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Reconstructing the history of biological productivity and atmospheric oxygen partial pressure (pO₂) is a fundamental goal of geobiology. Recently, the mass-independent fractionation of oxygen isotopes (O-MIF) has been used as a tool for estimating pO₂ and productivity during the Proterozoic. O-MIF, reported as ∆¹⁷O, is produced during the formation of ozone and destroyed by isotopic exchange with water by biological and chemical processes. Atmospheric O-MIF can be preserved in the geologic record when pyrite (FeS₂) is oxidized during weathering, and the sulfur is redeposited as sulfate. Here, sedimentary sulfates from the ∼1.4-Ga Sibley Formation are reanalyzed using a detailed one-dimensional photochemical model that includes physical constraints on air-sea gas exchange. Previous analyses of these data concluded that pO₂ at that time was ∼1% PAL (times the present atmospheric level). Our model shows that the upper limit on pO₂ is essentially unconstrained by these data. Indeed, pO₂ levels below 0.8% PAL are possible only if atmospheric methane was more abundant than today (so that pCO₂ could have been lower) or if the Sibley O-MIF data were diluted by reprocessing before the sulfates were deposited. Our model also shows that, contrary to previous assertions, marine productivity cannot be reliably constrained by the O-MIF data because the exchange of molecular oxygen (O₂) between the atmosphere and surface ocean is controlled more by air-sea gas transfer rates than by biological productivity. Improved estimates of pCO₂ and/or improved proxies for ∆¹⁷O of atmospheric O₂ would allow tighter constraints to be placed on mid-Proterozoic pO₂.

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Significance

Constraining the abundance of molecular oxygen (O₂) in Earth’s atmosphere over time is a problem of central importance for understanding the evolution of complex life. Here, we refine previous analyses of the rare oxygen isotope composition of sedimentary sulfates to develop improved estimates of atmospheric O₂ during Earth’s mid-Proterozoic era. Previous analyses of these data had predicted O₂ concentrations well below 1% present atmospheric level. Our new calculations suggest that this value is closer to a lower limit on atmospheric oxygen partial pressure unless the climate was warmed significantly by biogenic methane. The calculations also show that marine productivity cannot be reliably estimated from these data because of the slow rate of transfer of O₂ across the air-sea interface.

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drivers (or, more likely, their interplay) in controlling the expansion of biological complexity and, in particular, the rise of animals (21–23). Understanding how primary productivity has changed through time as atmospheric O₂ rose is also a fundamentally unanswered question about Earth’s history (e.g., refs. 24 to 26).

Here, we employ a tool for estimating ancient pO₂ and primary productivity in deep time: the triple oxygen isotope composition of marine and lacustrine sedimentary rocks. This approach utilizes oxygen isotope signatures that deviate significantly from the usual mass-dependent fractionation (MDF) line. Today, about 30% of this oxygen MIF (O-MIF) signal originates from ozone (O₃) photochemistry, and we expect that this percentage was considerably higher in the past (SI Appendix, section 1.2). The O-MIF value can be defined by the relationship (27)

\[
\frac{\Delta^{17} \text{O}}{1000} \equiv \ln \left( \frac{\delta^{17} \text{O}}{1000} + 1 \right) - \lambda_{RL} \cdot \ln \left( \frac{\delta^{18} \text{O}}{1000} + 1 \right).
\]  

[1]

Here, \( \delta \text{O} \) represents the deviation in parts per thousand (‰) or “permil” from the \( ^{16} \text{O} / ^{18} \text{O} \) ratio in an isotopic standard, and \( \lambda_{RL} \) is a reference line slope that we take to be equal to 0.528, following Young et al. (28) and Pack (27). For small fractions, this reduces to

\[
\Delta^{17} \text{O} \equiv \delta^{17} \text{O} - \lambda_{RL} \cdot \delta^{18} \text{O}.
\]  

[2]

We use the logarithmic form (Eq. 1) in all calculations, as the fractionation in ozone is not small. The positive \( \Delta^{17} \text{O} \) signal from ozone (~20‰ at the surface) is transferred to CO₂, and O₂ acquires a negative \( \Delta^{17} \text{O} \) signal (~−0.43‰ at the surface) by mass balance (27). The \( \Delta^{17} \text{O} \) signal from atmospheric O₂ can be transferred to the rock record via weathering of pyrite, FeS₂, and the subsequent burial of oxidized sulfur phases at Earth’s surface (25, 29, 30). Some authors have recently suggested that H₂O₂ may be responsible for oxidizing pyrite in rivers draining the Himalayas (31), so we keep track of \( \Delta^{17} \text{O} \) of H₂O₂ as well. Small changes in \( \Delta^{17} \text{O} \) can also be induced by mass-dependent processes with different values for \( \lambda_{RL} \), as discussed further below (see the section Dilution of the O-MIF Signal in O₂ and CO₂ via Biospheric Recycling). We use the term “O-MIF” only to refer to the large changes induced by ozone formation.

On the present Earth, \( \Delta^{17} \text{O} \) values are small, roughly ~0.05‰ in seawater sulfate (32, 33) and ~0.43‰ in tropospheric O₂ (27). By comparison, the existing oxygen isotope record from sedimentary sulfate minerals deposited during the Proterozoic shows values as light as ~0.9‰ (25), requiring tropospheric O₂ values significantly lighter than those of the modern atmosphere. The overall magnitude of these signals is controlled by atmospheric O₂ and CO₂, which act to control the production and storage of isotopic anomalies in the atmosphere and by the globally integrated productivity of the biosphere, which acts to eliminate MIF (34, 35). As a result, if one knows (or can assume) atmospheric pCO₂, one can either use an assumed atmospheric pO₂ to estimate global gross primary production, GPP (25, 36), or invert for an estimate of atmospheric pO₂ (15, 37). (GPP is the total rate of synthesis of fresh organic matter, which, for an aerobic ecosystem, is just the rate of oxygenic photosynthesis.) However, previous attempts to solve for pO₂ (ibid.) used a box modeling approach that mischaracterized the effect of stratosphere–troposphere gas exchange at low pO₂, made potentially problematic assumptions about the link between GPP and air–sea O₂ transfer, and left out other key aspects of atmospheric chemistry.

Here, we revisit this problem with a detailed one-dimensional photochemical and ocean–atmosphere gas exchange model. This approach includes several advances that allow for a more realistic representation of the oxygen cycle. First, our photochemical model explicitly calculates the lowering of the ozone layer as atmospheric O₂ decreases (38) and directly simulates the photochemically catalyzed isotopic exchange between O₂ (or O₃) and gaseous H₂O. Second, our model includes limitations imposed by gas exchange rates across the air–sea interface. At O₂ levels lower than today, the gas transfer rate, rather than GPP itself, should control the extent of biospheric recycling of \( \Delta^{17} \text{O} \) values.

