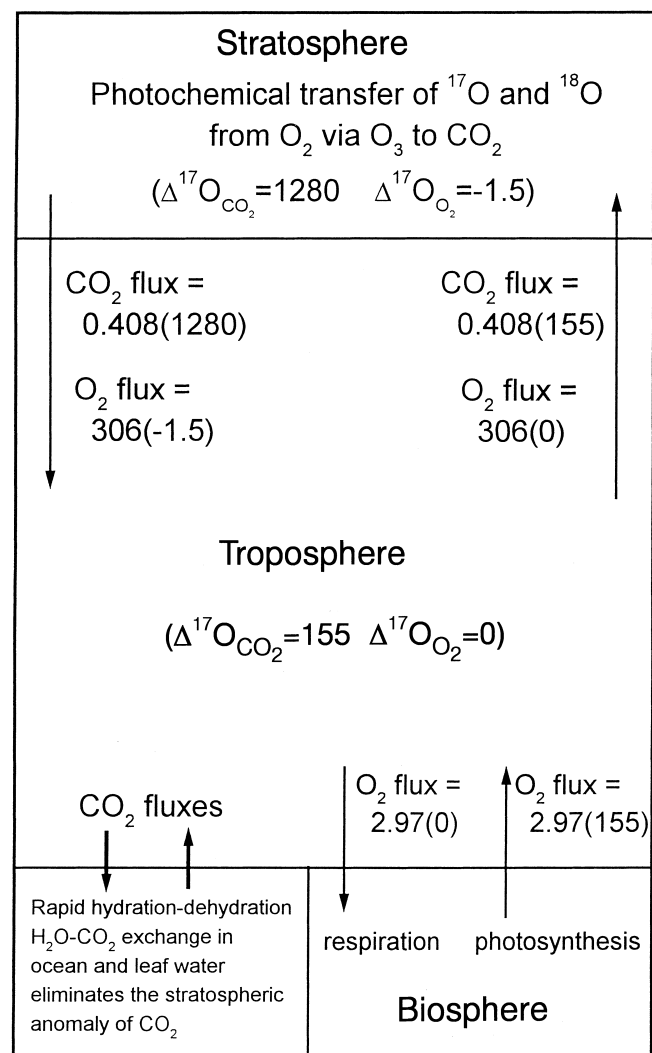
Figure 2 Simplified O_2, CO_2 and $\Delta^{17}O$ cycle. The values of $\Delta^{17}O_{O_2}$ and $\Delta^{17}O_{CO_2}$ (in units of per meg with respect to HLA) are indicated for the stratosphere and the troposphere. The fluxes shown are in units of $10^{16}\,\text{mol yr}^{-1}$ and the values in parenthesis are $\Delta^{17}O_{O_2}$ and $\Delta^{17}O_{CO_2}$. The tropospheric value of $\Delta^{17}O_{CO_2}$ is taken as equal to $\Delta^{17}O$ of ocean and leaf water (155 per meg, see text). Note that the net positive anomaly flux in CO_2 ($1280 \times 0.408 - 155 \times 0.408$) 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).

Figure content:

Stratosphere

Photochemical transfer of ^{17}O and ^{18}O from O_2 via O_3 to CO_2

($\Delta^{17}O_{CO_2}$=1280 $\Delta^{17}O_{O_2}$=-1.5)

CO_2 flux = 0.408(1280) CO_2 flux = 0.408(155)

O_2 flux = 306(-1.5) O_2 flux = 306(0)

Troposphere

($\Delta^{17}O_{CO_2}$=155 $\Delta^{17}O_{O_2}$=0)

CO_2 fluxes O_2 flux = 2.97(0) O_2 flux = 2.97(155)

