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$^{18}O^{13}C^{16}O$ in Earth's atmosphere

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Abstract—The chemistry and budgets of atmospheric gases are constrained by their bulk stable isotope compositions (e.g., $\delta^{13}C$ values), which are based on mixing ratios of isotopologues containing one rare isotope (e.g., $^{16}O^{13}C^{16}O$). Atmospheric gases also have isotopologues containing two or more rare isotopes (e.g., $^{18}O^{13}C^{16}O$). These species have unique physical and chemical properties and could help constrain origins of atmospheric gases and expand the scope of stable isotope geochemistry generally. We present the first measurements of the abundance of $^{18}O^{13}C^{16}O$ from natural and synthetic sources, discuss the factors influencing its natural distribution and, as an example of its applied use, demonstrate how its abundance constrains the sources of CO_2 in the Los Angeles basin. The concentration of $^{18}O^{13}C^{16}O$ in air can be explained as a combination of ca. 1‰ enrichment (relative to the abundance expected if C and O isotopes are randomly distributed among all possible isotopologues) due to enhanced thermodynamic stability of this isotopologue during isotopic exchange with leaf and surface waters, ca. 0.1‰ depletion due to diffusion through leaf stomata, and subtle (ca. 0.05‰) dilution by $^{18}O^{13}C^{16}O$-poor anthropogenic CO_2. Some air samples are slightly (ca. 0.05‰) lower in $^{18}O^{13}C^{16}O$ than can be explained by these factors alone. Our results suggest that $^{18}O^{13}C^{16}O$ abundances should vary by up to ca. 0.2‰ with latitude and season, and might have measurable sensitivities to stomatal conductances of land plants. We suggest the greatest use of Δ_{47} measurements will be to "leverage" interpretation of the $\delta^{18}O$ of atmospheric CO_2. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

The budget and chemistry of atmospheric CO_2 are constrained by its concentration, $\delta^{13}C$, $\delta^{18}O$, and $\delta^{17}O$ values, the O_2/N_2 ratio of air, and various indirect arguments based on biomass inventories and ocean models (Francey and Tans, 1987; Keeling et al., 1993; Ciais et al., 1995; Ciais and Meijer, 1998; Gruber and Keeling, 2001; Kaplan et al., 2002; Riley et al., 2002; Ito, 2003; Scholze et al., 2003). However, the most significant sources and sinks of CO_2 (photosynthesis, respiration, anthropogenic emissions, dissolution in and exsolution from the oceans) vary in flux and isotope signature (Kaplan et al., 2002; Riley et al., 2002), such that the atmospheric budget cannot be rigorously defined by inversion of isotopic and concentration records alone. Therefore, additional constraints would help in determining the overall atmospheric budget and in understanding the mechanisms of CO_2 production and consumption in model systems.

In principle, the stable isotopic composition of atmospheric CO_2 could provide a large number of independent constraints on its global budget because there are twelve stable isotopologues (Table 1), each of which has unique thermodynamic and kinetic properties that could cause them to be fractionated from one another during natural processes (Gibbs, 1928; Bigeleisen and Mayer, 1947; Urey, 1947). However, eight of these (all but $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{18}O^{12}C^{16}O$, and $^{17}O^{12}C^{16}O$) have not been previously analyzed in the atmosphere, principally because of their low concentrations in air (mole fractions of ca. 1.7×10^{-8} to 6×10^{-13}). All of these unmeasured species contain two or more rare isotopes; hereafter, we refer to them as multiply substituted isotopologues.

This study reports measurements of $^{18}O^{13}C^{16}O$ in natural and synthetic sources, and discusses their significance for studies of the atmospheric budget of CO_2. One previous study reports data for $^{12}CD_4$ and/or $^{13}CD_3H$ concentrations in air (suggesting $\geq$500-fold enrichments relative to those expected for a random distribution of stable C and H isotopes among all methane isotopologues; Mroz et al., 1989), and two previous studies have attempted to predict atmospheric abundances of multiply substituted methane (Kaye and Jackman, 1990) and N_2O (Kaiser et al., 2003). However, to the best of our knowledge, this is the first report of precise (sub-per mil level) measurements of abundances of multiply substituted species in nature. Therefore, we devote much of this paper to documenting and discussing unusual features of the geochemistry of multiply substituted molecules.

2. METHODS

We measured the stable isotope composition of CO_2, including mass 47, using a Finnigan MAT 253 gas source stable isotope ratio mass spectrometer configured to measure ion beams corresponding to M/z = 44 through 49, inclusive. This instrument registers the ion beam for mass 47 through a 10^{12} Ohm resistor, such that the ~pA ion beams generated from typical sample sizes (10's of μmoles) generate signals on the order of volts. See the Appendix for further instrumental details. This instrument routinely measures ratios of mass 47 to mass 44 (hereafter referred to as R^{47}) in natural CO_2 with internal precision of ca. 0.06 to 0.1‰, 1σ, (based on multiple sample-standard comparisons within a single analysis) and external precision of ca. 0.02 to 0.04‰, 1σ, (defined by repeat analyses of a single sample, where each analysis is the average of multiple sample-standard comparisons). These reproducibilities depend predictably on analytical protocol (i.e., length of integration per sample-standard comparison, number of comparisons per analysis), and therefore, generally can be kept near their lower limits.

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Table 1. Natural abundances of CO_2 isotopologues#.

Mass*	Isotopologue	Abundance fraction of CO_2	Volume fraction of atmosphere
44	$^{16}O-^{12}C-^{16}O$	98.4%	370 ppm
45	$^{16}O-^{13}C-^{16}O$	1.1%	4.1 ppm
	$^{17}O-^{12}C-^{16}O$	760 ppm	290 ppb
46	$^{18}O-^{12}C-^{16}O$	0.41%	1.5 ppm
	$^{17}O-^{13}C-^{16}O$	8.5 ppm	3.2 ppb
	$^{17}O-^{12}C-^{17}O$	150 ppb	56 ppt
47	$^{18}O-^{13}C-^{16}O$	46 ppm	17 ppb
	$^{18}O-^{12}C-^{17}O$	1.6 ppm	600 ppt
	$^{17}O-^{13}C-^{17}O$	1.6 ppb	0.62 ppt
48	$^{18}O-^{12}C-^{18}O$	4.3 ppm	1.6 ppb
	$^{17}O-^{13}C-^{18}O$	18 ppb	6.3 ppt
49	$^{18}O-^{13}C-^{18}O$	48 ppb	18 ppt

Based on stochastic distribution and average $\delta^{13}C$ and $\delta^{18}O$ of CO_2.

* Nominal cardinal mass in AMU.

In reporting data for abundances of mass-47 CO_2, we define the variable Δ_{47} as the difference in per mil between the measured value of R^{47} and the value of R^{47} expected in that sample if its stable C and O isotopes are randomly distributed among all isotopologues—a case we refer to as the stochastic distribution. Values of R^{47} expected for the stochastic distribution can be calculated based on bulk stable isotope composition (known by conventional measurements of $\delta^{18}O_{VSMOW}$ and $\delta^{13}C_{PDB}$) and principles from elementary sampling theory. R^{47} values for the stochastic distribution can be described by:

$$\frac{2\cdot[18]\cdot[16]\cdot[13]+[17]^2\cdot[13]+2\cdot[18]\cdot[17]\cdot[12]}{[16]^2\cdot[12]} \tag{1}$$

where [16], [17], and [18] are the concentrations of ^{16}O, ^{17}O, and ^{18}O in the pool of all oxygen atoms, and [12] and [13] are the concentrations of ^{12}C and ^{13}C in the pool of all carbon atoms contributing to a given population of CO_2 molecules. Note that 97% of the mass-47 isotopologues in atmospheric CO_2 are $^{18}O^{13}C^{16}O$ (Table 1), and thus variations in its abundance dominate R^{47} variations.

