

Triple oxygen isotope composition of tropospheric carbon dioxide as a tracer of terrestrial gross carbon fluxes

K. J. Hoag,¹ C. J. Still,² I. Y. Fung,¹ and K. A. Boering¹

Received 14 July 2004; revised 12 November 2004; accepted 9 December 2004; published 19 January 2005.

[1] Stratospheric photochemistry leads to anomalous oxygen isotope enrichments in CO₂ (for which $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.516 \times \delta^{18}\text{O} \neq 0$). This isotope anomaly is not lost until air returns to the troposphere and CO₂ undergoes isotope exchange with water primarily in the terrestrial biosphere and oceans. A two-box model is used to investigate the contribution of stratospheric production and contemporary surface carbon fluxes to tropospheric $\Delta^{17}\text{O}_{\text{CO}_2}$. The predicted magnitude of $\sim 0.15\%$ is large enough that measurement of a globally averaged tropospheric $\Delta^{17}\text{O}_{\text{CO}_2}$ should provide a new constraint for gross carbon exchanges between the biosphere and atmosphere in terrestrial carbon cycle models. Importantly, $\Delta^{17}\text{O}_{\text{CO}_2}$ should be complementary to the primary isotopic tracer of gross carbon exchanges, $\delta^{18}\text{O}_{\text{CO}_2}$, but is not dependent on numerous hydrologic variables. Furthermore, with improved measurement precision, $\Delta^{17}\text{O}_{\text{CO}_2}$ could serve as a direct tracer of gross carbon exchanges and their variations. **Citation:** Hoag, K. J., C. J. Still, I. Y. Fung, and K. A. Boering (2005), Triple oxygen isotope composition of tropospheric carbon dioxide as a tracer of terrestrial gross carbon fluxes, *Geophys. Res. Lett.*, 32, L02802, doi:10.1029/2004GL021011.

1. Introduction

[2] The terrestrial biosphere plays a dominant role in controlling atmospheric CO₂ on annual and interannual timescales and is responsible for about half of the net global carbon sink for anthropogenic CO₂. This net sink and its variability on short time scales are governed primarily by the gross fluxes of CO₂ into and out of the atmosphere due to respiration and photosynthesis, respectively. Because the net sink is the small difference between these large fluxes and is more easily constrained by observations, large uncertainties remain in the global magnitudes and the temporal and spatial variability of these gross fluxes [e.g., Gurney *et al.*, 2002]. Moreover, the climate sensitivities of these gross fluxes are a key uncertainty in climate change predictions since understanding the distinct responses of photosynthesis versus respiration to changing environmental conditions is critical to predicting how carbon storage by the terrestrial biosphere will respond to global change [e.g., Friedlingstein *et al.*, 2003; Cox *et al.*, 2000; Schimel *et al.*, 2001].

¹Department of Earth and Planetary Science and Department of Chemistry, University of California, Berkeley, California, USA.

²Department of Geography, University of California, Santa Barbara, California, USA.

[3] While net CO₂ exchanges between the atmosphere, biosphere, and ocean are studied using observations of the concentrations and $\delta^{13}\text{C}$ values of CO₂ [e.g., Francey *et al.*, 1995] or measuring the local net fluxes of CO₂ directly [e.g., Goulden *et al.*, 1998], observations and modeling of $\delta^{18}\text{O}$ of tropospheric CO₂ have received increasing attention as a means to constrain gross carbon exchanges since both the gross photosynthetic uptake of carbon and the total ecosystem respiration play dominant and often opposing roles in determining $\delta^{18}\text{O}_{\text{CO}_2}$ [e.g., Farquhar *et al.*, 1993; Ciais *et al.*, 1997]. Francey and Tans [1987] first suggested that isotope exchange between CO₂ and water in the chloroplasts of leaves during photosynthesis largely determines tropospheric $\delta^{18}\text{O}_{\text{CO}_2}$. While $\sim 1/3$ of atmospheric CO₂ entering leaves is assimilated, the remainder diffuses back out with a new $\delta^{18}\text{O}$ value determined largely by $\delta^{18}\text{O}_{\text{leaf-H}_2\text{O}}$. Farquhar *et al.* [1993] related this isotope exchange process to gross primary productivity (GPP) in a model which included a large number of isotopic, physical, hydrologic, and biological variables. Subsequent modeling studies confirmed that land biota are the primary determinant of $\delta^{18}\text{O}_{\text{CO}_2}$ [e.g., Ciais *et al.*, 1997; Cuntz *et al.*, 2003a, 2003b]. Table 1 summarizes the isotope exchange processes in the global $\delta^{18}\text{O}_{\text{CO}_2}$ cycle. Among the current aims of modeling efforts is to use $\delta^{18}\text{O}$ observations of CO₂ and H₂O to improve estimates of GPP and respiration, both globally and locally [e.g., Cuntz *et al.*, 2003a, 2003b; Riley *et al.*, 2003].

