

The atmospheric oxygen cycle: The oxygen isotopes of atmospheric CO₂ and O₂ and the O₂/N₂ ratio

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Introduction

Oxygen is the most abundant element in the earth's crust, it accounts for 89% of the mass of the ocean, and it is the second most abundant element in the earth's atmosphere. Much work on the oxygen cycle has focused on the question of the origin of atmospheric O₂ and its variations over geologic time [see *Kump et al.*, 1991, and references therein]. This review focuses on several other aspects of the oxygen cycle including the short-term controls on the oxygen isotopic abundance of atmospheric CO₂ and O₂, and the short-term variability in the O₂/N₂ ratio.

These aspects of the oxygen cycle depend mainly on material exchanges between the atmosphere and living organisms at the earth's surface or in the ocean. Like several other atmospheric variables which have received much attention recently, e.g., the abundances of CO₂, CH₄, and N₂O, the oxygen isotopic content of CO₂ and O₂ and the O₂/N₂ ratio have atmospheric lifetimes that are long relative to the time scale of atmospheric mixing and thus reflect an integration of material exchanges over the globe. Recently, our knowledge of these variables has expanded through laboratory experiments exploring the exchange pathways, and through measurements on contemporary air samples or in ancient air samples extracted from polar ice cores. This review summarizes recent literature on these subjects, and also emphasizes how these aspects of the global oxygen cycle can provide new information on the material exchanges between the atmosphere and biota integrated over large areas.

The ¹⁸O/¹⁶O Ratio of Atmospheric CO₂

The oxygen isotopic content of atmospheric CO₂ is mainly determined by interactions between CO₂ and the global reservoirs of liquid water. This follows because direct gas phase interactions of CO₂ with O₂ and H₂O vapor do not result in O atom exchange [*Francey and Tans*, 1987]. When CO₂ dissolves in water, oxygen atoms are exchanged through a mechanism that involves the hydration of dissolved CO₂ to form carbonic acid (H₂CO₃). The time scale for dissolved CO₂

to come to isotopic equilibrium with liquid water is the same as the time scale for hydration, i.e., around 30 seconds [*Mills and Urey*, 1940]. The ¹⁸O/¹⁶O ratio of CO₂ in equilibrium with water at 25°C is 1.041 times higher than the ¹⁸O/¹⁶O ratio of the water. This equilibrium fractionation factor varies slightly with temperature.

Isotopic ratios are generally reported according to

$$\delta = ({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{standard}} - 1 \quad (1)$$

where the δ value is customarily multiplied by 1000 and expressed in per mille (‰). *Bottinga and Craig* [1969] suggested using a standard based on CO₂ in equilibrium with the Standard Mean Ocean Water (SMOW) at 25°C [*Craig and Gordon*, 1965]. Most recent measurements have been reported relative to the ¹⁸O/¹⁶O ratio of CO₂ derived from the Pee-Dee Belemnite (PDB) carbonate standard. This standard has an ¹⁸O/¹⁶O ratio that is 0.22‰ higher than the Bottinga and Craig standard [*Friedman and O'Neil*, 1977].

The ¹⁸O/¹⁶O ratio of atmospheric CO₂ is primarily determined by exchanges with leaf water, soil water, and surface sea water [*Francey and Tans*, 1987; *Farquhar et al.*, 1993]. Oxygen atom exchange with leaf water occurs because a significant fraction of the CO₂ which diffuses into the chloroplasts of leaf cells is not assimilated but diffuses back into the air, and this fraction will have equilibrated isotopically with chloroplast water. Equilibration occurs in spite of the short (< 1 second) residence time of CO₂ in leaves because of the presence of the enzyme carbonic anhydrase, which is concentrated in the chloroplasts of leaf cells and which dramatically speeds up the hydration reaction. Oxygen atom exchange with soil water occurs primarily through CO₂ which is released into the soil by below-ground respiration and which subsequently diffuses into the atmosphere. Oxygen atom exchange with seawater occurs through the exchange of CO₂ molecules across the air-sea interface.

The oxygen isotopic composition of soil water and leaf water vary considerably. Soil water isotopic composition tends to follow the composition of precipitation which is progressively depleted in ¹⁸O relative to seawater towards high latitudes and towards the interior of continents. Chloroplast water, in turn, tends to be enriched in ¹⁸O relative to soil water by evaporation from leaves because H₂¹⁶O evaporates preferentially relative to H₂¹⁸O. This enrichment of chloroplast water is sensitive to relative humidity and temperature, which can be highly variable [*Dongmann et al.*, 1974; *Förstel*, 1978; *Zundel et al.*, 1978].

