

# Oxygen isotopic composition of carbon dioxide in the middle atmosphere

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The isotopic composition of long-lived trace molecules provides a window into atmospheric transport and chemistry. Carbon dioxide is a particularly powerful tracer, because its abundance remains >100 parts per million by volume (ppmv) in the mesosphere. Here, we successfully reproduce the isotopic composition of CO<sub>2</sub> in the middle atmosphere, which has not been previously reported. The mass-independent fractionation of oxygen in CO<sub>2</sub> can be satisfactorily explained by the exchange reaction with O(<sup>1</sup>D). In the stratosphere, the major source of O(<sup>1</sup>D) is O<sub>3</sub> photolysis. Higher in the mesosphere, we discover that the photolysis of <sup>16</sup>O<sup>17</sup>O and <sup>16</sup>O<sup>18</sup>O by solar Lyman- $\alpha$  radiation yields O(<sup>1</sup>D) 10–100 times more enriched in <sup>17</sup>O and <sup>18</sup>O than that from ozone photodissociation at lower altitudes. This latter source of heavy O(<sup>1</sup>D) has not been considered in atmospheric simulations, yet it may potentially affect the “anomalous” oxygen signature in tropospheric CO<sub>2</sub> that should reflect the gross carbon fluxes between the atmosphere and terrestrial biosphere. Additional laboratory and atmospheric measurements are therefore proposed to test our model and validate the use of CO<sub>2</sub> isotopic fractionation as a tracer of atmospheric chemical and dynamical processes.

biogeochemical cycles | CO<sub>2</sub> | mesosphere | stratosphere

Of the many trace molecules that can be used to examine atmospheric transport processes and chemistry [e.g., CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>, and the chlorofluorocarbons (CFCs)], carbon dioxide is unique in the middle atmosphere, because of its high abundance [ $\approx$ 370 parts per million by volume (ppmv) in the stratosphere, dropping to  $\approx$ 100 ppmv at the homopause]. The mass-independent isotopic fractionation of oxygen first discovered in ozone (1–5) is thought to be partially transferred to carbon dioxide (3, 6–11) via the reaction O(<sup>1</sup>D) + CO<sub>2</sub> in the middle atmosphere (12, 13). Indeed, whereas the reactions of trace molecules with O(<sup>1</sup>D) usually lead to their destruction (14), the O(<sup>1</sup>D) + CO<sub>2</sub> reaction regenerates carbon dioxide. This “recycled” CO<sub>2</sub> is unique in its potential to trace the chemical [reactions involving O(<sup>1</sup>D) in either a direct or indirect way] and dynamical processes in the middle atmosphere. When transported to the troposphere, it will produce measurable effects in biogeochemical cycles involving CO<sub>2</sub> (15) and O<sub>2</sub> (16).

In plots of the <sup>17</sup>O vs. <sup>18</sup>O content of atmospheric trace gases (so-called “three-isotope” plots), the mass-dependent fractionation of oxygen has a slope of  $\delta^{17}\text{O}/\delta^{18}\text{O} = m \approx 0.5$ . Weighted least-squares fits to the first stratospheric/mesospheric measurements of  $[\delta^{17}\text{O}(\text{CO}_2) - \delta^{17}\text{O}(\text{CO}_2)_t]/[\delta^{18}\text{O}(\text{CO}_2) - \delta^{18}\text{O}(\text{CO}_2)_t]$  at 30°N by Thieme *et al.* (10) give  $m = 1.37 \pm 0.12$  ( $2\sigma$ ) when the errors in both  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are included (7); where  $\delta^{17}\text{O}(\text{CO}_2)$  and  $\delta^{18}\text{O}(\text{CO}_2)$  are the isotopic composition of CO<sub>2</sub> relative to that in a selected standard (in parts per thousand) and  $\delta^{17}\text{O}(\text{CO}_2)_t$  and  $\delta^{18}\text{O}(\text{CO}_2)_t$  denote the isotopic composition of CO<sub>2</sub> in the troposphere. Subsequent stratospheric measurements at latitudes of 43.7° and 67.9°N (8) revealed larger values of both  $\delta^{17}\text{O}(\text{CO}_2)$  and  $\delta^{18}\text{O}(\text{CO}_2)$  than those seen at 30°N over a similar altitude range and a slope of  $m = 1.72 \pm 0.22$  ( $2\sigma$ ). Over smaller altitude intervals, a similar analysis yields  $m = 2.06 \pm$

1.16 ( $2\sigma$ ) for samples from the Arctic vortex (6) and  $1.64 \pm 0.38$  ( $2\sigma$ ) from the lower stratosphere (7). Slopes near 1.6–1.7 have been successfully reproduced in laboratory photochemical experiments under approximately stratospheric conditions (17).