[4] Clearly, using $\delta^{18}\text{O}_{\text{CO}_2}$ as a constraint on terrestrial GPP requires estimates and/or detailed modeling of $\delta^{18}\text{O}$ values for numerous water pools which can be difficult to ascertain. $\delta^{18}\text{O}$ of leaf water, e.g., depends on plant anatomy, the vertical distribution of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in soils, the humidity in the canopy and its $\delta^{18}\text{O}$, and other factors such as precipitation and temperature. In contrast, the anomalous relationship between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of tropospheric CO₂, or $\Delta^{17}\text{O}_{\text{CO}_2}$ defined below, does not depend directly on values for $\delta^{18}\text{O}$ or $\delta^{17}\text{O}$ of soil and leaf H₂O and may therefore be easier to link directly to GPP and to deconvolve the response of GPP to interannual changes in, e.g., temperature and precipitation.

[5] Stratospheric CO₂ is anomalously enriched in ¹⁷O and ¹⁸O [e.g., Lämmerzahl *et al.*, 2002; Boering *et al.*, 2004]. Most physical and chemical processes fractionate isotopes in a mass-dependent manner for which $\delta^{17}\text{O} = \lambda \times \delta^{18}\text{O}$, with $\lambda = 0.500$ to 0.529 [e.g., Thieme, 1999]. However, for stratospheric CO₂, $\delta^{17}\text{O} \sim 1.7 \times \delta^{18}\text{O}$, and the magnitude of the CO₂ isotope anomaly may be defined as

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \times \delta^{18}\text{O} \quad (1)$$

Table 1. Processes Controlling $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of Tropospheric CO₂

Process	Total CO ₂ Flux (PgCyr ⁻¹)	Variables to Model $\delta^{18}\text{O}_{\text{CO}_2}$	Variables to Model $\Delta^{17}\text{O}_{\text{CO}_2}$
Leaf water (in, out)	272, 170 ^a	$\delta^{18}\text{O}$ of leaf H ₂ O & flux	Flux
Respiration	102 ^a	$\delta^{18}\text{O}$ of soil H ₂ O & flux	Flux
Soil water - invasion	4.4 ^b	$\delta^{18}\text{O}$ of soil H ₂ O & flux	Flux
Ocean (in, out)	92, 90 ^a	$\delta^{18}\text{O}$ of ocean H ₂ O & flux	Flux
Fossil fuel	6.0 ^a	Flux	Flux
Stratosphere to troposphere	30 to 102 ^c	Flux of $\delta^{18}\text{O}_{\text{CO}_2}$ from the stratosphere	Flux of $\Delta^{17}\text{O}_{\text{CO}_2}$ from the stratosphere

^aCiais *et al.* [1997].^bStern *et al.* [2001].^cUsing air mass fluxes from Holton [1990] and Appenzeller *et al.* [1996].

where $\lambda = 0.516$ [Boering *et al.*, 2004]. This CO₂ isotope anomaly likely arises from anomalous kinetic isotope effects in the formation of O₃ [e.g., Mauersberger *et al.*, 1999], which can be photochemically transferred to CO₂ via O(¹D) from O₃ photolysis [e.g., Yung *et al.*, 1997]. Since there is, in effect, no stratospheric sink for $\Delta^{17}\text{O}_{\text{CO}_2}$, anomalous CO₂ produced in the stratosphere is transported to the troposphere where the isotope anomaly is destroyed by isotope exchange with water and diluted by inputs of non-anomalous CO₂. Importantly, when CO₂ equilibrates with mass-dependently fractionated H₂O, $\Delta^{17}\text{O}_{\text{CO}_2}$ is reset to zero.