**Production of the O-MIF (\( \Delta^{17} \text{O} \)) Signal during Ozone Formation**

O-MIF in Earth’s atmosphere is mainly produced by the ozone formation reaction (39–41)

\[
O + O₂ + M \rightarrow O₃ + M.
\]  

[3]

Here, “O” is the ground state of atomic oxygen, and “M” represents a third molecule needed to carry off the excess energy of the collision. Ozone is a bent molecule with a resonant double bond between three oxygen atoms (SI Appendix, Table S6). If we let “O” represent a minor isotope of O (i.e., \( ^{17} \text{O} \) or \( ^{18} \text{O} \)), the isotopic analogs of reaction [3] can be written as

\[
O + OQ + M \rightarrow OOQ + M,
\]  

[4]

\[
O + OO + M \rightarrow OOO + M.
\]  

[5]

and

\[
Q + O₂ \leftrightarrow OO + O.
\]  

[7]

Two different forms of ozone are created: asymmetric OOO (reactions [4] and [6]) and symmetric OOQ (reaction [5]). The rate constants for these reactions are given in SI Appendix, Table S2. Asymmetric ozone in reaction [4] forms ~16% faster than symmetric ozone in reaction [5] (the so-called “η effect” in the chemical physics literature (40, 42–44). This effect depends on both temperature (45) and pressure (46). Reaction [6] forms asymmetric ozone as well, but its rate constant is roughly equal to that of reaction [3] (for \( ^{17} \text{O} \)), or even slower (for \( ^{18} \text{O} \)), for reasons that are related to the rapid isotopic exchange reaction

\[
Q + O₂ \leftrightarrow OO + O.
\]  

[7]

The rate of isotope exchange as well as the rate of ozone formation is influenced by the symmetry number of two for the O₂ molecule and by the vibrational zero-point energy difference between lighter OO and heavier OQ. The net result is that O₃ becomes enriched in minor isotopes (O atoms) by about 70‰ (\( ^{17} \text{O} \)) and 75‰ (\( ^{18} \text{O} \)), producing \( \Delta^{17} \text{O} \) values of ~30‰, following Eq. 1. This large enrichment has been confirmed by stratospheric observations made from balloon flights (47–49). The enrichment is then transferred to CO₂ via the reaction sequences (50)

\[
OOQ + hv \rightarrow O₂ + Q(1D)
\]  

[8]

and

\[
Q(1D) + CO₂ \rightarrow COO + O.
\]  

[9]

Here, hv represents an ultraviolet photon, and Q(1D) is an excited electronic state of atomic oxygen. Thus, atmospheric CO₂ acquires positive \( \Delta^{17} \text{O} \) inherited from ozone. The excess Q atoms in CO₂ are ultimately derived from O₂; hence, O₂ acquires negative \( \Delta^{17} \text{O} \). However, because O₂ is ~500 times more abundant than CO₂ in the modern atmosphere, the negative \( \Delta^{17} \text{O} \) values in O₂ are much smaller than the positive \( \Delta^{17} \text{O} \) values in CO₂. Q(1D) can also react with other species (e.g., H₂O and CH₄), thereby spreading the O-MIF signal throughout the photochemical network.
Dilution of the O-MIF Signal in O₂ and CO₂ via Biospheric Recycling

Recycling by the Marine Biosphere. The O-MIF signal in O₂ and CO₂ can be diluted by processing through the terrestrial and marine biospheres (35). Consider the marine biosphere first. CO₂ dissociates in solution to form carbonic acid and other forms of dissolved inorganic carbon (DIC), all of which readily exchange O atoms with water. The time scale for isotopic exchange is essentially equal to the time scale for CO₂ hydration, which is of the order of minutes (51). By comparison, the residence time of CO₂ in the surface ocean is ~20 d, as shown in SI Appendix, section 2.1.2. (CO₂ and O₂ behave similarly because their air-sea transfer velocities are nearly the same). Whenever O₂ is dissolved in water, it loses its O-MIF signal. However, the situation is quite different for O₂. Dissolved oxygen does not exchange O atoms with water unless it is used for respiration (35), which can be represented by reaction [10] running to the right:

\[ \text{CH}_2\text{O} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}. \]  

The reverse of respiration is photosynthesis, which is represented by reaction [10] running to the left.

Respiration dilutes the O-MIF signal in O₂ by reducing much of it to water and adding some O atoms to other molecules. However, it also creates a small Δ¹⁷O signal by way of a phenomenon called the “Dole effect.” Respiration induces strong MDF (52). This causes atmospheric O₂ to be enriched in minor isotopes by ~23.5‰ for ¹⁸O and ~12.5‰ for ¹⁷O (28). The slope of the MDF line for respiration is ~0.515 (28), which is slightly lower than the slope of the normal terrestrial MDF line given by Eq. 1. This difference imparts a negative Δ¹⁷O signal to O₂, which is important when we compare our model to observed values in the modern Earth. This process is less of a complication at low pO₂ levels because air-sea gas transfer rates decrease while the O-MIF in O₂ signal becomes substantially larger; hence, we have elected to ignore it in our low-O₂ calculations. We justify this assumption explicitly in SI Appendix, section 1.2.

The processing of the O-MIF signal by the marine biosphere is complicated because air-sea gas transfer limitations also play a role. The net downward flux of gas X across the atmosphere–ocean interface can be expressed as a “piston velocity,” kₓ, times a concentration difference over a thin boundary layer at the ocean’s surface:

\[ \Phi(X) = k_X \cdot \{\alpha_X \cdot pX - [X]_{aq}\}. \]  

The piston velocity can be related to the product of the 10-m average wind speed and the Schmidt number of the fluid (53) (SI Appendix, section 2.1.2). The remaining terms in Eq. 11 are the Henry’s Law coefficient α and the species atmospheric partial pressure pX. [X]ₐq is the dissolved concentration of the gas in the surface ocean. We found that, kO₂ ≈ 5.0 m · d⁻¹, and kCO₂ ≈ 4.7 m · d⁻¹.

Note that Φ(X) in Eq. 11 is a net flux, the difference between a gross downward flux proportional to αXpX and a gross upward flux proportional to [X]ₐq. The upward and downward fluxes are independent (i.e., they do not impede each other). Thus, for CO₂, which exchanges O atoms upon contact with water, the dilution term is straightforward: it is equal to the gross downward flux kCO₂ · αCO₂ · pCO₂, which can be used to calculate a maximum deposition velocity in the photochemical model (SI Appendix, Eq. S4). Thus, for CO₂, the dilution term is entirely independent of GPP. We explain how this is implemented in Methods.