Despite the large uncertainties in  $m$ , induced by the challenges associated with the sample collection and mass spectrometry of middle atmospheric O<sub>3</sub> (2, 5) and CO<sub>2</sub> (8, 10, 11), it is worth examining the potential sources of variation in the isotopic composition of carbon dioxide, both to better understand the atmosphere and as a guide for future observations. Yung *et al.* (13), for example, have suggested that the upwelling of tropospheric air from the tropics along with downwelling near 30°N could dilute the magnitude of the fractionation induced by photochemistry. It is beyond the scope of this work to provide a detailed explanation of the effect of transport on the isotopic composition of CO<sub>2</sub>. Briefly, the key concept is the “age of air,” with the clock being set to zero at the tropopause. As the air parcel travels to the middle atmosphere, it ages, and there is more time for photochemical equilibrium to be reached. Morgan *et al.* (18) discuss these issues at length and give a heuristic relation between the intrinsic enrichment factor ( $\varepsilon$ ) and the resulting isotopic composition ( $\delta$ ) for the one-dimensional (1D) diffusion-limited transport case:

$$\delta = \varepsilon (1 + [r/(1+r)]^{1/2})/2, \quad [1]$$

where  $r = \tau_{\text{chem}}/4\tau_{\text{trans}}$  with  $\tau_{\text{chem}}$  = chemical lifetime (here the isotopic exchange time) and  $\tau_{\text{trans}}$  = transport time (here the eddy mixing time).

In this work (a 1D diffusive model), the transport time  $\tau_{\text{trans}}$  is defined by  $H_{\text{atm}}^2/K_{\text{zz}}$ , where  $H_{\text{atm}}$  and  $K_{\text{zz}}$  are the atmospheric scale height and eddy mixing coefficient, respectively. The  $K_{\text{zz}}$  profile used in this work is taken from Allen *et al.* (19). Depending on the relative rates of (photo)chemistry vs. transport, the  $\delta$  values achieved in the atmosphere can therefore be reduced by up to factors of two from those measured in the laboratory (20). The vertical transport time across the tropopause is on the order of years, but drops to approximately weeks in the upper stratosphere. The lifetime for CO<sub>2</sub> isotopic exchange is much slower than the transport time at all altitudes, whereas the photochemical production and quenching rates for O(<sup>1</sup>D) are much faster than transport processes. For example, at an altitude of  $\approx$ 45 km, where O(<sup>1</sup>D) peaks,  $\tau_{\text{chem}}$  is  $\approx 10^8$  s for O(<sup>1</sup>D) + CO<sub>2</sub> but only  $\approx 10^{-5}$  s for the collisional quenching of O(<sup>1</sup>D); that for  $\tau_{\text{trans}}$  is  $\approx 10^7$  s, and the age of air entering from the troposphere is  $\approx 10^8$  s (21). During the time air ascends from the tropopause to this altitude, vertical mixing acts to dilute the isotopic fractionation of CO<sub>2</sub>. Thus, the isotopic composition of

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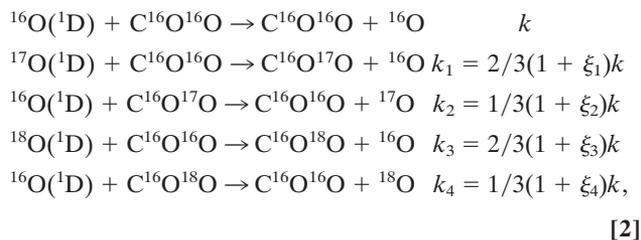
stratospheric CO<sub>2</sub> should reflect both the variety of transport histories of air parcels and the sources of O(<sup>1</sup>D).

The magnitude of δ<sup>17</sup>O(CO<sub>2</sub>) or δ<sup>18</sup>O(CO<sub>2</sub>) in principle can be used to determine how the air parcels are transported, but only if all sources of O(<sup>1</sup>D) are accounted for. As we discuss below, whereas ozone photolysis is the dominant source of O(<sup>1</sup>D) in the stratosphere, other sources, which were not included in previous models, must be considered at higher altitudes. Curves of δ<sup>17</sup>O(CO<sub>2</sub>) or δ<sup>18</sup>O(CO<sub>2</sub>) alone vs. altitude therefore reflect both the transport and chemical history of the air parcels. Precise measurements of both δ<sup>17</sup>O(CO<sub>2</sub>) and δ<sup>18</sup>O(CO<sub>2</sub>) that are well sampled spatially and seasonally could break the ambiguity between the sources of O(<sup>1</sup>D) and history of the air parcels, but they are clearly sometime into the future.

Fortunately, limits to the slope *m* can be estimated by assuming photochemical equilibrium between CO<sub>2</sub> and O(<sup>1</sup>D), because transport from the troposphere will only dilute the magnitude of both δ<sup>17</sup>O and δ<sup>18</sup>O with equal proportionality. Here we present such an analysis along with a simple 1D diffusive transport simulation to assess the relative importance of stratospheric and mesospheric sources of O(<sup>1</sup>D) to the isotopic composition of CO<sub>2</sub> in the middle atmosphere. To avoid uncertainties due to stratosphere–troposphere exchange processes, possible contamination from tropospheric water, and seasonal and latitudinal variations of tropospheric CO<sub>2</sub> isotopologues, we place our focus here only on the data that have been taken well above the tropopause (8, 10).

