

Observations of the anomalous oxygen isotopic composition of carbon dioxide in the lower stratosphere and the flux of the anomaly to the troposphere

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Received 18 August 2003; revised 14 November 2003; accepted 30 December 2003; published 12 February 2004.

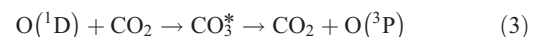
[1] Measurements of the triple oxygen isotopic composition of stratospheric CO₂ in whole air samples from the NASA ER-2 aircraft show anomalous enrichments in ¹⁷O and ¹⁸O. The compact correlation of the isotope anomaly (defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.516 \times \delta^{18}\text{O}$) with simultaneous N₂O measurements demonstrates that $\Delta^{17}\text{O}_{\text{CO}_2}$ is a long-lived tracer with a stratospheric source. These characteristics, and an isotopic link to O₃ production, make $\Delta^{17}\text{O}_{\text{CO}_2}$ potentially useful as a tracer of integrated stratospheric chemistry and transport. The $\Delta^{17}\text{O}_{\text{CO}_2}$:N₂O correlation is also used to estimate a net $\Delta^{17}\text{O}_{\text{CO}_2}$ flux to the troposphere of $3.6 \pm 0.9 \times 10^{15}\%$ mol CO₂ yr⁻¹. This flux is required to predict and understand the CO₂ and O₂ isotope anomalies in the troposphere and their use as tracers of gross carbon exchanges between the atmosphere and biosphere on interannual to glacial-interglacial time scales. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions. **Citation:** Boering, K. A., T. Jackson, K. J. Hoag, A. S. Cole, M. J. Perri, M. Thiemens, 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.

1. Introduction

[2] Oxygen has 3 stable isotopes, ¹⁶O, ¹⁷O, and ¹⁸O. Most kinetic and equilibrium isotope effects alter ¹⁷O/¹⁶O ratios by half the degree to which the ¹⁸O/¹⁶O ratios change [e.g., Thiemens, 1999]. However, anomalous or “mass-independent” isotope effects, which result in ¹⁷O isotopic compositions that are not related to the ¹⁸O isotopic composition by a factor of ~0.5, are evident in many atmospheric species, including O₃ [e.g., Lammerzahl *et al.*, 2002] and stratospheric CO₂ [Thiemens *et al.*, 1991;

Thiemens *et al.*, 1995a, 1995b; Alexander *et al.*, 2001; Lammerzahl *et al.*, 2002]. The CO₂ isotope anomaly is of interest for its potential as a tracer of stratospheric processes [e.g., Yung *et al.*, 1997; Alexander *et al.*, 2001; Lammerzahl *et al.*, 2002] and of gross carbon exchanges between the atmosphere and biosphere and their sensitivity to climate change on annual [Hoag *et al.*, 2002] to millennial [Luz *et al.*, 1999; Blunier *et al.*, 2002] time scales.

[3] The CO₂ isotope anomaly originates in whole or in part from transfer from O₃ via Equations (1)–(3) [e.g., Yung *et al.*, 1991].



Unusual isotope effects in Equation (1) result in large, anomalous enrichments in ¹⁷O and ¹⁸O in O₃. While the underlying theory is still under investigation [e.g., Gao and Marcus, 2001; Babikov *et al.*, 2003], the isotope effects themselves are now well-quantified by laboratory measurements [e.g., Mauersberger *et al.*, 1999]. O(¹D) from (2) can exchange isotopes with CO₂ in (3). Whether an additional anomalous isotope effect occurs in (3) remains controversial [e.g., Wen and Thiemens, 1993; Yung *et al.*, 1997; Barth and Zahn, 1997]. For full application of the CO₂ isotope anomaly as a tracer of stratospheric and biogeochemical processes, additional information on the source and production rate of the anomaly is required.