For O₂, the situation is more complicated because isotopes are not exchanged unless the O₂ is taken up by respiration, so one cannot simply use the gross upward and downward fluxes implied by Eq. 11. The relevant air–sea exchange flux should include only the O₂ that is reprocessed by respiration and photosynthesis. Furthermore, O₂ that is produced by photosynthesis within the surface ocean and then consumed in situ by respiration should not be counted as contributing to this exchange flux. An additional consideration is that the time-averaged net O₂ flux at the atmosphere–ocean interface must be approximately zero if the system is to remain in steady state. (We can neglect the ~10 Tmol · yr⁻¹ of O₂ that is consumed by oxidative weathering on the continents [table 10.1 in ref. 54].) Thus, the surface ocean must remain near Henry’s Law equilibrium with the atmosphere on average according to Eq. 11. However, in reality, the surface ocean departs substantially from equilibrium at different localities and at different seasons, driving measurable atmosphere–ocean O₂ exchange (55).

We can account for these complex O₂ exchange processes in our globally averaged model by following an approach pioneered by Bender et al. (52). On the modern Earth, marine GPP produces ~12,000 Tmol · O₂ · yr⁻¹ (52), a value that falls nicely in between more recent estimates of 8,000 to 17,000 Tmol · yr⁻¹ (56). We use the older values here because they have been used by other authors (25, 34, 35, 37), so one can compare with their results. Bender et al. (52) estimate that 12% of marine GPP is recycled internally within the surface ocean, so the relevant sea–air (or air–sea) flux of O₂ is 12,000 × 0.88 = 10,600 Tmol · O₂ · yr⁻¹.

To estimate the recycled O₂ fraction at lower pO₂ levels, one must understand the logic by which Bender et al. (52) calculated their 12% modern value. They compared the timescale for air–sea exchange of O₂ with that for uptake by respiration. The timescale for air–sea exchange is the dissolved O₂ reservoir size in the ocean mixed layer divided by the (gross) upward O₂ flux from Eq. 11. Both quantities are proportional to pO₂ (at least on a time average), so the exchange timescale is just a constant equal to the depth of the ocean mixed layer divided by the piston velocity. The timescale for uptake by respiration is equal to the dissolved O₂ reservoir divided by GPP, so it depends linearly on pO₂ if GPP remains constant. Today, the timescale for air–sea exchange is ~1/14 that for respiration, so most photosynthetically generated O₂ escapes to the atmosphere. At lower O₂ levels, this ratio decreases, so more photosynthetically O₂ is recycled. The calculation is shown explicitly in SI Appendix, section 2.1.2. The results are shown in Fig. 1. Importantly, GPP is assumed to remain constant all the way down to 0.01 PAL O₂, thereby maximizing dilution of the Δ¹⁷O signal.

At pO₂ levels of 1% PAL and below, the O₂ exchange flux calculated by this method approaches the “piston velocity (PV)” limit, so we simply use the latter value as we do for CO₂. Again, this maximizes the rate of air–sea O₂ transfer, and thus minimizes the Δ¹⁷O signal in O₂. The limiting O₂ flux, ΦPVT, is readily calculated by setting the dissolved O₂ concentration equal to zero in Eq. 11: ΦPVT = kO₂ · αO₂ · pO₂ ≈ 6.5 × (pO₂/1 bar) moles · m⁻² · d⁻¹, using the O₂ solubility from SI Appendix, Table S1. Converting time units to years and multiplying by the area of the surface ocean, 5.1 × 10¹⁰ m², yields the PV limit values shown in SI Appendix, Table S3 and in Fig. 1. More details about model implementation are shown in Methods.

Critically, our estimated air–sea O₂ exchange fluxes at low pO₂ levels are only weakly connected to marine GPP. The exchange flux could be lower than calculated here if Proterozoic GPP was substantially lower than today, but it cannot be higher unless Proterozoic GPP was higher than today, and pO₂ was also relatively high. This same reasoning implies that the O-MIF data from sedimentary sulfates are largely independent of marine GPP. Thus, previous attempts to estimate Proterozoic GPP from such data (e.g., ref. 25) need to be rethought.

Recycling by the Terrestrial Biosphere. According to Farquhar et al. (57) and Bender et al. (52), modern terrestrial GPP is
Δ accelerates hydration (51). Therefore, we assume that the in plants of the enzyme carbonic anhydrase, which greatly however, this problem is alleviated by the ubiquitous presence often shorter than the time scale (minutes) for CO2 hydration. Thus, terrestrial uptake of O2 rises to 20,400 Tmol · yr⁻¹ when this process is considered (52). CO2 is not produced by photorespiration, so the recycling of CO2 by land plants should go at the slower, uncorrected GPP rate. Isotope exchange between CO2 and plant water is complicated by the fact that the residence time of CO2 in leaves is often shorter than the time scale (minutes) for CO2 hydration. However, this problem is alleviated by the ubiquitous presence in plants of the enzyme carbonic anhydrase, which greatly accelerates hydration (51). Therefore, we assume that the Δ¹⁷O signal in CO2 is almost zeroed out by this process as it is by recycling through the marine biosphere.

The processing of atmospheric O2 by the terrestrial biosphere should have been slower during the mid-Proterozoic because vascular plants had not yet evolved. That said, significant portions of the exposed land surface may have been covered by microbial mats composed largely or partly of O2-generating cyanobacteria (37, 60). Estimating the GPP of such mats is problematic because it is difficult to determine what fraction of the land surface should have been covered and because the area of the continents may have changed over time. Hence, we present calculations both with and without terrestrial mats. Based on a detailed study of a modern microbial mat in Indonesia, Finke et al. (60) estimated a terrestrial microbial mat GPP of 20 to 200 Tmol · O2 · yr⁻¹ for an Archean Earth with 1/6 the current land area. This translates to 120 to 1,200 Tmol · O2 · yr⁻¹ if the continents had grown to their present size by 1.4 Ga. Other authors have estimated Proterozoic microbial mat fluxes as high as 4,000 Tmol · O2 · yr⁻¹ (26). We use a terrestrial O2 flux of 660 Tmol · yr⁻¹ (~5% of modern terrestrial GPP) in the calculations discussed in the next paragraph and shown in Fig. 4B. This number is close to the midrange terrestrial O2 flux in Planavsky et al. (26).

