Measurements of $^{18}$O$^{18}$O and $^{17}$O$^{18}$O in the atmosphere and the role of isotope-exchange reactions

Laurence Y. Yeung,1 Edward D. Young,1 and Edwin A. Schauble1

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Of the six stable isotopic variants of O$_2$ to together during photosynthesis. In addition, the observations of natural variations in $^{16}$O$^{18}$O$^{18}$O and $^{16}$O$^{17}$O$^{18}$O$^{16}$O ratios have led to insights in atmospheric, oceanographic, and paleoclimate research. Complementary measurements of the exceedingly rare $^{18}$O$^{18}$O and $^{17}$O$^{18}$O isotopic variants might therefore broaden our understanding of oxygen cycling. Here we describe a method to measure natural variations in these multiply substituted isotopologues of O$_2$. Its accuracy is demonstrated by measuring isotopic effects for Knudsen diffusion and O$_2$ electrolysis in the laboratory that are consistent with theoretical predictions. We then report the first measurements of $^{18}$O$^{18}$O and $^{17}$O$^{18}$O proportions relative to the stochastic distribution of isotopes (i.e., $\Delta_{36}$ and $\Delta_{35}$ values, respectively) in tropospheric air. Measured enrichments in $^{18}$O$^{18}$O and $^{17}$O$^{18}$O yield $\Delta_{36} = 2.05 \pm 0.24\%$ and $\Delta_{35} = 1.4 \pm 0.5\%$ (2σ).

Based on the results of our electrolysis experiment, we suggest that autocatalytic $^{18}$O$^{3}$P + O$_2$ isotope exchange reactions play an important role in regulating the distribution of $^{18}$O$^{18}$O and $^{17}$O$^{18}$O in air. We constructed a box model of the atmosphere and biosphere that includes the effects of these isotope exchange reactions, and we find that the biosphere exerts only a minor influence on atmospheric $\Delta_{36}$ and $\Delta_{35}$ values. $^{18}$O$^{3}$P + O$_2$ isotope exchange in the stratosphere and troposphere is therefore expected to govern atmospheric $\Delta_{36}$ and $\Delta_{35}$ values on decadal timescales. These results suggest that the ‘clumped’ isotopic composition of atmospheric O$_2$ in ice core records is sensitive to past variations in atmospheric dynamics and free-radical chemistry.

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1. Introduction

[2] The global budget of atmospheric O$_2$ is governed on millennial timescales by the biosphere: O$_2$ is produced by photosynthesis and consumed primarily by respiration. Glacial-interglacial fluctuations in its bulk isotopic composition (i.e., its $^{18}$O$/^{16}$O and $^{17}$O$/^{16}$O ratios) over the last 800,000 years are associated with hydrosphere-biosphere feedbacks such as changes in ice sheet volume, evapotranspiration, and primary productivity integrated over ~1,200,000 years periods [Bender et al., 1994; Keeling, 1995; Blunier et al., 2002; Hoffmann et al., 2004; Severinghaus et al., 2009; Landais et al., 2010; Luz and Barkan, 2011]. Stratospheric photochemistry also influences the bulk isotopic composition of O$_2$ by transferring heavy isotopes of oxygen into CO$_2$; those heavy oxygen isotopes are eventually sequestered in the hydrosphere [Yeung et al., 1991; Thiemens et al., 1995; Yung et al., 1997; Luz et al., 1999]. Records of only three O$_2$ isotopic variants, however, are not sufficient to deconvolve these and other feedbacks.

[3] Measurements of $^{18}$O$^{18}$O and $^{17}$O$^{18}$O in atmospheric O$_2$ could offer independent isotopic constraints on O$_2$ budgets. For instance, the isotopic signature of atmosphere-biosphere interactions could potentially be resolved from that of the hydrosphere because the tendency for $^{18}$O$^{18}$O and $^{17}$O$^{18}$O bonds to form upon photosynthesis should be insensitive to the isotopic composition of the source water. Water has no O-O bonds to pass on, so photosynthetic chemistry alone should determine the extent to which $^{18}$O and $^{17}$O ‘clump’ together during photosynthesis. In addition, the mass dependence of respiration for $^{18}$O$^{18}$O and $^{17}$O$^{18}$O could be used in concert with well-known mass dependences for $^{16}$O$^{18}$O and $^{16}$O$^{17}$O with $^{18}$O$^{16}$O to understand oxygen consumption mechanisms in terrestrial and marine environments.

[4] While $^{18}$O$^{18}$O and $^{17}$O$^{18}$O are exceedingly rare (4 ppm and 1.6 ppm, respectively, in O$_2$; see Table 1), recent advances in gas-source mass spectrometry suggest that their variations can be measured with “normal” (i.e., low-resolution) isotope-ratio mass spectrometers (IRMS). The routine analysis of rare ‘clumped’ isotopic variants of CO$_2$ to high precision (i.e., $\leq 0.02\%$ in $^{18}$O$^{18}$C$^{18}$O, which is 46 ppm in CO$_2$ [Eiler and Schauble, 2004; Eiler, 2007; Huntington et al.,]...
Table 1. Properties of O2 Isotopologues in Air

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Mass (amu)</th>
<th>(e_{\gamma-32})</th>
<th>Relative Abundance</th>
<th>Atmospheric Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{16}\text{O}^{16}\text{O})</td>
<td>31.99829</td>
<td>1</td>
<td>1</td>
<td>0.2095</td>
</tr>
<tr>
<td>(^{16}\text{O}^{17}\text{O})</td>
<td>32.994046</td>
<td>0.98466</td>
<td>7.8 \times 10^{-4}</td>
<td>1.6 \times 10^{-5}</td>
</tr>
<tr>
<td>(^{16}\text{O}^{18}\text{O})</td>
<td>33.994076</td>
<td>0.97007</td>
<td>4.1 \times 10^{-3}</td>
<td>8.6 \times 10^{-4}</td>
</tr>
<tr>
<td>(^{17}\text{O}^{16}\text{O})</td>
<td>33.998263</td>
<td>0.97001</td>
<td>1.5 \times 10^{-7}</td>
<td>3.2 \times 10^{-8}</td>
</tr>
<tr>
<td>(^{17}\text{O}^{18}\text{O})</td>
<td>34.998293</td>
<td>0.95605</td>
<td>1.6 \times 10^{-6}</td>
<td>3.4 \times 10^{-7}</td>
</tr>
<tr>
<td>(^{18}\text{O}^{18}\text{O})</td>
<td>35.998322</td>
<td>0.94268</td>
<td>4.2 \times 10^{-6}</td>
<td>8.8 \times 10^{-7}</td>
</tr>
</tbody>
</table>

2. Clumped-Isotope Systematics of O2

2.1. Notation

\(^{18}\text{O}^{18}\text{O}\) and \(^{17}\text{O}^{18}\text{O}\) distributions are reported against the stochastic (random) distribution of isotopes as defined by the following relationships:

\[
\frac{^{33}R_{\text{stochastic}}}{^{16}\text{O}^{17}\text{O}} = \frac{^{17}\text{O}^{16}\text{O}}{^{16}\text{O}^{16}\text{O}} = 2 \frac{^{17}\text{O}}{^{16}\text{O}} = 2^{17}R \tag{1a}
\]

\[
\frac{^{34}R_{\text{stochastic}}}{^{16}\text{O}^{16}\text{O}} = 2 \frac{^{18}\text{O}}{^{16}\text{O}} + \frac{^{17}\text{O}^{17}\text{O}}{^{16}\text{O}^{16}\text{O}} = 2^{18}R + (^{17}R)^2 \tag{1b}
\]

\[
\frac{^{35}R_{\text{stochastic}}}{^{16}\text{O}^{16}\text{O}} = 2 \frac{^{18}\text{O}^{18}\text{O}}{^{16}\text{O}^{16}\text{O}} = 2^{18}R^{17}R \tag{1c}
\]

\[
\frac{^{36}R_{\text{stochastic}}}{^{16}\text{O}^{16}\text{O}} = \frac{^{18}\text{O}^{18}\text{O}}{^{16}\text{O}^{16}\text{O}} = (^{18}R)^3 \tag{1d}
\]

\[
\Delta_{35} = \frac{^{35}R_{\text{measured}}}{^{35}R_{\text{stochastic}}} - 1 \tag{2a}
\]

\[
\Delta_{36} = \frac{^{36}R_{\text{measured}}}{^{36}R_{\text{stochastic}}} - 1 \tag{2b}
\]

in accordance with the recent recommendations by Coplen [2011] and conventions for reporting ‘clumped’ isotope distributions [Huntington et al., 2009; Dennis et al., 2011]. Enrichments and deficits in \(\Delta\)-notation, reported in per mil (%o), reflect proportional deviations from a canonical relationship derived from the bulk isotopic composition, similar to the way in which \(\Delta^{18}\text{O}\) or \(\Delta^{17}\text{O}\) values are derived from \(\delta^{18}\text{O}\) and \(\delta^{17}\text{O}\) values [Miller, 2002; Young et al., 2002]. In this case, the canonical relationship is the random occurrence of isotopes in a molecular species.

[7] Conceptually, \(\Delta\) quantifies the abundances of rare isotopic variants relative to those predicted by chance for a given collection of stable isotopes; \(\Delta = 0\) represents the random distribution of isotopes, whereas a nonzero \(\Delta\) value represents on over- or under-abundance of the indicated rare isotopologue relative to the random distribution. In many instances, this over- or under-abundance of rare isotopologues can be thought of as an excess or deficit in bond ordering, i.e., the tendency of two (or more) rare isotopes to occur as neighbors on the same bond. This definition of \(\Delta\) as an ordering parameter can be misleading, however, when variations in \(\Delta\) occur not through intramolecular bond scission or synthesis, but rather by fractionation of isotopologues. In the latter case, bond ordering is unchanged, but the expected stochastic distribution (e.g., \(^{36}R_{\text{stochastic}}\)) is altered by changing the overall (bulk) isotopic composition of the ensemble (e.g., \(^{18}R\) [Eiler, 2007]).

[8] In effect, \(\Delta\) can change either by altering bond ordering in molecules or by altering the reference stochastic composition. The \(\Delta\) values so defined are not conserved quantities precisely because the stochastic distribution changes with bulk isotopic composition. Apparent isotopic bond ordering can therefore be modified by both bond-altering processes and bond-preserving processes. Atmospheric budgets are affected by mechanisms that fall into both categories [Affek and Eiler, 2006; Affek et al., 2007; Yeung et al., 2009], so we will discuss the isotopic systematics of O2 separately in each context.

2.2. Bond-Ordering Equilibrium: Breaking and Making Bonds, but Preserving Atomic Abundances

[9] The familiar carbonate clumped-isotope paleothermometer [Eiler, 2011] relies on the change in isotopic bond ordering resulting from a bond-breaking/bond-making process: carbonate mineral growth at equilibrium. In that case, intraphase isotope-exchange equilibrium, when achieved [Wang et al., 2004; Ghosh et al., 2006; Eagle et al., 2010], results in a bond-ordering signature that is independent of the isotopic mass balance between the carbonate and its source water. Bond ordering in the carbonate mineral system, consequently, would then depend only on the temperature of equilibration, and thus would be independent of bulk isotopic composition. These equilibrium bond-ordering values are typically enrichments of up to one per mil in \(\Delta\) because heavy isotopes usually prefer to bond with each other at low temperatures [Wang et al., 2004].