[4] In this study, we report 29 measurements of the anomalous isotopic composition of stratospheric CO₂ from whole air samples collected by the NASA ER-2 aircraft. These measurements complement the existing 52 published measurements on samples collected from a C-141 aircraft [Thiemens *et al.*, 1995a], balloons [Thiemens *et al.*, 1991; Alexander *et al.*, 2001; Lammerzahl *et al.*, 2002] and rockets [Thiemens *et al.*, 1995b]. The correlation of the CO₂ isotope anomaly with N₂O mixing ratios provides new insight into the source of the anomaly, its distribution in the stratosphere, and its potential as a tracer of integrated stratospheric chemistry and transport. It also allows the flux of the anomaly to the troposphere to be estimated from the global N₂O loss rate. An

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Table 1. ER-2 Measurements

Flight Date	Altitude (km) ^a	Latitude ^b	Potential Temp (K)	N ₂ O (ppb) ^c	δ ¹⁷ O _{CO₂} ‰	δ ¹⁸ O _{CO₂} ‰	Δ ¹⁷ O _{CO₂} ‰
970426	19.1	72.2	502	154	25.13	41.52	3.71
	19.2	75.6	503	187	23.70	40.27	2.92
	19.2	79.0	506	249	22.28	40.15	1.56
	19.2	82.5	505	205	22.93	39.78	2.40
	19.2	86.1	502	128	24.31	39.14	4.11
	19.1	88.7	501	97	26.19	40.76	5.16
	15.6	89.0	421	217	23.46	40.74	2.44
	17.7	87.4	463	141	26.28	42.71	4.24
	19.6	84.5	513	131	25.31	40.41	4.45
	16.8	78.2	461	263	22.28	40.63	1.32
970506	19.4	74.2	513	198	23.92	41.03	2.75
	19.4	64.5	505	218	23.71	41.40	2.35
970509	13.7	62.9	388	292	20.58	38.57	0.68
970511	11.3	64.3	357	303	21.11	39.78	0.58
	18.6	75.5	488	195	22.86	39.05	2.71
970626	16.4	75.9	441	237	21.74	38.54	1.86
	18.9	73.7	493	170	23.78	39.51	3.40
	18.4	57.4	472	223	23.15	40.84	2.08
	19.7	54.5	500	220	23.05	40.38	2.21
970629	20.5	48.4	505	239	23.06	41.03	1.89
	20.8	60.4	527	104	28.20	43.75	5.63
	14.5	63.7	394	296	19.24	36.43	0.44
970630	18.6	66.5	480	260	22.31	40.67	1.32
	20.6	64.1	524	82	28.61	43.57	6.13
	19.3	78.6	506	211	23.66	41.16	2.43
970707	19.4	81.6	504	205	23.37	40.34	2.55
	19.2	89.6	497	195	24.62	41.83	3.04
	15.8	64.0	421	274	21.83	40.38	1.00
970710	20.0	65.9	514	210	22.93	40.05	2.26

^aAverage range: 0.08 ± 0.08 km (max = 0.27, typical <0.05).

^bRange: 0.01 to 0.44°.

^cAverage range: 3.7 ± 3.9 ppbv.

accurate flux is required for using CO₂ and O₂ isotope anomalies as new constraints on gross carbon exchanges.

2. Measurement Description

[5] Whole air samples were collected during the POLARIS campaign [Newman *et al.*, 1999] by an automated sampler with 29 electropolished 1.6-liter stainless steel canisters and a 4-stage metal bellows pump [Flocke *et al.*, 1999]. The pump pressurized the canisters to 40 psia, resulting in collection times of 15–180 s at altitudes of 9–21 km, respectively, and a ~4.5 ℓ STP sample volume. After trace gas mixing ratios were measured by GC/MS, 2 to 4 ℓ of sample remained, half of which was transferred to a glass flask for isotopic analyses of N₂O, CH₄, H₂, and N₂. CO₂ was cryogenically separated from the other half and immediately analyzed or stored in a glass ampoule.

[6] Due to isobaric interference between ¹⁷O¹²C¹⁶O and ¹⁶O¹³C¹⁶O, the purified CO₂ samples were converted to O₂ by reaction with BrF₅ at 800°C for 45 hours [Thiemens *et al.*, 1991] prior to analysis on a Finnigan MAT 251 dual inlet isotope ratio mass spectrometer at UCSD in 1997–8. The isotope compositions are reported as δ¹⁷O and δ¹⁸O on the V-SMOW scale where δ^xO = 1000([(^xO/¹⁶O)_{sample}/^x(^xO/¹⁶O)_{VSMOW} – 1). Measurement precision for the isotope anomaly (defined in Equation (4) below) is estimated to be ±0.1‰. Measurements of δ¹⁵N of N₂ at Princeton (M. Bender, personal communication) yield an upper limit of 0.1‰ for fractionation of δ¹⁸O_{CO₂} due to sample collection and handling. Tests of standards

in the canisters suggest that δ¹⁸O is altered by <0.1‰ after short- or long-term storage in dry canisters under laboratory conditions. Measurements of δ¹³C are not available for these samples since CO₂ was converted to O₂ prior to isotopic analysis.