Terrestrial microbial mats are subject to gas exchange constraints analogous to those imposed at the atmosphere–ocean interface. The surface of a water-saturated mat is much less permeable, though, than the turbulent ocean surface. Based on observations of the dissolved O2 profile within a modern, water-saturated microbial mat by Finke et al. (60), we estimate that the effective PV for O2 exchange between the mat and the atmosphere is about 1/60 that for atmosphere–ocean exchange (SI Appendix, section 2.2.8). The O2 storage capacity for a mat is also much smaller than that of the surface ocean, so more of its photosynthetically produced O2, ~70%, should be released to the atmosphere under low-pO2 conditions (60). Because of the low exchange velocity, this O2 could not have easily flowed back into the mat if pO2 was low. Thus, to balance O2 release, productive mats must also have released CH4 (61) or H2/CO (62) in stoichiometrically equivalent amounts; otherwise, that O2 would have accumulated in the atmosphere. Here, we assume that the O2 flux from mats was balanced by CH4. The 660 Tmol(O2) · yr⁻¹ produced in our simulations that include mats corresponds to a CH4 flux of 330 Tmol · yr⁻¹, or about 10 times the modern CH4 flux (SI Appendix, section 1.3).

Results
Fits to Modern Earth. We implemented the chemistry and transport described in Production of the O-MIF (Δ¹⁷O) Signal during Ozone Formation and Dilution of the O-MIF Signal in O2 and CO2 via Biospheric Recycling in a recent version of our one-dimensional photochemical (main) model (63), now linked to an isotopic model which duplicates this same chemistry for species containing one minor O isotope, either ¹⁷O or ¹⁸O. O2 and CO2 were treated as variables in both the main code and the isotopic code, but their boundary conditions were handled differently (see Methods). For our modern atmosphere calculations, the surface O2 mixing ratio was set to 0.21 in the main code, and the CO2 mixing ratio was set to 300 ppmv. We henceforth define these concentrations as 1 PAL. A relatively low value of pCO₂ near the preindustrial level of 280 ppmv, is appropriate for these calculations because the Δ¹⁷O signal in modern atmospheric O₂ has been gradually accumulating on a timescale commensurate with the lifetime of O₂ against isotopic recycling, ~1,200 y (35). In both the main code and the isotopic code, O₂ and CO₂ were given biospheric recycling fluxes using numbers from Dilution of the O-MIF Signal in O2 and CO₂ via
Biospheric Recycling. The O₂ flux from the combined marine and terrestrial biosphere was set equal to 31,000 Tmol · yr⁻¹, which represents the sum of a gross marine flux calculated from the downward part of Eq. 11 along with a flux equal to terrestrial GPP.

Model predictions for Δ¹⁷O of O₂, O₃, and CO₂ are compared with measurements in Fig. 2. The stratospheric ozone measurements are from balloon flights carried out over the last ∼40 y (see ref. 49 and references therein). They measure bulk ozone, separated cryogenically from air and converted quantitatively to O₂. Isotopic measurements of surface ozone were made indirectly by oxidizing nitrite and measuring the composition of the resulting nitrate (64). This measures only the transferrable (end atom) isotopic composition of O₃. Symmetric ozone (OQQO) was assumed by those authors to have Δ¹⁷O = 0%. The fractionation values in the ozone data are affected by local meteorological factors such that the records from different places and times vary significantly. The shape of the modeled Δ¹⁷O profile for ozone reflects temperature- and pressure-dependent correction factors described in SI Appendix. The US 1976 Standard Atmosphere temperature profile was used in all calculations (SI Appendix, Fig. S7), including those at lower pO₂ levels.

Sensitivity studies were performed to determine the effect on our results (SI Appendix, Fig. S7). Importantly, to generate Fig. 2, the rate constant for the formation of asymmetric [O₃]⁻¹ has been adjusted downward by a factor β = 0.9772 (SI Appendix, Table S2).

Fig. 2. Comparison between model-generated Δ¹⁷O values for our present-day simulation (curves) and atmospheric observations (symbols). Filled blue squares, blue circles, and the blue star are O₂ measurements for different altitudes from Pack et al. (67), Thiemens et al. (68), and Pack (27), respectively. The blue curves are model-predicted values with (solid) and without (dotted) corrections for the Dole effect. Measurements for CO₂ are from Kawagucci et al. (66), with filled black circles showing measurements from Kiruna, Sweden (68° N) on February 22, 1997, and open black circles showing measurements from Sanriku, Japan (39° N) on August 31, 1994. Measurements for O₃ are from Krankowsky et al. (49), with filled green circles, open green circles, and filled green squares showing measurements from Brazil, France, and Sweden, respectively. The green star is the measured surface fractionation of bulk O₃ from Vicars and Savarino (64). The light green curve shows the Δ¹⁷O of stratospheric O₃ calculated by Liang et al. (65). Note the scale change at Δ¹⁷O = 0%.

Fig. 3. Vertical profiles of (A) ozone (O₃) number density, (B) Δ¹⁷O of O₃, (C) Δ¹⁷O of O₂, and (D) Δ¹⁷O of CO₂ from photochemical model across a range of assumed ground-level atmospheric pO₂ values (in PAL). All results assume an atmospheric pCO₂ of 300 ppmv.
Without this correction factor, our model predicts $\Delta^{17}O$ values of \(-37^{\circ}\) for $O_3$ at 25 km altitude, which is well above the average of the data. With the correction, $\Delta^{17}O$ is $\sim$ 28$^{\circ}$ at that altitude, which is within the range of observations; however, we underpredict $\Delta^{17}O$ of $O_3$ above 30 km. The correction also brings us closer to the tropospheric ozone data (see Fig. 2). We feel justified in making this correction because we are ultimately interested in $\Delta^{17}O$ of $O_3$, not $O_2$. Overpredicting the (positive) $\Delta^{17}O$ of $O_2$ would cause us to also overpredict the magnitude of the (negative) $\Delta^{17}O$ value of $O_2$. Young et al. (28) employed a similar strategy because their model also overpredicted $\Delta^{17}O$ of $O_2$ and because they were also focused on $O_2$.

The model of Liang et al. (65) overpredicted $\Delta^{17}O$ of stratospheric $O_3$ as well (Fig. 2). Even with this correction factor, our model still slightly overpredicts $\Delta^{17}O$ of surface ozone: we get $\sim$ 27.5$^{\circ}$, whereas the reported value is $\sim$ 26$^{\circ}$ (64). The actual value of $\Delta^{17}O$ for surface ozone depends strongly on the $\Delta^{17}O$ of symmetric $O_3$, which has not been measured experimentally. The discrepancy between calculation and measurement will only be resolved when we fully understand the isotopic fractionation in reactions [4–6].