### Mechanism

The photochemical modification of the isotopic composition of atmospheric CO<sub>2</sub> follows from its interactions with O(<sup>1</sup>D). Provided that all of the O atoms in the CO<sub>3</sub><sup>\*</sup> activated complex are equivalent (12, 13), the appropriate chemical rate coefficients are as follows:



where the product O is either O(<sup>1</sup>D) or O(<sup>3</sup>P) (elastic or inelastic collisions). The ξ<sub>1</sub>–ξ<sub>4</sub> account for the isotopic deviations from a purely statistical accounting of the reaction probability and include both the changes in the collisional rates predicted by the kinetic theory of gases (–21.8, –3.0, –41.6, –5.8 per mil) as well as the quenching of O(<sup>1</sup>D) by O<sub>2</sub>/N<sub>2</sub> (19.8/18.9 and 37.7/36.0 per mil for δ<sup>17</sup>O(<sup>1</sup>D) and δ<sup>18</sup>O(<sup>1</sup>D), respectively). These contributions to ξ<sub>1</sub>–ξ<sub>4</sub> are of opposite sign and similar in magnitude, and so the overall reduced mass effect in the reaction kinetics of O(<sup>1</sup>D) and CO<sub>2</sub> is small. As we will show below, the isotopic exchange reaction between CO<sub>2</sub> and O(<sup>1</sup>D) can satisfactorily explain the observed isotopic composition of CO<sub>2</sub> in the middle atmosphere, suggesting that kinetic fractionation in the O(<sup>1</sup>D) + CO<sub>2</sub> → CO<sub>3</sub><sup>\*</sup> → O + CO<sub>2</sub> system is small. In addition, the reproduction of the CO<sub>2</sub> isotopic composition in the middle atmosphere further verifies the assumption of the equally weighted branching in the photodissociation of asymmetric ozone adopted in our previous modeling (22).

The resulting isotopic composition of CO<sub>2</sub> in photochemical equilibrium (in the absence of transport) is then determined simply by that of O(<sup>1</sup>D) or [C<sup>16</sup>O<sup>17</sup>O]/[C<sup>16</sup>O<sup>18</sup>O] = (k<sub>1</sub>k<sub>4</sub>)/(k<sub>2</sub>k<sub>3</sub>) [δ<sup>17</sup>O(<sup>1</sup>D)]/[δ<sup>18</sup>O(<sup>1</sup>D)]. To convert from the fractionation factors associated with (k<sub>1</sub>k<sub>4</sub>)/(k<sub>2</sub>k<sub>3</sub>) to δ values, isotopic standards must

be chosen. In this work, we follow the convention of Lämmerzahl *et al.* (8) and Liang *et al.* (22), who discuss the isotopic fractionation of trace gases referenced to atmospheric O<sub>2</sub>, unless otherwise stated. In this framework, the isotopic composition of stratospheric and mesospheric CO<sub>2</sub> reduces to (using the approximation that 1/(1 + δ) = 1 – δ)

$$\delta^{17}\text{O}(\text{CO}_2) \approx \xi_1 - \xi_2 + \delta^{17}\text{O}({}^1\text{D}) \tag{3}$$

$$\delta^{18}\text{O}(\text{CO}_2) \approx \xi_3 - \xi_4 + \delta^{18}\text{O}({}^1\text{D}). \tag{4}$$

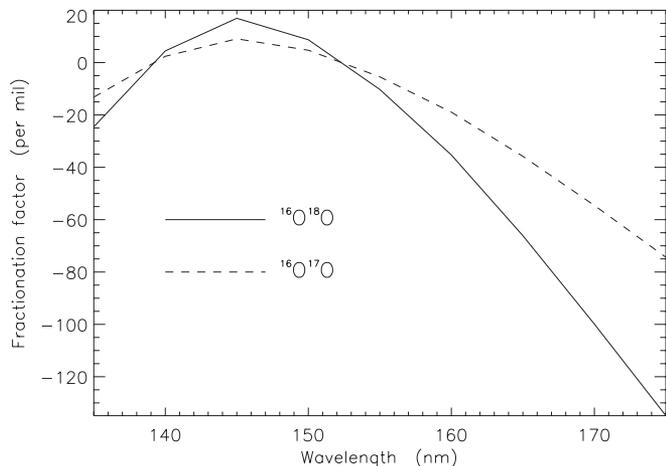
Thanks to the small contributions of ξ<sub>1</sub> – ξ<sub>4</sub> the slope *m* is well approximated by [δ<sup>17</sup>O(CO<sub>2</sub>) – δ<sup>17</sup>O(CO<sub>2</sub>)<sub>t</sub>]/[δ<sup>18</sup>O(CO<sub>2</sub>) – δ<sup>18</sup>O(CO<sub>2</sub>)<sub>t</sub>], where δ<sup>17</sup>O(CO<sub>2</sub>)<sub>t</sub> ≈ 9 and δ<sup>18</sup>O(CO<sub>2</sub>)<sub>t</sub> ≈ 17 per mil [or 21 and 41 per mil referenced to Vienna-standard mean ocean water (V-SMOW) (10)] are the mean δ values of tropospheric CO<sub>2</sub>, if transport is neglected. In the analysis that follows, δ<sup>17</sup>O(CO<sub>2</sub>)<sub>t</sub> and δ<sup>18</sup>O(CO<sub>2</sub>)<sub>t</sub> have been subtracted from the measured and predicted δ<sup>17</sup>O(CO<sub>2</sub>) and δ<sup>18</sup>O(CO<sub>2</sub>) values, again in accordance with Lämmerzahl *et al.* (8). The simulations also solve the full algebraic equations to predict the isotopic composition of CO<sub>2</sub> and O(<sup>1</sup>D); no approximations are invoked.