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Paper number 95RG00438.
8755-1209/95/95RG-00438\$15.00

A global steady-state budget for $\delta^{18}\text{O}$ of atmospheric CO_2 is shown in Figure 1. This budget uses figures from Farquhar *et al.* [1993] for fluxes and isotopic exchanges of atmospheric CO_2 with leaf, soil, and sea water. One significant source of uncertainty here is the global average isotopic composition of chloroplast water. Logically, the $\delta^{18}\text{O}$ of chloroplast water should be intermediate between that of soil water and water at the evaporating surface in the leaves where the maximum isotopic enrichment occurs. A critical question

is where does chloroplast water fall in this range. Farquhar *et al.* [1993] present results based on isotope exchange experiments with several varieties of fruit trees that suggest the isotopic composition of chloroplast water is virtually identical to that of water at the evaporating surfaces in leaves. The budget in Figure 1 is based on this assumption, taking into account the variability of leaf water over the surface of the earth. In contrast, Yakir and coworkers have conducted isotope exchange experiments on sunflowers that indicate that

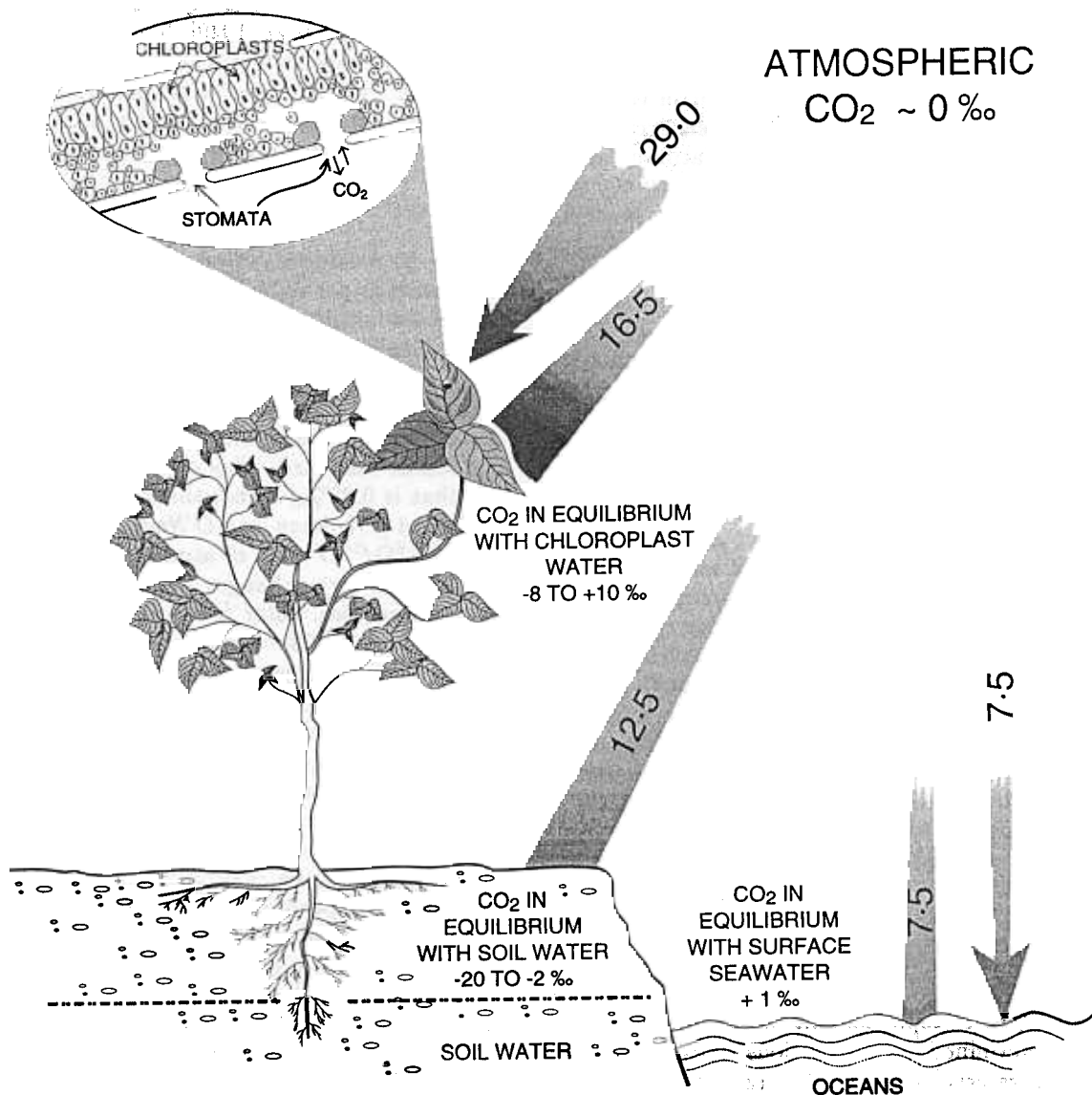


Figure 1. The global "pre-anthropogenic" steady-state budget for the oxygen isotopes of atmospheric CO_2 based on Farquhar *et al.* [1993] showing annual fluxes of CO_2 in units of 10^{15} moles of carbon and showing the isotopic composition of CO_2 in equilibrium with dominant exchangeable water reservoirs [see also Keeling, 1993]. CO_2 exchange with soil water involves uptake of CO_2 by leaves, respiration within the soil, and diffusion of the respiratory CO_2 out through the soil. The budget shown here assumes that the kinetic isotope fractionation that results from diffusion through stomata and through the soil cancel each other out (see also Table 2, Eq. (F)). According to this budget, the bulk composition of atmospheric CO_2 can be explained by assuming that 45% of the oxygen atoms come from chloroplast water at an average isotopic composition of $+5\text{‰}$, 34% come from soil water at an average of -7‰ , and 21% come from sea water at an average of $+1\text{‰}$. This combination yields atmospheric CO_2 at approximately 0‰ . All numbers here are relative to the PDB standard.

chloroplast water is typically 6 to 10‰ depleted in ^{18}O compared to water at the evaporating surface [Yakir *et al.*, 1993; Yakir *et al.*, 1994]. The difference in $\delta^{18}\text{O}$ between chloroplasts and evaporation sites probably varies significantly from species to species [Yakir *et al.*, 1993].