Predicted $\Delta^{17}O$ values for $CO_2$ increase from 0$^{\circ}$ at the surface to $\sim$ 10$^{\circ}$ at 40 km, in agreement with the data from Sweden but not as close to the data from Japan (66). $CO_2$ is expected to be unfractionated near the surface because of rapid exchange of $O$ isotopes with seawater. Comparisons of $\Delta^{17}O$ between model and observations for $H_2O_2$ and nitrate are shown in SI Appendix, Fig. S1.

For $O_2$, the $\Delta^{17}O$ value predicted near the surface by our model, $\sim$ 0.14$^{\circ}$, is well above observed values. The $O_2$ data are scattered, but Pack (27) suggests that $\sim$ 0.43$^{\circ}$ is a reasonable average value. This discrepancy is expected because according to Young et al. (28), 2/3 of the isotopic signal in modern $O_2$ is caused by the Dole effect, described in Dilution of the O-MIF Signal in $O_2$ and $CO_2$ via Biospheric Recycling. Accordingly, we subtract 0.29$^{\circ}$ from our calculated values to produce the solid curve in Fig. 2, which agrees well with the observations (27, 67, 68). Recall that this correction is expected to be smaller at lower $pO_2$ levels (Dilution of the O-MIF Signal in $O_2$ and $CO_2$ via Biospheric Recycling).

**Results for Lower $pO_2$ Levels (Marine Biosphere Only).** In a second set of calculations, we lowered atmospheric $pO_2$ from 1 to $10^{-3}$ PAL, keeping $pCO_2$ constant at 1 PAL. The interpretation of model results becomes complicated at $pO_2 < 10^{-3}$ PAL because terms other than air–sea exchange become important in the $O_2$ budget. In these simulations and in the ones described in the next section, we set the $O_2$ surface exchange flux equal to the values shown in SI Appendix, Table S3 using the $PV$-limited flux when $pO_2$ is lower than 0.03 PAL. Surface fluxes of other trace gases ($CH_4$, $N_2O$, $CO$, and $H_2$) were kept equal to their modern values (see Methods). The selected results are shown in Fig. 3. Notably, as $O_2$ decreases, the ozone layer moves downward, and its peak density decreases (Fig. 3A), consistent with earlier results (38, 69, 70).

Because the $CO_2$ mixing ratio is held constant in these calculations, the $O_2$:CO2 ratio decreases at lower $O_2$ levels, causing $O_2$ to become more negatively fractionated (e.g., the $\Delta^{17}O$ in surface $O_2$ is about $-8.5^{\circ}$ at $10^{-3}$ PAL $pO_2$) (Fig. 3C). This depletion in $\Delta^{17}O$ in $O_2$ can be transferred to $O_3$, so the fractionation in ozone also decreases with decreasing $O_2$. For example, the surface ozone fractionation decreases from 27.5 to 19.3$^{\circ}$ as $O_2$ decreases from 1 to $10^{-3}$ PAL. Tropospheric $CO_2$ stays near 0$^{\circ}$ because isotopic exchange with seawater remains rapid in all these calculations. The large decrease in $\Delta^{17}O$ for tropospheric $O_2$ at low $O_2$ levels is a result of mass balance. In today’s atmosphere, the positive $\Delta^{17}O$ signal in $O_3$ is transferred to $CO_2$ in the stratosphere as discussed in Production of the O-MIF ($\Delta^{17}O$) Signal during Ozone Formation. $CO_2$ then flows downward into the troposphere and ultimately transfers that signal to seawater. Residual $O_2$ becomes negative in $\Delta^{17}O$ as a result. However, at low $pO_2$, the ozone layer moves lower in the stratosphere or even into the troposphere (38, 70). $CO_2$ remains neutral or even slightly negative in $\Delta^{17}O$ (Fig. 3D), while ozone transfers its positive $\Delta^{17}O$ signal to water vapor—and from there to the ocean—by way of the

**Fig. 4.** Calculated $\Delta^{17}O$ values for $O_2$ in the marine biosphere–only simulations (A) and the terrestrial biosphere–included simulations (B). The red-contoured interval represents the range of values that are consistent with the 1.4-Ga Sibley sulfate data, assuming 8 to 15% incorporation of $O_2$. The dashed lines represent various suggested constraints on $pCO_2$ discussed in the text.
HO\textsubscript{3} chemistry described in SI Appendix, section 2.2.5. This latter process is highly efficient, and the atmospheric O\textsubscript{2} reservoir is small, so O\textsubscript{2} becomes strongly negative in $\Delta^{17}$O.

Next, we repeated our calculations over a grid with $p$O\textsubscript{2} ranging from 1 to 10$^{-3}$ PAL and with $p$CO\textsubscript{2} from 1 to 300 PAL, yielding 42 assumed $p$O\textsubscript{2}/$p$CO\textsubscript{2} combinations. Following the methodology described earlier in this section and in Methods, CO\textsubscript{2} surface exchange fluxes remain at the PV limit, so they become large at high $p$CO\textsubscript{2} values. The O\textsubscript{2} exchange fluxes were taken from SI Appendix, Table S3. The calculated $\Delta^{17}$O values for ground-level O\textsubscript{2} are shown in Fig. 4A. Some authors (e.g., ref. 31) have suggested that the main oxidizing agent for pyrite is H\textsubscript{2}O\textsubscript{2}, not O\textsubscript{2}. The $\Delta^{17}$O value of H\textsubscript{2}O\textsubscript{2} tracks that of O\textsubscript{2} closely (SI Appendix, Fig. S4), however, suggesting that it may not matter which species actually causes the oxidation.