Values of Δ_{47} for unknown samples are determined by (1) measuring their $\delta^{13}C$, $\delta^{18}O$, and R^{47} values by comparison with an intralaboratory standard that has a known bulk isotopic composition and that has been heated at 1000°C to produce the stochastic distribution (so that its R^{47} value can be accurately calculated only knowing its $\delta^{18}O$ and $\delta^{13}C$ values), see Appendix for details; (2) calculation of the R^{47} value *expected* for the sample if it had the stochastic distribution, based on its measured $\delta^{18}O$ and $\delta^{13}C$ values; and (3) calculation of Δ_{47} values using the formula:

$$\Delta_{47} = (R^{47}_{measured}/R^{47}_{stochastic} - 1)\cdot 1000 \tag{2}$$

Note that $\delta^{18}O$ and $\delta^{13}C$ values are calculated from measurements of R^{45} and R^{46} by assuming the stochastic distribution (Allison et al., 1995; Gonfiantini et al., 1995). Therefore, the scheme outlined above involves an internal inconsistency or circularity that might require an iterative calculation to circumvent. However, mass-47 isotopologues make up only ca.40 ppm of natural CO_2 (Table 1), and $\delta^{18}O_{VSMOW}$ or $\delta^{13}C_{PDB}$ values are effectively independent of Δ_{47} when it is within a few per mil of 0 (as is the case for all measurements reported here).

External precision of Δ_{47} values generally averages 0.007 to 0.015‰, 1σ, unless contaminants are present (see Appendix). We infer that Δ_{47} values are more reproducible than R^{47} values because analytical errors in R^{45}, R^{46}, and R^{47} (all of which figure, directly or indirectly in calculation of Δ_{47}) are correlated with one another. In this respect, measurements of Δ_{47} are analogous to measurements of $\Delta^{17}O$, which depend on both $\delta^{17}O$ and $\delta^{18}O$ and typically have external precision better than either of these controlling variables for analyses of pure gases (e.g., Miller et al., 1999).

Carbon dioxide samples were extracted from air or purified from experiments using standard vacuum cryogenic techniques and then further cleaned by gas chromatography; the samples were also occasionally cleaned by UV photolysis followed by additional vacuum cryogenic purification. External precision of Δ_{47} for repeat extractions of CO_2 from samples collected at the same time and place averages 0.012‰, 1σ (Table 2). Laboratory experiments on labeled gases and gases equilibrated at known, high temperatures before extraction and analysis demonstrate that CO_2 generally does not re-equilibrate during these sample purification procedures. Carbon dioxide was generally extracted from whole-air samples within hours of collection to minimize isotopic exchange with water adsorbed or condensed on flask walls; two samples that we suspect underwent such postcollection exchange are discussed below. Analyses of atmospheric CO_2 in Table 2 have been ion-corrected for interferences from N_2O, based on measured N/C ratios of samples and comparison with measurements of standards having known N_2O/CO_2 ratios. These corrections average $+0.102 \pm 0.011$‰ for $\delta^{13}C$, $+0.146 \pm 0.016$‰ for $\delta^{18}O$ and -0.047 ± 0.006 for Δ_{47} (all variations are 1σ). See the Appendix for further analytical details.

3. RESULTS AND DISCUSSION

Table 2 presents measurements of the stable isotope composition, including Δ_{47} values, of CO_2 from air and CO_2 produced or processed in laboratory experiments. In the following paragraphs, we first evaluate various physical and biologic processes potentially influencing atmospheric $^{18}O^{13}C^{16}O$, beginning with relatively simple physical processes and followed by more complex biologic processes that combine several fractionation mechanisms. Afterwards, we present measurements of $^{18}O^{13}C^{16}O$ in air from the Los Angeles basin and discuss the balance of sources and fractionations responsible for these observations.

3.1. The Stochastic Distribution and Mixing Relationships

Figure 1 plots R^{47} values in CO_2 having the stochastic distribution and a range of $\delta^{13}C$, $\delta^{17}O$, and $\delta^{18}O$ values typical of natural terrestrial materials. This field of predicted abundances appears flat at the plotted scale, but has a subtle saddle-shaped curvature. Consequentially, mixing two populations of CO_2 molecules, each of which has the stochastic distribution, without exchange of isotopes between isotopologues (i.e., if mixing is conservative with respect to all isotopologues), produces a mixed population having higher or lower R^{47} than expected for the stochastic abundance in the new bulk composition. That is, the mixture will have a higher or lower Δ_{47} value than the end members (Fig. 1, inset A). We confirmed this effect by measuring Δ_{47} values of two CO_2 samples that differed greatly from one another in $\delta^{18}O$ and $\delta^{13}C$, and by measuring a mixture of these two gases (Table 2). As expected, mixing of these gases generates a positive Δ_{47} anomaly. This experiment demonstrates that multiply substituted isotopologues of CO_2 behave conservatively during gas mixing and through the various steps of our sample purification and analysis.

Because abundances of multiply substituted isotopologues have predictable dependences on mixing, they can be used to identify gases that are mixtures of two isotopically distinct end members, and to constrain the properties and proportions of those end members. Such information cannot be obtained based on bulk stable isotope data (e.g., $\delta^{13}C$ and $\delta^{18}O$ values) alone. Given the typical $\delta^{13}C$ and $\delta^{18}O$ values of major components of the CO_2 budget (Ciais and Meijer, 1998), mixing alone could

Table 2. Stable isotope composition, including Δ_{47}, of natural and synthetic CO_2.

Sample	$\delta^{13}C$	$\delta^{18}O$	Δ_{47}	Notes
Mixing				
Starting gas #1	−40.09	−14.65	0.95	CO_2 equilibrated with SLAP at 25°C
Starting gas #2	−2.88*	176.84	0.70*	CO_2 labeled with ^{18}O*
Mixture of #1 and #2	−30.25*	35.98	1.99*	Predicted Δ_{47} = 2.24
Thermodynamic equilibrium				
Calculated	$\Delta_{47} = -0.95 + 560\ T^{-1}$ (T in K); 0.99‰ at 289 K.			Fit to calculation from Wang et al., 2004; T of 10–40°C.
Air equilibrated with water at 25°C	−9.36	44.79	0.97	
High-temperature gases				
Car Exhaust #1	−22.46 ± 0.08	24.24 ± 0.18	0.06 ± 0.08	Corrected for contamination; see Supp. Inf.
Natural gas combustion	−39.66	23.14	−0.04	
Calcined calcite	−3.63	10.18	0.04	
Car Exhaust #2	−25.18	26.55	0.70@	Re-equilibrated with condensed water in flask?
Diffusive fractionation				
Diffused gas #1	−38.22	−14.54	0.85	Predicted Δ_{47} (diffused) − Δ_{47} (residue) = 0.49‰
Residual gas #1	−28.01	6.18	0.38	
Respiration				
Compost	−20.93	41.74	0.86	
Human Breath	−23.76	35.18	0.66	
Residues of photsynthetic uptake				
Antirrhinum majus	−6.99	44.61	0.65	From 390 to 318 ppm CO_2; initial Δ_{47} = 0.75
Viburnum davidii	−7.59	46.40	0.79	From 385 to 335 ppm CO_2; initial Δ_{47} unknown
Buxus microphylla japonica	−8.38	46.33	0.45	From 380 to 357 ppm CO_2; initial Δ_{47} unknown
Air				
3-28-03 Santa Monica	−9.35	41.25	0.68	
3-31-03 Pasadena	−10.07	41.06	0.67	
4-4-03, AM Pasadena	−8.81	41.63	0.62	
4-4-03, PM Pasadena	−8.61	41.84	0.63	
4-9-03 Pasadena	−9.74	41.43	0.65	
4-15-03 Pasadena	−11.17	39.97	0.75	
4-23-03 Pasadena	−8.65	42.48	0.71	
4-23-03 Pasadena	−8.67	42.46	0.67	(Repeat)
5-2-03, AM Pasadena	−8.72	41.71	0.66	
5-2-03, AM Pasadena	−8.76	41.49	0.73	(Repeat)
5-2-03, AM Pasadena	−8.79	41.64	0.69	(Repeat)
5-2-03, PM Pasadena	−8.90	41.71	0.93	
5-2-03, PM Pasadena	−8.92	41.68	0.93	(Repeat)

* The ^{18}O-labeled CO_2 used in this experiment has non-terrestrial ^{17}O content for its $\delta^{18}O$. The $\delta^{13}C$ and Δ_{47} values for this gas, and the mixture to which it was added, are ion - corrected based on the known amount of synthetic, pure ^{18}O they contain.

@ This sample spent several hours in a flask containing water condensed from the collected car exhaust; we speculate that its Δ_{47} reflects approach toward thermodynamic equilibrium at room temperature rather than the initial value at the time of collection.

generate Δ_{47} values in atmospheric CO_2 of up to + 0.10‰, but generally less than +0.05‰.