[6] Thus, modeling a global cycle for $\Delta^{17}\text{O}$ in tropospheric CO₂ to investigate gross fluxes to and from the terrestrial biosphere is analogous to that for $\delta^{18}\text{O}_{\text{CO}_2}$ but is considerably less complex. In particular, explicit values for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of leaf water are not required since $\Delta^{17}\text{O}$ for CO₂ retro-diffusing out of leaves during photosynthesis is reset to zero (if isotopic equilibration is complete) or some fraction of $\Delta^{17}\text{O}_{\text{CO}_2}$ (if equilibration is incomplete). Likewise, explicit values for $\delta^{18}\text{O}$ of soil H₂O are not required since respired CO₂ and the CO₂ associated with the invasion flux of atmospheric CO₂ into the soil [e.g., Miller *et al.*, 1999] are not anomalous. Therefore, tropospheric $\Delta^{17}\text{O}_{\text{CO}_2}$ may provide a tracer of gross carbon fluxes that is complementary to $\delta^{18}\text{O}_{\text{CO}_2}$ but which does not depend on explicit values of $\delta^{18}\text{O}$ for numerous water pools and is decoupled from potential ambiguities due to correlated changes in $\delta^{18}\text{O}$ of leaf and soil water with changing temperature or precipitation patterns. Moreover, while $\Delta^{17}\text{O}$ of O₂ has been proposed as a constraint on GPP on millennial time scales [Luz *et al.*, 1999], tropospheric $\Delta^{17}\text{O}_{\text{CO}_2}$ may provide information on annual to decadal time scales. In this first study, a two-box model is used to investigate the feasibility of using $\Delta^{17}\text{O}_{\text{CO}_2}$ as a constraint on gross CO₂ fluxes to and from the terrestrial biosphere.

2. Model Description

[7] A two-box model representing the northern and southern hemispheres (NH and SH) was chosen since there are several flux asymmetries between the hemispheres. Carbon mass balance requires that the rate of change in CO₂ inventory in the NH troposphere (M^N) is the sum of the sources and sinks (Q_j^N) of CO₂ within the hemisphere and the interhemispheric exchanges of CO₂:

$$\frac{dM^N}{dt} = \sum_j Q_j^N - \frac{M^N - M^S}{\tau} \quad (2)$$

In (2), τ is 1.1 yrs, the interhemispheric exchange time from ⁸⁵Kr observations [Jacob *et al.*, 1987].

[8] The mass balance equation for $\Delta^{17}\text{O}_{\text{CO}_2}$ in the NH troposphere, expressed as $\Delta^{17}\text{O}^N$, is given by (3):

$$\frac{d(M^N \times \Delta^{17}\text{O}^N)}{dt} = \sum_j (\Delta^{17}\text{O}_j \times Q_j^N) - \frac{(\Delta^{17}\text{O}^N \times M^N) - (\Delta^{17}\text{O}^S \times M^S)}{\tau} \quad (3)$$

Equations (2) and (3) yield (4) for the $\Delta^{17}\text{O}^N$ tendency in the NH.

$$\frac{d(\Delta^{17}\text{O}^N)}{dt} = \frac{1}{M^N} \left\{ \sum_j [(\Delta^{17}\text{O}_j - \Delta^{17}\text{O}^N) Q_j^N] + (\Delta^{17}\text{O}^S - \Delta^{17}\text{O}^N) \frac{M^S}{\tau} \right\} \quad (4)$$

The carbon sources and sinks are expressed as the sum of fluxes into and out of the NH:

$$Q^N = \sum_j Q_j^N = \{F_{SA}^N + F_{AS}^N\} + \{F_{OA}^N + F_{AO}^N\} + \{F_{LA}^N + F_{AL}^N + F_{resp}^N\} + F_{ff}^N + F_{landuse}^N \quad (5)$$

where F_{XY} represents the flux from a donor reservoir X to receiver reservoir Y , with the subscript S denoting the stratosphere, A the troposphere, O the ocean, and L leaves. F_{AL} and F_{LA} are the CO₂ fluxes between the troposphere and leaves of plants and are proportional to GPP. F_{resp} , F_{ff} , and $F_{landuse}$ are unidirectional CO₂ fluxes from stem and soil respiration, fossil fuel combustion, and land use, respectively. Analogous equations were used to calculate M^S and $\Delta^{17}\text{O}^S$.