When pyrite is oxidized to sulfur by O\textsubscript{2}, only 8 to 15% of the oxygen in the sulfate comes from O\textsubscript{2}; the rest comes from water (71). By contrast, Killingsworth et al. (72) suggest that the incorporated O\textsubscript{2} fraction is 18 ± 9%. We use the lower numbers from Balci et al. (71) here to remain consistent with previous studies (25, 37). Higher O\textsubscript{2} incorporation in sulfate would lead to higher predicted $p$O\textsubscript{2} values. The 1.4-Ga Sibley sulfates were deposited in a shallow evaporative setting (25). The most negative $\Delta^{17}$O value observed in these sediments is −0.9%, but all of these data are below −0.3%, below the range of Proterozoic sulfates (25). The O\textsubscript{2} needed to produce this fractionation must therefore have $\Delta^{17}$O values in the range of −6 to −11‰. Most of this O\textsubscript{2} is taken up in the last oxidation step going from sulfate to sulfide (71), so we assume that a similar uptake fraction would apply to H\textsubscript{2}O\textsubscript{2} (SI Appendix, Fig. S4). This range is represented by the red-contoured interval in Fig. 4A. The $\Delta^{17}$O values higher than −6‰ in O\textsubscript{2} are excluded by the Sibley data, assuming that the Balci et al. (71) oxidant incorporation factors are correct. The $\Delta^{17}$O values lower than −11‰ in O\textsubscript{2} cannot be excluded, but they would require bacterial reprocessing of dissolved sulfate and consequent dilution of the O-MIF signal within the water column beneath which the sulfates were deposited. We ignore the Dole effect correction to $\Delta^{17}$O of O\textsubscript{2} at $p$O\textsubscript{2} levels below 1 PAL. More than half of this correction comes from the terrestrial biosphere, which would have been greatly diminished at 1.4 Ga if $p$O\textsubscript{2} was low (Recycling by the Terrestrial Biosphere). Any Dole effect caused by the marine biosphere at that time would push our calculated $\Delta^{17}$O values lower for O\textsubscript{2}, causing our predicted $p$O\textsubscript{2} values to be higher than those estimated in this section.

Not surprisingly, predicted $\Delta^{17}$O values for O\textsubscript{2} depend on both $p$O\textsubscript{2} and $p$CO\textsubscript{2}. Thus, estimating $p$O\textsubscript{2} from Proterozoic data depends on having an accurate estimate for $p$CO\textsubscript{2}. Unfortunately, constraints on $p$CO\textsubscript{2} span an order of magnitude. A credible lower limit on $p$CO\textsubscript{2} can be inferred from climate considerations, but the upper limit on $p$CO\textsubscript{2} is unclear. The two dashed horizontal lines in Fig. 4A indicate a range of plausible $p$CO\textsubscript{2} levels. The lower line is at $\sim$12 PAL (3,550 ppmv), and the upper line is at $\sim$24 PAL (7,100 ppmv). These estimates come from three-dimensional climate model simulations (73). According to their (zero-CH\textsubscript{4}) climate model results, 3,550 ppmv CO\textsubscript{2} at 1.42 Ga would have produced a glacial climate with a mean surface temperature of 10.7 °C, whereas 7,100 ppmv CO\textsubscript{2} would have produced a mean surface temperature of 18.6 °C—sufficient to keep the continents (but not the poles) ice free. These calculations account for the fact that solar luminosity at that time was −90% of the present value (74).

If one considers these values to be lower and upper bounds on $p$CO\textsubscript{2} and assumes no dilution of the O-MIF signal, $p$O\textsubscript{2} should be in the range of 0.8 to 20% PAL (Fig. 4A). These values are roughly an order of magnitude higher than the 0.1 to 1% PAL values estimated by Planavsky et al. (37) from these same data. Part of the difference is attributable to the more detailed photochemical model used here and to our improved treatment of air–sea gas exchange. However, much of it stems from our more restricted range of plausible $p$CO\textsubscript{2} values. Planavsky et al. (37) assumed a range of $p$CO\textsubscript{2} values randomly distributed between 2 and 500 PAL, along with a substantial terrestrial oxygen flux. If we allow $p$CO\textsubscript{2} values as low as 2 PAL, our predicted $p$O\textsubscript{2} could be 0.1% PAL or even lower. These low $p$CO\textsubscript{2} levels would have resulted in global glaciation unless Earth’s greenhouse effect at that time was supplemented by large amounts of CH\textsubscript{4} and/or N\textsubscript{2}O (73, 75). However, N\textsubscript{2}O photolyzes rapidly below ~0.1 PAL O\textsubscript{2}, so its greenhouse contribution should have been modest (63, 76). CH\textsubscript{4} is a more likely Proterozoic greenhouse gas; its possible effect is considered in the following section.

A weakness in the above argument is that Liu et al. (73) considered their 24 PAL $p$CO\textsubscript{2} estimate to be a lower limit for mid-Proterozoic $p$CO\textsubscript{2} (assuming no methane), not an upper limit. The climate record suggests that the “Boring Billion” period between 1.8 to 0.8 Ga was ice free, except for a few possible exceptions. Glaciations have been reported in the King Leopold formation in northwestern Australia at 1.8 Ga (77) and in the Vazante Group in Brazil, which was once considered Neo-proterozoic in age but which has been redated at 1.1 to 1.3 Ga (78). Atmospheric CO\textsubscript{2} levels above ~30 PAL would permit $p$O\textsubscript{2} values as high as today, according to Fig. 4A. Thus, other arguments are needed to place an upper limit on $p$CO\textsubscript{2} if we wish to constrain mid-Proterozoic $p$O\textsubscript{2} levels.

Additional Results for Lower $p$O\textsubscript{2} Levels (Terrestrial Biosphere Included). Finally, we repeated the calculations shown in Fig. 4 but with a terrestrial (microbial mat) biosphere included. Terrestrial GPP was set at 660 Tmol O\textsubscript{2} · yr$^{-1}$ with an accompanying CH\textsubscript{4} flux equal to half that value (see Recycling by the Terrestrial Biosphere). We assumed O\textsubscript{2} exchange rates with the marine biosphere were the same as in Results for Lower $p$O\textsubscript{2} Levels (Marine Biosphere Only). The effect on $\Delta^{17}$O of O\textsubscript{2} is shown in Fig. 4B. The red contours at −6 and −11‰ shift upward, particularly at low $p$O\textsubscript{2} levels where air–sea O\textsubscript{2} exchange is slow. Most of this change is caused by higher rates of O\textsubscript{2} recycling, which dilutes the O-MIF signal.

However, the interpretation of these results is changed even more if one considers the effect of higher CH\textsubscript{4} levels on climate. The high CH\textsubscript{4} flux assumed here, 10 times the modern value, causes atmospheric CH\textsubscript{4} to increase from 1.6 ppmv in the base, 1 PAL O\textsubscript{2} model to as much as 60 ppmv at some O\textsubscript{2} levels (SI Appendix, Fig. S5). The nonlinear response of CH\textsubscript{4} concentration to its surface input rate has been seen in other models [e.g., Pavlov et al. (79)]. Even at low $p$O\textsubscript{2}, the calculated CH\textsubscript{4} mixing ratio is 15 to 20 ppmv, enough to generate 2 to 3 °C of greenhouse warming (76). One CO\textsubscript{2} doubling produces roughly this same temperature increase when the climate is relatively warm; consequently, we reduced the lower $p$CO\textsubscript{2} limit in Fig. 4B from 12 to 6 PAL. When this change is made, the permissible range for $p$O\textsubscript{2} extends all the way down to 0.1% PAL or lower. If the CO\textsubscript{2} level and CH\textsubscript{4} flux assumed here are correct for the mid-Proterozoic, few constraints can be placed on $p$O\textsubscript{2} from the existing O-MIF data. Terrestrial GPP values of 4,000 Tmol · yr$^{-1}$ or higher (26) can be ruled out, though, because they produce $\Delta^{17}$O values in O\textsubscript{2} less negative than −6‰ (SI Appendix, Fig. S6).