3.2. Thermodynamic Fractionations

Multiply substituted isotopologues generally have lower zero-point energies than their isotopically normal and singly substituted relatives (Bigeleisen and Mayer, 1947; Urey, 1947; Wang et al., 2004, this volume). Therefore, a population of isotopologues that is thermodynamically equilibrated at earth-surface temperatures will generally have greater abundances of multiply substituted isotopologues than predicted by the stochastic distribution (i.e., they will have positive Δ_{47} values; Fig. 1, inset B). Calculations based on reduced partition coefficients of CO_2 isotopologues (Wang et al., 2004, this volume) indicate that this thermodynamic elevation in Δ_{47} varies between ca. 1.1 and 0.85‰ between temperatures of 273 and 303 K, respectively (Table 2). Natural air exposed to condensed water in the laboratory at 298 K was found to contain CO_2 with a Δ_{47} value of +0.97‰, consistent with these calculations (Table 2). Isotopic exchange with plant leaf water and seawater are large components of the CO_2 budget (Francey and Tans, 1987) and, in the absence of other fractionations, should drive atmospheric CO_2 toward a mean Δ_{47} value of + 0.93‰ for the global mean temperature of 289 K. Somewhat higher or lower values are expected if CO_2 undergoes a disproportionately large amount of isotopic exchange with water at temperatures different from this mean (see below for details).

Carbon dioxide collected from car exhaust created by combustion in the laboratory (the plume above a natural gas torch), or created by calcining calcite, has, with one exception, Δ_{47} values near 0.0‰ (Table 2). These results are consistent with the close approach to a stochastic distribution expected for thermodynamic equilibrium at temperatures in excess of several hundred degrees centigrade (Wang et al., 2004, this volume), and they suggest that high-temperature processes involved in fossil-fuel emissions and cement manufacture should produce CO_2 having the stochastic distribution. One sample of car exhaust yielded a higher Δ_{47} value inconsistent with this generalization. However, exhaust contains abundant water that can catalyze low-temperature re-equilibration of CO_2 if it con-

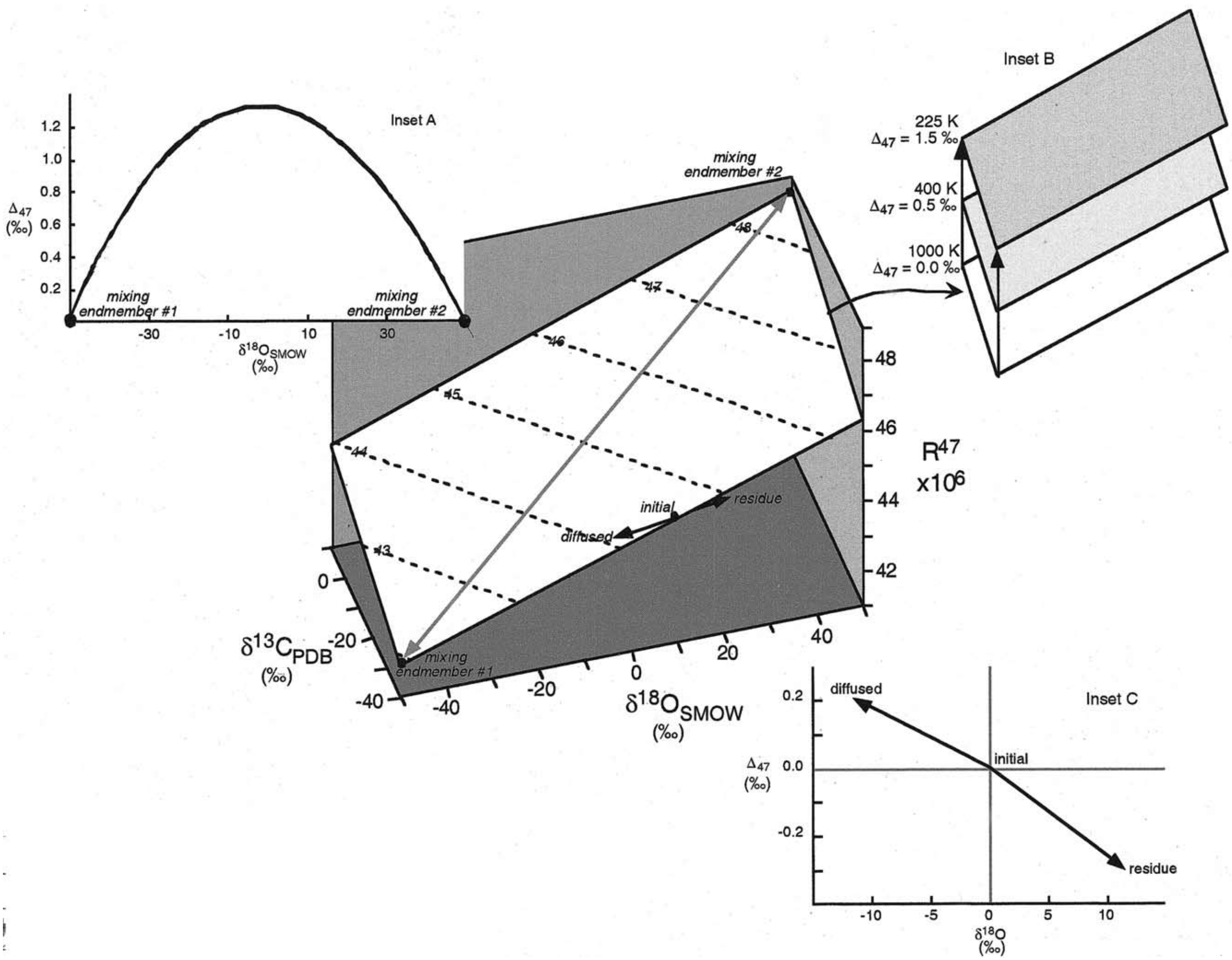

Fig. 1. The unfilled field on the central, three-dimensional diagram illustrates the ratio of mass-47 to mass-44 isotopologues (R^{47}) predicted for the stochastic distribution, as a function of bulk $\delta^{18}O_{SMOW}$ and $\delta^{13}C_{PDB}$ of CO_2. Dashed light lines contour $10^6 x R^{47}$ on the surface of that field. All compositions falling on that field have Δ_{47} values of 0, by definition. Compositions above or below the field have positive or negative Δ_{47} values, respectively. The field has a subtly saddle-shaped curvature (not visible at the plotted scale), such that mixing lines between points on the field generally will produce mixtures lying above or below it. For example, the heavy gray line links two end members lying on the field of stochastic compositions and different from one another in bulk isotopic composition. Inset A shows that mixing of these two end members produces new compositions having positive Δ_{47} values. Thermodynamic equilibrium at earth-surface temperatures produces mass-47 isotopologues in excess of the stochastic distribution. Inset B schematically illustrates this effect by showing fields of equilibrium compositions at 400 and 225 K lying above (to higher Δ_{47}) the field for the stochastic distribution, which is indistinguishable from equilibrium at very high temperature (1000 K). Many kinetically limited processes are predicted to produce gases not having the stochastic distribution. For example, arrows on the central figure and Inset C show that Knudsen diffusion produces gas that is lower in $\delta^{18}O$ and $\delta^{13}C$ but higher in Δ_{47} than its residue.

denses on the walls of the collection vessel. We speculate that our efforts to cryogenically remove water from this sample during its collection failed.

It is beyond the scope of this study to discuss in detail the abundances of multiply substituted isotopologues for species other than CO_2. However, we note that carbonate species (e.g., H_2CO_3, HCO_3^-, $CO_3^=$, calcite) at earth-surface temperatures are expected to contain concentrations of ^{13}C-^{18}O bonds ~0.5‰ greater than the stochastic distribution. We speculate that CO_2 evolved from aqueous solution might preserve the carbonate-ion isotope distribution (Δ_{47} equivalent of ~ 0.5‰) rather than the gaseous CO_2 equilibrium (Δ_{47} ~ 1.0‰) if the kinetics of isotopic redistribution among CO_2 isotopologues are slow compared to the rate of degassing.