Rapid hydration-dehydration H_2O-CO_2 exchange in ocean and leaf water eliminates the stratospheric anomaly of CO_2

respiration   photosynthesis

Biosphere

Table 1 Calculation of the $\Delta^{17}O$ of atmospheric O_2

Mass flux of air from the stratosphere (10^{17} kg yr^{-1})	Stratospheric turnover time (yr)	[N$_2$O] returning to troposphere (p.p.b.v.)	$\Delta^{17}O_{CO_2}$ (per meg)#	$P[\Delta^{17}O_{CO_2}]$ (per meg yr^{-1})	$P[\Delta^{17}O_{O_2}]$ (per meg yr^{-1})	Estimated 1,200-yr accumulation of $\Delta^{17}O_{O_2}$ (per meg)††
2.0*	–	246‖	1,550	67☆	−0.091	−109
6.8†	–	292‖	530	80☆	−0.109	−131
–	2.6‡	250¶	1,460	63**	−0.086	−104
–	1.0§	294¶	500	76**	−0.103	−124

* 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 mbar (5.2×10^{17} kg, based on ref. 20).
§ Stratosphere defined as mass of atmosphere above 380 K (6.8×10^{17} kg, based on ref. 21).
‖ Calculated using an N$_2$O loss rate of 12.5 Mt N yr^{-1} and a growth rate of 0.3 Mt 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.
¶ [N$_2$O] for stratospheric air with a mean age equivalent to the turnover time in column 2, derived from simultaneous observations of stratospheric CO$_2$ and N$_2$O mixing ratios[18].
# Extrapolating from observations[6,7,28] of the correlation of $\Delta^{17}O_{CO_2}$ with N$_2$O mixing ratios (or CH$_4$ and the relation between stratospheric CH$_4$ and N$_2$O) to the values of N$_2$O in column 3.
☆ Annual production rate of $\Delta^{17}O_{CO_2}$ in the troposphere by transport from the stratosphere, including dilution factors (mass flux from stratosphere/mass of the troposphere) of 0.043 and 0.153, respectively, for the mass fluxes in column 1.
** Annual production rate of $\Delta^{17}O_{CO_2}$ in the troposphere by transport from the stratosphere given by $\Delta^{17}O_{CO_2}$ in column 4 divided by the turnover time and including a dilution factor (annually averaged mass of the atmosphere above 100 mbar or 380 K/mass of the atmosphere below) of 0.113 and 0.153, respectively.
†† Note that using a more realistic time-varying CO$_2$ time series over the past 1,200 years, and integrating CO$_2$ 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 [O$_3$] 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 35 km and below 25 km.

year accumulation of anomalous O_2 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 CO_2 with excess ^{17}O enters the troposphere and brings a net anomaly flux ([1,280 × 0.408 − 155 × 0.408]10^{16} per meg mol yr^{-1}). A parallel negative anomaly flux of the same absolute magnitude is carried by O_2 ($−1.5 × 306 × 10^{16}$ per meg mol yr^{-1}). The anomaly in the CO_2 flux is removed by hydration–dehydration exchange with water, and the negative flux in O_2 is balanced by a positive anomaly flux from the biosphere ($155 × 2.97 × 10^{16}$ per meg mol yr^{-1}). The value of $\Delta^{17}O_{CO_2}$ in air returning from the stratosphere was calculated as 1,280 per meg ($−\Delta^{17}O_{O_2}/f + 155$, 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 $\Delta^{17}O_{O_2}$ anomaly reflects the ratio between two important global processes—biospheric O_2 production and stratospheric photochemistry involving O_2, O_3 and CO_2.

In an attempt to learn about past variations in global biosphere production, we have analysed ice-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:

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

where $\Delta^{17}O_{O_2}^* = \Delta^{17}O_{O_2} − 155$ per meg, $[CO_2]$ is the atmospheric CO_2 concentration, k is a proportionality constant relating the rate of anomalous O_2 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 O_2 in the stratosphere is proportional to the CO_2 mixing ratio, and that k is constant between glacial and interglacial times. Of course, k enfolds contributions from both the stratospheric circulation and isotope photochemistry involving ultraviolet flux, O_3 and CO_2, and there are significant uncertainties in predicting these aspects of past atmospheres. Crutzen and Bruhl[22] and Martiniere et al.[23] predict that perturbations to stratospheric ozone from changes in temperature and chemistry (for example, due to changes in [N$_2$O] 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 uncertain[24]. 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 $\Delta^{17}O$ 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_t/P_o, as follows, where the subscript t denotes time before present and subscript 0 denotes present:

$$P_t/P_o = k_t/k_o([CO_2]_t/[CO_2]_o) × (\Delta^{17}O_{O_2}^*)_o/(\Delta^{17}O_{O_2}^*)_t \qquad (3)$$