Discussion

Geologic Constraints on Mid-Proterozoic $p$CO\textsubscript{2}. Past atmospheric CO\textsubscript{2} concentrations can be inferred from geologic data as well as from climate models (54). One approach is to study the composition of ancient soils preserved as paleosols. The two samples that are closest in time to the period of interest are the
Flin Flon paleosol at 1.8 Ga (80) and the Sturgeon Falls paleosol at 1.1 Ga (81). The original authors used the fact that these paleosols retained iron during weathering to derive estimates for \( p_{O_2} \). Sheldon (82) reanalyzed them for \( p_{CO_2} \) using a similar kinetic approach. Interpolating between his (very high) \( p_{CO_2} \) value at 1.5 Ga and his much lower value at 1.1 Ga yielded a \( p_{CO_2} \) of 3,600 ppmv (12 PAL in our units) at 1.4 Ga (82). This value should be considered as a lower limit, as Sheldon’s analysis method assumes that all the \( CO_2 \) that enters the soil reacts with silicate minerals. A reanalysis of earlier Archean paleosols by Kanzaki and Murakami (83) using a different methodology yields \( p_{CO_2} \) values that are 10 to 20 times higher than those calculated by Sheldon for those same samples. Thus, the paleosol data support the lower limit on \( p_{CO_2} \) shown in Fig. 4b but may not provide a useful upper limit.

Our lower limit on mid-Proterozoic \( p_{CO_2} \) is also supported by a study of the carbon isotopic composition of microfossils preserved in the Ruyang Group in Shaxi Province, China (84). Carbon isotope fractionation decreases when \( CO_2 \) is less available; hence, the highly depleted \( \delta_{13}C \) values (−32 to −36‰) measured in the microfossils require relatively high \( p_{CO_2} \). They estimate a lower limit of 3,600 ppmv (12 PAL) at 1.4 Ga, similar to Sheldon’s estimate from paleosols.

Upper limits on mid-Proterozoic \( p_{CO_2} \) have been estimated by looking at fossil cyanobacteria as well as their effect on the nature of the sedimentary record. Riding (85) argued that a decline in \( p_{CO_2} \) below 10,000 ppmv (33 PAL) at ~1,400 to 1,300 Ma resulted in blooms of planktic cyanobacteria that induced “whitings” of carbonate mud in the water column whose sedimentary accumulation began to dominate carbonate platforms at that time. A later study of cyanobacterial sheath calcification suggests that 3,600 ppmv (12 PAL) is an upper limit on \( p_{CO_2} \) at 1.2 Ga (86). These authors argue that falling \( CO_2 \) levels led to the evolution of intracellular carbon-concentrating mechanisms that pumped \( CO_2 \) into cell carboxysomes, raising the pH of the surrounding cytosol and triggering in vivo carbonate deposition.

We conclude that atmospheric \( p_{CO_2} \) was likely falling during the mid-Proterozoic and that concentrations of 12 to 24 PAL at 1.4 Ga are in the right ballpark based on geoecology proxy data. If so, then the very low \( p_{O_2} \) levels allowed by Fig. 4b may not be supported. Moving the lower limit on \( p_{CO_2} \) back to 12 PAL in Fig. 4b would imply a lower limit of ~0.5% PAL for \( p_{O_2} \). However, even this limit would not be firm because of possible dilution of the O-MIF signal during sulfate precipitation in the water column.

**Additional Thoughts on Mid-Proterozoic \( CH_4 \).** Our results depend critically on the concentration of atmospheric \( CH_4 \). When \( CH_4 \) is low, that is, when the biogenic methane flux is comparable to (or lower than) today, we can derive a lower limit on mid-Proterozoic \( p_{O_2} \) ~0.8% PAL, from the Sibley data if we assume no recycling of the O-MIF signal in the water column (Results for Lower \( p_{O_2} \) Levels (Marine Biosphere Only)). At 10 times the current methane flux, we get no lower limit on \( p_{O_2} \) whatsoever (Additional Results for Lower \( p_{O_2} \) Levels (Terrestrial Biosphere Included)). In the latter calculations, we assumed a substantial methane flux from terrestrial microbial mats. This assumption is speculative for two reasons: 1) The fractional land coverage and productivity of such mats during the mid-Proterozoic is uncertain. 2) Whether mats grown under low \( p_{O_2} \) could actually generate this much methane is unclear. The cultivation of mats under such conditions might help to answer the latter question.

Some authors (e.g., ref. 79) have also suggested that methane could have been generated in significant amounts in Proterozoic marine sediments. Their argument was that, if GPP was relatively high and the recycling of organic matter by aerobic decay and sulfate reduction were both low, more of the organic matter should have been recycled by fermentation and methanogenesis. This argument has been criticized by other researchers (87–89) who argue that methane production in sediments remains low even under low-\( O_2 \), low-sulfate conditions, partly because of the fact that biological productivity must have been lower because of slower recycling of critical nutrients such as phosphorus (88, 89). Unless this objection can be countered, we accept that marine methane production must have been low.

**Conclusions**

We provide a more mechanistically grounded framework for interpreting the triple oxygen isotope record through Earth’s history. Our model improves on the treatment of atmospheric ozone photochemistry and introduces key constraints on air–sea gas exchange. The O-MIF record provides a measure of the atmospheric ratio of \( O_2:CO_2 \), not of \( p_{O_2} \) itself. A reasonable lower limit on \( p_{CO_2} \) at 1.4 Ga, ~3,600 ppmv or 12 PAL, can be estimated from climate models and is supported by geochemical proxy data. \( CO_2 \) partial pressures lower than this value can be tolerated climatically but only if \( CH_4 \) concentrations were high (>15 ppmv). Given \( p_{CO_2} \) ≥ 12 PAL and low \( CH_4 \), mid-Proterozoic \( O_2 \) should have been >0.8% PAL if the Sibley data are taken at face value. The dilution of the \( \Delta^{17}O \) signal by the reprocessing of sulfate within the water column above where the sulfates were deposited could decrease this lower limit on \( p_{O_2} \), but there is no easy way to quantify this effect. High \( CH_4 \) and lower \( p_{CO_2} \) would also allow \( p_{O_2} \) to have been lower.