3.3. Diffusion

Processes that lead to kinetic isotope fractionations (such as gas-phase diffusion) are predicted to yield populations of molecules with nonstochastic abundances of multiply substituted isotopologues because the mass dependences of diffusive fractionations differ from the slope of the field of stochastic distributions over most of its range (Fig. 1, inset C). For example, the kinetic theory of gases (Gibbs, 1928) predicts that a population of CO_2 molecules diffusing through a small aperture (Knudsen diffusion) is depleted in heavy isotopes relative to the residual gas it leaves behind, with a mass dependence given by the equation:

$$R^j_{diffused} = R^j_{residue} . (M_i/M_j)^{0.5} \quad (3)$$

Where R^j is the ratio of the concentration of isotopologue j to the concentration of isotopologue i, and M_i and M_j are the masses of isotopologues i and j, respectively. This fractionation law predicts that a "diffused" population of CO_2 will be 11.2‰ lower in $\delta^{13}C$, 22.2‰ lower in $\delta^{18}O$, but 0.5‰ *higher* in Δ_{47} than the residual gas. Diffusion of one gas through another ("gas-phase diffusion") leads to fractionations with magnitudes and mass dependences that vary with the mean molecular mass of the ambient atmosphere (Gibbs, 1928). These fractionations are smaller than those arising from Knudsen diffusion, but have a similar proportionality among changes in $\delta^{13}C$, $\delta^{18}O$, and Δ^{47}. For example, diffusion of CO_2 through air leads to fractionations of −4.4, −8.7, and +0.3‰, respectively.

We conducted an experiment to confirm the effects of diffusive fractionations on Δ_{47} values by cryogenically collecting CO_2 leaked through a needle value into vacuum, followed by isotopic analysis of the "diffused" and residual CO_2. We infer this experiment approximates Knudsen diffusion because the mean-free path of CO_2 in a low vacuum approaches the width of the aperture in a needle valve when it is slightly opened. The measured differences in $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} between diffused CO_2 and residual gas closely approach those predicted for Knudsen diffusion (Table 2).

Diffusion of CO_2 in and out of leaf stomata are the largest gross fluxes in the global atmospheric budget (Farquhar et al., 1993; Ciais et al., 1997; the residence time of atmospheric CO_2 with respect to leaf interaction is ca. 2 yr). Stomatal diffusion generally takes place following the "gas-phase" rather than "Knudsen" diffusion law because stomata are large relative to the mean-free path of CO_2 in air (except under conditions of water stress). Therefore, if we neglect any other mechanisms of isotopic fractionation, diffusion-mediated air-leaf interaction should decrease the Δ_{47} value of residual atmospheric CO_2 by an amount equal to the "gas-phase" diffusive fractionation (0.27‰) multiplied by the fraction of CO_2, entering leaves, that gets fixed (ca. 1/3), or ca. 0.1‰, overall. See below for a more detailed model of air-leaf interaction.

3.4. Respiration

Trapped air collected from within a compost heap contains CO_2 having Δ_{47} consistent with thermodynamic equilibrium at its ambient temperature (Table 2). This is understandable because the high surface area, available condensed water, warm temperatures, and relatively high residence time of respired CO_2 in constricted pore spaces should promote approach to equilibrium. This result suggests that CO_2 produced by soil respiration should have a Δ_{47} value equal to the equilibrium value at the soil temperature. In the absence of any other isotopic fractionations, this should drive the atmosphere toward a Δ_{47} value equal to that for the average earth surface temperature (0.93‰; see above). Respired CO_2 must diffuse through soils before escaping to the atmosphere, and it is possible that this results in an additional isotopic fractionation. Arguments presented in the preceding section suggest this process could increase Δ_{47} values of escaping CO_2 by up to 0.27‰. However, soils are complex systems and we speculate that additional experiments will be needed before their Δ_{47} budget can be confidently understood.

Human breath contains CO_2 that has a Δ_{47} value significantly lower than thermodynamic equilibrium at body temperature (0.66 vs. 0.90‰; Table 2). We expect that diffusive fractionation during exsolution of CO_2 out of blood and into the lungs should tend to increase rather than lower Δ_{47} (and, in any event, liquid-phase diffusion of CO_2 generates only very small isotopic fractionations), so we have no simple explanation of the measured offset from equilibrium. It is possible it reflects a metabolic fractionation that discriminates against generation of $^{18}O^{13}C^{16}O$, although our intuition is that such isotope effects would not be preserved through the acid-base chemistry associated with transport of respired CO_2 through blood. It is also possible that this phenomenon reflects exsolution of CO_2 having an abundance of ^{13}C-^{18}O bonds inherited from carbonate ions in solution (as was discussed above). More experimental work will be required to test these hypotheses.

3.5. Photosynthesis

Photosynthesis in leafy plants involves gas-phase diffusion of CO_2 into leaves through stomata, isotopic exchange with leaf water facilitated by carbonic anhydrase, fixation of ca. 1/3 of the CO_2 within leaves, and retro diffusion of the remainder back out of the leaf and into the atmosphere (Farquhar and Lloyd, 1993). If isotopic exchange between CO_2 within leaves and leaf water is sufficiently rapid, it should maintain the Δ_{47} value of that CO_2 at or near the equilibrium value for the temperature of exchange, despite fractionations of bulk isotopic composition (e.g., $\delta^{13}C$ value) due to metabolic carbon fixation. Therefore, we expect that interaction between leaves and air should have an effect on Δ_{47} of atmospheric CO_2 that reflects a dynamic balance between diffusive fractionations into and out of leaves and isotopic exchange between the CO_2 inside leaves and leaf water. A box model of air-leaf interaction based on this assumption (Fig. 2) predicts that this process will drive residual CO_2 toward a Δ_{47} value equal to the equilibrium value at the temperature of the leaf, minus a fraction of the diffusive fractionation equal to the fraction of CO_2 entering leaves that is fixed. For example, assuming a leaf temperature of 289 K and fixation of 1/3 of the CO_2 entering leaves, this model predicts that air-leaf interaction will drive Δ_{47} of residual CO_2 towards values of 0.84‰ (if diffusion through stomata follows the "gas-phase" diffusion mass dependence) or 0.77‰ (if diffusion follows the Knudsen diffusion mass dependence).

We suspect, based on previous studies of the activity of carbonic anhydrase in leaves (Gillon and Yakir, 2001), that the assumptions behind the model presented in Figure 2 are valid often but not always. In cases where carbonic anhydrase activity is low (so gaseous CO_2 within leaves is not buffered by isotopic exchange with leaf water), kinetic isotope effects associated with metabolic carbon fixation might generate distinctive, nonequilibrium Δ_{47} values in residual CO_2. Similarly, in these cases abundances of ^{13}C-^{18}O bonds in carbonate species dissolved in leaf water might imaginably impact Δ_{47} values of