[9] Table 2 lists the estimated magnitude of each Q_j , its NH:SH ratio, and its $\Delta^{17}\text{O}_j$ value used in the “base” model scenario, while Table 3 lists sensitivity tests. The carbon budget for (2) is chosen to be that for the 1990s, with $dM/dt = 3.2$ PgCyr⁻¹, and $[\text{CO}_2]_0^A = 370$ ppm. The annual stratosphere-troposphere carbon exchange fluxes for each hemisphere, $F_{SA}^{N,S}$ and $F_{AS}^{N,S}$, are the products of air mass fluxes from Appenzeller *et al.* [1996] and the tropospheric CO₂ concentration, $[\text{CO}_2]^A$, calculated from M^N and M^S . This prescribes a stratospheric CO₂ mixing ratio, $[\text{CO}_2]^S$, equal to $[\text{CO}_2]^A$; a time lag between $[\text{CO}_2]^S$ and $[\text{CO}_2]^A$ of 1–2 years

Table 2. Carbon Sources and Sinks (Q_j) Controlling $\Delta^{17}O^A$

Source or Sink	Symbol	Q_j^a (PgCyr ⁻¹)	NH:SH	$\Delta^{17}O_i$ (‰ vs VSMOW)
From Stratosphere	F_{SA}	6.8×10^{17} kg air yr ⁻¹ \times $[CO_2]^S(t)$	52:48	0.420 ^b
To Stratosphere	F_{AS}	-6.8×10^{17} kg air yr ⁻¹ \times $[CO_2]^A(t)$	52:48	$\Delta^{17}O^A$
From Ocean	F_{OA}	F_{AO} – net ocean sink	60:40	0.0
To Ocean	F_{AO}	$-90.0 \times [CO_2]^A(t)/[CO_2]_0^A$	60:40	$\Delta^{17}O^A$
Fossil Fuel	F_{ff}	6.0	96:4	-0.155
Land Use Change	$F_{landuse}$	1.6	50:50	0.0
From Leaf	F_{LA}	152.5 ^c	66:34	0 for $F_{LA,eq}$; $\Delta^{17}O^A$ otherwise
To Leaf	F_{AL}	-240.5 ^c	66:34	$\Delta^{17}O^A$
Stem and Root Respiration	F_{resp}	82.7 ^c	62:38	0.0

^a $Q_j > 0$ denote sources to the troposphere and $Q_j < 0$ denote sinks; magnitudes are the global values.

^bInitial value, increases as $\Delta^{17}O^A$ increases.

^cInitial value, increases as $[CO_2]^A$ increases.

does not change the carbon budget nor $\Delta^{17}O^{N,S}$ significantly. The fossil fuel flux F_{ff} is 6 PgCyr⁻¹, with 96% in the NH [Marland *et al.*, 2003]. Land use modification is assumed to occur mainly in the tropics, with $F_{landuse} \sim 1.6$ PgCyr⁻¹ split evenly between the NH and SH [Schimel *et al.*, 2001]. The gross CO₂ flux to the ocean is calculated at each timestep as $F_{AO} = 90$ PgCyr⁻¹ \times $[CO_2]^A(t)/[CO_2]_0^A$. A constant net ocean sink of 2 PgCyr⁻¹ is assumed and therefore $F_{OA}(t) = F_{AO}(t) - 2$. F_{AO} and F_{OA} are divided between the hemispheres using the partitioning of net ocean fluxes from the mean of the TransCom3 models [Gurney *et al.*, 2003].

[10] The background equilibrium terrestrial biosphere is represented by net carbon assimilation during photosynthesis (A) balanced by stem and soil respiration ($A_0 + F_{resp} = 0$). Here A is the difference between CO₂ to and from leaves ($A = F_{AL} + F_{LA}$) with the fluxes given by:

$$F_{LA} = A \times C_c / (C_a - C_c) \quad (6)$$

$$F_{AL} = -A \times C_a / (C_a - C_c) \quad (7)$$

(6) and (7) follow from Farquhar and Lloyd [1993] and Ciais *et al.* [1997]; C_c and C_a are the CO₂ concentrations in the chloroplasts and the atmosphere. Typical values for the C_c/C_a ratio are 2/3 for C₃ plants and 1/3 for C₄ plants [Pearcy and Ehleringer, 1984], with the assumption that $C_c \sim C_i$, the intracellular [CO₂]. The leaf flux estimates in Table 2 assume a global annual magnitude for GPP of 100 PgCyr⁻¹ [Cramer *et al.*, 1999]. The hemispheric distribution of GPP is assumed to be the same as that for net