[10] The relevant intraspecies isotopic equilibrium state for \(\text{O}_2\) in the atmosphere is gas-phase \(\text{O}_2 + \text{O}_2\) isotope-exchange equilibrium wherein the bulk isotopic composition (and therefore the stochastic distribution) is constant. Bond re-ordering during isotope exchange leads only to changes in \(\Delta_{36}\) and \(\Delta_{35}\) values. Theoretical equilibrium \(\Delta_{36}\) and \(\Delta_{35}\)
values are 1.5–3.0% for $\Delta_{36}$ and 0.8–1.6% for $\Delta_{35}$, between 300 and 200 K [Wang et al., 2004]. Thus, any process that breaks and re-forms O-O bonds without consuming or producing O$_2$ could, in principle, drive $\Delta_{36}$ and $\Delta_{35}$ toward equilibrium values with no measurable change in $\delta^{18}$O and $\delta^{17}$O. Possible mechanisms resulting in equilibration include the reversible decomposition of alkali-earth peroxides (Section 3.2), catalytic isotope exchange on zeolites (Section 3.3) [Starokon et al., 2011], and gas-phase O ($P$) + O$_2$ isotope exchange reactions (Section 4.2) [Kaye and Strobel, 1983].

2.3. Physical Fractionation: Preserving O-O Bonds

[11] The simplest bond-preserving process relevant to the atmosphere is two-component mixing. The isotopic composition (e.g., $^{18}$R and $^{36}$R$_{measured}$) varies linearly with mixing fraction, yet the stochastic distribution, i.e., $^{36}$R$_{stochastic} = (^{18}$R)$^2$, varies nonlinearly with mixing fraction. So, even if a mixture consists of two gases with the same initial $\Delta_n$ values, mixing yields $\Delta_n$ anomalies; $\Delta_n$ is not conserved. Mixing equal parts O$_2$ with $^{18}$O$_{water}$ (e.g., ocean water) and $^{18}$O$_{atmospheric}$ O$_2$, both starting with $\Delta_{36} = 0$, yields an anomaly of +0.15‰ in $\Delta_{36}$ (see Figure 1). This feature of $\Delta_n$ notation has been demonstrated in previous work on CO$_2$ [Eiler and Schauble, 2004]. Only in rare cases, such as when the mixing end-members have the same bulk isotopic composition, are $\Delta_n$ values conserved upon mixing. Mixing-based budgets for atmospheric $\Delta_n$ values are therefore less straightforward than traditional budgets based solely on bulk isotopic $\delta$-notation.

[12] An intuitive relationship between isotopologue fractionation and $\Delta_n$ values for O$_2$ for bond-preserving processes can be derived from the familiar parlance of mass-dependent isotope effects. Here, we follow the practice of describing fractionation factors $\alpha$ related by mass dependences $\beta$ [Young et al., 2002]:

$$\alpha_m = (\alpha_i)^{R_{m}/R_{i}}$$  

where the numerical subscripts describe fractionation factors between different O$_2$ isotopologues of mass $m_i$ and $m_j$ and $^{18}$O/^{16}$O ($m = 31.989829$). In equation (3), a fractionation that preserves $\Delta_{36}$ and $\Delta_{35}$ has mass dependences of $\beta_{36/34} = 0.500$ and $\beta_{35/34} = 0.66$, respectively. While $\beta_{36/34} = 0.500$ preserves $\Delta_{36}$ as a natural consequence of its definition, $\beta_{35/34}$ values that preserve $\Delta_{35}$ vary somewhat with $\beta_{34/33}$ due to the presence of two different rare stable isotopes in $^{18}$O/^{16}$O. We derive these relationships in Appendix A. Graphically, $\Delta_n$ values are approximated by horizontal excursions on a triple-isotopologue plot relative to the mass-dependent relationship for the stochastic distribution, i.e., $\delta^{36}$ excursions relative to a $\beta_{36/34} = 0.500$ line on a $^{35}$O versus $^{34}$O plot (see Figure 2). Examples of these mass dependences can be found in gravitational fractionation and Knudsen diffusion.

[13] A stagnant air column in a gravitational potential will have a higher partial pressure of heavy isotopologues at the base. This fractionation depends on mass according to the barometric formula. For a species of mass $m$, its partial pressure $P$ at a height $z$ and temperature $T$ can be related to the surface partial pressure $P_0$ by the equation:

$$P = \frac{m}{P_0} = e^{\frac{w}{R_T}}$$  

where $g$ is the acceleration due to gravity (9.81 m s$^{-2}$) and $R_G$ is the gas constant. This equation can be recast to reflect isotopic ratios:

$$\alpha_{m,gravitation} = \frac{m_{diffused}}{m_{initial}} = (m_{atm} - m_{ocean})Z$$  

where $m_{32}$ is the mass of $^{16}$O/^{16}$O. One can now recognize that because the mass difference between $^{16}$O/^{16}$O$ and $^{17}$O/^{16}$O$, $(m_{32} - m_{33})$, is exactly half the mass difference between $^{18}$O/^{16}$O$ and $^{16}$O/^{16}$O$, $(m_{32} - m_{33})$, we have $(m_{34})^2 = m_{36}$. Therefore, $\alpha_{34} = (\alpha_{36})^{0.5}$, or $\beta_{36/34} = 0.5$, and gravitational fractionation has a negligible effect on $\Delta_{36}$ (even when including the contribution from $^{17}$O/^{16}$O$; see Appendix A). A similar argument can be made to show that $\beta_{35/34} = 0.666$, resulting in no fractionation for $\Delta_{35}$. This behavior for $\Delta_{36}$ and $\Delta_{35}$ is distinct from the bulk-isotope fractionations of 0.1–1‰ in natural systems [Craig et al., 1988; Severynhaus et al., 1996].

[14] Knudsen diffusion, in contrast, leads to changes in both $\Delta_{36}$ and $\Delta_{35}$. Graham’s law of effusion states that the flux of gas through an orifice smaller than the mean free path of that gas will be inversely proportional to the square root of its mass. For pure O$_2$ gas, the isotopic fractionation factor is:

$$\alpha_{m, m_{32}}_{effusion} = \frac{m_{diffused}}{m_{initial}} = \sqrt{\frac{m_{32}}{m_{34}}}$$  

Mass dependences for effusion can be derived from these $\alpha$ values to be $\beta_{36/34} = 0.515$ and $\beta_{35/34} = 0.676$ (see Table 1),
Figure 2. Example of a bond-preserving fractionation process that can generate $\Delta_{36}$ anomalies. Knudsen diffusion subject to Rayleigh fractionation has $\beta_{36/34} = 0.522$ in the residue, which generates a $\Delta_{36} < 0$ anomaly relative to the stochastic distribution ($\beta_{36/34} = 0.500$). The arrow depicts an anomaly of $\Delta_{36} = 0.4\%$. 

which lead to $\Delta_{36}$ and $\Delta_{35}$ increases in the isotopically lighter diffused population: $O_2$ that has leaked through a critical orifice from an infinite reservoir is lower in $^{18}O$ and $^{17}O$ by 29.9 and 15.3, respectively, but higher in $\Delta_{36}$ and $\Delta_{35}$ by 1.7 and 0.9, respectively, than the reservoir. This fractionation is a classic example of ‘clumped’ isotope signatures changing due to shifts in the stochastic reference frame (i.e., the bulk isotopic composition of the gas).

[15] In a finite system, the residue population will be fractionated in the opposite direction: Higher in $^{18}O$ and $^{17}O$, but lower in $\Delta_{36}$ and $\Delta_{35}$ (see Figure 2). Furthermore, this closed system has $\beta$ values that are slightly larger than the infinite system due to the effective $\alpha$ values derived from Rayleigh fractionation relationships:

$$R_{\text{residue}} = R_{\text{initial}} f^{\alpha_{\text{effective}} - 1}$$

$$R_{\text{diffused}} = R_{\text{initial}} \frac{1 - f^{\alpha_{\text{effective}}}}{1 - f}$$

where $f$ represents the fraction of the initial gas remaining, and $\alpha$ for the Rayleigh system is defined by $R_{\text{initial}}$ [Young et al., 2002]. $\beta_{36/34}$ and $\beta_{35/34}$ values, defined by connecting the $R_{\text{diffused}}$ and $R_{\text{residue}}$ corresponding to a single $f$ value, range from 0.515–0.522 and 0.676–0.681, respectively, depending on $f$. We explore these particular systematics experimentally in Section 4.1.

3. Methods

[16] To analyze $^{18}O$ and $^{17}O$ in $O_2$, argon was first removed from samples using gas chromatography at sub-ambient temperatures. Next, the purified $O_2$ was analyzed against a working reference gas on an IRMS, where the residual Ar content was also measured (as a $m/z = 40$ voltage ratio). Then, standard gases with similar bulk isotopic composition, but a ‘clumped-isotope’ composition near the stochastic distribution, were prepared and analyzed over a range of Ar concentrations. Reported $\Delta_{36}$ and $\Delta_{35}$ values correspond to the excesses or deficits in $^{18}O$/$^{16}O$ and $^{17}O$/$^{16}O$ ratios relative to the stochastic distribution of isotopes after correction for the residual Ar signals and deviations from a purely stochastic distribution in the reference gases (see Appendix B).

3.1. Sample Handling and Purification

[17] $O_2$ samples (150–200 $\mu$mol $O_2$) were transferred to and from a gas chromatographic system through two glass U-traps at $-196^\circ$C on a high-vacuum glass line pumped by a diaphragm-backed turbomolecular pump (Pfeiffer HiCube), which had a typical baseline pressure of $\approx 5 \times 10^{-6}$ mbar. Purified $O_2$ samples were adsorbed for 10 min onto small glass fingers filled with molecular sieve 5A pellets at $-196^\circ$C before analysis on the IRMS.

[18] The gas chromatographic (GC) system, which was designed to separate $O_2$ from Ar and N$_2$, consisted of a reconditioned HP 5890 Series II GC capable of cryogenic cooling with liquid nitrogen and thermal conductivity detection. First, samples were adsorbed onto degassed silica gel pellets in a U-trap at $-196^\circ$C for ~30 min. The U-trap was then immersed in warm water ($\approx 60^\circ$C) while an ultrahigh-purity helium carrier gas ($>99.9995$%; Grade 5.5) flowed through it to desorb the sample. The desorbed sample was then injected onto the GC column (3 m, molecular sieve 5A, 80/100 mesh; Restek) using two 4-way VICI/Valco switching valves. As an additional precaution against atmospheric leaks, the switching valves were isolated in He-flushed “jackets.” The eluent from the GC column was collected on a second silica gel U-trap downstream from the GC column at $-196^\circ$C. Air samples were passed through the GC system a second time to remove residual Ar remaining from the first pass. A diagram of the vacuum/GC extraction and purification system is shown in Figure 3.

[19] Baseline separation of Ar, $O_2$, and N$_2$ was achieved at $T \leq -65^\circ$C, and routine separations were carried out at $-80^\circ$C. The volumetric flow rate was 25 mL min$^{-1}$ (~23 psi He carrier). Argon typically eluted near 30 min, while $O_2$ eluted near 38 min (see Figure 3); collection of $O_2$ lasted 23–25 min, starting near minute 37. After collection of $O_2$, the column temperature was raised to 200°C and the He pressure was raised to 40 psi to elute N$_2$.

[20] The conditions for $O_2$/Ar separation were chosen to minimize both residual Ar and total sample preparation time. Higher $O_2$/Ar elution temperatures decreased the $O_2$/Ar peak resolution and also increased the amount of Ar in the purified product. For instance, raising the temperature to 25°C after the Ar peak eluted, which reduced the $O_2$ collection time to ~15 min, actually increased the Ar content relative to a 25-min collection at $-80^\circ$C. Furthermore, using a 6-m molecular sieve 5A column yielded no improvements in $O_2$/Ar separation efficiency due to on-column dispersion and a longer $O_2$ collection time. However, installing a U-trap to purify the helium carrier filled with molecular sieve 5A and
a 6-ft silica gel column (45–60 mesh; SRI International), both at −196°C, resulted in a twofold improvement in Ar removal. Consequently, we believe that Ar impurities in the helium stream ultimately limited O2 purity in the current system. Typical air preparations with two passes through our system resulted in 1–5 ppm 40Ar (i.e., 3–17 ppb 36Ar) in O2. Additional small ion corrections at m/z = 36 were necessary for high-precision measurements of 18O18O (see Appendix B).