[7] Mixing ratios of N₂O and O₃ were measured in situ by the Airborne Tunable Diode Laser Spectrometer [Podolske and Loewenstein, 1993] and the O₃ UV spectrophotometer [Proffitt and McLaughlin, 1983]. The in situ N₂O and O₃ data are averaged over the WAS collection period weighted by the canister fill rate.

3. Results and Discussion

[8] Measurements of δ¹⁷O and δ¹⁸O of CO₂ from the ER-2 (Table 1) are plotted in Figure 1 with previous measurements. Clearly, CO₂ is anomalously fractionated since the δ¹⁷O:δ¹⁸O slope is significantly larger than slopes of 0.50 to 0.529 for mass-dependent fractionation [e.g., Thiemens, 1999]. Assuming errors of 0.5‰ for both δ¹⁷O and δ¹⁸O, a weighted least squares regression [Williamson, 1968] of the ER-2 data yields a slope of 1.47 ± 0.28 (2σ), or 1.64 ± 0.38 excluding the lowest δ¹⁸O datum. For comparison, the same regression and assumed errors yield slopes of 1.21 ± 0.16 for the Thiemens *et al.* [1995b] rocket data, 1.72 ± 0.22 for the Lammerzahl *et al.* [2002] balloon data, 2.06 ± 1.16 for the Alexander *et al.* [2001] balloon data, and 1.37 ± 0.12 for the combined rocket data from Thiemens *et al.* [1995b] and Zipf and Erdman [1994]. Scatter in the ER-2 data is discussed below.

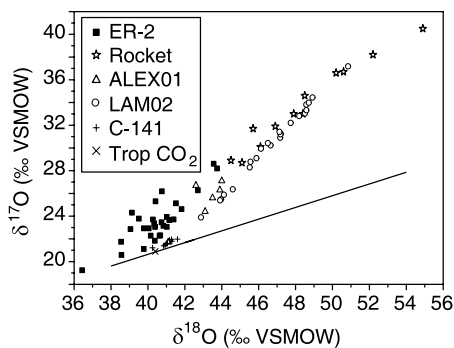


Figure 1. $\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ of CO₂ from the ER-2, rocket [Thiemens *et al.*, 1995b], balloon [Alexander *et al.*, 2001; Lammerzahl *et al.*, 2002], and C-141 [Thiemens *et al.*, 1995a]. Tropospheric CO₂ [Thiemens *et al.*, 1991] and the mass-dependent fractionation line with slope = 0.516 are also shown.

[9] To examine the distribution of the CO₂ isotope anomaly in the stratosphere, we define its magnitude as

$$\Delta^{17}\text{O}_{\text{CO}_2} = \delta^{17}\text{O} - 0.516 \times \delta^{18}\text{O} \quad (4)$$

where 0.516 was selected empirically to best represent $\Delta^{17}\text{O}_{\text{CO}_2}$ in air entering the stratosphere ($\sim 0.1\text{‰}$ for N₂O ~ 315 ppbv). In Figure 2, $\Delta^{17}\text{O}_{\text{CO}_2}$ is plotted against altitude. $\Delta^{17}\text{O}_{\text{CO}_2}$ generally increases with altitude but is highly variable, ranging from 1.9 to 9‰ at 20 km. Such variability is typical of long-lived tracers measured with high spatial resolution in the extratropics, a result of transport of air filaments between different regions, reversible air displacements, and the stratospheric circulation bringing older air down from higher altitudes [e.g., Boering *et al.*, 1996]. If the local chemical time scales controlling $\Delta^{17}\text{O}_{\text{CO}_2}$ are long compared to transport times, such variability can be removed by plotting $\Delta^{17}\text{O}$ against another long-lived tracer [Plumb and Ko, 1992] such as N₂O, which is slowly photolyzed and photo-oxidized by O(¹D) with time and altitude. Figure 3 shows $\Delta^{17}\text{O}_{\text{CO}_2}$ versus N₂O from the ER-2 and Thiemens *et al.* [1995b] rocket samples, the only datasets for which N₂O is available. N₂O and $\Delta^{17}\text{O}_{\text{CO}_2}$ from the ER-2 are tightly correlated, with a nearly linear increase in $\Delta^{17}\text{O}_{\text{CO}_2}$ as N₂O decreases. Interestingly, the ER-2 and rocket observations overlap despite gaps of 9 km