primary production (NPP) calculated by the terrestrial biogeochemistry model CASA [Randerson *et al.*, 1997]. We assume that plants use 12% of GPP as leaf respiration [Ciais *et al.*, 1997] so that A_0 is 88 PgCyr⁻¹. The global distribution of C₃:C₄ plant coverage is from Still *et al.* [2003]. Furthermore, isotope equilibration between CO₂ and H₂O in chloroplasts is incomplete. We therefore partitioned F_{LA} into equilibrated ($F_{LA,eq} = \Theta \times F_{LA}$) and non-equilibrated fluxes, with the degree of equilibration (Θ) for C₃ and C₄ plants of 0.93 and 0.38, respectively [Gillon and Yakir, 2000]. We assumed that the land sink of 2.4 PgCyr⁻¹ required to balance the contemporary carbon budget is due to enhanced GPP, with $A(t) = A_0 \times [CO_2]^A(t)/[CO_2]_0^A$, and $F_{resp}(t) = A(t) - 2.4$. As $\Delta^{17}O^A$ is influenced by gross fluxes, our calculations show that assigning the net land sink to retarded respiration has little impact on $\Delta^{17}O^A$ (not shown).

[11] Solving (4) requires values for $\Delta^{17}O_j$ for each carbon flux. Fluxes leaving the troposphere (F_{AS} , F_{AO} , F_{AL}) carry the isotopic value of the troposphere ($\Delta^{17}O = \Delta^{17}O^A$) and therefore do not contribute to (4). For the stratosphere-to-troposphere flux, $\Delta^{17}O^S$ was estimated using $\Delta^{17}O^A$ and an initial net $\Delta^{17}O_{CO_2}$ flux of 42.9‰PgCyr⁻¹ [Boering *et al.*, 2004]. $\Delta^{17}O_j$ for the surface fluxes to the atmosphere, F_{OA} , $F_{LA,eq}$, and F_{resp} , are assumed to be zero since the CO₂ is equilibrated with mass-dependently fractionated water pools. The non-equilibrated CO₂ flux, $(1 - \Theta) \times F_{LA}$, exits the leaf with an unchanged tropospheric $\Delta^{17}O^A$. $\Delta^{17}O$ for fossil fuel CO₂ is assumed to be that for atmospheric O₂ ($\Delta^{17}O_{O_2} = -0.155$ ‰ [Luz *et al.*, 1999]), as in $\delta^{18}O$ modeling

Table 3. Model Results and Sensitivities: $\Delta^{17}O^A$ for Model yr = 20

Parameter (units)	Base Scenario Value	Change	NH $\Delta^{17}O^N$ (‰)	SH $\Delta^{17}O^S$ (‰)	Global $\Delta^{17}O^A$ (‰)
Base Scenario	–	–	0.14	0.15	0.14
Strat-trop air mass flux (kg air yr ⁻¹)	6.8×10^{17}	2.0×10^{17a}	0.13	0.15	0.14
Net strat-trop isotope flux (‰PgCyr ⁻¹)	42.9	32	0.10	0.11	0.11
		54	0.17	0.19	0.18
Θ	$\Theta_{C3} = 0.93$ $\Theta_{C4} = 0.38$	$\Theta_{C3} = \Theta_{C4} = 1.0$	0.13	0.14	0.14
dM/dt (PgCyr ⁻¹)	3.2	2	0.14	0.15	0.14
		4	0.14	0.15	0.14
Soil invasion (PgCyr ⁻¹)	0	4.4	0.13	0.15	0.14
GPP (PgCyr ⁻¹)	100	90	0.15	0.16	0.15
		110	0.13	0.14	0.13
		50	0.21	0.23	0.22
		150	0.10	0.11	0.11

^aHolton [1990].