Upper limits on \( p_{O_2} \) during the mid-Proterozoic are difficult to estimate from the O-MIF data, again because of uncertainties in \( p_{CO_2} \). Marine GPP cannot be estimated reliably from sedimentary O-MIF data because of complications imposed by constraints on air–sea gas transfer. Terrestrial microbial mat GPP is constrained by similar considerations. If atmospheric \( p_{O_2} \) was low, then terrestrial GPP could only have been high if mats emitted large quantities of \( CH_4 \) or \( H_2 \) to the atmosphere to soak up the emitted \( O_2 \). Despite all these limitations, the sedimentary O-MIF record remains a useful tool for investigating the composition of the Precambrian atmosphere. If better proxies for \( p_{CO_2} \) can be obtained, along with more direct measures of \( \Delta^{17}O \) of atmospheric \( O_2 \), the O-MIF record may eventually lead to a quantitative understanding of the history of atmospheric \( O_2 \).

**Methods**

Our photochemical model includes a main model for normal chemical reactions and an isotopic model designed for oxygen isotope reactions. The main model is derived from Stanton et al. (63). It extends from the ground up to 100 km in altitude and contains full atmospheric chemistry for CHONS (carbon, hydrogen, oxygen, nitrogen, and sulfur) species (up through \( C_5 \) for carbon). Chlorine chemistry has been removed from the model, as it is less important for the preindustrial atmosphere than for today. The main model includes 42 species linked by 175 chemical reactions (SI Appendix). Boundary conditions for the long-lived species are described later in this section. The main model is run to steady state, assuming a fixed solar zenith angle and using a fully implicit time integration scheme.

The boundary conditions in the model are critical and must be chosen carefully. At the upper boundary (100 km), most species are given fixed mixing ratios in the main model. They serve as control variables for the long-lived species or are described later in this section. The main model is run to steady state, assuming a fixed solar zenith angle and using a fully implicit time integration scheme.

Some authors (e.g., ref. 79) have also suggested that methane could have been generated in significant amounts in Proterozoic marine sediments. Their argument was that, if GPP was relatively high and the recycling of organic matter by aerobic decay and sulfate reduction were both low, more of the organic matter should have been recycled by fermentation and methanogenesis. This argument has been criticized by other researchers (87–89) who argue that methane production in sediments remains low even under low-\( O_2 \), low-sulfate conditions, partly because of the fact that biological productivity must have been lower because of slower recycling of critical nutrients such as phosphorus (88, 89). Unless this objection can be countered, we accept that marine methane production must have been low.
given mixing ratios equal to their observed values (SI Appendix, section 2.1.1). The main model then calculates surface fluxes needed to sustain them. At lower \(\text{CO}_2\) levels, these fluxes are held constant in both the main and isotopic models. For \(\text{CH}_4\), the modern mixing ratio is fixed at 1.6 ppmv; this yields a corresponding upward flux of 33 Tmol yr\(^{-1}\), which is comparable to estimates for the \(\text{CH}_4\) flux on modern Earth (91). In the calculations that include terrestrial microbial mats (Additional Results for Lower \(\text{CO}_2\) Levels (Terrestrial Biosphere Included)), the \(\text{CH}_4\) flux was increased to 330 Tmol yr\(^{-1}\), balancing the assumed \(\text{CO}_2\) flux.

The key to calculating the dilution of the O-MIF signal by biospheric recycling is to give special treatment to \(\text{O}_2\) and \(\text{CO}_2\). Unlike shorter-lived gases such as \(\text{CH}_4\), their surface mixing ratios do not depend in a simple way on their surface fluxes. The surface fluxes calculated by the photochemical model, given fixed mixing ratio boundary conditions, are tiny compared to the recycling fluxes described in Dilution of the O-MIF Signal in \(\text{O}_2\) and \(\text{CO}_2\) via Biospheric Recycling. Hence, in the (globally averaged) photochemical model, each gas must be flowing either up or down at the lower boundary, whereas, on the real Earth, \(\text{O}_2\) and \(\text{CO}_2\) are flowing both upward and downward in different places and at different times of the year. We simulate this exchange by inserting fictitious tropospheric chemical production terms for \(\text{O}_2\) and \(\text{CO}_2\) equal to their calculated recycling fluxes (SI Appendix, Table 53) in both main and isotopic codes. These sources are distributed evenly between 0 and 11 km, as should be appropriate for a long-lived gas injected into a rapidly mixed reservoir. The injected \(\text{O}_2\) and \(\text{CO}_2\) have nowhere to go except down through the lower boundary. Dividing those downward fluxes by the number density of each gas yields a deposition velocity, which is then saved for use in the isotopic code. For \(\text{O}_2\) \(\leq 1\%\) PAL, to ensure that we maximize the rate of \(\text{O}_2\) exchange, we gradually increase the fictitious production term until the calculated \(\text{O}_2\) deposition velocity equals the \(\text{O}_2\) described in Recycling by the Marine Biosphere (also see SI Appendix, Table 59).

The structure of the isotopic model is like that of the main model but with significant deviations in the chemical scheme and boundary conditions. The isotopic model contains 358 reactions that duplicate the chemistry in the main model but for isotopically substituted species (SI Appendix, Tables 55 and 58). Both minor O isotopes, \(\text{O}^{17}\) and \(\text{O}^{18}\), are represented in the isotopic model by the total number of O atoms in the molecule. The boundary conditions for the species in the isotopic model are the same as in the main model except for \(\text{O}_2\) and \(\text{CO}_2\) (SI Appendix, Table 59). Instead of assuming fixed mixing ratios, we use fixed deposition velocities for \(\text{O}_2\) and \(\text{CO}_2\) (SI Appendix, Table 59). Each gas is given the same deposition velocity as that derived in the main code, along with the same distributed tropospheric recycling flux. Thus, their surface concentrations can now change in response to fractionating chemistry that occurs within the atmosphere. Because they start close to the solution, the isotopic equations can be iterated to steady state using Newton’s method. SI Appendix, Table 59 shows the boundary conditions used in the main/isotope codes and a flowchart of the model operation described in this section. Further details on the methodology are provided in SI Appendix. Data Availability. All model output data and code are available on Zenodo with the identifier https://doi.org/10.5281/zenodo.4609604.

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