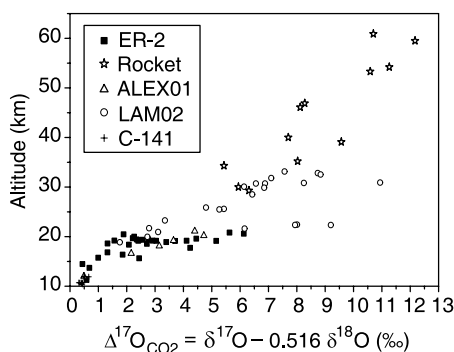


Figure 2. $\Delta^{17}\text{O}_{\text{CO}_2}$ for data in Figure 1 vs altitude.

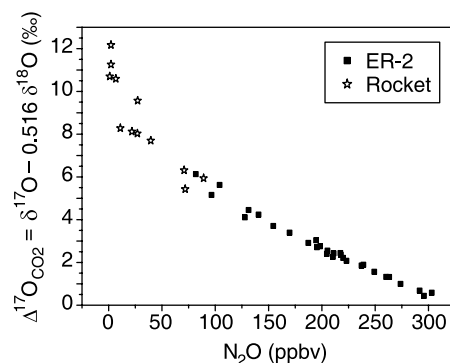


Figure 3. $\Delta^{17}\text{O}_{\text{CO}_2}$ vs N₂O mixing ratio from the ER-2 and rocket [Thiemens *et al.*, 1995b].

and 7 years in sample collection. In contrast, Figure 4 demonstrates that $\Delta^{17}\text{O}_{\text{CO}_2}$ does not correlate with O₃, a tracer with a 1–3 month lifetime at 20 km.

[10] The $\Delta^{17}\text{O}_{\text{CO}_2}$:N₂O correlation provides new insight into the production rate and variation of $\Delta^{17}\text{O}_{\text{CO}_2}$ in the stratosphere. First, the tight correlation for N₂O > 80 ppb demonstrates that $\Delta^{17}\text{O}_{\text{CO}_2}$ is a long-lived tracer. Thus, while it has been suggested [Thiemens *et al.*, 1995b; Thiemens, 1999] that the negative $\Delta^{17}\text{O}_{\text{CO}_2}$:N₂O correlation results from a common connection with O(¹D), the correlation would result from transport even in the absence of this commonality. This conclusion is further supported by the tight correlation of $\Delta^{17}\text{O}_{\text{CO}_2}$ with mean ages derived from ER-2 CO₂ mixing ratios [not shown; see Andrews *et al.*, 2001], which are not influenced by O(¹D), and by the larger scatter in the correlation in the upper stratosphere and mesosphere (i.e., for N₂O < 50 ppb), where the N₂O lifetime is comparable to the transport time scales.

[11] Second, the $\Delta^{17}\text{O}_{\text{CO}_2}$:N₂O correlation is consistent with Yung's chemical mechanism (1)–(3) coupled with stratospheric transport. Production of $\Delta^{17}\text{O}_{\text{CO}_2}$ is probably most rapid in the upper tropical stratosphere where production rates of O₃ and O(¹D) are highest. When air descends via the stratospheric circulation, the large upper stratospheric signal in $\Delta^{17}\text{O}_{\text{CO}_2}$ is long-lived even far from the main source region. Thus, large values of $\Delta^{17}\text{O}_{\text{CO}_2}$ in the lower stratosphere result from the stratospheric circulation and not from “particle precipitation” (cosmic ray) events in the polar regions which could generate large amounts of O(¹D)