A global model describing oxygen atom exchanges of CO_2 with terrestrial ecosystems has been developed by Farquhar *et al.* [1993] (see Table 1, Equation G). This model is based on a formulation in which the oxygen-atom exchanges with leaf water are described using an effective fractionation factor Δ_A (see Table 1) against ^{18}O on net uptake of CO_2 . The isotopic exchange flux between the atmosphere and leaves is thus obtained by multiplying Δ_A by net flux of CO_2 into the leaves (basically equal to gross primary production, GPP). The factor Δ_A is not a true fractionation factor because it depends on the isotopic composition of atmospheric CO_2 . Δ_A is nevertheless useful because it can be measured in controlled experiments as well as modeled over the surface of the earth [Farquhar *et al.*, 1993].

The latitudinal distribution of Δ_A as estimated by Farquhar *et al.* [1993], is shown in Figure 2. Also shown is the latitudinal variation of CO_2 in equilibrium with surface seawater (δ°), the isotopic composition of CO_2 returned to the atmosphere through soils (δ_r), the sum $\delta_r + \Delta_A$, and the annual mean surface values of $\delta^{18}\text{O}$ of atmospheric CO_2 . Exchanges with leaves and soils tend to drive the local $\delta^{18}\text{O}$ of atmospheric CO_2 towards the sum $\delta_r + \Delta_A$. This sum tends to decrease towards high latitudes in the northern hemisphere, following the depletion of $^{18}\text{O}/^{16}\text{O}$ of precipitation. The latitudinal gradient in $\delta_r + \Delta_A$ can account qualitatively for the latitudinal gradient in $^{18}\text{O}/^{16}\text{O}$ of CO_2 that was observed by Francey and Tans [1987], although the actual profile in the air is smoothed by atmospheric mixing.

In addition to exhibiting a gradient with latitude, the $^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 is known to undergo a seasonal cycle in the northern hemisphere [Keeling, 1961; Friedli *et al.*, 1987] with a maximum in early summer and a minimum in early winter. This seasonal cycle probably results mostly from the seasonality of exchanges with terrestrial ecosystems. These exchanges will tend to cause a decrease in $^{18}\text{O}/^{16}\text{O}$ of CO_2 during the warmer months when atmospheric CO_2 exchanges most rapidly with leaf and soil reservoirs which are depleted in $^{18}\text{O}/^{16}\text{O}$ at middle and high northern latitudes. The ratio will tend to increase during other seasons as a result of transport of higher $^{18}\text{O}/^{16}\text{O}$ ratios from more southern latitudes. Other factors, such as seasonal variations in soil water $^{18}\text{O}/^{16}\text{O}$ ratios, in leaf water isotopic enrichment, and in the ratio of CO_2 exchange rate with leaves and soils probably also play a role. Modeling this seasonal cycle remains an important area of future work.