3.2. Standardization

[21] The use of a stochastic reference frame for O2 isotope-abundance requires that one develop methods to generate laboratory standards with known ∆36 and ∆35 values over a range of bulk isotopic composition [Huntington et al., 2009; Dennis et al., 2011]. High-temperature standards, reflecting ∆36 ∼ ∆35 ∼ 0, are a convenient reference close to the stochastic distribution. We utilized the reversible decomposition of BaO2 to generate Ar-free O2 at high-temperature isotopic equilibrium:

$$2\text{BaO}_2(s) = 2\text{BaO}(s) + \text{O}_2(g)$$  (9)

Argon can be pumped out at low temperatures so O2 will evolve exclusively from the lattice when the peroxide is heated above 600°C [Tribelhorn and Brown, 1995]. The oxygen atoms in each product O2 molecule originate from different peroxide groups in the mineral lattice [Tribelhorn and Brown, 1995], and the process is reversible, so BaO2 decomposition at high temperatures should produce a ‘clumped-isotope’ distribution in the evolved O2 reflecting high-temperature equilibrium; experimental studies indicate that equilibrium can be maintained at T < 1000°C at low heating/cooling rates [Tribelhorn and Brown, 1995; Jorda and Jondo, 2001]. This method is general to alkali-earth peroxides, and is similar to that used by Asprey [1976] to synthesize pure F2 gas from the reversible decomposition of solid K2NiF6 KF, i.e., 2(K2NiF6 KF)solid = 2(K3NiF6)solid + F2.

[22] To estimate the clumped-isotope composition of O2 derived from BaO2 decomposition, theoretical models for bond-ordering in O2 and BaO2 were used. A comparative model of isotopologue ordering in O2 was calculated using the same method and data as Wang et al. [2004], using the harmonic frequency of 16O16O [Huber and Herzberg, 1979]. Vibrational frequencies of isotopologues were determined from their reduced masses, and the resulting estimate was essentially identical to the harmonic model of Wang et al. [2004]. We note that Wang et al. [2004] showed that inclusion of anharmonic terms has a minor effect on ordering equilibria for O2, <0.01‰ at room temperature.

[23] BaO2 is predicted to be much less enriched in multiply substituted isotopologues than O2 is at all temperatures (see Figure 4 and Appendix C). It is also predicted to have lower 18O/16O and 17O/16O ratios. Above 600°C, ∆36 and ∆35 are both predicted to be <0.01‰ in BaO2, whereas they

Figure 3. Schematic of the GC and vacuum-line extraction and purification system. During sample purification, helium flows through both silica gel traps. After GC separation, the switching valves are rotated to isolate the vacuum prep line from the helium flow. Also shown is a typical gas chromatogram of O2/Ar separation for ~20 cm3 samples of air. N2 was eluted from the column at higher temperatures after collection of O2.

Figure 4. Calculated ‘clumped’ isotopic fractionation for the BaO2 and O2 systems relative to atomic O vapor.
are predicted to be $\leq 0.08\%$ in O$_2$. As with the C-O bonding system, there appears to be a strong correlation between equilibrium constants and bond order, with double-bonded species (e.g., CO$_2$ and O$_2$) showing larger enrichments in multiply substituted isotopologues than species with lower-order bonds (e.g., C–O bonds in carbonate and bicarbonate and O–O bonds in peroxide) [Wang et al., 2004; Schauble et al., 2006; Eagle et al., 2010].

[24] To decompose BaO$_2$ in the laboratory, BaO$_2$ powder was first loaded into 1/4" OD quartz tubes and pumped to $10^{-5}-10^{-5}$ mbar overnight. Afterwards, the quartz tubes were sealed with a torch and placed in a tube furnace at 800°C for 2.5 h (calculated $\Delta_{36} = 0.03\%$ and $\Delta_{35} = 0.02\%$). Hot breakseals were quenched immediately when plunged into cold water. As a test of the breakseal method, we also performed experiments in which BaO$_2$ was heated to 800°C for 2.5 h in an evacuated 9-mm ID quartz-and-glass tube that extended from the interior of the tube furnace to an aliquot volume. In this arrangement, the evolved O$_2$ was allowed to equilibrate with BaO and BaO$_2$ only at high temperatures, unlike the breakseal-quenching process, in which some low-temperature isotope exchange might be present. We did not observe significant differences beyond typical experimental scatter in the resulting $\Delta_{36}$ and $\Delta_{35}$ values measured ($\pm 0.1-0.3\%$, depending on the isotopologue), consistent with the breakseal method yielding O$_2$ at high-temperature equilibrium.

[25] A second method for generating high-temperature O$_2$ standards in breakseals was also developed. In that method, O$_2$ was collected into breakseals with molecular sieve 5A and Platinum wire and heated to 1000°C (expected $\Delta_{36} = 0.02\%$ and $\Delta_{35} = 0.01\%$). Hot breakseals were again quenched immediately by plunging them into cold water.

While we cannot rule out a lower ‘blocking’ temperature for gases prepared in this manner, high O$_2$ concentrations should passivate platinum when $T < 500$°C [Brewer, 1953], where $\Delta_{36} = 0.11\%$ and $\Delta_{35} = 0.06\%$, so O$_2$ standards prepared in this manner are still expected to be near the stochastic distribution, and nearly indistinguishable from it within the analytical uncertainty. We note that this method altered the bulk isotopic composition of O$_2$, probably by isotopic exchange with the molecular sieve and/or quartz, but the bulk isotopic fractionation was relatively consistent.

3.3. Other Sources of Isotopic Reordering

[26] While the oxygen-oxygen bond in O$_2$ is not easily broken (bond dissociation enthalpy 118 kcal mol$^{-1}$), any isotopic reordering during sample preparation and analysis will result in an alteration of $\Delta_{36}$ and $\Delta_{35}$. Thus, we performed experiments with O$_2$ samples enriched in $^{18}$O to quantify the extent of isotopic reordering in our sample preparation scheme.

[27] The extent of isotopic reordering in the source of the IRMS was determined by measuring the isotopic composition of our O$_2$ standard gas “spiked” with an aliquot of $\geq 97\%$ $^{18}$O (Cambridge Isotope Labs). Significant isotopic reordering in the IRMS source would result in a significant increase in $\delta^{34}$ (500–600‰ for our $^{18}$O spike size), with little change in $\delta^{38}$ relative to the unspiked O$_2$, due to fragmentation-recombination reactions such as

$$^{16}$O$^{16}$O + e$^-$ $\rightarrow$ $^{16}$O$^+$ + $^{16}$O$^2-$ \hspace{1cm} (10)$$

$$^{18}$O$^{16}$O + $^{16}$O$^+$ $\rightarrow$ $^{16}$O$^{18}$O + $^{18}$O$^+$. \hspace{1cm} (11)$$

Zero isotopic reordering would yield (i) no change in $\delta^{18}$O beyond any $^{16}$O$^{18}$O present in the $\geq 97\%$ $^{18}$O gas and (ii) a large change in the $m/z = 36$ voltage. In our experiment, we observed only a small change in $\delta^{34}$ (9‰) and a relatively large change in $\delta^{38}$ ($3.4 \times 10^{-6}$‰), indicating that the extent of O$_2$ isotopic reordering in the IRMS source was small. We further quantified the extent of isotopic reordering in the IRMS source by the method of standard additions (see Figure 5). The results were consistent with only 1% of the bonds being reordered toward an (probably high-temperature) isotope-exchange equilibrium in the IRMS source.

[28] Similar $^{18}$O$^{18}$O spike-reordering tests were performed with molecular sieve adsorbents because O$_2$ can exchange isotopes with the molecular sieves and/or reorder its isotopes on the surface of molecular-sieve zeolites at low temperatures [Starokon et al., 2011]. Adsorption of O$_2$ onto the molecular sieve 5A at $-196$°C, followed by desorption at 240°C for 30 min, resulted in $\sim 1\%$ isotopic reordering. Passing gas through the GC system only reordered isotopes in O$_2$ after the column was baked with a helium flow at 350°C overnight ($\sim 12$h). In that case, the bond ordering resembled equilibrium at the GC temperature, $-80$°C. During a typical air preparation, O$_2$ was exposed to molecular sieve four times (twice through the GC and twice in a sample finger), which would result in a reduction in $\Delta_{36}$ signal magnitude of $\sim 4\%$ (i.e., $\sim 0.08\%$ for $\Delta_{36} = 2\%$). We observed some evidence for isotopic reordering ($2-3\%$) upon exposure to a pressure gauge that had both Pirani-type and inverted magnetron...
During our sample preparation.

\[ \frac{P_{ds}}{P_{us}} = 0 \]

(i.e., diffusion through a critical orifice lead to measured \( \Delta_{36} = 1.33 \)) also yielded gas flow properties in the transition regions. 

d values do not change with temperature from \( T = 296 \) to \( T = 196 \text{C} \) (total volume \( V = 5 \text{L} \) before being collected onto a silica gel trap at \( T = 196 \text{C} \) for purification on the GC system. The purpose of the second 5-L bulb was to reduce back-diffusion through the critical orifice, as adsorption of \( \text{O}_2 \) onto silica gel is a slow process. The steady state pressure on the “diffused” side of the apparatus was \( \leq 10^{-1} \text{ mbar} \) during the experiment. After 3 h of diffusion, both bulbs were isolated from the critical orifice, and the diffused population was allowed to adsorb onto the silica gel trap for another 60 min. Both the diffused and residue population were analyzed on the IRMS.

The results of the diffusion experiment are shown in Figure 6 and Table 2. As predicted for a diffusion-limited system, the diffused gas exhibited decreases in \( \delta^{18}O \) and \( \Delta_{36} \) and increases in \( \Delta_{35} \). In addition, using equation (12) with \( \frac{P_{ds}}{P_{us}} = 0.2 \) yields good agreement between theory and experiment. The measured isotopic fractionations yield a \( \beta_{36/34} \) value of 0.517 \( \pm \) 0.002 \( \sigma \), consistent with the predicted \( \beta_{36/34} \) of 0.518. An assumption of no back-diffusion, i.e., \( \frac{P_{ds}}{P_{us}} = 0 \), instead predicts bulk-and clumped-isotope fractionations that are smaller, and an \( f \) value that is larger, than the measured values.

Back-diffusion of order 20% is possible given the relatively slow \( \text{O}_2 \) adsorption rate onto silica gel, which resulted in the relatively high steady state downstream pressure of \( \leq 10^{-1} \text{ mbar} \). However, the size of our critical orifice \( (D/L = 1.33) \) also yielded gas flow properties in the transition region between purely molecular (Knudsen) and purely viscous (Poiseuille) flows. Because viscous flow does not fractionate isolopologues, while Knudsen diffusion fractionates isolopologues according to Graham’s law, a small amount of viscous flow probably reduces Graham’s law of fractionation factors could be described by the equation [Benedict, 1947; Naylor and Backer, 1955]:

\[
\alpha_{m_i-m_j} = \left( \frac{m_{ij}}{m_i} - 1 \right) \left( 1 - \frac{P_{ds}}{P_{us}} \right) 
\]

where \( P_{ds}/P_{us} \) is the ratio of pressures in the downstream and upstream volumes.