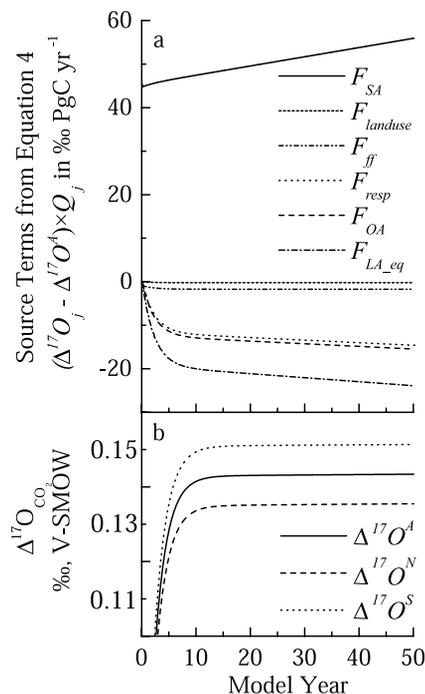


Figure 1. (a) Source terms in (4) vs model year showing the influence of each source on $\Delta^{17}O^A$. (b) Predicted $\Delta^{17}O_{CO_2}$ in the NH, SH, and global troposphere.

[Ciais *et al.*, 1997]. Finally, processes that contribute to $F_{landuse}$ are assumed to produce CO₂ with $\Delta^{17}O = 0$.

3. Results and Discussion

[12] The base scenario was run for 50 yrs. The magnitude of each CO₂ isotope source term in (4), calculated as $(\Delta^{17}O_j - \Delta^{17}O^A) \times Q_j$, is plotted in Figure 1a, showing the dominance of the stratospheric input and terrestrial biospheric exchange in determining $\Delta^{17}O^A$. After a 20-year spin-up, the model yielded a small but measurable global average tropospheric value for $\Delta^{17}O^A = 0.50 \times (\Delta^{17}O^N + \Delta^{17}O^S)$ of 0.14‰ with very small hemispheric differences (Figure 1b and Table 3). The modeled trend and Figure 1a indicate that the increasing isotope flux of $\Delta^{17}O_{CO_2} > 0$ from the stratosphere due to increased CO₂ mixing ratios (F_{SA}) has a larger impact on tropospheric $\Delta^{17}O_{CO_2}$ than the fossil fuel isotope flux with $\Delta^{17}O_{CO_2} < 0$. Also, F_{LA} , F_{resp} , and F_{OA} dilute tropospheric $\Delta^{17}O_{CO_2}$. Thus, any trend in tropospheric $\Delta^{17}O_{CO_2}$ could not be predicted from the Suess effect for ¹³C and ¹⁴C for which the addition of fossil fuel CO₂ acts as a dilution.

[13] Results of sensitivity tests are given in Table 3. The sensitivity of $\Delta^{17}O^A$ to the strat-trop air mass flux and to uncertainty in the net strat-trop isotope flux resulted in changes in $\Delta^{17}O^A$ of $<0.01\%$ and $\sim 0.04\%$, respectively. Assuming complete equilibration of retro-diffused CO₂ for both C₃ and C₄ plants or including a soil invasion flux of 4.4 PgCyr⁻¹ [Stern *et al.*, 2001] both decreased $\Delta^{17}O^A$ by $<0.01\%$. Changing dM/dt from 2 and 4 PgCyr⁻¹ had no significant effect. Finally, varying GPP by $\pm 10\%$ and $\pm 50\%$ yielded changes in $\Delta^{17}O^A$ of $\pm 0.01\%$ and $-0.04/+0.08\%$, respectively. For comparison, interannual variations in GPP

over the past 40 years are predicted to be on the order of $\pm 5\%$ while uncertainty in the absolute magnitude of global GPP is as large as $\pm 50\%$ [Schaefer *et al.*, 2002; K. Schaefer, personal communication, 2004].