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

Depth (m)	Gas age (kyr)	Climate	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)*	$\delta^{17}O$ (‰)*	$\Delta^{17}O_{O_2}$ (per meg)	[CO$_2$] (p.p.m.v.)†	P_t/P_o‡
	0.15	Interglacial				0	280	1.00
1,907	18.67	Glacial	0.41	1.050	0.584	37	190	0.89
2,039	25.78	Glacial	0.36	0.822	0.467	39	190	0.91
2,212	36.67	Interstadial	0.39	0.413	0.236	21	210	0.87
2,492	56.17	Interstadial	0.42	0.365	0.226	35	210	0.97
2,668	82.03	Interglacial	0.32	0.236	0.135	12	235	0.91

* The oxygen isotope data shown were corrected for gravitational fractionation[27] by subtraction of the $\delta^{15}N$ value from the measured $\delta^{17}O$ and by subtraction of 2($\delta^{15}N$) from the measured $\delta^{18}O$.
† From ref. 29.
‡ 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 present (Table 2). Since terrestrial-biosphere production during glacial times was probably somewhat lower than today (due to glacier-ice advance, colder temperatures, lower p_{CO_2}, and drier climates), ocean productivity was apparently similar to or higher than today. For example, samples from the Last Glacial Maximum have normalized gross production of 0.9. Meyer[25] estimated that net productivity of the land-biosphere was 0.75 times today's. Terrestrial gross production of O_2 may have been a few per cent higher, since photorespiration would have been proportionally faster in response to lower CO_2 (D. Yakir, personal communication). Oceanic 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 $\Delta^{17}O$ as a tracer of global biospheric production, $\Delta^{17}O$ of dissolved O_2 ($\Delta^{17}O_{diss.O_2}$) can be used for inferring the rate of O_2 production by aquatic organisms. The $\Delta^{17}O_{diss.O_2}$ in the photic zone of oceans and lakes depends on the relative rates of air–water gas exchange (which introduces the stratospheric anomaly to dissolved O_2) and biological-O_2 cycling (which removes this anomaly). Our measurements of $\Delta^{17}O_{diss.O_2}$ over a range of biological productivity demonstrate this point. In the Dead Sea, where at present photosynthesis is zero, $\Delta^{17}O_{diss.O_2}$ with respect to HLA is −7 per meg. This value, as expected, is identical within the analytical error to atmospheric oxygen. In the Red Sea (Station A near Eilat, 10 m depth, May 1998), $\Delta^{17}O_{diss.O_2}$ was 51 per meg, indicating moderate production. In the highly productive Sea of Galilee (3 m depth; February–April 1998), $\Delta^{17}O_{diss.O_2}$ values ranged from 114 to 136 per meg and clearly demonstrate the effect of rapid biological production. Infinitely rapid production would completely eliminate the anomaly, and $\Delta^{17}O_{diss.O_2}$ would equal $\Delta^{17}O$ of H_2O (taken as 155 per meg).