Assuming no back diffusion, i.e., \( P_{ds}/P_{us} = 0 \), and \( f = 0.5 \), the difference in \( \delta^{18}O \) and \( \Delta_{35} \) between the diffused and residue populations is calculated to be -41.9‰, -21.4‰, +2.7‰, and +1.4‰, respectively. For \( P_{ds}/P_{us} = 0.1 \) and \( f = 0.5 \), the difference between the diffused and residue populations is calculated to be -37.7‰, -19.2‰, +2.5‰, and +1.3‰, respectively. Because the mass dependence of diffusion governs both forward and back-diffusion, \( \beta_{36/34} \) and \( \beta_{35/34} \) values do not change appreciably for \( f = 0.5 \) (i.e., \( \beta_{36/34} = 0.5170 \) versus 0.5174 for \( P_{ds}/P_{us} = 0 \) versus 0.1, respectively). Thus, back-diffusion mainly reduces the bulk isotopic fractionation relative to the unidirectional Rayleigh limit.

In our pinhole diffusion experiment, we allowed \( \text{O}_2 \) gas to diffuse from a 5-L glass bulb through an orifice of known diameter into a vacuum. We measured the isotopic composition of both the diffused and residue populations. The initial pressure in the 5-L bulb was 1.0 mbar, resulting in a mean free path, \( \lambda \), of 100 \( \mu \text{m} \). Molecular oxygen diffused through a laser-drilled orifice (Lenox Laser) with a diameter, \( D \), of 75 \( \pm \) 7.5 \( \mu \text{m} \). It then passed through a length of flexible bellows tubing and a second 5-L bulb and two U-traps at \( T = 196 \text{C} \) (total volume \( V = 5 \text{L} \)) before being collected onto a silica gel trap at \( T = 196 \text{C} \) for purification on the GC system. The purpose of the second 5-L bulb was to reduce back-diffusion through the critical orifice, as adsorption of \( \text{O}_2 \) onto silica gel is a slow process. The steady state pressure on the “diffused” side of the apparatus was \( \leq 10^{-1} \text{ mbar} \) during the experiment. After 3 h of diffusion, both bulbs were isolated from the critical orifice, and the diffused population was allowed to adsorb onto the silica gel trap for another 60 min. Both the diffused and residue population were analyzed on the IRMS.

4. Experiments

4.1. Knudsen Diffusion: Mass Fractionation While Preserving O-O Bonds

[20] We performed experiments to induce shifts in \( \Delta_{36} \) and \( \Delta_{35} \) by Knudsen diffusion of \( \text{O}_2 \). These experiments provide a useful test of our analytical methods because the changes in \( \Delta_{36} \) and \( \Delta_{35} \) due to diffusion are readily calculable. We showed, in Section 2.3, that fractionation factors \( \alpha \) for \( \text{O}_2 \) diffusion through a critical orifice lead to measured effective \( \beta_{36/34} \) and \( \beta_{35/34} \) values of between 0.515-0.522 and 0.676-0.681, respectively, for a system subject to Rayleigh fractionation. In a laboratory setting, back-diffusion through the critical orifice can also alter effective \( \alpha \) and \( \beta \) values: Because the “downstream” volume is never ideal (finite size and pressure), gas can travel “upstream” into the high-pressure volume. This back-diffusion is subject to the same isotopic fractionation described in equations (6)-(8), but with a time-dependent \( R_{\text{initial}} \) value corresponding to the changing \( R_{\text{diffused}} \) in a Rayleigh system; Benedict showed
fractionations with a scaling factor on \((\alpha - 1)\) similar to the effect of back-diffusion in equation (12). Furthermore, theoretical calculations by Wahlbeck [1971] suggest that gas flux through the orifice is enhanced by \(\sim 20\%\), presumably due to increasing viscous flow, relative to the flux predicted for purely molecular flow at \(\lambda D = 1.33\). Thus, we are unable to distinguish between back-diffusion and partially viscous flow leading to a \(20\%\) reduction in \((\alpha - 1)\) values in this experiment. Decreasing the orifice size to achieve purely molecular flow \((\lambda D \geq 10, i.e., D \leq 10 \mu m \text{ at 1 mbar})\) would reduce the mass flow rate through the orifice more than 50-fold, increasing the experiment’s duration to about a week. Such timescales are impractical for this experiment because atmospheric leaks would have become important. Cryo-trapping the diffused \(O_2\), however, would eliminate back-diffusion and isolate the viscous-flow contribution to the observed diffusive isotope fractionation.

4.2. \(O_2\) Electrolysis: Bond-Ordering Equilibration

Independent of Bulk Isotopic Composition

\[Q^3P + O_2 \rightarrow OOQ \rightarrow Q^3P + OQ\]  

\[M + OQQ\]

where \(Q\) denotes an isotope of oxygen and \(M\) is a third body such as another \(O_2\) molecule. In a closed system, the bulk isotopic composition is determined by the \(O_2/O_3\) mass balance and isotopic effects in \(O_3\) formation [Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001], while oxygen atoms in their ground electronic state, \(O^3P\), act as catalysts for bond reordering in molecular oxygen.

When a ground-state oxygen atom forms a bond with an \(O_2\) molecule, it has three possible fates: ozone formation, inelastic scattering, and isotopic exchange. A stable ozone molecule forms only when a third body, \(M\), absorbs the excess energy released during \(O-O\) bond formation. Without that third body, the metastable \(O_3\) can redissociate to \(O^3P\) + \(O_2\). If the \(O-O\) bond that breaks is the one that just formed, then inelastic scattering results. If the other bond breaks, then isotopic exchange occurs. In either case, the liberated \(O^3P\) atom perpetuates an autocatalytic cycle. Consequently, reaction (13a) occurs at rates at least several hundred times faster than that of (13b) at pressures of \(\sim 50\) mbar [Kaye and Strobel, 1983; Johnston and Thiemen, 1997; Wiegel et al., 1997]. This difference in rates will decouple \(\Delta_{36}\) and \(\Delta_{35}\) values from the bulk isotopic composition of \(O_2\): While \(R_{\text{measured}}^{36}\) and \(R_{\text{measured}}^{35}\) change with every applicable isotope-exchange event, \(R_{\text{stochastic}}^{36}\) and \(R_{\text{stochastic}}^{35}\) vary only with \(\delta^{18}O\) and \(\delta^{17}O\), which is governed by the \(O_2/O_3\) mass balance.

\[\text{Excited atomic oxygen, } O^1D, \text{ could also exchange isotopes with } O_2, \text{ but } O^3P \text{ chemistry should dominate the bond-ordering budget in most systems. Nearly all } O^3P \text{ atoms would be quenched to } O^1P \text{ eventually by } N_2 \text{ or } O_2, \text{ after which isotope exchange proceeds autocatalytically. Even in the presence of unconventional chemical physics on } O_3 \text{ potential energy surface, the large number of } O^3P + O_2 \text{ isotope exchange reactions occurring is predicted to yield an isotopic distribution in } O_2 \text{ that is controlled by differences in zero-point energies in the } O_3 \text{ isotopologues [Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001]. } \Delta_{36} \text{ and } \Delta_{35} \text{ values, as measures of bond ordering and not bulk isotopic composition, are therefore expected to reflect mass-dependent isotopic equilibrium, while } \delta^{18}O \text{ and } \delta^{17}O, \text{ being measures of bulk isotopic composition only, will reflect the mass-independent isotopic fractionation that dominate ozone-formation chemistry.}\]

\[O^3P + O_2 \rightarrow OOQ \rightarrow Q^3P + OQ\]

\[M + OQQ\]

where \(Q\) denotes an isotope of oxygen and \(M\) is a third body such as another \(O_2\) molecule. In a closed system, the bulk isotopic composition is determined by the \(O_2/O_3\) mass balance and isotopic effects in \(O_3\) formation [Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001], while oxygen atoms in their ground electronic state, \(O^3P\), act as catalysts for bond reordering in molecular oxygen.

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\[\text{To realize } O^3P + O_2 \text{ isotope exchange in the laboratory, } O_2 \text{ was electrolyzed with a radio-frequency discharge in a manner similar to the classic experiments of Heidenreich and Thiemen [1983]. We fabricated a vessel out of a 100-mL round-bottom flask, a tungsten electrode (1.5 cm exposed to vacuum), and a 9-mm Louwers-Hapert vacuum valve outfitted with fluorinated-elastomer O-rings (Markez). The exterior wire lead was jacketed so the entire vessel could be immersed in a cold bath without wetting the wire. Electrolysis was initiated by setting a Tesla coil at its lowest audible level for one hour. Pressures inside the vessels were 50 to 60 mbar at } 25^\circ C, \text{ resulting in a mean free path } \lambda \leq 30 \mu m \text{ versus the vessel’s } 2-cm \text{ radius; under these conditions, } O^3P + O_2 \text{ reactions should primarily occur in the gas phase with only a minor contribution from surface chemistry. After the experiment, } O_3 \text{ was cryogenically separated from } O_2, \text{ which was passed through the GC system twice to remove residual } O_3 \text{ and any contaminants.}\]

\[\text{Electrolysis experiments were performed at three bath temperatures: } 25^\circ C, -30^\circ C, \text{ and } -80^\circ C. \text{ The vessel temperature was maintained by submerging the round-bottom flask into a water bath (25°C experiment) or ethanol bath (}-30^\circ C \text{ and } -80^\circ C \text{ experiments}). \text{ Because the Tesla coil added heat to the vessel, the bath temperature was monitored and, if necessary, the bath was cooled, every 10 to 15 min. This procedure yielded stable bath temperatures to within } \pm 3^\circ C. \text{ Temperatures inside the reaction vessel were not measured, but we performed several additional blank experiments to...\]
estimate the effective internal temperatures: A thermocouple was inserted into the reaction vessel while it was open to atmosphere (P ∼ 1 bar) and the temperature was monitored for 10 min with the Tesla coil on, simulating experimental conditions. Internal temperatures increased monotonically in all cases, by +10°C, +16°C, and +18°C for the 25°C, −30°C, and −80°C baths, respectively. Therefore, we estimate that effective, time-integrated temperatures inside the reaction vessel were +5°C, +8°C, and +9°C warmer than the 25°C, −30°C, and −80°C baths, respectively.

Figure 7. O + O2 isotope exchange rapidly re-orders 16O-18O and 17O-18O bonds in O2. Electrolysis of pure, stochastically ordered O2 (i.e., Δ36 ≈ Δ35 = 0) at low temperatures with a RF discharge resets Δ36 and Δ35 near their equilibrium values. Error bars show analytical 2σ uncertainties.

Table 3. Results of Electrolysis Experiments

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Δ36</th>
<th>Δ35</th>
<th>Δ36 Predicted</th>
<th>Δ35 Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/14/11</td>
<td>23.398</td>
<td>11.912</td>
<td>1.91</td>
<td>1.1</td>
</tr>
<tr>
<td>10/19/11</td>
<td>23.477</td>
<td>11.961</td>
<td>2.04</td>
<td>1.6</td>
</tr>
<tr>
<td>10/20/11</td>
<td>23.307</td>
<td>11.869</td>
<td>2.14</td>
<td>1.4</td>
</tr>
<tr>
<td>10/21/11</td>
<td>23.552</td>
<td>12.003</td>
<td>2.01</td>
<td>1.6</td>
</tr>
<tr>
<td>10/24/11</td>
<td>23.388</td>
<td>11.914</td>
<td>2.13</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Average ± 2 s.e. 23.424 ± 0.083 11.932 ± 0.046 2.05 ± 0.08 1.4 ± 0.2

*Dates are given as mm/dd/yy.

The δ36 and δ35 are reported against VSMOW using a laboratory standard gas calibrated with San Carlos Olvina (δ18O = 5.2‰, δ17O = 2.7‰). Our results are consistent with previous direct determination of the O2 bulk isotopic composition (δ18O = 23.51‰ and δ17O = 12.18‰) [Thiemens and Meagher, 1984]. A more recent measurement has reported δ18O = 23.88‰ and δ17O = 12.08‰ [Barkan and Luz, 1991].

External standard error of replicate gas preparations; systematic uncertainties increase 2σ limits to ±0.24‰ and ±0.5‰ in Δ36 and Δ35, respectively.

are controlled by two different mechanisms in this system, one of which [O(3P) + O2 isotope exchange] equilibrates Δ36 and Δ35 despite persistent disequilibrium in the O2/O3 system.