### Sources of O(<sup>1</sup>D)

In the stratosphere, quantitative calculations of the three-isotope slope *m* are obtained through recent kinetic calculations that model the isotopic fractionation of ozone vs. altitude (22). Contributions to the enrichments of isotopically heavy ozone follow from two processes: chemical formation (1, 4, 23) and UV photolysis (22, 24–26). Using the model that reproduces the observed enrichments in a three-isotope plot of O<sub>3</sub> (22), the computed photochemical equilibrium values of *m* (in the absence of transport) at altitudes between 30 and 60 km range from 1.3 to 3.0. After taking atmospheric transport into account, the slope *m*, calculated over the same altitude range as that of the CO<sub>2</sub> measurements in the stratosphere, is 1.60 (see below), which is in good agreement with the measured value of ≈1.7 (8).

At altitudes of >70 km, however, the photodissociation of O<sub>2</sub> becomes the dominant source of O(<sup>1</sup>D). Exchange of O(<sup>1</sup>D) with CO<sub>2</sub> at these altitudes could therefore modify the slope *m* if the O(<sup>1</sup>D) from O<sub>2</sub> photolysis is isotopically distinct from that generated in the stratosphere. Using a semianalytical calculation of the photolysis-induced fractionation (24, 25) in the Schumann–Runge bands of O<sub>2</sub>, the calculated δ of heavy O(<sup>1</sup>D) is <100 per mil (Fig. 1), dependent on altitude. However, a recent laboratory measurement of O<sub>2</sub> dissociation near Lyman-α (121.567 nm) has shown that the cross-section and O(<sup>1</sup>D) yield are strong functions of wavelength and suggests extremely large isotopic dependence (27). Although the cross-section near Lyman-α is 2–3 orders of magnitude less than those in the Schumann–Runge bands, the solar flux is correspondingly enhanced, compared with the flux in the Schumann–Runge bands.

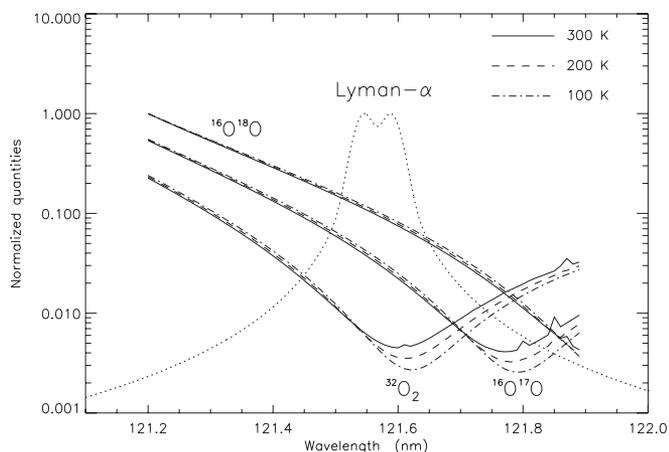
For *T* = 100–300 K, we have computed the isotopic dependence of the O<sub>2</sub> dissociation cross-section and O(<sup>1</sup>D) yield near Lyman-α (Fig. 2), by using coupled-channel Schrödinger equation calculations that accurately reproduce the experimental data for <sup>16</sup>O<sup>16</sup>O (27) and the well known rovibrational constants of oxygen isotopologues. These cross-sections, together with the solar spectrum, yield enormous fractionation factors and calculated values of δ<sup>17</sup>O(<sup>1</sup>D) and δ<sup>18</sup>O(<sup>1</sup>D) resulting from O<sub>2</sub> photolysis that peak at ≈80 km with sizes of 3137.1 and 10578.6 per mil, respectively. The resulting *m* ≈ 0.3 means that even small amounts of mixing of mesospheric air with the *m* = 1.6 gas that characterizes the stratosphere can provide an explanation for the *m* ≤ 1.2 fractionation observed in CO<sub>2</sub> by Thiemens *et al.* (10). We stress that Lyman-α photolysis of O<sub>2</sub> as a source of heavy O(<sup>1</sup>D) has not been considered in previous models. The ob-