What can we learn from measurements of $^{18}\text{O}/^{16}\text{O}$ ratios of CO_2 ? Farquhar *et al.* [1993] propose using the measurements to distinguish between CO_2 exchanges with different biomes and between terrestrial ecosystems and the oceans. This application is suggested be-

Table 1. Summarizing Two Alternative Formulations for Describing Exchanges of Oxygen Isotopes of CO_2 with Terrestrial Ecosystems

NOTATION:	
C_a	Atmospheric CO_2 partial pressure ($p\text{CO}_2$)
C_c	$p\text{CO}_2$ in chloroplast
$^{18}\text{C}_a$	Atmospheric $\text{C}^{18}\text{O}^{16}\text{O}$ partial pressure
R_a	$^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric CO_2
R_c	$^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 in equilibrium with chloroplast water
R_s	$^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 in equilibrium with soil water
R_{PDB}	$^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 derived from the carbonate standard Pee-Dee Belemnite [see Friedman and O'Neil, 1977]
δ_a	$(R_a - R_{\text{PDB}})/R_{\text{PDB}}$
δ_c	$(R_c - R_{\text{PDB}})/R_{\text{PDB}}$
δ_s	$(R_s - R_{\text{PDB}})/R_{\text{PDB}}$
δ_r	$\delta_s + \epsilon_{\text{soil}}$
F_{in}	Gross flux of CO_2 into stomata
F_{out}	Gross flux of CO_2 out of stomata
R	Flux of CO_2 out of soil from root and soil respiration
α_{sto}	Fractionation factor of diffusion through stomata (same both directions)
α_{soil}	Fractionation factor for diffusion out of soil
ϵ_{sto}	$\alpha_{\text{sto}} - 1$ [$-\bar{a}$ per Farquhar <i>et al.</i> , 1993]
ϵ_{soil}	$\alpha_{\text{soil}} - 1$
A	Gross primary production ($A = F_{\text{in}} - F_{\text{out}}$)
Δ_A	Effective discrimination against $\text{C}^{18}\text{O}^{16}\text{O}$ relative to net CO_2 assimilation [Farquhar <i>et al.</i> , 1993]; $\Delta_A = -\epsilon_{\text{sto}} + [C_c/(C_a - C_c)](\delta_c - \delta_a)$
M	Number of moles of air in the atmosphere
N	Net ecosystem production ($N = F_{\text{in}} - F_{\text{out}} - R$)
EQUATIONS:	
Mass balance of atmospheric CO_2 :	
$M dC_a/dt = F_{\text{out}} - F_{\text{in}} + R$	(A)
Mass balance of atmospheric $\text{C}^{18}\text{O}^{16}\text{O}$:	
$M d(R_a C_a)/dt = \alpha_{\text{sto}} R_c F_{\text{out}} - \alpha_{\text{sto}} R_a F_{\text{in}} + \alpha_{\text{soil}} R_s R$	(B)
Flux/gradient proportionality:	
$F_{\text{out}}/(F_{\text{in}} - F_{\text{out}}) = C_c/(C_a - C_c)$	(C)
Combining (A) and (B):	
$M C_a dR_a/dt = \alpha_{\text{sto}}(R_c - R_a)F_{\text{out}} - R_a(\alpha_{\text{sto}} - 1)(F_{\text{in}} - F_{\text{out}}) + (\alpha_{\text{soil}} R_s - R_a)R$	(D)
Rearranging (D):	
$M C_a dR_a/dt = \alpha_{\text{sto}}(R_c - R_a)F_{\text{out}} + (\alpha_{\text{soil}} R_s - \alpha_{\text{sto}} R_a)R + R_a(\alpha_{\text{sto}} - 1)(R - F_{\text{in}} + F_{\text{out}})$	(E)
FORMULATION 1 (results from converting (D) to δ -notation): ¹	
$M C_a d\delta_a/dt = (\delta_c - \delta_a)F_{\text{out}} + (\delta_s + \epsilon_{\text{soil}} - \delta_a - \epsilon_{\text{sto}})R - \epsilon_{\text{sto}}N$	(F)
FORMULATION 2 (combining (C) and (D), and converting to δ -notation): ¹	
$M C_a d\delta_a/dt = A \Delta_A + (\delta_r - \delta_a)R$	(G)

¹ See Tans *et al.*, 1993, for example of approximations used.