[40] Autocatalytic O(3P) + O2 isotope exchange is the most likely mechanism to equilibrate Δ36 and Δ35 because of (i) its high bimolecular reaction rate, (ii) the paucity of permanent O(3P) sinks in the experiment, (i.e., surfaces, O3, or another O(3P)), and (ii) its minimal effects on δ18O and δ17O of O2. Furthermore, we observe nearly quantitative agreement between our measured Δ36 and Δ35 values and those expected from theory [Hathorn and Marcus, 2000; Wang et al., 2004]. Wall/surface effects cannot be ruled out, but the results from a previous study of O2 chemistry by Morton et al. [1990] suggest wall effects are insignificant in our apparatus. For example, the surface of the tungsten electrode during electrolysis likely resembles a high-temperature plasma, so significant oxygen-isotope exchange on that surface would probably reflect high temperatures rather than the low temperatures consistent with our results. Experimental deviations from theory were 0.1–0.3‰ in Δ36, similar to our stated measurement uncertainty; therefore, at most, high-temperature isotope exchange occurred at 10% the rate of gas-phase oxygen-isotope exchange. Isotope effects in other reactions involving excited-state species (e.g., O(1D) and O3(Δg)) could also lead to deviations from isotopic equilibrium, but this system appears to be dominated by O(3P) + O2 isotope exchange reactions. Future experiments with UV photolysis of O2 and O3 may yield further insight.

5. 18O18O and 17O18O in Tropospheric Air

5.1. Measurements

[41] We measured Δ36 and Δ35 in ~20 cm3 samples of tropospheric air collected at the UCLA Court of Sciences in October 2011. Our measurements yield Δ36 = 2.05 ± 0.24‰ and Δ35 = 1.4 ± 0.5‰ (2σ; see Table 4), where quoted uncertainties reflect propagation of both random and systematic errors in the analysis. Reproducibility between sample preparations is ±0.08‰ and ±0.2‰ for Δ36 and Δ35 (2 s.e., n = 5), respectively. This external precision includes
the corrections for residual $^{36}$Ar and relatively small composition-dependent nonlinearity (see Appendix B).

[42] Atmospheric O$_2$ is in a non-equilibrium steady state between oxygen photosynthesis and respiration. Its bulk oxygen-isotope composition ($\delta^{18}$O = 23–24‰) reflects biosphere processes on millennial timescales [Bender et al., 1994], plus a small contribution (~0.3‰ in $\delta^{18}$O) from stratospheric photochemistry and subsequent oxygen-isotope transfer to CO$_2$ [Yung et al., 1991; Luz et al., 1999; Luz and Barkan, 2011]. Most of the $\delta^{18}$O enrichment in atmospheric O$_2$ arises from respiration, but its effects on $\Delta^{36}$ and $\Delta^{35}$ are not known because $\beta_{36}$ and $\beta_{35}$ values for respiration have not yet been measured.

[43] The effects of photosynthesis and respiration on $\Delta_{16}$ and $\Delta_{35}$ could be rendered insignificant, however, even when the biosphere dominates the bulk isotopic budget, if isotopic reordering of the atmospheric O$_2$ reservoir occurs on timescales shorter than O$_2$ cycling through the biosphere. Therefore, one must consider the role of O(3P) + O$_2$ isotope exchange reactions in the bond-ordering budget of atmospheric O$_2$. As we showed in Sections 2 and 4.2, O(3P) + O$_2$ isotope exchange reactions can drive $\Delta_{36}$ and $\Delta_{35}$ toward equilibrium values in a closed system with a negligible effect on the bulk isotopic composition of O$_2$ in that system.

The atmosphere, too, can be considered a closed system with respect to the oxygen isotopes in O$_2$ on sub-millennial timescales, with a O$_2$/O$_3$ mass balance yielding $\delta^{18}$O, $\Delta^{17}$O $\approx$ 0.3‰ [Luz et al., 1999; Young et al., 2002; Luz and Barkan, 2011]. Our reported tropospheric $\Delta_{36}$ and $\Delta_{35}$ values are consistent with isotopic equilibrium near 255 K, which is similar to the globally averaged tropospheric temperature of 251 K [Vinnikov and Grody, 2003], but O(3P) + O$_2$ isotope exchange in the stratosphere probably has an influence on the tropospheric budget. Ultimately, a full consideration of the atmospheric $\Delta_{36}$ and $\Delta_{35}$ budgets will require an accounting of the biosphere’s effects as well. We will evaluate not only the relative rates of isotope-exchange and biological processes, but also the range of expected biological fractionations, in Section 5.2, with the aim of presenting testable hypotheses for future study.

5.2. Model for $^{18}$O$^{18}$O and $^{17}$O$^{18}$O in the Atmosphere

[44] We constructed a model of the atmosphere to investigate the balance of photosynthesis, respiration, and O(3P) + O$_2$ isotope exchange on the bond-ordering budget for O$_2$ in the troposphere. The mole fraction of $^{18}$O$^{18}$O in the troposphere, $\chi^{36}$, at steady state, can be described by the mass balance equation:

$$F_{TS} \chi^{36} - F_{TS} \chi^{36} + F_P \chi^{36} + F_R \chi^{36} \alpha_{36,R} - E(\chi^{36} - \chi^T_{36,qr}) = 0$$

(14)

In equation (14), $\chi^{36}$ is the oxygen fraction of $^{18}$O$^{18}$O for the photosynthetic end-member, $\alpha_{36,R}$ is the respiratory fractionation factor, and $\chi^T_{36,qr}$ and $\chi^{36}$ are the oxygen fractions of $^{18}$O$^{18}$O for the tropospheric-equilibrium and stratospheric mixing end-members, respectively. The downward ($F_{TS}$) and upward ($F_{TS}$) troposphere-stratosphere fluxes are in balance, i.e., $F_{TS} = F_{TS} = 4.9 \times 10^{18}$ mol O$_2$ yr$^{-1}$ [Appenzeller et al., 1996; Hoag et al., 2005], as are the photosynthetic ($F_P$) and respiratory ($F_R$) fluxes, i.e., $F_P = F_R = 3.0 \times 10^{16}$ mol O$_2$ yr$^{-1}$ [Luz et al., 1999; Blunier et al., 2002]. We have also included $E$, the rate of O$_2$ equilibration in the troposphere (in mol O$_2$ yr$^{-1}$), in the mass balance equation. Inclusion of this term is supported by predictions of an O(3P) concentration of order $10^3$ cm$^{-3}$, constrained by tropospheric NO$_x$ and O$_3$ concentrations [Brasseur et al., 1990; Liang et al., 2006]. A summary of model parameters can be found in Figure 8 and Table 5. Similar mass balance equations can be written for all the other O$_2$ isotopologues and are not shown here.

[45] In the following sections, we will discuss the likely consequences of the transport of stratospheric air (5.2.1), tropospheric isotope exchange reactions (5.2.2), and biological processes (5.2.3) on the tropospheric budget of $\Delta_{36}$. We then conduct a sensitivity test (5.2.4) to determine the primary influences on tropospheric $\Delta_{36}$. The arguments that follow will also be valid for $\Delta_{35}$, but we will confine our discussion to $\Delta_{36}$ because of better analytical precision in our measurements. For simplicity, we have omitted the loss of $^{18}$O and $^{17}$O atoms from the O$_2$ reservoir via O(3D) + CO$_2$ isotope exchange in the stratosphere, which should decrease $\delta^{18}$O and $\delta^{17}$O by ~0.3‰ [Luz et al., 1999; Luz and Barkan, 2011]; while the primary source of stratospheric O(3D), O$_3$ photolysis, affects the O$_2$ mass balance, the O(3D) + CO$_2$ reaction does not generate additional bond-ordering fractionation because it does not involve O$_2$.

5.2.1. Flux of High-$\Delta_{36}$ O$_2$ From the Stratosphere

[46] First, we estimate the stratospheric end-member, $\chi^{36}$, which is expected to be an equilibrium-like value facilitated by O(3P) + O$_2$ isotope exchange reactions. High O(3P) and O$_2$ concentrations in the stratosphere suggest that O(3P) + O$_2$ isotope exchange occurs there readily (see Figure 9): Average expected chemical lifetimes of O$_2$ with respect to
Table 5. Description of Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{IT}$</td>
<td>Flux from stratosphere to troposphere</td>
<td>$4.9 \times 10^{16}$ mol O$_2$ yr$^{-1}$</td>
<td>Appenzeller et al. [1996], Hoag et al. [2005]</td>
</tr>
<tr>
<td>$F_{TP}$</td>
<td>Flux from troposphere to stratosphere</td>
<td>$4.9 \times 10^{14}$ mol O$_2$ yr$^{-1}$</td>
<td>Appenzeller et al. [1996], Hoag et al. [2005]</td>
</tr>
<tr>
<td>$F_p$</td>
<td>Flux out of biosphere from photosynthesis</td>
<td>$3.0 \times 10^{11}$ mol O$_2$ yr$^{-1}$</td>
<td>Luc et al. [1999], Blunier et al. [2002]</td>
</tr>
<tr>
<td>$F_b$</td>
<td>Flux into biosphere due to respiration</td>
<td>$3.0 \times 10^{10}$ mol O$_2$ yr$^{-1}$</td>
<td>Luc et al. [1999], Blunier et al. [2002]</td>
</tr>
<tr>
<td>$E$</td>
<td>Tropospheric $\Delta_e$ equilibration rate</td>
<td>$k_{0-2O}[O(P)]<em>{avg} \times V</em>{troposphere}$</td>
<td>This study</td>
</tr>
<tr>
<td>$\chi_{36}^{18}$</td>
<td>Fraction of $^{18}O^{18}O$ in stratospheric O$_2$</td>
<td>See section 4.4.1 ($\Delta_{36} = 3.0%o$)</td>
<td>This study</td>
</tr>
<tr>
<td>$\chi_{35}^{18}$</td>
<td>Fraction of $^{18}O^{17}O$ in tropospheric O$_2$</td>
<td>See section 4.3 ($\Delta_{35} = 2.6%o$)</td>
<td>This study</td>
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<tr>
<td>$\alpha_{18}$</td>
<td>Fraction of $^{18}O^{18}O$ in O$_2$ at isotope-exchange equilibrium in the troposphere</td>
<td>See section 4.4.2 ($\Delta_{36} = 1.7-2.1%o$)</td>
<td>This study</td>
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<tr>
<td>$\alpha_{18}$</td>
<td>$^{18}O^{18}O$/$^{18}O^{16}O$ fractionation for respiration</td>
<td>See section 4.4.3</td>
<td>This study</td>
</tr>
</tbody>
</table>

Oxygen isotope exchange, $\tau_{O2}$, range from 160 days at 15 km to several minutes at 50 km (see Figure 2) [Brasseur et al., 1990; Wiegell et al., 1997; Brasseur and Solomon, 2005]. These short $\tau_{O2}$ times suggest that a typical air parcel, which upwells into the O($^3P$)-rich stratosphere at tropical latitudes, will have its O-O bonds re-ordered before it re-enters the O($^3P$)-poor troposphere in the middle and high latitudes >1 year later [Holton et al., 1995; Plumb, 2007; Engel et al., 2009; Holzer et al., 2012]. O$_2$ chemistry involving other short-lived species (e.g., HO$_x$, NO$_x$, and ClO$_x$) may have a minor influence. Because rates of transport across the tropopause are generally much slower than rates of O($^3P$) + O$_2$ isotope exchange, we expect that $\Delta_{36}$ and $\Delta_{35}$ will be temperature-stratified until a “horizon” is reached where the timescale of stratosphere-troposphere exchange (STE) is much shorter than that of isotopic equilibration at the in situ temperature. This isotope-exchange horizon probably lies in the climatological tropopause layer (~15 km; $T = 190–200$ K), where $\tau_{O2}$ is comparable to the dynamical STE lifetime of days to months. A descent velocity of 0.2–0.4 mm s$^{-1}$ from stratospheric residual circulation at the mid-latitude tropopause [Rosenlof, 1995] implies that the average sinking air parcel descends 1 km altitude in 30–60 days ($\Delta T \sim 5$ K, or 0.1%o in $\Delta_{36}$). This transit time, $\tau_{1km}$, is comparable to $\tau_{O2}$ between 15–20 km ($T \sim 200$ K).