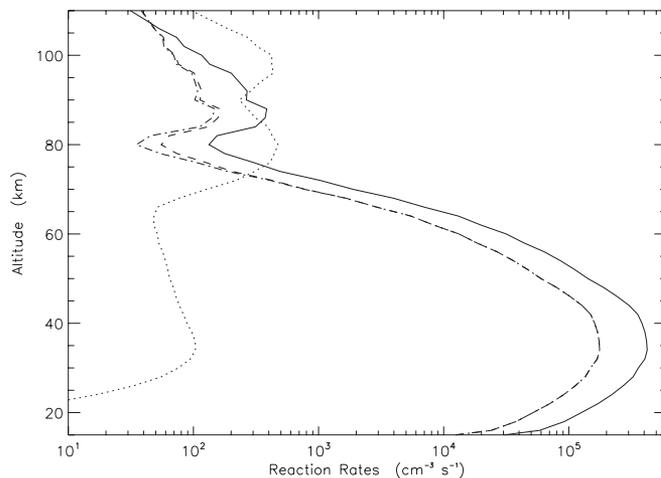
**Fig. 1.** Fractionation factors of molecular oxygen in the vacuum UV calculated by using the model described in Liang *et al.* (25). The fractionation factor is defined by  $1,000 \times (\sigma/\sigma_0 - 1)$ , where  $\sigma_0$  and  $\sigma$  are the photoabsorption cross-sections of normal and isotopically substituted molecules, respectively. The absorption cross-section of normal  $O_2$  is taken from the literature (30–33).

served depletion of  $\delta^{18}O(O_2)$  at 53.3 and 59.5 km (10) is also likely the consequence of this  $O_2$  Lyman- $\alpha$  photolysis.

In addition to the mechanism of transferring heavy oxygen atoms from  $O_3$  and  $O_2$  to  $CO_2$ , we also include the effect of  $CO_2$  photolysis using a semianalytic model of photodissociation (24, 25). Although the photolysis-induced fractionation of oxygen in  $CO_2$  can be as large as 100 per mil at selected wavelengths (28), the overall effect of UV photolysis is always insignificant compared with that induced by (photo)chemical exchange. Shown in Fig. 3 are vertical profiles for two processes,  $CO_2$  photolysis and  $CO_2 + O(^1D)$  exchange reactions. Below  $\approx 70$  km, although the fractionation factors for  $CO_2$  photodissociation are  $>100$  per mil, the photolysis rates are negligible compared with the exchange reaction rates. At  $>70$  km, the photolysis-induced fractionation is small, because most of absorption happens near the maximum of absorption cross-section, where only small fractionation factors are seen (24, 25), and the contribution from the Lyman- $\alpha$  photolysis (see the dashed vs. dash-dotted lines in Fig. 3) of  $O_2$  becomes important.



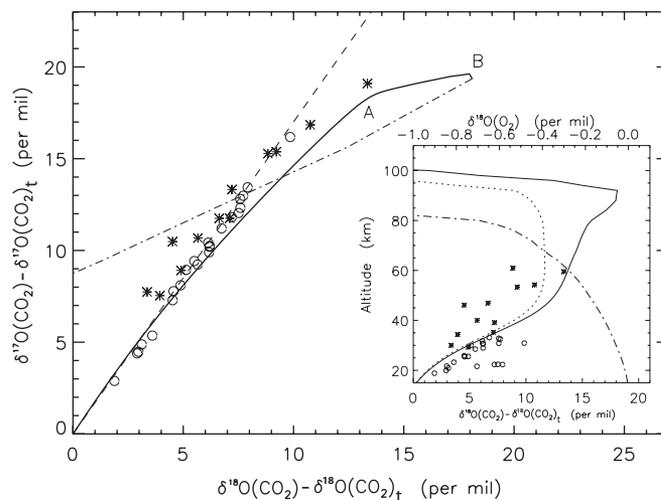
**Fig. 2.** Absorption cross-sections for the production of  $O(^3P)$  and  $O(^1D)$  near Lyman- $\alpha$ . The solar profile is shown by the dotted line. All quantities are normalized. Normalization factors for the Lyman- $\alpha$ , cross-sections at 100, 200, and 300 K are  $5.1 \times 10^{11}$  photons  $cm^{-2} s^{-1} \text{\AA}^{-1}$ , and  $1.73 \times 10^{-18}$ ,  $1.75 \times 10^{-18}$ , and  $1.76 \times 10^{-18}$   $cm^2$ , respectively.



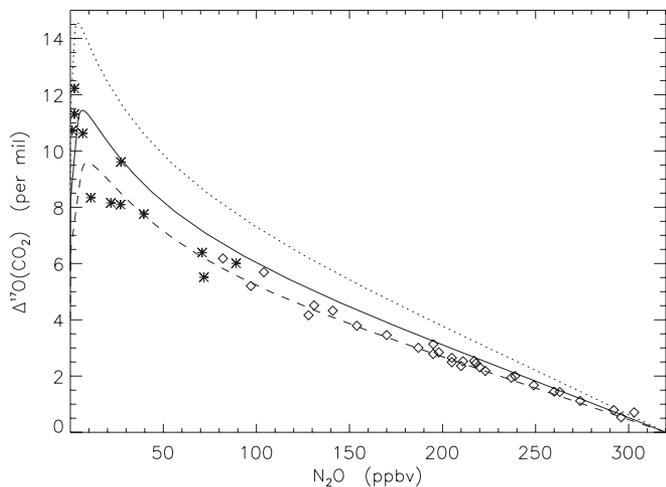
**Fig. 3.** Vertical reaction rate profiles for the  $O(^1D) + CO_2$  chemical exchange (solid line) and  $CO_2$  photolysis (dotted line). Dashed and dash-dotted lines represent  $O(^1D)$  production rates for cases with and without including  $O_2$  Lyman- $\alpha$  photolysis, respectively.