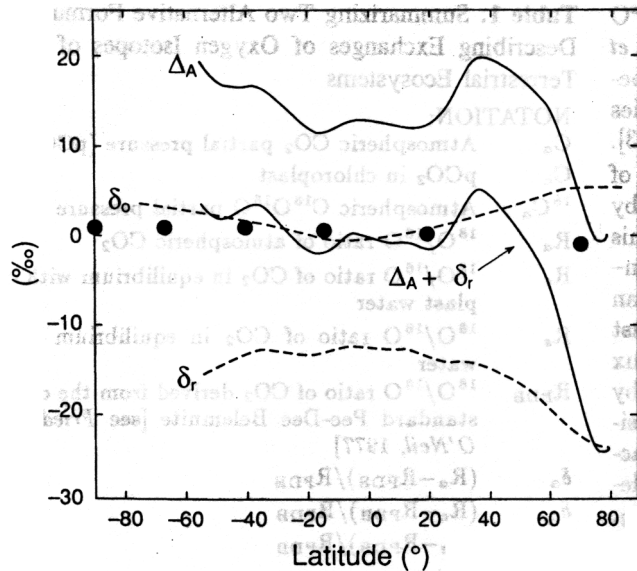


Figure 2. Latitudinal averages of the effective discrimination factor on uptake of CO_2 by leaves Δ_A , the $\delta^{18}O$ of CO_2 emitted by soils (δ_r), the $\delta^{18}O$ of CO_2 in equilibrium with surface seawater δ_0 , and the observed atmospheric $\delta^{18}O$ of atmospheric CO_2 (circles), and the sum ($\delta_r + \Delta_A$), from Farquhar *et al.* [1993]. Here δ_r was computed from the isotopic composition of precipitation minus 7.6‰. Latitudinal averages for Δ_A and δ_r are weighted by GPP. δ_r and δ_0 are expressed relative to the PDB standard.

cause of the large variability in the effective discrimination factor Δ_A between different biomes.

Further insight into what can be learned from measurements of oxygen isotopes of CO_2 can be obtained by the formulation shown in Table 1 (Equation F) which divides the isotopic exchanges with terrestrial ecosystems into three separate terms. The first term is proportional to the gross flux of CO_2 out of leaves which is related to stomatal conductance. The second is proportional to the flux of CO_2 out of soils which, for an ecosystem which is neither gaining or losing carbon, is closely related to ecosystem gross primary production (GPP). The third is proportional to the net flux of CO_2 into the ecosystem, i.e., to net ecosystem production (NEP). The first two terms depend on gross (i.e., two-way) exchanges of CO_2 while the third term depends on the net (one-way) CO_2 exchange. The third term is present because net CO_2 uptake by the ecosystem results in discrimination against ^{18}O in CO_2 as the CO_2 diffuses into stomata. Under some circumstances, e.g., over a diurnal cycle, the instantaneous value of this third term may be comparable in magnitude to the first two terms. On a time averaged basis, however, this term will be relatively unimportant because NEP is generally at least an order of magnitude smaller than the flux of CO_2 out of soils or leaves. (Figure 1 was drawn assuming this term is zero). What this means is that $\delta^{18}O$ of CO_2 is mainly sensitive to gross rather than net exchanges [see also Yakir *et al.*, 1993]. The unique value of the $\delta^{18}O$ measurements therefore lies in providing new

information on rates of gross primary production and stomatal conductance, as these exchanges can produce large variations in $\delta^{18}O$ without producing variations in atmospheric CO_2 concentration or carbon isotopes of CO_2 .

At present, several research programs are engaged in measuring the $^{18}O/^{16}O$ ratio of atmospheric CO_2 . These measurements will be useful for validating global-scale numerical models including physiologically based exchanges of H_2O and CO_2 with leaves and soils. The $^{18}O/^{16}O$ measurements can be expected to provide information on rates of gross primary production and stomatal conductance integrated over large spatial scales and in variations in these quantities in response to climate change, increasing atmospheric CO_2 , or other global variables.

The $^{18}O/^{16}O$ Ratio of Atmospheric O_2 : The Dole Effect

The $^{18}O/^{16}O$ ratio of atmospheric O_2 is higher than that of average seawater H_2O by 23.5‰ [Kroopnick and Craig, 1972]. This observation was first made independently by Dole [1935] and Morita [1935] and has become known as the Dole effect. It is caused mainly by discrimination against ^{18}O during respiration, as was realized in early investigations [Lane and Dole, 1956]. By this reasoning, photosynthesis produces O_2 from H_2O with the same $^{18}O/^{16}O$ ratio as the H_2O , while respiration preferentially removes $^{16}O_2$ from the air. A steady-state balance is achieved when the $^{18}O/^{16}O$ ratio of atmospheric O_2 is enriched relative to photosynthetic O_2 by the discrimination factor associated with respiration.