[47] We therefore estimate that O$_2$ entering the stratosphere from the stratosphere has $\chi_{36}^{18}$ and $\chi_{35}^{18}$ corresponding to $\Delta_{36,5} = 3.0\%o$ and $\Delta_{35,5} = 1.6\%o$, the equilibrium values at $T \sim 200$ K. While our predicted value is uncertain due to a simplified STE scheme ignoring seasonal variations and isotropic STE [Holton et al., 1995], isotope-exchange lifetimes of less than a day above 25 km suggest that air entering the troposphere from the stratosphere is unlikely to have $\Delta_{36}$ values lower than 2.7%o. Furthermore, the effects of a changing $^{18}O$ and $^{17}O$ inventory in the O$_2$/O$_3$ system are limited because sequestration of oxygen isotopes in CO$_2$ via $O(^1D) + CO_2$ isotope-exchange reactions occurs much more slowly in the stratosphere than O($^3P$) + O$_2$ isotope exchange (due to low O($^1D$) and CO$_2$ concentrations [Yang et al., 1991; Boering et al., 2004; Liang et al., 2007]). Future measurements of stratospheric air, combined with 2-D modeling of intrastratospheric transport, should provide a more accurate stratospheric end-member. Note that the STE flux of $4.9 \times 10^{16}$ mol O$_2$ yr$^{-1}$ [Appenzeller et al., 1996; Hoag et al., 2005] would cycle through a mass of O$_2$ equivalent to the atmospheric inventory ($3.7 \times 10^{19}$ mol O$_2$) in 7.6 years; autocatalytic oxygen-isotope exchange in the stratosphere would therefore alter the tropospheric O$_2$ bond-ordering signature on decadal timescales.

5.2. Gas-Phase Isotope-Exchange Reactions in the Troposphere

[48] In the troposphere, O($^3P$) chemistry could drive $\Delta_{36}$ and $\Delta_{35}$ toward equilibrium values at tropospheric temperatures. The troposphere’s equilibrium $^{18}O^{18}O$ and $^{17}O^{18}O$ fractions in O$_2$, $\chi_{36}^{18}$ and $\chi_{35}^{18}$, might reflect the global

Figure 9. Temperature, O($^3P$), and $\tau_{O2}$ profiles derived from Brasseur and Solomon [2005]. O($^3P$) and $\tau_{O2}$ below 15 km are considered highly uncertain. Also shown (yellow area) is the estimated $\tau_{1km}$ range for downwelling stratospheric air (30–60 days), which implies a stratospheric O($^3P$) + O$_2$ exchange horizon at 15–20 km.
average tropospheric temperature of 251 K ($\Delta_{36} = 2.1\%$ and $\Delta_{35} = 1.1\%$ [Vinnikov and Grody, 2003]) because the troposphere is well-mixed on timescales of about a year. The main tropospheric $O(3P)$ source, NO$_2$, however, is emitted primarily at the surface by combustion processes and biological denitriﬁcation. NO$_2$ is also produced by lightning $^{18}O$ must be enriched in $D$ with a mass of 10 cm$^{-1}$. The presence of that vertical transport barrier suggests that $\Delta_{36}$ and $\Delta_{35}$ may be sensitive to the vertical distribution of NO$_2$. Weighing the tropospheric temperature profile by a vertical proﬁle of NO$_2$ would yield an effective temperature of 281 K ($\Delta_{36} > 0.98$ and $\Delta_{35} = 0.9\%$). In any case, tropospheric $O(3P)$ concentrations are related to $E$ using known isotope-exchange rate coefficients ($k_{O_{1+O_2}} \sim 3 \times 10^{-12}$ cm$^{-3}$ s$^{-1}$ [Wiegell et al., 1997]), O$_2$ concentrations, and an estimate of the volume of the troposphere ($V_{\text{troposphere}} \approx 7.7 \times 10^{8}$ km$^3$):

$$E \approx k_{O_{1+O_2}}[O_{2}]_{\text{avg}}[O(3P)]_{\text{avg}} \times V_{\text{troposphere}} \quad (15)$$

Using this equation, $[O(3P)]_{\text{avg}} = 1 \times 10^{-3}$ cm$^{-3}$, $[O_2]_{\text{avg}} = 4.0 \times 10^{18}$ cm$^{-3}$, and 12 h of photochemistry each day, tropospheric $O(3P) + O_2$ isotope exchange cycles through $2.4 \times 10^{18}$ mol O$_2$ per year, or a mass equivalent to the tropospheric O$_2$ inventory in 15 years.

5.2.3. O$_2$ Flux to and From the Biosphere

[40] The annual flux of O$_2$ to and from the biosphere, at $\sim 1/160$ the size of the STE flux [Lue et al., 1999; Hoag et al., 2005], may only be a minor contribution to the tropospheric $\Delta_{36}$ and $\Delta_{35}$ budgets. Stil1, the potential fractionations associated with the biosphere are important. Water oxidation during photosynthesis may yield O$_2$ with $\chi_{36}$ and $\chi_{35}$ near the stochastic distribution because photosynthesis does not discriminate between oxygen isotopes [Guy et al., 1993; Helman et al., 2005]. However, O$_2$ cannot inherit a bond-ordering signature from water because H$_2$O contains no O-O bonds. Respiration leaves the O$_2$ residue between 10 and 30% enriched in $^{18}O$ with a mass dependency $\beta_{34/33} \approx 0.516$ [Lane and Dole, 1956; Guy et al., 1989; Kidson et al., 1993; Angert et al., 2003; Helman et al., 2005]. These fractionations resemble those of closed-system Knudsen diffusion ($\beta_{34/33} = 0.512$), which would lead to $\chi_{36}^{O_{36,R}}$ and $\chi_{35}^{O_{35,R}}$ that are depleted relative to the stochastic distribution in the residue (i.e., $\Delta_{36} \approx -2\%$ and $\Delta_{35} \approx -1\%$ using $\beta_{36/34} = 0.52$ and $\beta_{35/34} = 0.68$; see Section 2.3). Oxygen consumption during photosynthesis, and possibly associated oxygen-atom recycling in certain autotrophs [Eisenstadt et al., 2010], could therefore alter the effective photosynthetic abundances, $\chi_{36}^{P}$ and $\chi_{35}^{P}$, coming from aquatic environments. Nonetheless, the overall biosphere signature likely yields $\Delta_{36}, \Delta_{35} < 0$. Laboratory experiments identifying the bond-ordering signatures of photosynthesis and respiration will allow one to constrain further their contributions to the atmospheric $\Delta_{36}$ and $\Delta_{35}$ budgets.

5.2.4. Interpretation of $^{18}O$ Measurements

[50] We tested the sensitivity of the tropospheric $\Delta_{36}$ budget to various fractionations using our box model (equation (14) and Figure 8) and the fluxes and mixing end-members justiﬁed in the preceding sections. The simpliﬁed biosphere in the model, with photosynthetic O$_2$ having a bulk isotopic composition $\delta^{18}O = 4\%o$ and $\alpha_{34,4R} = 0.98$ ($e = -20\%$), yielded a steady state $\delta^{18}O = 24.4\%o$. Subtracting $0.3\%o$ due to O-atom transfer to CO$_2$ in the stratosphere yields $\delta^{18}O = 24.1\%o$, similar to previous measured and modeled values [Barkan and Luz, 2005; Luz and Barkan, 2011]. While our measured $\delta^{18}O$ of O$_2$ is less than this value (see Table 1), the difference is attributable to the assumed bulk isotopic composition in our primary standard (San Carlos Olivine, $\delta^{18}O = 5.2\%o$). The interpretation of $\Delta_{36}$ is not affected by this subtle difference in bulk isotopic composition between model and the data.

[51] First, we will consider the biosphere alone in the absence of gas-phase bond-ordering equilibration due to $O(3P) + O_2$ isotope exchange reactions. Using $\chi_{36}^{P}$ corresponding to the stochastic distribution, the measured tropospheric $\Delta_{36}$ value ($+2.05\%$) can only be obtained with $\beta_{36/34} = 0.476$ for respiration, which is a value lower than the theoretical limit for gas-phase kinetic processes involving O$_2$ [Young et al., 2002] and much lower than the value suggested in Section 5.2.3. Moreover, after including the effects of $O(3P) + O_2$ isotope exchange in the stratosphere, respiration alone was unable to balance the ﬂux of $\chi_{36}^{P}$ from the stratosphere for any value of $\beta_{36/34}$; the STE ﬂux is too large. Increasing the biosphere-atmosphere ﬂux of O$_2$ only modest decreases in tropospheric $\Delta_{36}$ (e.g., $2.7\%o$ for tenfold increases in $F_{P}$ and $F_{P}$ versus $3.0\%o$ for the base estimate). Alternately, $\chi_{36}^{P}$ would need to yield photosynthetic O$_2$ with $\Delta_{36} \approx -160\%o$ (when $\beta_{36/34} = 0.515$ for respiration) to balance the high-$\Delta_{36}$ air entering the troposphere from the stratosphere. Given that primary O$_2$ evolution does not discriminate between $^{16}O^{18}O$, $^{16}O^{17}O$, and $^{18}O^{18}O$ [Guy et al., 1993; Helman et al., 2005], a 160% disparity between $^{18}O^{18}O$ and $^{18}O^{18}O$ is implausible.

[52] Including tropospheric $O(3P) + O_2$ isotope exchange, however, can balance the STE flux of high-$\Delta_{36}$ air. To explain $\Delta_{36} \leq 2.29\%o$, the $2\sigma$ upper limit to our measured tropospheric $\Delta_{36}$, $E$ must be $\geq 2 \times 10^{19}$ mol O$_2$ yr$^{-1}$, corresponding to $[O(3P)]_{\text{avg}} \geq 4 \times 10^{3}$ cm$^{-3}$. A vertical gradient in tropospheric $O(3P)$ would alter these estimates: Weighting the tropospheric temperature proﬁle by a vertical proﬁle of NO$_2$ (see Section 5.2.2), yields $E = 0.6 - 5 \times 10^{12}$ mol O$_2$ yr$^{-1}$, and $[O(3P)]_{\text{avg}} = 1 - 10 \times 10^{2}$ cm$^{-3}$ can explain the entire $2\sigma$ range in measured $\Delta_{36}$. A similar tropospheric $O(3P)$ concentration range is obtained even if we use our lower estimate of $\chi_{36}^{P}$ corresponding to $\Delta_{36} = 2.78\%o$. O$_2$ coming from the stratosphere. These $O(3P)$ concentrations, derived using our two-box model, are thus consistent with global models [Brasseur et al., 1990; Brasseur and Solomon, 2005; Liang et al., 2006].

[53] Based on our analysis of $\Delta_{36}$ and $\Delta_{35}$, $O(3P) + O_2$ isotope exchange appears to exert the primary influence on isotopic bond ordering in tropospheric O$_2$. While the effects of O$_2$ production and consumption by the biosphere are yet to be determined, gas-phase chemistry in the stratosphere and troposphere is sufﬁcient to explain our measured value of $\Delta_{36}$ in tropospheric air. Future detailed studies on $\Delta_{36}$ and $\Delta_{35}$ in tropospheric O$_2$, photochemistry, and isotopic...
fractionation associated with the biosphere will lay the groundwork for applications relevant to the atmospheric chemistry and biogeochemical cycling of \( \text{O}_2 \).