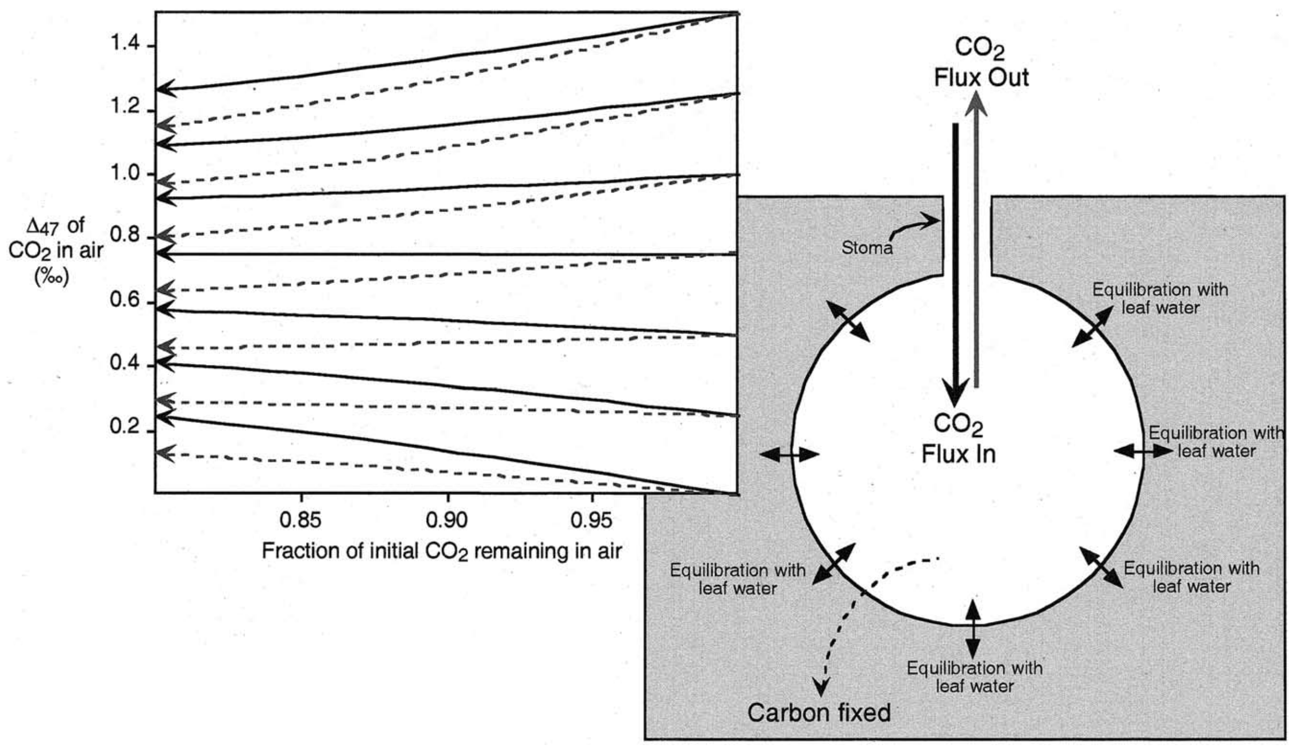

Fig. 2. Schematic illustration of a box model (right) describing the effect of air-leaf interactions on the Δ_{47} value of atmospheric CO_2, and calculated results of that model (left) assuming a range of initial Δ_{47} values from 0.0 to 1.5‰; Knudsen diffusion through stomata (one could similarly assume a fractionation following the gas-phase diffusion law); a temperature of 289 K (such that the equilibrium Δ_{47} equals 0.93‰); and a fraction of CO_2 entering the leaf that is equal to either 1/3 (solid black arrows) or 1/2 (dashed gray arrows). This model assumes that CO_2 inside the leaf undergoes rapid isotopic exchange with leaf water such that its Δ_{47} is continuously maintained at the equilibrium value, despite any changes in bulk isotopic composition that might result from metabolic carbon fixation, and regardless of the Δ_{47} of CO_2 entering the leaf. The predicted change in Δ_{47} in atmospheric CO_2 exposed to leaves depends on its initial value, the temperature of exchange, the mass-dependence of diffusive fractionations (i.e., the gas-phase vs. Knudsen laws), and particularly, the fraction of CO_2 entering leaves that is fixed.

CO_2 retro diffusing from leaves (see above). We cannot yet assess the importance or predict the magnitudes of these effects, and they will need to be evaluated by more focused experimental studies.

Our measurements of CO_2 residual to photosynthesis yield Δ_{47} values of between 0.45 and 0.79‰. In the one case where the Δ_{47} value of the initial CO_2 is known (the experiment on Antirrhinum majus), we find it decreased from 0.75 to 0.65‰ for 20% CO_2 uptake (Table 2). This is consistent with the box model presented in Figure 2. The experiment on Viburnum davidii yielded a Δ_{47} value (0.79‰) below that for thermodynamic equilibrium at the temperature of the experiment (0.90‰), and higher than the value typical of air in the place this experiment was done (ca. 0.70‰; see below). This result is consistent with, but does not provide any clear evidence in favor of, the model in Figure 2. The experiment on Buxus microphylla japonica yielded an exceptionally low Δ_{47} value of 0.45‰ after only 6% CO_2 uptake. We do not know the Δ_{47} of the starting air for this experiment, but all samples taken at the site before and after are higher than 0.62‰. Thus, it seems likely that Δ_{47} decreased by at least 0.17‰. The model in Figure 2 cannot explain this observation, and we suspect it reflects a kinetic isotope effect associated with metabolic carbon fixation and/or abundances of ^{13}C-^{18}O bonds in inorganic carbon in leaf water.

3.6. Air in the Los Angeles Basin

Collectively, the physical and biologic fractionations of $^{18}O^{13}C^{16}O$ examined above suggest that measurements of Δ_{47} in atmospheric CO_2 can help constrain the chemistry and budget of atmospheric CO_2, including (but perhaps not limited to) the temperature of isotopic exchange between atmosphere and surface or leaf waters, the role of diffusive fractionations associated with transport of CO_2 through leaf stomata, and mixing proportions of anthropogenic CO_2. We illustrate the influences of these processes in controlling the Δ_{47} of natural CO_2 through study of air from the Los Angeles basin.

Near-surface air samples collected between March 28th, 2003, and May 2nd, 2003, in southern California have Δ_{47} values of $+0.72 \pm 0.10$ (1σ;Table 2). Eight of these nine samples are essentially indistinguishable from each other, averaging $+0.68 \pm 0.04$‰; the outlier collected on the afternoon of May 2nd, 2003, could reflect natural variability, although taken alone it provides little basis for speculating on its cause. We focus on the average of the tightly grouped majority. It is