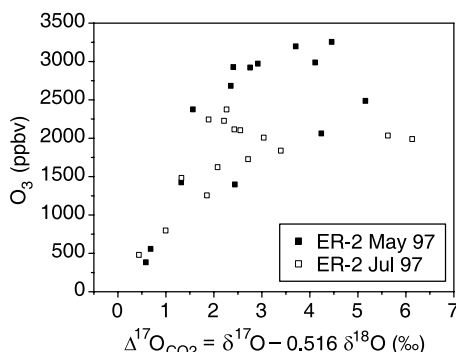


Figure 4. O₃ mixing ratios vs $\Delta^{17}\text{O}_{\text{CO}_2}$ from the ER-2.

in the lower stratosphere, an alternative hypothesis of *Lammerzahl et al.* [2002] to explain the large $\Delta^{17}\text{O}_{\text{CO}_2}$ values they observed near 22 km.

[12] Third, the negative $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ correlation demonstrates that $\Delta^{17}\text{O}_{\text{CO}_2}$ has a stratospheric source but weak, if any, sink. The primary sink for $\Delta^{17}\text{O}_{\text{CO}_2}$ (and (1)–(3) in general) should be mass-dependent isotope exchange with liquid water in plant leaves, soils, and the ocean [e.g., *Farquhar et al.*, 1993, based on $\delta^{18}\text{O}$]. While *Yung et al.* [1991] and *Alexander et al.* [2001] have suggested that $\Delta^{17}\text{O}_{\text{CO}_2}$ could be a tracer of O(¹D) abundances and of transport in regions where tracers like N₂O and CH₄ are losing their dynamic range, the applications of a tracer with a stratospheric source but weak to no sink may be even broader ranging. For example, when the molecular-level details of the isotope chemistry producing $\Delta^{17}\text{O}_{\text{CO}_2}$ are known, a tracer with such a stratospheric source may serve as a new diagnostic for transport errors in 2D and 3D models and in predicting the build-up of pollutants from stratospheric aircraft [e.g., *Hall et al.*, 1999]. Furthermore, if $\Delta^{17}\text{O}_{\text{CO}_2}$ arises solely from transfer from O₃ (i.e., no anomalous isotope effect in (3)), then $\Delta^{17}\text{O}_{\text{CO}_2}$ is a tracer with production and transport terms that are proportional to those of odd oxygen but with no free radical loss term. Thus, $\Delta^{17}\text{O}_{\text{CO}_2}$ could be used to account for integrated O₃ production and transport while leaving integrated O₃ chemical loss as the free parameter to compare with model results and instantaneous loss rates from free radical measurements. In the meantime, simply the unusual curvilinear $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ correlation may provide additional constraints on transport and mixing in the stratosphere to mesosphere that are complementary to those from other tracer:tracer combinations.

[13] Fourth, the $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ correlation can be used to quantify the flux of $\Delta^{17}\text{O}_{\text{CO}_2}$ to the troposphere. The slope of two long-lived tracers is equal to the ratio of their net vertical fluxes [*Plumb and Ko*, 1992]. For N₂O, the net vertical flux is the global N₂O loss rate, or 13 TgNyr⁻¹ ± 25% [*Prather and Ehhalt*, 2001]. Fluxes to the troposphere have been estimated in this manner for NO_y and O₃ [*Murphy and Fahey*, 1994; *McLinden et al.*, 2000] and, using a small, unpublished subset of the ER-2 data reported here, for $\Delta^{17}\text{O}_{\text{CO}_2}$ [*Luz et al.*, 1999]. Here, we apply the *Plumb and Ko* relationship to the ER-2 data for N₂O > 195 ppb, restricting N₂O for several reasons. First, mixing in the vortex, confirmed by CH₄ and N₂O isotope measurements from POLARIS [*McCarthy et al.*, 2003; *Park et al.*, 2003], results in a slightly larger variability in the $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ correlation for N₂O between 80 and 150 ppbv. Second, higher N₂O values are most relevant for air returning to the troposphere [*Olsen et al.*, 2001]. The resulting net isotope flux of $\Delta^{17}\text{O}_{\text{CO}_2}$ is 3.6 ± 0.9‰ PmolCO₂ yr⁻¹. The net flux is independent of the mass flux of air and in general is the quantity needed for biogeochemistry applications. A stratosphere-to-troposphere flux can be derived using air mass flux calculations from, e.g., *Holton* [1990] or *Appenzeller et al.* [1996], yielding fluxes for $\Delta^{17}\text{O}_{\text{CO}_2}$ of 3.9 and 4.4‰ Pmol CO₂ yr⁻¹, respectively. Overall, the largest uncertainty for both the downward and net $\Delta^{17}\text{O}_{\text{CO}_2}$ fluxes is the N₂O loss rate. Uncertainty in the $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ fit is 3%, and the slope is expected to be robust with respect to both season and latitude