### 1D Model

To provide an assessment of the probable impact of the multiple sources of  $O(^1D)$  and the role of transport in the isotopic composition of  $CO_2$ , the results of a 1D atmospheric model are summarized in Figs. 4 and 5. In the three-isotope plot presented in Fig. 4, the dominant slope of  $\approx 1.6$ – $1.7$  is produced by the  $O(^1D)$  from ozone photolysis, which is also responsible for the strong correlation of  $\Delta^{17}O(CO_2)$  with the stratospheric  $N_2O$  mixing ratio shown in Fig. 5 [where  $\Delta^{17}O(CO_2) = \delta^{17}O(CO_2) -$



**Fig. 4.** Three-isotope plot of oxygen in  $CO_2$ , from which the mean tropospheric values have been subtracted. The atmospheric measurements are from balloon measurements of Lämmerzahl *et al.* (8) (circles) and the full rocket data set first reported by Thiemens *et al.* (10) (asterisks). The solid line depicts the model, and the change in slope at A corresponds to an altitude of  $\approx 55$  km. At higher altitudes (and for fractionations greater than these fiducial values), the slope  $m(A-B)$  is  $\approx 0.3$ , as expected from oxygen photolysis. Another change of slope in the calculation occurs at B for altitudes of  $\approx 90$  km and higher. Over this range, molecular diffusion dominates, and the slope becomes mass dependent, that is  $\approx 0.5$  (dash-dotted line). (Inset) Vertical profiles of  $\delta^{18}O(CO_2)$  with (solid) and without (dotted) including the fractionation of  $O(^1D)$  induced by  $O_2$  Lyman- $\alpha$  photolysis. For comparison, the vertical profile of  $\delta^{18}O$  in  $O_2$  is shown by the dash-dotted line, which can be satisfactorily explained by eddy and molecular diffusion processes for this photochemically steady-state atmosphere.



**Fig. 5.** A plot of the value of the mass-independent isotopic fractionation in atmospheric CO<sub>2</sub> vs. the nitrous oxide abundance. Rocket (asterisks) and airborne (diamonds) data are taken from Thiemens *et al.* (10) and Boering *et al.* (7), and the solid line presents the results of our standard 1D simulations using the canonical eddy diffusion coefficient of Allen *et al.* (19). The dotted and dashed lines represent cases for a 30% reduction and enhancement of the eddy diffusion constant of <40 km, respectively.

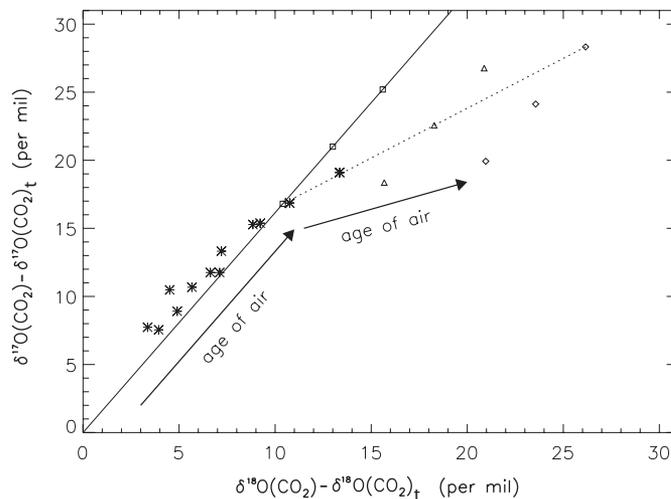
0.515 × δ<sup>18</sup>O(CO<sub>2</sub>) is the “anomalous” or mass-independent isotopic signature in CO<sub>2</sub>]. As Fig. 4 *Inset* shows, however, the heavy O atoms from O<sub>2</sub> Lyman-α photolysis can greatly modify the expected isotopic composition of CO<sub>2</sub> at altitudes >40 km.

We stress that such simple 1D simulations cannot fully capture the coupled impact of chemistry and transport on the isotopic composition of long-lived atmospheric trace gases, but they are useful in assessing the relative importance of various (photo)chemical processes. To provide bounds on the importance of transport, we carried out additional simulations (see Fig. 5) in which the eddy coefficients <40 km are reduced and enhanced by 30% compared with the prescription of Allen *et al.* (19). The disagreement of the 1D model vertical profiles shown in Fig. 4 with the measurements of Thiemens *et al.* (10) is due to circulation cells between the tropics and ≈30°N, where the air is significantly younger than that at higher latitudes with similar altitudes (refs. 13 and 21 and M.-C.L., G.A.B., and Y.L.Y., unpublished data). Indeed, we expect that multilatitude and, especially, additional mesospheric measurements of *m*, when combined with proper models, should be able to refine our understanding of atmospheric transport and chemical processes, especially in the remote regions of the mesosphere.