It is now recognized that additional processes also contribute to the Dole effect. While careful investigations have confirmed that photosynthesis produces O_2 without fractionation [Stevens *et al.*, 1975; Guy *et al.*, 1993], the isotopic composition of photosynthetic water can vary, and these variations will be passed on to the O_2 produced by photosynthesis. On average, this leads to an increased Dole effect because of evaporative enrichment of ^{18}O in leaf water [Dongmann, 1974]. Additional processes which influence the Dole effect are the equilibrium fractionation of $^{18}O/^{16}O$ between dissolved and gaseous O_2 , which is relevant because O_2 consumed by respiration is derived from dissolved O_2 , and photochemical processes in the stratosphere which lead to a slight decrease in $\delta^{18}O$ of O_2 through exchanges of oxygen atoms between O_2 and CO_2 [Bender *et al.*, 1994a].

Estimating the effective average fractionation factor for global respiration is complicated because O_2 consumption can occur via several distinct biochemical pathways [Guy *et al.*, 1989; Guy *et al.*, 1993; Bender *et al.*, 1994a] including the light reactions, such as the Mehler reactions and photorespiration reactions, and the dark reactions, such as the cytochrome pathway and the alternative cyanide-resistant pathway. To compute the global respiratory contribution to the Dole effect it

is necessary to know the fractionation factors and the relative O₂ consumption for each pathway at the global scale [Berry, 1992; Bender *et al.*, 1994a].

Respiration in the deep sea requires special consideration because here respiratory O₂ utilization depletes a significant fraction of the O₂ originally present in the water. If total depletion occurred, then the effective fractionation for respiration in the deep sea would be zero because the ¹⁸O/¹⁶O ratio of the removed O₂ would be equal to the ¹⁸O/¹⁶O ratio of the O₂ originally dissolved in the water. In the case where O₂ is only partially depleted, the effective respiratory fractionation factor can be calculated based on the percentage O₂ depletion that actually occurs [Bender *et al.*, 1994a].

A recent budget of the global contributions to the Dole effect by Bender *et al.* [1994a] is presented in Figure 3. This budget adopts the value of 4.4‰ [Farquhar *et al.*, 1993] for the average enrichment of terrestrial chloroplast water relative to SMOW. The budget takes account of respiratory fractionation using fractionation factors from Guy *et al.* [1989], Guy *et al.* [1993], Kiddon *et al.* [1993], and Bender [1990], and using estimates of the global O₂ uptake on land and in the ocean from Farquhar *et al.* [1980], Guy *et al.* [1993], and Keeling and Shertz [1992].

Interestingly, this budget yields an estimate for the global Dole effect of 20.8‰ which is significantly smaller than the observed value of 23.5‰. The difference may