[14] Based on these initial modeling results, we conclude the following. First, we predict that tropospheric $\Delta^{17}O_{CO_2}$ is small but measurable by current techniques (with precisions of $\sim 0.1\%$ [e.g., Boering *et al.*, 2004]). Second, we predict that any $\Delta^{17}O_{CO_2}$ trend in the troposphere is dominated by the increasing flux of $\Delta^{17}O_{CO_2}$ from the stratosphere and by the terrestrial biosphere, with a smaller contribution from the oceans, and not by fossil fuel burning. Therefore, the largest changes in a tropospheric time series for $\Delta^{17}O_{CO_2}$ should result from variations in the terrestrial gross fluxes. Third, measurements and modeling of a global average value for tropospheric $\Delta^{17}O_{CO_2}$ can serve as a new constraint for GPP and ecosystem respiration in carbon isotope models by providing an average value for $\Delta^{17}O_{CO_2}$ that should be consistent with $\delta^{18}O_{CO_2}$ yet is independent of $\delta^{18}O_{H_2O}$. Fourth, these model results provide motivation and a benchmark for challenging yet feasible improvements in measurement precision that will allow the full potential of $\Delta^{17}O_{CO_2}$ as an independent tracer of the magnitude and variability of gross carbon exchanges to be realized. Fifth, since tropospheric $\Delta^{17}O_{CO_2}$ is predicted to be small, future work should include small variations in the mass-dependent fractionation factors for isotope exchange with H₂O since a difference between the value for λ used in (1) and a slightly different λ resulting from isotope exchange with water reservoirs [e.g., Angert *et al.*, 2003] could lead to an apparent non-zero $\Delta^{17}O_{CO_2}$. Sixth, these modeling results may aid in the interpretation of the time series of $\Delta^{17}O_{CO_2}$ measurements from La Jolla, CA and the NOAA/CMDL flask network (M. Thieme, personal communication, 2004).

[15] **Acknowledgment.** Support from NSF (ATM-0096504), the David and Lucile Packard Foundation, and a NASA Earth System Science Fellowship (KJH) and suggestions from an anonymous reviewer are gratefully acknowledged.

References

- Angert, A., S. Rachmilevitch, E. Barkan, and B. Luz (2003), Effects of photorespiration, the cytochrome pathway, and the alternative pathway on the triple isotopic composition of atmospheric O₂, *Global Biogeochem. Cycles*, 17(1), 1030, doi:10.1029/2002GB001933.
- Appenzeller, C., *et al.* (1996), Seasonal variation of mass transport across the tropopause, *J. Geophys. Res.*, 101, 15,071–15,078.
- Boering, K. A., T. Jackson, K. J. Hoag, A. S. Cole, M. J. Perri, M. Thieme, and E. Atlas (2004), Observations of the anomalous oxygen isotopic composition of carbon dioxide in the lower stratosphere and the flux of the anomaly to the troposphere, *Geophys. Res. Lett.*, 31, L03109, doi:10.1029/2003GL018451.
- Ciais, P., *et al.* (1997), A three-dimensional synthesis study of $\delta^{18}O$ in atmospheric CO₂: 1. Surface fluxes, *J. Geophys. Res.*, 102, 5857–5872.
- Cramer, W., *et al.* (1999), Comparing global models of terrestrial NPP, *Global Change Biol.*, 5, suppl. 1, 1–15.
- Cox, P. M., *et al.* (2000), Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model, *Nature*, 408, 184–187.
- Cuntz, M., P. Ciais, G. Hoffmann, and W. Knorr (2003a), A comprehensive global three-dimensional model of $\delta^{18}O$ in atmospheric CO₂: 1. Validation of surface processes, *J. Geophys. Res.*, 108(D17), 4527, doi:10.1029/2002JD003153.
- Cuntz, M., P. Ciais, G. Hoffmann, C. E. Allison, R. J. Francey, W. Knorr, P. P. Tans, J. W. C. White, and I. Levin (2003b), A comprehensive global three-dimensional model of $\delta^{18}O$ in atmospheric CO₂: 2. Mapping the atmospheric signal, *J. Geophys. Res.*, 108(D17), 4528, doi:10.1029/2002JD003154.