### Three-Box Model

Finally, we use a three-box model to evaluate the potential impact of transport on the slope and magnitude of the CO<sub>2</sub> isotopic fractionation. Box 1 (fresh air from the troposphere) has δ<sup>17</sup>O(CO<sub>2</sub>)<sub>t</sub> = 9 and δ<sup>18</sup>O(CO<sub>2</sub>)<sub>t</sub> = 17 per mil. Box 2 (the stratosphere) has δ<sup>17</sup>O(CO<sub>2</sub>)<sub>s</sub> = δ<sup>17</sup>O(<sup>1</sup>D) = 93 and δ<sup>18</sup>O(CO<sub>2</sub>)<sub>s</sub> = δ<sup>18</sup>O(<sup>1</sup>D) = 69 per mil, with the values defined by photochemical steady-state with O(<sup>1</sup>D) from O<sub>3</sub>. Box 3 (the mesosphere) has δ<sup>17</sup>O(CO<sub>2</sub>)<sub>m</sub> = δ<sup>17</sup>O(<sup>1</sup>D) = 3137 and δ<sup>18</sup>O(CO<sub>2</sub>)<sub>m</sub> = δ<sup>18</sup>O(<sup>1</sup>D) = 10579 per mil, with the values predicted from the Lyman-α photolysis of O<sub>2</sub>. The isotopic composition of CO<sub>2</sub> is determined by the mixing of air from these boxes, or

$$\delta^{17}\text{O}(\text{CO}_2) = x_t \delta^{17}\text{O}(\text{CO}_2)_t + x_s \delta^{17}\text{O}(\text{CO}_2)_s + x_m \delta^{17}\text{O}(\text{CO}_2)_m \quad [5]$$



**Fig. 6.** A three-box mixing model for CO<sub>2</sub> in the middle atmosphere. The tropospheric δ values of CO<sub>2</sub> have been subtracted. The symbols denote additional mixing with box 3 to varying extent. Squares, no mixing with box 3; triangles, 0.05% of air from box 3; diamonds, 0.1% of air from box 3. Asterisks are taken from Thiemens *et al.* (10). The solid line illustrates the fractionation expected from the interaction of CO<sub>2</sub> and O<sub>3</sub> only, and the dotted line presents an example of how the three isotope slope can be flattened by the mixing of air from boxes 2 (stratosphere) and 3 (mesosphere).

$$\delta^{18}\text{O}(\text{CO}_2) = x_t \delta^{18}\text{O}(\text{CO}_2)_t + x_s \delta^{18}\text{O}(\text{CO}_2)_s + x_m \delta^{18}\text{O}(\text{CO}_2)_m \quad [6]$$

where *x<sub>t</sub>*, *x<sub>s</sub>*, and *x<sub>m</sub>* are the fractions of air from boxes 1, 2, and 3, and *x<sub>t</sub>* + *x<sub>s</sub>* + *x<sub>m</sub>* = 1. For atmospheric CO<sub>2</sub>, *x<sub>m</sub>* ≪ *x<sub>s</sub>* < *x<sub>t</sub>*. As expected, the magnitude of δ<sup>17</sup>O(CO<sub>2</sub>) increases with the age of the air parcel, i.e., more CO<sub>2</sub> exchanging with O(<sup>1</sup>D) from boxes 2 and 3.

The mixing of boxes 1 and 2 produces a slope of 1.6, as shown in the solid line in Fig. 6. When mixing in air from box 3, the slope is modified, and the dotted line represents the cases for which (*x<sub>t</sub>*, *x<sub>m</sub>*) = (0.80, 0), (0.75, 0.0005), and (0.70, 0.001). The two extreme data points from Fig. 4 that are overplotted by asterisks can be explained by only ≈0.02% mixing with box 3. Similar analyses can be applied to the rest of the data. In general, we predict that in the middle atmosphere air recently entrained from the troposphere would have CO<sub>2</sub> isotopic compositions characterized by stratospheric ozone, whereas the O(<sup>1</sup>D) from O<sub>2</sub> photolysis would play a part in air parcels exposed to the mesosphere.

In summary, we have demonstrated that Δ<sup>17</sup>O(CO<sub>2</sub>), the anomalous isotopic composition of CO<sub>2</sub>, can serve as a powerful tracer of atmospheric dynamics and chemistry well into the mesosphere. Furthermore, this “recycled” CO<sub>2</sub> carries a long-lived isotopic composition that is distinct from that in the troposphere and as such has the potential to constrain biogeochemical cycles involving carbon dioxide and oxygen, in particular those involving the terrestrial biosphere (15). Recent three-isotope measurements of O<sub>2</sub> in closed systems (29), for example, have shown that a nearly universal respiration curve can be used to extract highly precise Δ<sup>17</sup>O values in both O<sub>2</sub> and CO<sub>2</sub> that are sensitive to the magnitude of the anomalous signature generated in the middle atmosphere and the relative rates of mass transport through the biosphere vs. atmospheric photochemistry. To the best of our knowledge, all existing estimates (16) for the changes of terrestrial biospheric production over millennial time scales, the window over which the tropospheric oxygen isotopic anomaly accumulates, are based on an assumption that the strength of stratosphere–troposphere exchange in paleoatmospheres is the