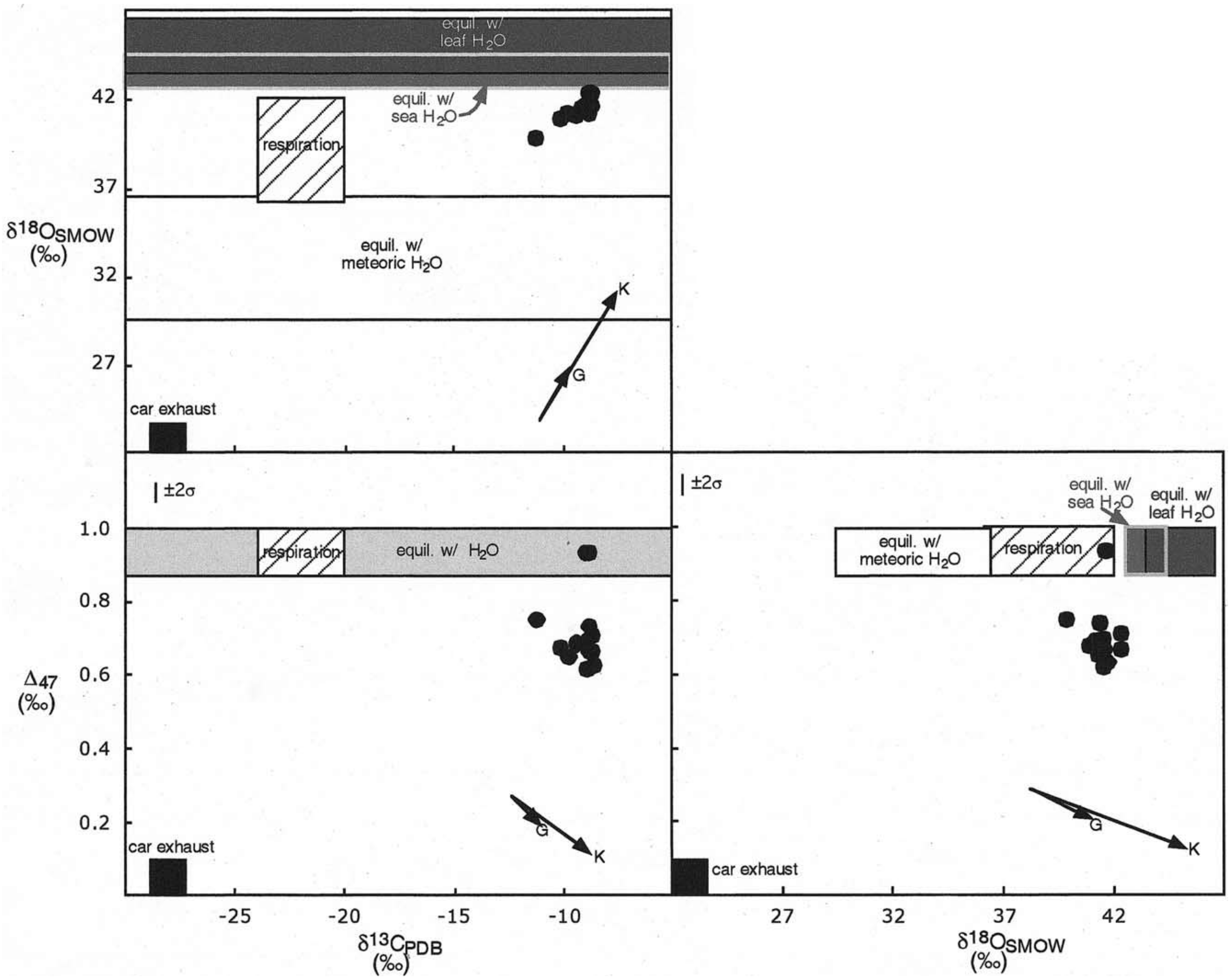

Fig. 3. Comparison of the isotopic compositions (including $\delta^{18}O_{SMOW}$, $\delta^{13}C_{PDB}$, and Δ_{47}) of atmospheric CO_2 samples (filled circles) to various end members and fractionations relevant to the atmospheric budget. Unfilled, light gray and dark gray boxes plot the compositions of CO_2 in thermodynamic equilibrium near 289 K with typical meteoric water, seawater, and leaf water, respectively, based on calculations from Wang et al. (2004), this volume, and estimates of the $\delta^{18}O$ of average waters from Kaplan et al. (2002). Black boxes indicate the expected compositions of car exhaust; diagonally ruled boxes indicate the composition of CO_2 expected for soil respiration, based on a measurement of compost soil gas. Note that human breath has a lower Δ_{47} value. Arrows indicate the vector changes in composition of CO_2 that is residual to 1/3 loss rate limited by diffusion (as is typical during photosynthesis; Farquhar and Lloyd, 1993; Farquhar et al., 1993); arrows labeled "G" indicate vectors for gas-phase diffusion; those labeled "K" are for Knudsen diffusion. The isotopic compositions of CO_2 in most samples from Pasadena and Santa Monica approach to thermodynamic equilibrium with surface and leaf waters, modulated by fractionations during diffusion in and out of leaves and additions of anthropogenic emissions. Most samples are ca. 0.05‰ lower in Δ_{47} than can be quantitatively explained by this combination of factors.

noteworthy that this outlier is the only sample to have a Δ_{47} equal to that expected for thermodynamic equilibrium at the temperatures of sample collection and purification, and we speculate that it might have undergone exchange with unnoticed water condensed on its flask walls. Figure 3 compares the Δ_{47}, $\delta^{13}C$, and $\delta^{18}O$ values of CO_2 from air with various sources and fractionations discussed above.

The average Δ_{47} value we observe is significantly below the range expected for thermodynamic equilibrium at the mean earth surface temperature of 289 K (0.93‰; this also equals the average spring temperature in and near southern California) and is lower than expected for CO_2 that undergoes isotopic exchange with leaf water mediated by stomatal diffusion (0.84‰, assuming 289 K, fixation of 1/3 of CO_2 entering leaves, and "gas phase" diffusive fractionations; Fig. 2). The concentration of CO_2 in air in the Los Angeles basin is enriched relative to the average troposphere by ca. 20 ppm, or 6%, relative, due to local anthropogenic emissions (Newman et al., 1999). Assuming this contribution is dominated by car exhaust having Δ_{47} of ca. 0, it should reduce the average Δ_{47} of air by ca. 0.05‰. The combination of this effect with our prediction of the typical Δ_{47} buffered by air-leaf interaction (Fig. 2) leads to an expected Δ_{47} value of +0.79 (for "gas phase" diffusion)—still subtly higher than our average value, and clearly higher than the average for the tightly grouped majority of our samples. A net predicted Δ_{47} value as low as + 0.72‰—equal to our average—is found if we assume isotopic exchange with leaf water is mediated by Knudsen diffusion, but this is an improbable limiting case.

We conclude that the Δ_{47} value of air in the Los Angeles basin largely reflects processes independently believed to dominate the atmospheric CO_2 budget (air-leaf interaction) modified by known local anthropogenic sources, but that it is also influenced by an unknown process(es) that subtly (ca. 0.05–0.09‰) reduces Δ_{47} values. One simple explanation of this discrepancy could be a systematic error in our estimation of the temperature dependence of isotope exchange reactions controlling Δ_{47} values at thermodynamic equilibrium. However, our measurement of air intentionally equilibrated with water agrees with this estimation, suggesting it is accurate. Mixing effects and sample contaminants (see Appendix) do not provide plausible explanations for this discrepancy because both should raise Δ_{47} values. It might reflect reduction of the Δ_{47} value of the atmosphere as a whole due to accumulated anthropogenic emissions, although these contribute less than 1% of the gross fluxes to the atmosphere, and we expect they should be overwhelmed by the air-sea and air-leaf exchange processes that drive the atmosphere toward thermodynamic equilibrium. Soil respiration does not appear to be a candidate for generating Δ_{47} values below those expected for thermodynamic equilibrium. We speculate that this discrepancy might reflect disequilibrium degassing of CO_2 from seawater, such that abundances of ^{13}C-^{18}O bonds partly or entirely reflect those for carbonate ions in solution.

4. OUTLOOK

More widespread analyses of $^{18}O^{13}C^{16}O$ in air have the potential to reveal new information about the global atmospheric CO_2 budget and about the mechanisms of CO_2 production and uptake in model systems. The real usefulness of Δ_{47} measurements for advancing these issues will not become clear until records are produced documenting variation in Δ_{47} of atmospheric CO_2 with time and location, and until more sophisticated experimental studies are made of complex model systems. Nevertheless, enough can be surmised from data presented in this study to speculate on the potential directions this work will take.

First, measurements of Δ_{47} can discriminate between CO_2 produced by respiration (expected Δ_{47} of ca. 0.8 to 1.0‰, depending on temperature and assuming soil CO_2 analyzed here is representative) and combustion ($\Delta_{47} \sim 0$‰). These sources are difficult to discriminate from one another based on $\delta^{13}C$ values alone. This difference would be most useful in studies of environments containing vigorous sources of both biogenic and anthropogenic CO_2 (e.g., Newman et al., 1999).

Second, variations in temperature with latitude and season should drive variations in Δ_{47} due to changes in thermodynamic equilibrium mediated by exchange with water. If we assume this exchange only takes place at temperatures above the freezing point of water, the possible range in observed Δ_{47} values is 0.21‰ (the difference between equilibrium at 305 and 273 K). This is a large multiple of external precision (avg. 0.012‰) and should be easily observed.

The residence time of CO_2 with respect to interaction with leaves and seawater (ca. 1.5–2 yr; Ciais and Meijer, 1998) is long compared to timescales of latitudinal mixing within either northern or southern hemisphere, and comparable to the timescale for interhemispheric mixing. Therefore, we expect that potential variations in Δ_{47} arising from the temperature dependence of thermodynamic equilibrium should be reduced by atmospheric mixing. Nevertheless, isotopic exchange with water is believed to be responsible for large-amplitude latitudinal gradients and seasonal cycles in the $\delta^{18}O$ of CO_2 (Ciais and Meijer, 1998). This leads us to suspect the same processes could lead to measurable variations in Δ_{47}.

One of the most important uses of Δ_{47} measurements will be to place a new constraint on the interpretation of the $\delta^{18}O$ of atmospheric CO_2, which depends on both temperature of CO_2-water isotopic exchange and the $\delta^{18}O$ of surface and leaf waters (as well as other factors). Values of Δ_{47} are sensitive to temperature but not to the $\delta^{18}O$ of water, and thus could be used to deconvolve the relative importance of these two controlling variables. For example, the average interhemispheric gradient in the $\delta^{18}O$ of CO_2 is ca. 2‰, and the largest seasonal cycles are nearly as large (Ciais and Meijer, 1998). If all of this variation were due to differences in average temperature of CO_2-water exchange (an improbable but useful reference case), it would be accompanied by variations in Δ_{47} of 0.060‰ with the same sign. That is, a ratio, $\partial(\Delta_{47})/\partial(\delta^{18}O)$, of 0.03 is distinctive of isotopic variations controlled by temperature-dependent exchange equilibria. This contrasts with the ratio of 0 resulting from variations in source-water $\delta^{18}O$, and also with the ratio of -0.03 resulting from diffusive fractionations.

We also think it is noteworthy that CO_2-water exchange is overwhelmingly dominated by leaves in the northern hemisphere, and thus should be modulated by diffusive fractionations as illustrated in Figure 2, whereas air-sea exchange is proportionately more important in the southern hemisphere. We have no direct information on the Δ_{47} of CO_2 outgassed from the ocean. However, if it reflects thermodynamic equilibrium of CO_2, Δ_{47} should be higher in the south than the north for a given temperature of exchange. If instead, Δ_{47} of outgassed CO_2 reflects thermodynamic equilibrium of dissolved carbonate species values, it could be lower in the south than in the north. Of course, it is possible that both factors counterbalance one another and no gradient will be observed.

The sensitivities of Δ_{47} values to factors other than temperature might also be used to better understand respiration and photosynthesis at ecosystem or larger scales. For example, "gas-phase" and "Knudsen" diffusive fractionations have different mass dependences, so variations in water stress (which influences stomatal conductance) should lead to subtle ($\leq$0.2‰) but potentially measurable differences in the Δ_{47} value of CO_2 residual to photosynthetic carbon fixation.