6. Conclusions and Outlook

[54] We have measured proportional enrichments in \( ^{18}\text{O}^{18}\text{O} \) and \( ^{17}\text{O}^{18}\text{O} \) of 2.05 ± 0.24‰ and 1.4 ± 0.5‰ (2σ), respectively, in tropospheric air. Based on our laboratory experiments and a box model for atmospheric \( \text{O}_2 \), we hypothesize that these enrichments are primarily driven by \( \text{O}^{3}P + \text{O}_2 \) isotope-exchange reactions occurring in the stratosphere and troposphere. Due to the sensitivity of tropospheric \( \Delta_{36} \) on the STE flux, atmospheric temperature profile, and \( \text{O}^{3}P \) concentration, we hypothesize that measurements of bond ordering in tropospheric \( \text{O}_2 \) may be able to constrain atmospheric dynamics and free-radical chemistry in the present, and perhaps also in the past.

[55] Temporal variations in \( \Delta_{36} \) and \( \Delta_{35} \) in the ice core record, specifically, may trace anthropogenic and climate-driven changes in atmospheric chemistry and circulation on decadal timescales. For instance, the main sources of tropospheric \( \text{O}^{3}P \) were greatly reduced, relative to today, during preindustrial times: \( \text{NO}_x \) emissions have been estimated to be as little as one-fifth those of the present-day, while tropospheric \( \text{O}_3 \) concentrations have also been reduced by half [Thompson, 1992; Martinerie et al., 1995]. Lower tropospheric \( \text{O}^{3}P \) concentrations would decrease the tropospheric bond-ordering equilibration rate (\( E \) in equation (14) and Figure 8), shifting the steady state tropospheric \( \Delta_{36} \) value up toward the stratospheric mixing end-member value. A fivefold reduction in tropospheric \( \text{O}^{3}P \) could result in as much as a 0.5‰ increase in tropospheric \( \Delta_{36} \) relative to the present-day value, depending on the effective tropospheric temperature used for \( \lambda_{\text{TRO}} \) and assuming no change in the STE flux. A recent prediction of only modest changes to tropopause temperature (\( \sim+1^\circ \text{C} \)) and STE flux during the Last Glacial Maximum could potentially also be tested [Rind et al., 2009].

[56] The triple-isotopologue mass dependences, \( \beta_{36/34} \) and \( \beta_{35/34} \), may also be used to constrain the oxygen budget in closed systems such as soils [Aggarwal and Dillon, 1998; Lee et al., 2003] and the ocean’s interior [Kroopnick and Craig, 1976; Bender, 1990]. Bulk isotopic fractionations of up to +15‰ have been observed, which may result in a change of −1.3‰ in \( \Delta_{36} \) of the residue (using \( \beta_{36/34} = 0.522 \)). Over this range in bulk isotopic composition, a \( \beta_{36/34} \) difference of 0.002 would result in a 0.1‰ difference in \( \Delta_{36} \). These triple-isotopologue \( \beta \) values provide additional information that augments the “triple-isotope” \( \beta_{34/33} \) values (i.e., relating \( ^{18}\text{O}^{18}\text{O} \) and \( ^{17}\text{O}^{18}\text{O} \) used to partition oxygen consumption fluxes into their component mechanisms [Angert and Luz, 2001; Young et al., 2002; Angert et al., 2003]), and may prove valuable where oxygen cycling mechanisms are poorly understood. Interpreting measured \( \Delta_n \) values using mass-dependent fractionation laws represents a general approach to multi-isotopologue systematics that can be applied to any environment where single-phase isotope-exchange equilibration is not the dominant process. The sensitivity of \( \Delta_{36} \) and \( \Delta_{35} \) to diffusion, and not gravitational fractionation, for example, may comprise a test of physical fractionation mechanisms in glacial firm and ice layers, including countercurrent flux [Severinghaus et al., 1996] and bubble close-off [Severinghaus and Battle, 2006].

[57] Finally, this study highlights the potential value of high-resolution gas-source IRMS instruments for understanding atmospheric systems. Our analyses of \( ^{18}\text{O}^{18}\text{O} \) and \( ^{17}\text{O}^{18}\text{O} \) in \( \text{O}_2 \) were possible on a low-resolution IRMS only after significant sample preparation and mass spectrometry of large gas samples. High-resolution instruments may be able to resolve \( ^{18}\text{O}^{18}\text{O} \) from \( ^{36}\text{Ar} \) well enough to reduce the sample handling artifacts and instrumental ion corrections that ultimately limit the precision in the present study. Detailed analyses of these species in \( \text{O}_2 \) trapped in ice cores, or in low-\( \text{O}_3 \) zones in the oceans, will likely require sensitivity and precision higher than what is currently available.

Appendix A: \( \beta \)-Values That Preserve \( \Delta_{36} \) and \( \Delta_{35} \)

[58] Here, we derive the triple-isotopologue mass dependences \( \beta_{36/34} \) and \( \beta_{35/34} \) that preserve \( \Delta_{36} \) and \( \Delta_{35} \) values. We will omit the contribution of \( ^{17}\text{O}^{18}\text{O} \) to mass-34 \( \text{O} \) for simplicity, as the errors it imposes on \( \Delta_{36} \) and \( \Delta_{35} \) in the case of gravitational fractionation are <10⁻⁶‰. References to mass-34 \( \text{O} \) herein describe \( ^{16}\text{O}^{18}\text{O} \) species exclusively.

[59] During an arbitrary fractionation process, isotopologue abundances change from \( R_i \) to \( R_f \) according to \( \alpha \) values for each isotopologue relative to \( ^{16}\text{O}^{18}\text{O} \):

\[
36R_f = 36R_i \times \alpha_{36} \quad (A1a)
\]

\[
35R_f = 35R_i \times \alpha_{35} \quad (A1b)
\]

\[
34R_f = 34R_i \times \alpha_{34} \quad (A1c)
\]

\[
33R_f = 33R_i \times \alpha_{33} \quad (A1d)
\]

In most cases, \( \text{O}_2 \) is near natural abundance and the \( ^{18}\text{O} \) and \( ^{16}\text{O}^{18}\text{O} \) \( \alpha \) values are comparable, yielding

\[
18R_f \approx 18R_i \times \alpha_{34} \quad (A2a)
\]

\[
17R_f \approx 17R_i \times \alpha_{33} \quad (A2b)
\]

The stochastic distributions for \( ^{18}\text{O}^{18}\text{O} \) and \( ^{17}\text{O}^{18}\text{O} \) in gases with composition \( R_f \) are therefore

\[
36R_{f,\text{stochastic}} = \left( ^{18}R_f \right)^2 \quad (A3a)
\]

\[
\equiv \left( 18R_i \times \alpha_{34} \right)^2 \quad (A3b)
\]

\[
\equiv \left( 36R_{i,\text{stochastic}} \right) \left( \alpha_{34} \right)^2 \quad (A3c)
\]

\[
35R_{f,\text{stochastic}} = 2 \times 18R_i \times 17R_i \quad (A4a)
\]

\[
\equiv 2 \times \left( ^{18}R_i \times \alpha_{34} \right) \left( ^{17}R_i \times \alpha_{33} \right) \quad (A4b)
\]

\[
\equiv \left( 35R_{i,\text{stochastic}} \right) \alpha_{34} \alpha_{33} \quad (A4c)
\]
fractionation preserves both $\Delta_{36}$ and $\Delta_{35}$, with $\beta_{36/34} = 0.500$, $\beta_{34/33} = 0.501$, and $\beta_{35/34} = 0.666$.

Appendix B: Mass Spectrometry

B1. Instrument Protocols

[61] Purified O$_2$ samples were analyzed on a dual-inlet Thermo-Finnigan MAT 253 IRMS equipped with 9 Faraday cups. The gas was equilibrated with the IRMS’s sample bellows at $\sim$240°C for 35 min. Passive equilibration yielded analyses that consistently fractionated light (0.3–1% in $\delta^{18}O$) relative to their known bulk isotopic composition. Therefore, we “mixed” the gas by alternating the bellows volume between 25% and 100% three times every 200 s during the equilibration. An operating system script was written to automate this task, which eliminated the bulk isotopic fractionation ($<0.02\%$ in $\delta^{18}O$).

[62] Two of the Faraday cups had wide geometries to accommodate multicollection of O$_2$ and CO$_2$ on the same detector array. Amplifier resistor values of $5 \times 10^7$, $1 \times 10^{11}$, $1 \times 10^{10}$, $3 \times 10^{11}$, and $1 \times 10^{12}$ $\Omega$ yielded nominal detection voltages of 4000, 5500, 3500, 45, and 400 mV at $m/z = 32$ (wide cup), 33, 34 (wide cup), 35, and 36, respectively, with an ion-source pressure of $\sim2.5 \times 10^{-7}$ mBar. A $3 \times 10^{11}$-$\Omega$ resistor was used for $m/z = 35$ detection because we identified an electronic noise source coming from a switch on its amplifier board, particular to this Faraday cup-amplifier configuration, which degraded the signal-to-noise ratio (SNR) at higher resistor values; the $3 \times 10^{11}$-$\Omega$ resistor on the $m/z = 35$ amplifier board yielded a SNR similar to that of a $1 \times 10^{12}$-$\Omega$ resistor on a switchless board. The resulting lower voltage on $m/z = 35$ was therefore the most sensitive to inaccuracies arising from long-term electronic drifts of order 1 mV (e.g., electronic offsets).

[63] Our working standard gas had a bulk isotopic composition of $\delta^{18}O = -12.404\%$ and $\delta^{17}O = -6.457\%$ against Vienna Standard Mean Ocean water, calibrated by assuming that San Carlos Olivine has a composition $\delta^{18}O = 5.200\%$ and $\delta^{17}O = 2.742\%$.

[64] Sample peak shapes are shown in Figure B1. Under typical ion-source pressures, we observed that all the minor ion beams had negative, pressure-sensitive baselines, or “pressure baselines,” that reduced the observed voltage relative to its true value. The magnitudes of these baselines varied with source pressure, conductance (modulated by the position of the “sulfur window”), extraction, and various tuning parameters, and they are qualitatively different from the zero-analyte backgrounds that were routinely subtracted as part of typical measurements. In general, these pressure baselines were negligible for $m/z = 33$ and 34 ($-6$ and $-2$ mV, respectively, resulting in errors of order 0.001‰ in $\delta^{18}O$ and $\delta^{17}O$), but significant for $m/z = 35$ and 36 (about $-18$ and $-75$ mV, respectively). They were affected by the presence of a strong magnetic field (i.e., a rare earth magnet) near the inlet to the Faraday cups. Secondary electrons inadequately quenched by the Faraday-cup electron suppressors and/or produced by collisions of ions with the sides of the IRMS flight tube are thought to be the source of these baselines.

[65] Pressure baselines were not of equal magnitude on either side of the molecular ion peaks. The high-voltage
(low-mass) side was typically more negative (see Figure B1). Placing a rare earth magnet on the flight tube near the detector array corrected this disparity, indicating that stray electron splatter may be its root cause. Measurements made with the magnet in place were consistent with those made without the magnet, albeit slightly noisier. Furthermore, the low-voltage (high-mass) side yielded the best reproducibility, so it was used, without the magnet, for pressure-baseline corrections.