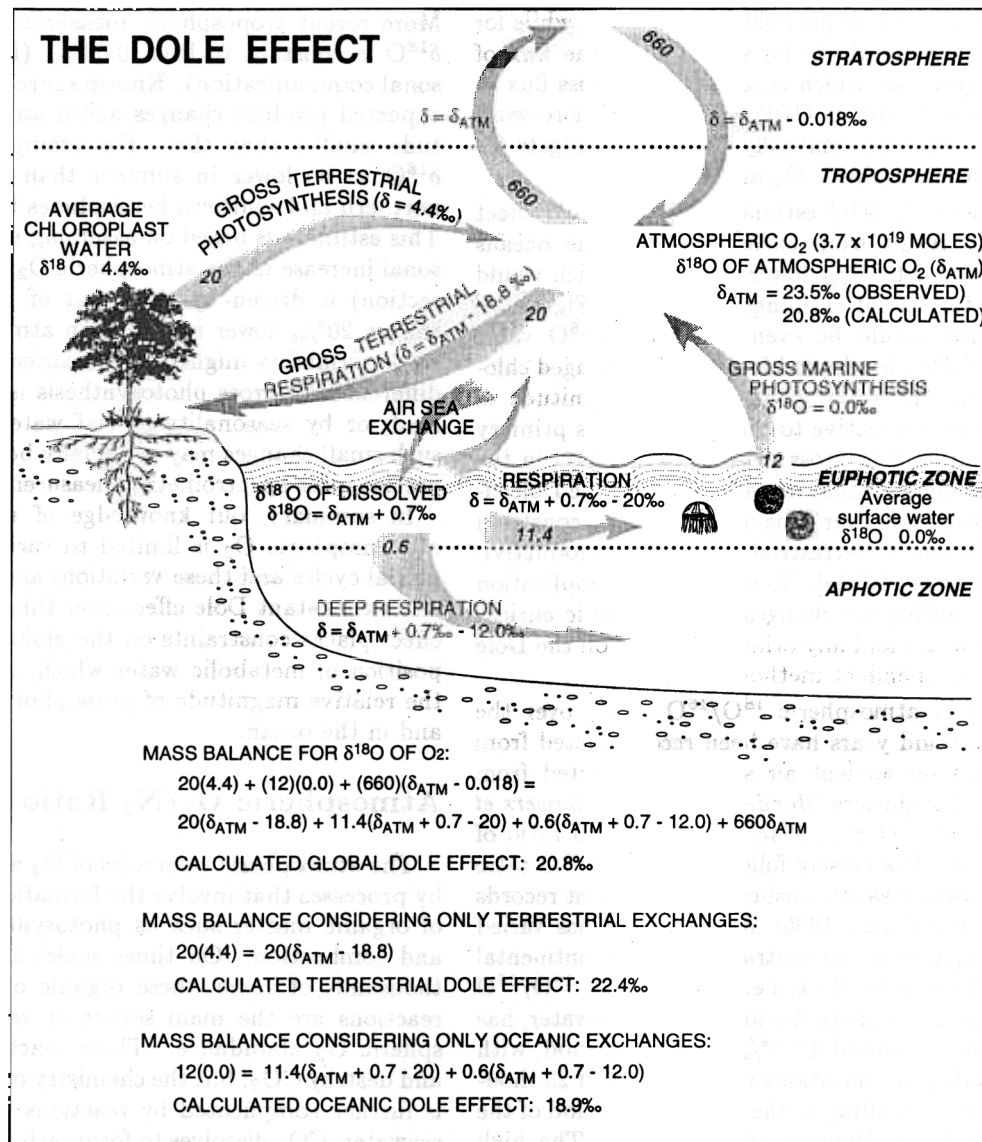


Figure 3. The global steady-state budget for the oxygen isotopes of atmospheric O₂ per Bender *et al.* [1994]. Fluxes are in units of 10¹⁵ moles O₂ yr⁻¹. The $\delta^{18}O$ values represent estimates of global averages of spatially and temporally variable quantities. Photorespiration and photooxidation reactions are grouped here as part of total terrestrial respiration. The O₂ flux from leaves thus exceeds the net O₂ production by leaves, i.e., the O₂ production associated with gross primary production, by the amount required by balance photorespiration and photooxidation reactions.

either reflect errors in the values adopted or unknown additional processes. A possible problem is the value of 4.4‰ adopted from *Farquhar et al.* [1993] for average chloroplast water. A value of 8.7‰ would bring the budget into balance, and *Bender et al.* [1994a], argue that a higher value is plausible given the uncertainties involved. In this case, however, the *Farquhar et al.* [1993] budget for $^{18}\text{O}/^{16}\text{O}$ of CO_2 would be out of balance. One possible way of reconciling both the CO_2 and O_2 isotope budgets might be by increasing the $\delta^{18}\text{O}$ of chloroplast water and decreasing the $\delta^{18}\text{O}$ of CO_2 leaving soils relative to the *Farquhar et al.* [1993] budget (M. Bender, personal communication). Some additional flexibility may be provided by the fact that the O_2 and CO_2 budgets depend on different weighted averages of chloroplast water. For the O_2 budget, the average needs to be weighted by GPP plus photorespiration, while for CO_2 the average needs to be weighted by the flux of CO_2 out of stomata, which is equal to the gross flux of CO_2 into stomata minus GPP. In any case more work is needed to construct mutually consistent budgets for $\delta^{18}\text{O}$ in both atmospheric O_2 and CO_2 .

Bender et al. [1994a] estimate that the Dole effect which would result from exchanges with the oceans alone is around 2 to 3‰ lower than that which would result from terrestrial exchanges alone (see Figure 3). This difference would be even larger if a $\delta^{18}\text{O}$ value higher than 4.4‰ is adopted for globally averaged chloroplast water. Either way, the overall magnitude of the Dole effect is sensitive to the ratio of gross primary production on land to gross primary production in the oceans. This suggests that measurements of the Dole effect and its variation over time may be used to constrain relative variations in terrestrial and marine productivities [*Bender et al.*, 1994a]. To succeed, this application requires accounting for changes in the isotopic enrichment in leaf water and any other influences on the Dole effect using independent methods.