Finally, it is interesting to consider whether multiply substituted CO_2 might be studied in materials other than modern air. It would be reasonable to guess that this is not possible because the concentration of a multiply substituted isotopologue is a "combinatorial" property that is likely disturbed by heterogeneous reactions, and thus should only be meaningful in materials which retain their original chemical form (e.g., as gas molecules) in the geological record. This condition is likely not satisfied for CO_2, which reacts with ice and is only preserved indirectly in rocks after dissolution in water and precipitation as carbonates (a possible exception is CO_2 in firn air, which might or might not reset its Δ_{47} values by interaction with surrounding snow and ice). Two related, and potentially more interesting questions are (1) whether carbonate minerals contain multiply substituted structural groups (e.g., $^{13}C^{18}O^{16}O_2^{=}$) in abundances that reflect their temperatures of growth or other environmental variables; and (2) whether those abundances can be studied meaningfully by analysis of CO_2 extracted from carbonates by acid digestion or some other method. If so, then many of the principles of the geochemistry of multiply substituted isotopologues discussed here with reference to gaseous CO_2 might also be applied to study of minerals and other condensed materials preserved in the geological record. The most obvious and potentially attractive target of this kind is the use of $^{13}C^{18}O^{16}O_2^{=}$ abundances in near-surface carbonates as a "paleothermometer" that has no dependence on bulk stable isotope compositions, and thus that could be applied to times and places where the $\delta^{18}O$ of water is unknown.

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APPENDIX

Instrument: Internal and External Precision

Measurements reported in this study were made using a Finnigan-MAT 253 gas source mass spectrometer equipped with a collection system for high-mass ions consisting of both the standard set of three faraday cups registered through 10^8 to 10^{11} Ohm resistors (for masses 44, 45 and 46) and three additional faraday cups registered through 10^{12} Ohm resistors (for masses 47, 48 and 49). Sample sizes were generally ca. 50 to 100 μmoles and currents registered for resulting ion beams were approximately as follows: mass 44—50 nA; mass 45—0.5 nA; mass 46—0.2 nA; mass 47—2 pA; mass 48—0.2 pA; and mass 49—ca. 3 to 10 fA. For the purposes of this study, masses 48 and 49 were only used to evaluate sample contamination, which leads to highly correlated shifts in masses 47, 48 and 49 (see below).

Measurements consisted of a set of eight comparisons of sample and standard, with each comparison consisting of 8 s counting on each. Internal statistics for these sets of comparisons (1σ standard deviation about the mean) are approximately as follows: $\delta45 = \pm0.01‰$; $\delta46 = \pm0.02‰$; $\delta47 = \pm0.1‰$, where δi refers to variations in the ratio of mass i to mass 44. Standard errors for these measurements were ca. 1/3 to 1/5 of these values, depending on analysis duration. External precision for repeat measurements of the same gases (including fractionations associated with repeated sample purification and vacuum transfer) are typically as follows: $\delta45 = \pm0.01‰$; $\delta46 = \pm0.02‰$; $\delta47 = \pm0.03‰$—comparable to values expected based on the internal statistics of each measurement. Drift in δ values between pairs of sample-standard comparisons within a given analysis was generally negligible, other than for samples contaminated by hydrocarbons (see below). Measurements of $\delta45$ and $\delta46$ have linearity within the limits standard for the Finnigan Mat 253 and negligible in comparison to other errors in our measurements. Measurements of $\delta47$ are also generally linear, although extreme differences between sample and standard (50‰ or more) lead to measurable nonlinearity that can be detected by analysis of stochastically equilibrated samples spanning a range of bulk compositions. Samples and standards examined in this study generally have $\delta47$ values within ca. 10‰ of each other, so this phenomenon appears to have no significance for our results and has been ignored.

Ion Corrections and Standardization

Ion corrections for interferences of $^{17}O^{12}C^{16}O$ on $^{16}O^{13}C^{16}O$ and of $^{17}O^{13}C^{16}O$ and $^{17}O^{12}C^{17}O$ on $^{18}O^{12}C^{16}O$ were made following standard protocols recommended by the IAEA (Santrock et al., 1985; Allison et al., 1995). Ion corrections for interferences of $^{17}O^{12}C^{18}O$ and $^{17}O^{13}C^{17}O$ on $^{18}O^{13}C^{16}O$ were made by assuming (1) the bulk oxygen isotope composition of the CO_2 sample lies on the terrestrial mass fractionation line (Robert et al., 1992); and (2) both $^{17}O^{12}C^{18}O$ and $^{17}O^{13}C^{17}O$ are enriched or depleted relative to their stochastic abundances in direct proportion to enrichments or depletions in $^{18}O^{13}C^{16}O$ (i.e., all mass-47 molecules are inferred to undergo the same fractionations). We think it is implausible that these assumptions lead to significant errors in our ion corrected results because both species together represent only ca. 3.5% of all collected ions having $M/z = 47$, and deviations of tropospheric CO_2 from the oxygen-isotope terrestrial fractionation line are small or negligible (Thiemens et al., 1995). For reference, a 1 per mil excess or deficit of ^{17}O relative to the terrestrial fractionation line (Robert et al., 1992), if not explicitly considered in our ion correction, would lead to an error of ca. 0.035 per mil in the estimated Δ_{47} value. This factor is only expected to be significant relative to analytical precision for analyses of CO_2 from stratospheric air (Thiemens et al., 1995).

Determinations of $\delta^{13}C$ and $\delta^{18}O$ of our unknown samples were standardized following established protocols using secondary laboratory standards whose compositions have been determined using IAEA-certified standards (Gonfiantini et al., 1995). Standardization of Δ_{47} measurements is less straightforward and requires that we define a reference frame. We propose that measured ratios of mass-47 to mass-44 isotopologues be reported relative to a hypothetical reference frame in which all C and O isotopes, in abundances defined by the known $\delta^{13}C$ and $\delta^{18}O$ values for a sample, are randomly distributed among all possible isotopologues. We refer to this condition as the stochastic distribution, the mathematics of which can be derived by statistical principles and are presented in detail in Wang et al. (2004), this volume. This reference frame requires that we produce standard gases having known bulk isotopic compositions and that are independently known to have the stochastic distribution. The following paragraphs summarize our methods for generating and characterizing such standards and our procedure for using them to standardize measurements of unknowns.

We acquired three isotopic end members, including of 99.8% pure $^{18}O^{12}C^{18}O$ (purchased from Matheson), CO_2 having a $\delta^{18}O$ of 22‰ and having a $^{12}C/^{13}C$ ratio near 0 (produced by combusting pure ^{13}C synthetic diamond with tank O_2), and UHP tank CO_2 having $\delta^{18}O_{SMOW}$ of 1.8‰ and $\delta^{13}C_{PDB}$ of $-32.1‰$. These gases were purified by standard vacuum cryogenic techniques and analyzed for their isotopic composition individually, in various unheated mixtures, and in various mixtures that were heated before analysis to promote isotopic exchange between isotopologues. These measurements of variably enriched gases were made on a gas source isotope ratio mass spectrometer using magnetic peak switching to sequentially collect each ion beam in a single faraday cup rather than standard multi-collection. Registered intensities of each beam were regressed as a function of measurement time to account for loss of sample pressure during analysis, and the isotope ratios calculated based on the zero-time intercepts of those regressions. External precision in measured isotope ratios for this method is typically ca. 0.1 to 1%, relative (depending on the ion beam intensity ratio in question).

Measurements of the three starting gases are consistent with expected abundances of isotopologues. Measurements of physical mixtures of these end members indicate that their constituent isotopologues do not undergo measurable isotopic exchange when mixed at room temperature for several hours, condensed together as ice at liquid nitrogen temperatures, or inlet together into the source of the mass spectrometer. For example, the 46/44 and 46/48 ratios of a 50:50 mixture of $^{18}O^{12}C^{18}O$ and tank CO_2 are both $\leq$ca. 0.005, consistent with the amount of $^{18}O^{12}C^{16}O$ in tank CO_2 and indicating no measurable progress of the reaction: $^{18}O^{12}C^{18}O + {}^{16}O^{12}C^{16}O = 2 \times {}^{18}O^{12}C^{16}O$ during sample preparation and analysis. Finally, mixtures of these gases that were heated to between 800 and 1000°C in the presence of Pt wire for tens of minutes or longer had a distribution of isotopologues consistent with the stochastic distribution. For example, the heated 50:50 mixture of $^{18}O^{12}C^{18}O$ and tank CO_2 was found to be ca. 25% mass 44, 50% mass 46, and 25% mass 48, yielding an equilibrium constant of 3.998 ± 0.003 for the reaction $^{18}O^{12}C^{18}O + {}^{16}O^{12}C^{16}O = 2.{}^{18}O^{12}C^{16}O$ (indistinguishable from the K_{eq} for the stochastic distribution of 4).