At the time of our sampling in the Sea of Galilee, the rate of air–lake gas exchange was about $0.15\ mol\ m^{-2}\ d^{-1}$ (based on the dependence of gas exchange in lakes on wind speed[26]). In April 1998, $\Delta^{17}O_{diss.O_2}$ was 136 per meg and the lake thus lost 136×0.15 per meg mol d^{-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 meg mol d^{-1}, and P can be calculated as $0.13\ mol\ d^{-1}$ ($136/155 \times 0.15$). This example shows that if the rate of air–water gas exchange is known, $\Delta^{17}O_{diss.O_2}$ 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 Tedlar in order to compensate for gas gains and losses and to keep constant ambient pressure. The light sources were fluorescent lamps (about $100\ \mu E\ m^{-2}\ s^{-1}$ with negligible ultraviolet flux). Terrarium PK contained water from the Sea of Galilee ($\delta^{18}O = -0.5‰$ vs V-SMOW), and terrarium PDS contained Dan River water ($\delta^{18}O = -6.6‰$ 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_2-free air was passed with a high purity He carrier ($30\ ml\ min^{-1}$) through a chromatographic column ($5\ m \times 2\ mm$ inside diameter stainless-steel tube packed with 45/60 mesh 5-Å molecular sieve and held at $0\ °C$). O_2 and Ar eluted completely in 15 min, and were collected by passing the carrier gas through a trap containing coarse 5-Å molecular sieve held at $-196\ °C$. The remaining He carrier was pumped out, the purified O_2 and Ar were transferred to stainless-steel tubes[27] and admitted to a multi-collector mass spectrometer (Finnigan Delta-Plus). The $\delta^{18}O$ and $\delta^{17}O$ of O_2 and $\delta O_2/Ar$ were measured against a reference O_2/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 cases, we analysed samples in duplicate. Corrections were applied in order to account for the sensitivity of ionization efficiencies of the three isotope species of oxygen to variations in the O_2/Ar ratio. Isotopic and O_2/Ar ratios are given as: $\delta O_2/Ar(‰) = [(O_2/Ar_{sample})/(O_2/Ar_{HLA}) - 1]10^3$; $\delta^*O(‰) = (^*O/^{16}O_{sample})/(^*O/^{16}O_{HLA}) - 1]10^3$ where $^*O$ denotes ^{17}O or ^{18}O; and $\Delta^{17}O\ (per\ meg) = (\delta^{17}O - 0.521\delta^{18}O)10^3$. The analytical precision (standard error) of $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$ 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 $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$ were 0.044‰, 0.029‰ and 7 per meg, respectively.