- Farquhar, G., and J. Lloyd (1993), Isotope effects in the exchange of CO₂ between terrestrial plants and the atmosphere, *Stable Isotopes and Plant Carbon-Water Relations*, edited by J. R. Ehleringer et al., pp. 47–70, Elsevier, New York.
- Farquhar, G., et al. (1993), Vegetation effects on the isotope composition of oxygen in atmospheric CO₂, *Nature*, *363*, 439–443.
- Francey, R., and P. Tans (1987), Latitudinal variation in ¹⁸O of atmospheric CO₂, *Nature*, *327*, 495–497.
- Francey, R. J., et al. (1995), Changes in oceanic and terrestrial carbon uptake since 1982, *Nature*, *373*, 326–330.
- Friedlingstein, P., et al. (2003), How positive is the feedback between climate change and the carbon cycle?, *Tellus, Ser. B*, *55*, 692–700.
- Gillon, J., and D. Yakir (2000), Naturally low carbonic anhydrase activity in C₄ and C₃ plants limits discrimination against ¹⁸O-CO₂ during photosynthesis, *Plant Cell Environ.*, *23*, 903–915.
- Goulden, M. L., et al. (1998), Sensitivity of boreal forest carbon balance to soil thaw, *Science*, *279*, 214–217.
- Gurney, K. R., et al. (2002), Towards robust regional estimates of CO₂ sources and sinks using atmospheric transport models, *Nature*, *415*, 626–630.
- Gurney, K. R., et al. (2003), TransCom 3 CO₂ inversion intercomparison: 1, *Tellus, Ser. B*, *55*, 555–579.
- Holton, J. R. (1990), On the global exchange of mass between the stratosphere and the troposphere, *J. Atmos. Sci.*, *47*, 392–395.
- Jacob, D. J., et al. (1987), Atmospheric distribution of ⁸⁵Kr simulated with a general circulation model, *J. Geophys. Res.*, *92*, 6614–6626.
- Lämmerzahl, P., T. Röckmann, C. A. M. Brenninkmeijer, D. Krankowsky, and K. Mauersberger (2002), Oxygen isotope composition of stratospheric carbon dioxide, *Geophys. Res. Lett.*, *29*(12), 1582, doi:10.1029/2001GL014343.
- Luz, B., et al. (1999), Triple-isotope composition of atmospheric O₂ as a tracer of biosphere productivity, *Nature*, *400*, 547–550.
- Marland, G., et al. (2003), *Trends: A Compendium of Data on Global Change*, CO₂ Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn.
- Mauersberger, K., et al. (1999), O₃ isotope enrichment: Isotopomer-specific rate coefficients, *Science*, *283*, 370–372.
- Miller, J. B., et al. (1999), Measurement of ¹⁸O/¹⁶O in the soil-atmosphere CO₂ flux, *Global Biogeochem. Cycles*, *13*, 761–774.
- Pearcy, R., and J. Ehleringer (1984), Comparative ecophysiology of C₃ and C₄ plants, *Plant Cell Environ.*, *7*, 1–13.
- Randerson, J., et al. (1997), The contribution of terrestrial sources and sinks to trends in the seasonal cycle of atmospheric CO₂, *Global Biogeochem. Cycles*, *11*, 535–560.
- Riley, W. J., et al. (2003), ¹⁸O composition of CO₂ and H₂O ecosystem pools and fluxes: Simulations and comparisons to measurements, *Global Change Biol.*, *9*, 1567–1581.
- Schaefer, K., A. S. Denning, N. Suits, J. Kaduk, I. Baker, S. Los, and L. Prihodko (2002), Effect of climate on interannual variability of terrestrial CO₂ fluxes, *Global Biogeochem. Cycles*, *16*(4), 1102, doi:10.1029/2002GB001928.
- Schimel, D. S., et al. (2001), Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems, *Nature*, *414*, 169–172.
- Stern, L., et al. (2001), Influence of soils on oxygen isotope ratio of atmospheric CO₂, *Global Biogeochem. Cycles*, *15*, 753–759.
- Still, C. J., J. A. Berry, G. J. Collatz, and R. S. DeFries (2003), Global distribution of C₃ and C₄ vegetation: Carbon cycle implications, *Global Biogeochem. Cycles*, *17*(1), 1006, doi:10.1029/2001GB001807.
- Thiemens, M. (1999), Mass-independent isotope effects in planetary atmospheres and the early solar system, *Science*, *283*, 341–345.
- Yung, Y., et al. (1997), CO₂ in the atmosphere: Isotopic exchange with O₃ and its use as a tracer in the middle atmosphere, *J. Geophys. Res.*, *102*, 10,857–10,866.

K. A. Boering, I. Y. Fung, and K. J. Hoag, Department of Earth and Planetary Science and Department of Chemistry, University of California, Latimer Hall, Berkeley, CA 94720-1460, USA. (khoag@uclink.berkeley.edu)

C. J. Still, Department of Geography, University of California, 3611 Ellison Hall, Santa Barbara, CA 93106-4060, USA.