High-precision measurements of natural CO_2 and synthetic CO_2 having unenriched isotopic abundances were made by direct or indirect (i.e., by way of an intermediate reference gas) comparison to unenriched intralaboratory standards that had been heated by the same protocols known to achieve the stochastic distribution in enriched gases. These intralaboratory standards are defined as having Δ_{47} values of 0, and thus have 47/44 ratios defined by their bulk isotopic compositions (independently known by standard methods of CO_2 stable isotope analysis; Allison et al., 1995; Gonfiantini et al., 1995) and the mathematics defining the stochastic distribution (Wang et al., 2004, this volume). We regularly measure two or more heated intralaboratory standards that differ from one another in bulk isotopic composition; the definition of one as having a Δ_{47} value of 0 routinely yields a Δ_{47} value for the other(s) that is indistinguishable from 0.

Extraction and Purification of CO_2 From Air

Carbon dioxide was extracted from air by bleeding 5-L air samples through a series of four triple U-traps immersed in liquid nitrogen, warming those traps by immersion in ethanol-dry-ice slush, and collection of the gases evolved from those traps in a fifth trap held at liquid nitrogen temperatures. Previous studies have shown this system is capable of routinely yielding accurate and precise determinations of $\delta^{13}C$, $\delta^{18}O$, and $[CO_2]$ on samples of zero-air spiked with CO_2 standards (Newman et al., 1999). Extraction of CO_2 from air in laboratory experiments used these same methods and apparatus, but often used smaller samples (ca. 500 cc).

Our measurements of $^{13}C^{18}O^{16}O$ place additional demands on sample purity that require further treatments before analysis. The chief contaminants that can interfere with mass 47 are $^{15}N^{16}O_2$, $^{15}N^{14}N^{18}O$, $^{14}N^{15}N^{18}O$, and fragments or recombination products of halocarbons (e.g., CCl^+ produced from CH_3Cl or CH_2Cl_2) and other hydrocarbons. All of the candidate contaminant species other than N_2O have sufficiently low vapor pressures that they should be retained in the ethanol-dry-ice traps used during initial CO_2 extraction. Nevertheless, it is possible that some fraction of these species passes these traps. Therefore, samples of CO_2 extracted from whole air were further cleaned by the following methods: (1) All CO_2 samples extracted from air reported in Table 2 were entrained in a He stream and passed over a 17.2 m, PoraPLOT Q gas chromatography column at ca. 25°C. This treatment is efficient at separating hydrocarbon and halocarbon contaminants from CO_2, and variably reduced N_2O/CO_2 ratios of eluted gas. N_2O/CO_2 ratios of sample gases, after cleaning, were estimated by measuring N/C ratios by magnetic peak switching on the same gas-source mass spectrometer used for isotope ratio analysis, referred to analyses of manometrically prepared CO_2-N_2O mixtures. Contributions of N_2O to ion beams for masses 44 to 47 were subtracted as part of our ion correction for these samples; (2) We also established that exposure of CO_2 to several hours of intense mid-UV radiation (at both 250 and 350 nm) followed by a second cryogenic purification using liquid nitrogen and a pentane-slush efficiently removes hydrocarbon and chlorinated hydrocarbon contaminants, and would be a suitable method for purifying samples that are inappropriate for gas chromatography (e.g., if they are too large or small for a given GC and gas recovery system or have high concentrations of hydrocarbons that might pollute a GC column). UV irradiation of CO_2 standards alone indicates that the distribution of its isotopologues is unaffected by this treatment. Analyses of air samples and standard gases intentionally contaminated with CH_2Cl_2 and/or C_5H_{12} showed that either (or both) of these treatments is effective at reducing intensities of ion beams with $M/z = 47$, 48, and 49 (and higher) produced by their fragments and recombination products.

Routine analysis of masses 48 and 49, in addition to masses 44 to 47, permits us to test for the influence of potential contaminants on measurements of Δ_{47} (defined in the text) because of systematic relationships between interferences various species make on masses 44 through 49. For example, addition of 1 ppm NO_2 to pure CO_2 (at the high end of the abundance ratios of these gases in whole air) leads to the following coupled changes in the isotopic composition of CO_2: $\delta^{13}C$ = unchanged; $\delta^{18}O = 0.25‰$ increase; $\Delta_{47} = 0.15‰$ decrease; $\Delta_{48} = 0.5‰$ increase (Δ_{48} is defined similarly to Δ_{47}; i.e., difference in per mil between measured 48/44 and 48/44 expected for the stochastic distribution); 49 intensity = no measurable change. These coupled changes in isotope composition can be compared with data to establish whether measured variations in unknown samples can be attributed to NO_2 (we see no evidence for such a contaminant vector in the air samples reported in Table 2). Similarly, addition of 100 ppm of N_2O to pure CO_2 will lead to the following changes: $\delta^{13}C = 0.35‰$ decrease; $\delta^{18}O = 0.5‰$ decrease; $\Delta_{47} = 0.15‰$ increase; Δ_{48} = no change; 49 intensity = no change (these effects have been ion-corrected based on measured N_2O/CO_2 ratios in each air sample, and we see no evidence in the corrected data for unaccounted-for N_2O contaminants).

It is less easy to predict the consequences of contamination by hydrocarbons and chlorinated hydrocarbons, so we have examined their effects through a series of experiments. Addition of CH_2Cl_2 and/or pentane to whole air samples or prepurified CO_2 produces linear and highly correlated trends of variations in Δ_{47}, Δ_{48}, and the intensity of the mass 49 ion beam. These trends are described by the following two empiric equations for typical instrument conditions and sample sizes: $\Delta_{47} = 0.735 \times$ [(mV mass 49 in sample −mV mass 49 in standard)]; $\Delta_{48} = 3.47 \times$ [(mV mass 49 in sample −mV mass 49 in standard)]. The r^2 is greater than 0.999 in both cases. This high degree of correlation despite differences in amounts and proportions of the two contaminants suggests to us that the relevant interfering masses are always produced by recombination of C-O-H-Cl species in the source with a fixed proportion of product species. A possible explanation of this is that these species all have the same core of heavy elements (e.g., CCl, C_2O) and vary only in the number of H atoms or ions added to that core. Samples appearing to contain natural halocarbon and hydrocarbon contaminants (based on drift during analyses, clearly anomalous mass 49 intensities, and associated unusual Δ_{47} and Δ_{48} values) exhibit a relationship between Δ_{47}, Δ_{48}, and the mass 49 voltage like those in intentionally contaminated standard CO_2 (above). We have generally excluded from Table 2 all measurements appearing to have such contamination, with the exception of one car exhaust sample (noted in Table 2 and its footnote). Data for this sample were corrected using the empiric relationships described above.

Other Analytical Artifacts

Experiments on isotopically labeled and other synthetic CO_2 reveal that several procedures can change the distribution of CO_2 isotopologues toward Δ_{47} values consistent with room temperature thermodynamic equilibrium. These include condensation onto and release from molecular sieve or other adsorptive substrates, and prolonged (several day) containment within sample collection vessels having condensed water on their walls. We suspect that re-equilibration during adsorption is mediated by co-adsorbed water, and thus is analogous to re-equilibration on other wet surfaces. This phenomenon raises the possibility that simply passing CO_2 vapor over glass or gas chromatography columns will promote isotopic exchange. However, repeated experiments on labeled and other synthetic CO_2 indicate this is not the case. For example, the "mixed" CO_2 reported in Table 2, which has a Δ_{47} value ca.1‰ greater than room temperature equilibrium, was passed over a Porplot-Q column four times without measurably changing its Δ_{47} value. Finally, CO_2 can undergo internal isotopic exchange while passing through the mass spectrometer capillaries if they are "wet" (for example, because the instrument was recently vented or contaminated by a water-rich sample). This phenomenon is avoided by aggressively heating capillaries with a torch while flowing He through them before analyses of CO_2 samples, and its presence is detected by changes in the measured difference in Δ_{47} between standards having the stochastic distribution and those equilibrated with water at 25°C.