To measure these pressure baselines, we employed an acceleration-voltage-switching protocol similar to one being developed for measurements of mass-47 CO$_2$ [He et al., 2012]. First, the sample and standard sides of the IRMS were pressure-balanced on $m/z = 32$ to within 15 mV at an acceleration voltage corresponding to the pressure baselines, i.e., 9.450 kV. Next, sample and standard pressure-baseline voltages for $m/z = 33–36$ were measured in three IRMS sample-standard measurement cycles. The acceleration voltage was then increased to a value corresponding to peaks in the analyte signal, i.e., 9.485 kV, for 10 IRMS measurement cycles. Last, the acceleration voltage was switched back to the previous pressure-baseline setting, and another three measurement cycles were taken. During each measurement cycle, sample and standard signals were each integrated for 10s after an idle time of 20s. Each acquisition block was composed of 6 pressure-baseline and 10 on-peak measurement cycles, yielding a total analysis time of ~25 min. Reported values are external averages and standard errors from 4–6 acquisition blocks.

An example of the $m/z = 36$ signal during an acquisition block is shown in Figure B2. The pressure-baseline voltage increases (gets less negative), while the on-peak voltage decreases (gets less positive) with time; calculating the magnitude of the molecular signal requires that one account for both trends simultaneously. The pressure baseline was interpolated from a linear regression of the background voltage from the measurement cycles before and after the 10 on-peak measurement cycles. Separate linear regressions were generated for the sample and standard sides to mitigate errors due to sample-standard pressure imbalance. The molecular signal on each side for a measurement cycle was then calculated as the difference between the on-peak voltages and the interpolated pressure-baseline voltages. Signals at $m/z = 35$ were derived in the same way using its observed and pressure-baseline voltages.

Signal hysteresis during the acceleration-voltage switching protocol is a potential concern; stray electronic capacitances of the order pF can increase the $RC$ signal relaxation time, $\tau_{RC}$, significantly from its nominal 2-s value on the $m/z = 36$ cup ($R = 1 \times 10^{12}$ $\Omega$ and $C = 2$ pF). If the electronic relaxation time exceeded the time in between switching, the contrast between the observed and pressure-baseline measurements would have been smaller than the true values, leading to a scale compression in the resulting $\Delta_{36}$ and $\Delta_{35}$ values. Using $\tau_{RC} = 2$ s and a 20-s idle time, we calculate that the signal contrast (i.e., $V_{36} \times \exp(20s/\tau_{RC})$) will decrease by 0.045‰ at most in $\Delta_{36}$, which is less than our reported precision. To evaluate if hysteresis was significant for our measurements, we tested a different method for calculating $V_{36}$ that was sensitive to longer-term (minutes to hours) instrumental drifts rather than the shorter-term (seconds to minutes) drifts of concern for the procedure depicted in Figure B2. The alternate method used pressure-baseline trends that were measured as separate 10-cycle
had that may be a general (0.1/C24 were offset, but parallel within the fit uncertainties. 

Values. These uncertainties were values. = 34.9 and 0.02 7 D values. These uncertainties were values.

Corrections lines for O

(D18306 and 0.03/C6 = 34.9/0 because it was still present at ppb levels in

value and a high-temperature (b1) reference gas and in gas samples. This ion correction lines, standard gases were passed through the GC system

subject to amplifier nonlinearities. To account for these uncertainties of their respective linear regressions. Plotting the uncertainties at (i.e., of

Corrections correspond to the same bulk composition

argon correction lines for were first calculated for the sample

of the two high-temperature gases of two different

value yields 0) reference bulk isotopic composition of both the

correction lines (i.e., of

36/stochastic

34/180‰

36/stochastic

36/stochastic

34/‰

36/stochastic

36/stochastic

34 values. Our reported Δ36 value was calculated using the equation:

Δ36 = Δ36 vs. working std − Δ36, stochastic

This equation can be used only when both terms in the difference correspond to the same bulk composition δ34. Therefore, b was first calculated for the sample’s δ34 (i.e., that for Δ36 vs. working std) using equation (B2), after which Δ36, stochastic was calculated for the sample’s V40,SA/V40,STD Atmospheric O2 had δ34 = 36.275 ± 0.080‰ (2 s.e.), close to one of our standard gases (δ34 = 34.9‰), where the nonlinearity correction was comparable to the 1σ total uncertainty in Δ18O (0.1‰).

For our Knudsen diffusion experiment (Section 4.1), some uncertainty in Δ36 arises from the composition-dependent nonlinearity relationship derived in the previous section, because the bulk isotopic composition of both the diffused and residue populations were significantly (>10‰ in δ18O) outside the range for which high-temperature gases were available. Because of the relative difficulty in generating low-argon O2 standards over a wider range of bulk isotopic composition, we are unable to include a larger range of bulk isotopic composition at this time. Still, we see excellent agreement, within our reported uncertainty, between our data and the model of the experiment using equation (12).

B3. Uncertainty Estimates

To estimate the uncertainty in final Δ36 values associated with these ion-correction and nonlinearity relationships, which dominated the total uncertainty, we built a Monte Carlo simulation of equation (9). We sampled 100,000 points on each of 4 different Gaussian distributions corresponding to the δ34 (abscissa) and b (ordinate) values. Uncertainties in the slope and intercept of equation (B1) were calculated this way, as were Δ36, stochastic uncertainties at specific V40,SA/V40,STD values. These uncertainties were added in quadrature with the analytical standard error in Δ36 vs. working std to obtain 1σ uncertainty limits for the final Δ36 values.
Figure C1. Calculated bulk isotopic fractionation for the BaO₂ and O₂ systems relative to atomic O vapor.

[74] For Δ₁₈ measurements, an argon correction was not necessary because m/z = 35 is not isotopic with an argon isotope. In addition, a composition-dependent nonlinearity was not identified, perhaps because the analytical precision of individual measurements was ±0.2‰ (1σ s.e.); that uncertainty may exceed the magnitude of composition-dependent nonlinearity over our range in δ₁₈ ≈ 30–57‰. External (multisample) averages for high-temperature gases with δ₁₈ = ±1‰ and 32 ± 2‰ (1 s.d.) yielded Δ₁₈ values that were not significantly different from each other. Therefore, because we could not rule out a composition-dependent nonlinearity for Δ₁₈, we used 2 external standard errors as the uncertainty bounds for the high-temperature standard when propagating uncertainty in Δ₁₈. Higher-precision measurements of Δ₁₈ should be possible with higher amplification on the m/z = 35 Faraday cup with a new detector array that does not have the SNR problems we experienced (see section B1).

Appendix C: BaO₂ Theory


[76] All DFT calculations were made with the Quantum Espresso code [Giannozzi et al., 2009] using a 50 Rydberg energy cutoff for the plane wave basis set. Electronic wave vectors in the Brillouin zone were sampled on a shifted 4 × 4 × 4 Monkhorst-Pack grid, and the phonon density of states was sampled using a shifted Monkhorst–Pack-like grid [Gonze et al., 2002] with three distinct wave vectors. Calculated vibrational frequencies were scaled downward by 3.5% so that the peroxide O-O stretching mode frequency matched Raman measurements in BaO₂ (843 cm⁻¹ [Efthimiopoulos et al., 2010]). This scale factor ignores anharmonicity in both the model and the Raman measurement, which is expected to have small effects on isotopic ordering [Wang et al., 2004; Schauble et al., 2006; Cao and Liu, 2012]. Anharmonicity-corrected frequencies don’t appear to be known for BaO₂.

[77] Trial calculations with higher plane wave cutoff energies and denser electronic wave vector grids yielded very similar energies and optimized crystal structures. The room temperature ¹⁸O–¹⁸O bond-ordering equilibrium calculated with a 1-wave vector phonon sample and different barium pseudopotential (Ba.pbe-nsp-van.UPF from http://www.quantum-espresso.org) are within ~0.01‰ of the present result, suggesting that the choice of barium pseudopotential is not critical. This is also consistent with the very low frequencies observed for all modes other than the O–O stretch; low-frequency modes are not expected to strongly affect isotopic ordering. The optimized crystal structure and frequencies of Raman-active vibrational modes are very close to those determined by a recent DFT study using projector-augmented waves [Efthimiopoulos et al., 2010].

Assuming anharmonicity of no more than a few percent in the O–O stretching mode, and that lattice modes do not contribute significantly to isotopic ordering in BaO₂, the calculated ¹⁸O₂ equilibrium might reasonably be expected to be accurate to ~0.02‰ to 0.03‰ at room temperature and above. Uncertainty in these calculations ought to scale with isotopologue mass, and therefore be correspondingly smaller for ¹⁷O¹⁸O and ¹⁷O¹⁷O: ~0.01–0.02‰ and ~0.01‰, respectively.

[78] Below (see also Figure C1) are the polynomials fit to estimated isotopologue and isotopic equilibria using temperatures in Kelvin. BaO₂ equilibria were fit for T ≥ 250 K, and show a maximum misfit of 0.003‰. For clumped O₂ isotopic equilibria, the fits are for T ≥ 170 K with a maximum misfit of 0.004‰ in Δ₆ values and 0.09‰ in α. BaO₂ (this study)

\[
\begin{align}
K_{eq} & \times 4 = (-7.5990 \times 10^{10})T^{-6} + (2.7366 \times 10^6)T^{-4} + (2.9633)T^{-2} + 1 \\
K_{eq} & \times 2 = (-4.0330 \times 10^{10})T^{-6} + (1.4422 \times 10^6)T^{-4} + (1.5856)T^{-2} + 1 \\
K_{eq} & \times 4 = (-2.1324 \times 10^{10})T^{-6} + (7.5848 \times 10^5)T^{-4} + (0.85513)T^{-2} + 1
\end{align}
\]
\[ \alpha_{18-16} = \left(1.0365 \times 10^{12}\right)T^6 \left(6.3615 \times 10^7\right)T^{-4} + (4.1690 \times 10^1)T^{-2} + 1 \]  
\[ \alpha_{17-16} = \left(5.9074 \times 10^{11}\right)T^6 \left(3.6056 \times 10^7\right)T^{-4} + (2.2105 \times 10^2)T^{-2} + 1 \]

\( \text{O}_2 \) (This study, adapted from Wang et al. [2004])

\[ 16^O \text{O}_2 + 16^O \text{O} \rightarrow 18^O \text{O}_2 + 16^O \text{O} \]

\[ K_{eq} \times 4 = \left(-4.30256 \times 10^{11}\right)T^6 + \left(9.07569 \times 10^9\right)T^{-5} - (7.21969 \times 10^7)T^4 + (2.47642 \times 10^3)T^{-3} - (1.85176 \times 10^2)T^2 + (4.56043 \times 10^{-2})T^{-1} + 1 \]

\[ 16^O \text{O}_2 + 16^O \text{O} \rightarrow 17^O \text{O}_2 + 16^O \text{O} \]

\[ K_{eq} \times 2 = \left(-2.28850 \times 10^{11}\right)T^6 + \left(4.80743 \times 10^9\right)T^{-5} - (3.80618 \times 10^7)T^4 + (1.29814 \times 10^5)T^{-3} - (9.61087 \times 10^2)T^2 + (2.34001 \times 10^{-2})T^{-1} + 1 \]

\[ 16^O \text{O}_2 + 16^O \text{O} \rightarrow 17^O \text{O}_2 + 16^O \text{O} \]

\[ K_{eq} \times 4 = \left(-1.21482 \times 10^{11}\right)T^6 + (2.54270 \times 10^9)T^{-5} - (2.00456 \times 10^7)T^4 + (6.80125 \times 10^4)T^{-3} - (4.98714 \times 10^1)T^{-2} + (1.20347 \times 10^{-2})T^{-1} + 1 \]

\[ \alpha_{18-16} = \left(4.7312 \times 10^9\right)T^4 + (3.0146 \times 10^6)T^{-3} + (1.4894 \times 10^6)T^{-2} - (9.1783 \times 10^1)T^{-1} + 1 \]

\[ \alpha_{17-16} = \left(-6.0449 \times 10^{11}\right)T^6 + (3.8369 \times 10^8)T^{-5} + (1.5213 \times 10^6)T^{-2} + (1.6937 \times 10^6)T^{-3} + (7.9791 \times 10^1)T^{-2} - (5.833 \times 10^{-1})T^{-1} + 1 \]

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