1. Guy, R. D., Fogel, M. L. & Berry, J. A. Photosynthetic fractionation of stable isotopes. *Plant. Physiol.* **101**, 37–47 (1993).
2. Dongmann, G. The contribution of land photosynthesis to the stationary enrichment of the ^{18}O in the atmosphere. *Radiat. Environ. Biophys.* **11**, 219–255 (1974).
3. Farquhar, G. D. et al. Vegetation effects on the isotope composition of oxygen in atmospheric CO_2. *Nature* **363**, 439–443 (1993).
4. Lane, G. & Dole, M. Fractionation of oxygen isotopes during respiration. *Science* **123**, 574–576 (1956).
5. Schueler, B., Morton, J. & Mauersberger, K. Measurement of isotopic abundances in collected stratospheric ozone samples. *Geophys. Res. Lett.* **17**, 1295–1298 (1990).
6. Thiemens, M. H., Jackson, T., Zipf, E. C., Erdman, P. W. & van Egmond, C. Carbon dioxide and oxygen isotope anomalies in the mesosphere and stratosphere. *Science* **270**, 969–972 (1995).
7. Thiemens, M. H., Jackson, T. L. & Brenninkmeijer, C. A. M. Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric CO_2, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere. *Geophys. Res. Lett.* **22**, 225–257 (1995).
8. Thiemens, M. H. Mass-independent isotope effects in planetary atmospheres and the early solar system. *Science* **283**, 341–345 (1999).
9. Li, W. J. & Meijer, H. A. J. The use of electrolysis for accurate $\delta^{17}O$ and $\delta^{18}O$ isotope measurements in water. *Isotopes Environ. Health Studies* **34**, 349–369 (1998).
10. 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. *Global Biogeochem. Cycles* **8**, 363–376 (1994).
11. Thiemens, M. H., Jackson, T., Maurersberger, K., Schueler, B. & Morton, J. Oxygen isotope fractionation in stratospheric CO_2. *Geophys. Res. Lett.* **18**, 669–672 (1991).
12. Thiemens, M. H. & Jackson, T. Pressure dependency for heavy isotope enhancement in ozone formation. *Geophys. Res. Lett.* **17**, 717–719 (1990).
13. Mauersberger, K., Erbacher, B., Kranowsky, D., Gunther, J. & Nickel, R. Ozone isotope enrichment: Isotopomer-specific rate coefficients. *Science* **283**, 370–372 (1999).
14. Yung, Y. L., Lee, A. Y. T., Irion, F. W., DeMore, W. B. & Wen, J. Carbon dioxide in the atmosphere: Isotopic exchange with ozone and its use as a tracer in the middle atmosphere. *J. Geophys. Res.* **102**, 10857–10866 (1997).
15. Wen, J. & Thiemens, M. H. First multi-isotope study of the $O(^1D) + CO_2$ exchange and stratospheric consequences. *J. Geophys. Res.* **98**, 12801–12808 (1993).
16. Francey, R. J. & Tans, P. P. Latitudinal variations in oxygen-18 of atmospheric CO_2. *Nature* **327**, 495–497 (1987).
17. Dole, M. & Jenks, G. Isotopic composition of photosynthetic oxygen. *Science* **100**, 409 (1944).
18. Minschwaner, K., Salawitch, R. J. & McElroy, M. B. Absorption of solar radiation by O_2: Implications for O_3 and lifetimes of N_2O, $CFCl_3$, and CF_2Cl_2. *J. Geophys. Res.* **98**, 10543–10561 (1993).
19. Boering, K. A. et al. Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide. *Science* **274**, 1340–1343 (1996).
20. Holton, J. R. On the global exchange of mass between the stratosphere and the troposphere. *J. Atmos. Sci.* **47**, 392–395 (1990).
21. Appenzeller, C., Holton, J. R. & Rosenlof, K. H. Seasonal variation of mass transport across the tropopause. *J. Geophys. Res.* **101**, 15071–15078 (1996).
22. Crutzen, P. J. & Bruhl, C. A model study of atmospheric temperatures and the concentrations of ozone, hydroxyl, and some other photochemically active gases during the glacial, the pre-industrial Holocene and the Present. *Geophys. Res. Lett.* **20**, 1047–1050 (1993).
23. Martinerie, P., Brasseur, G. P. & Granier, C. The chemical composition of ancient atmospheres: A model study constrained by ice-core data. *J. Geophys. Res.* **100**, 14291–14304 (1995).
24. Rind, D. & Lacis, A. The role of the stratosphere in climate change. *Surv. Geophys.* **14**, 133–165 (1993).
25. Meyer, M. K. *Net Primary Productivity Estimates for the Last 18,000 years Evaluated from Simulations by a Global Climate Model.* Thesis, Univ. Wisconsin (1988).
26. Clark, J. F. et al. in *Air-Water Gas Transfer* (eds Jaehne, B. & Monahan, E. C.) 785–800 (Aeon, Hanau, 1995).
27. Sowers, T., Bender, M. & Raynaud, D. Elemental and isotopic composition of occluded O_2 and N_2 in polar ice. *J. Geophys. Res.* **94**, 5137–5150 (1989).
28. Brenninkmeijer, C. A. M., Lowe, D. C., Manning, M. R., Sparks, R. J. & van Velthoven, P. F. J. The ^{13}C, ^{14}C and ^{18}O isotopic composition of CO, CH_4, and CO_2 in the higher southern latitudes lower stratosphere. *J. Geophys. Res.* **100**, 26163–26172 (1995).
29. Barnola, J. M., Pimienta, P., Raynaud, D. & Korotkevich, Y. S. CO_2–climate relationship as deduced from the Vostok ice core—A reexamination based on new measurements and on a reevaluation of the air dating. *Tellus B* **43**, 83–90 (1991).