based on the ER-2 CH₄ and N₂O isotope analyses noted above. Thus, these fluxes should be accurate to 25% as well as precise. Finally we note that, using the ER-2 data reported here, estimates of the stratospheric contribution to the current O₂ isotope anomaly in *LUZ99* do not change.

[14] Several significant uncertainties remain. While the slope and 2σ uncertainty of the ER-2 $\delta^{17}\text{O}:\delta^{18}\text{O}$ relationship is within the estimated 2σ uncertainties of slopes from the other datasets, there is significantly more scatter in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ than in *Lammerzahl et al.* [2002] and *Thiemens et al.* [1995b]. The scatter could perhaps be explained by mixing in the lower stratosphere or a seasonal variation in tropospheric CO₂ isotope compositions [*Trolier et al.*, 1996] entering the stratosphere. However, seasonal variations should damp out for N₂O < ~275 ppbv [e.g., *Andrews et al.*, 2001] and the scatter does not, and mixing alone cannot explain how $\delta^{18}\text{O}$ lighter than tropospheric CO₂ could result. The tight $\Delta^{17}\text{O}_{\text{CO}_2}:\text{N}_2\text{O}$ correlation suggests that the $\delta^{17}\text{O}:\delta^{18}\text{O}$ scatter is mass-dependent. Measurements of $\delta^{15}\text{N}$ of N₂ indicate this mass-dependent fractionation cannot be due to sample handling. One explanation for the scatter, if not real atmospheric variability, is fractionation in the BrF₅ CO₂-O₂ conversion (e.g., see Figure 2j of *Brenninkmeijer et al.* [1995]: $\delta^{18}\text{O}_{\text{CO}_2}$ varied by 0.3‰ in a set of samples before BrF₅ conversion to O₂ and by 1.4‰ after), although laboratory controls suggest this is not a problem. Another explanation is isotopic exchange with water on the surface of ER-2 canisters. During cryogenic separation, excess residual water was found in several samples; excluding these samples reduces but does not eliminate the scatter in Figure 1. It also cannot be ruled out that exchange with collected stratospheric H₂O can occur; we calculate that 360 ppmv of CO₂ exchanging with 6 ppmv of highly isotopically-depleted H₂O in the lower stratosphere [*Johnson et al.*, 2001] could alter $\delta^{18}\text{O}$ by 2‰ while changing $\Delta^{17}\text{O}_{\text{CO}_2}$ by only 0.1‰. Future analyses using different CO₂-O₂ conversion techniques and on samples which were rapidly removed from dry canisters should help to address this uncertainty. Finally, questions remain as to whether there is an additional anomalous isotope effect in (3) and what molecular details determine the magnitude of $\Delta^{17}\text{O}_{\text{CO}_2}$. Further stratospheric observations, combined with continuing laboratory experiments and modeling, should help to resolve these remaining questions and provide an understanding sufficient to use $\Delta^{17}\text{O}_{\text{CO}_2}$ as a tracer of stratospheric processes and as the basis for new proxies of gross carbon exchanges between the atmosphere and biosphere.

[15] **Acknowledgments.** We thank S. Schauffler and R. Lueb for WAS support, M. Bender for $\delta^{15}\text{N}_{\text{N}_2}$ data and advice, K. Mauersberger and D. Krankowsky for advice, M. Loewenstein for N₂O, J. Margitan for O₃. We gratefully acknowledge support to UCB from NASA(NAG21483), NSF(ATM0096504), and the Packard Foundation, to UCSD from NSF(ATM0111714), to NCAR from NASA and NSF. NCAR is operated by the University Corporation for Atmospheric Research under NSF sponsorship.

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