same as that at present. We suggest that the simultaneous measurements of CO<sub>2</sub> and O<sub>2</sub> isotopologues can largely reduce this ambiguity and provide a more reasonable assessment for millennial bioproductivity, especially if they can be extended to ice core records. Better constraints on the potential role of the large isotopic fractionation in O<sub>2</sub> resulting from Lyman- $\alpha$  photolysis will require further atmospheric measurements of O<sub>2</sub> and CO<sub>2</sub> either in the mesosphere or polar regions in which downwelling air is prevalent. Experimentally, laboratory measurements of the dissociation cross-sections of isotopically substituted O<sub>2</sub> near Lyman- $\alpha$  (121.567 nm) are needed to confirm and refine the coupled-channel Schrödinger equation predictions, whereas that of the isotopic equilibration time constant between CO<sub>2</sub> and water ice is needed to assess whether the isotopic

composition of CO<sub>2</sub> recorded in ice bubbles can be used to examine millennial time scale fluctuations in troposphere-stratosphere exchange rates. Theoretically, 2D and 3D atmospheric simulations should significantly expand our understanding of the dynamical and chemical history of trace molecules in the atmosphere.

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- Mauersberger K, Erbacher B, Krankowsky D, Gunther J, Nickel R (1999) *Science* 283:370–372.
- Mauersberger K, Lammerzähl P, Krankowsky D (2001) *Geophys Res Lett* 28:3155–3158.
- Thiemens MH (2006) *Annu Rev Earth Planet Sci* 34:217–262.
- Thiemens MH, Heidenreich JE (1983) *Science* 219:1073–1075.
- Mauersberger K (1987) *Geophys Res Lett* 14:80–83.
- Alexander B, Vollmer MK, Jackson T, Weiss RF, Thiemens MH (2001) *Geophys Res Lett* 28:4103–4106.
- Boering KA, Jackson T, Hoag KJ, Cole AS, Perri MJ, Thiemens M, Atlas E (2004) *Geophys Res Lett* 31:L03109.
- Lämmerzahl P, Rockmann T, Brenninkmeijer CAM, Krankowsky D, Mauersberger K (2002) *Geophys Res Lett* 29:1582.
- Thiemens MH (1999) *Science* 283:341–345.
- Thiemens MH, Jackson T, Zipf EC, Erdman PW, Vanegmond C (1995) *Science* 270:969–972.
- Zipf EC, Erdman PW (1994) *NASA Upper Atmosphere Research Program: Research Summaries, 1992–1993. Report to the Congress and the Environmental Protection Agency, January* (Natl Aeronautics Space Admin, Washington, DC), Tech Rep N-92-34099.
- Yung YL, Demore WB, Pinto JP (1991) *Geophys Res Lett* 18:13–16.
- Yung YL, Lee AYT, Irion FW, DeMore WB, Wen J (1997) *J Geophys Res Atmos* 102:10857–10866.
- Cliff SS, Brenninkmeijer CAM, Thiemens MH (1999) *J Geophys Res Atmos* 104:16171–16175.
- Hoag KJ, Still CJ, Fung IY, Boering KA (2005) *Geophys Res Lett* 32:L02802.
- Luz B, Barkan E, Bender ML, Thiemens MH, Boering KA (1999) *Nature* 400:547–550.
- Chakraborty S, Bhattacharya SK (2003) *J Geophys Res Atmos* 108:4724.
- Morgan CG, Allen M, Liang MC, Shia RL, Blake GA, Yung YL (2004) *J Geophys Res Atmos* 109:D04305.
- Allen M, Yung YL, Waters JW (1981) *J Geophys Res Space Phys* 86:3617–3627.
- Rahn T, Zhang H, Wahlen M, Blake GA (1998) *Geophys Res Lett* 25:4489–4492.
- Hall TM, Waugh DW, Boering KA, Plumb RA (1999) *J Geophys Res Atmos* 104:18815–18839.
- Liang MC, Irion FW, Weibel JD, Miller CE, Blake GA, Yung YL (2006) *J Geophys Res Atmos* 111:D02302.
- Gao YQ, Marcus RA (2001) *Science* 293:259–263.
- Blake GA, Liang MC, Morgan CG, Yung YL (2003) *Geophys Res Lett* 30:1656.
- Liang MC, Blake GA, Yung YL (2004) *J Geophys Res Atmos* 109:D10308.
- Bhattacharya SK, Chakraborty S, Savarino J, Thiemens MH (2002) *J Geophys Res Atmos* 107:4675.
- Lacoursiere J, Meyer SA, Faris GW, Slanger TG, Lewis BR, Gibson ST (1999) *J Chem Phys* 110:1949–1958.
- Bhattacharya SK, Savarino J, Thiemens MH (2000) *Geophys Res Lett* 27:1459–1462.
- Luz B, Barkan E (2005) *Geochim Cosmochim Acta* 69:1099–1110.
- Anbar AD, Allen M, Nair HA (1993) *J Geophys Res Planets* 98:10925–10931.
- Lee LC, Slanger TG, Black G, Sharpless RL (1977) *J Chem Phys* 67:5602–5606.
- Nicolet M (1984) *Planet Space Sci* 32:1467–1468.
- Samson JAR, Rayborn GH, Pareek PN (1982) *J Chem Phys* 76:393–397.