Variations in atmospheric $^{18}\text{O}/^{16}\text{O}$ of O_2 over the past 130 thousand years have been reconstructed from measurements on ancient air samples extracted from bubbles in polar glaciers [*Bender et al.*, 1985; *Sowers et al.*, 1991; *Bender et al.*, 1994c]. The $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric O_2 has closely followed the $^{18}\text{O}/^{16}\text{O}$ ratio of surface seawater as established from sediment records [*Shackleton and Pisias*, 1985], which in turn has varied due to the expansion and contraction of the continental ice sheets. The Dole effect, i.e., difference in $^{18}\text{O}/^{16}\text{O}$ ratio between atmospheric O_2 and surface seawater, has been constant to around $\pm 0.5\%$ over this period, with possible small cyclic variations with a period of 23 thousand years corresponding to the precession period of the earth's orbital axis [*Bender et al.*, 1994a]. The high degree of constancy can probably be explained only if some of the factors controlling the Dole effect changed in ways that compensated for each other. This could occur, for example, if reductions in terrestrial productivity during glacial conditions were accompanied by reductions in marine productivity [*Bender et al.*, 1994a]. The similarity in the patterns of $\delta^{18}\text{O}$ variations in ice

core O_2 and sediment records has made it possible to establish more firmly the age of the air extracted from ice cores relative to the sediment chronologies [*Sowers et al.*, 1991].

Variations in $\delta^{18}\text{O}$ of atmospheric O_2 must lag behind variations of $\delta^{18}\text{O}$ in surface seawater by the turnover time of atmospheric O_2 with respect to gross photosynthesis and respiration. If the sediment and ice core chronologies were improved sufficiently, this turnover time, currently estimated at 1500 years, could be directly determined [*Bender et al.*, 1985; *Bender et al.*, 1994a].

How variable is $\delta^{18}\text{O}$ of atmospheric O_2 on shorter time scales? Temporal and spatial surveys [*Dole et al.*, 1954; *Kroopnick and Craig*, 1972] showed that $\delta^{18}\text{O}$ in the present atmosphere is constant to at least 0.25‰. More recent tropospheric measurements indicate that $\delta^{18}\text{O}$ is constant to at least 0.03‰ (M. Theimens, personal communication). Known sources of variability are expected produce changes about an order of magnitude smaller than this. For example, we can expect $\delta^{18}\text{O}$ to be lower in summer than in winter in both northern and southern hemispheres by about 0.002‰. This estimate is based on assuming that the 0.01% seasonal increase in the atmospheric O_2/N_2 ratio (see next section) is driven by the input of photosynthetic O_2 that is 20‰ lower in ^{18}O than atmospheric O_2 . Seasonal variability might also be caused by seasonal phase differences in gross photosynthesis in the oceans or on land, or by seasonality in leaf water $\delta^{18}\text{O}$. Detecting such small changes may eventually be feasible with very precise mass spectrometric measurements.

In summary, our knowledge of variations in $\delta^{18}\text{O}$ of atmospheric O_2 is limited to variations over recent glacial cycles and these variations are largely consistent with a constant Dole effect over this period. The Dole effect places constraints on the globally averaged composition of metabolic water which, in turn, constrains the relative magnitude of gross photosynthesis on land and in the ocean.

Atmospheric O_2/N_2 Ratio

The atmospheric reservoirs of O_2 and CO_2 are linked by processes that involve the formation and destruction of organic matter such as photosynthesis, respiration, and combustion. On times scales shorter than many thousands of years, these organic oxidation-reduction reactions are the main source of variability in atmospheric O_2 abundance. These reactions also produce and destroy CO_2 , but the chemistry of atmospheric CO_2 is further complicated by reactions with seawater. In seawater, CO_2 dissolves to form carbonic acid which can react to form basic compounds like carbonate and bicarbonate ions. These acid-base reactions have no effect on oxygen abundance so that atmospheric oxygen variations essentially reveal how atmospheric carbon dioxide would behave if the acid-base reactions did not occur.

The difference between the geochemistry of atmospheric O_2 and CO_2 can be quantified in terms of the

relative fluxes of O₂ and CO₂ expected from certain types of processes, as summarized in Table 2. One important difference between CO₂ and O₂ is that the uptake of fossil-fuel CO₂ by the ocean essentially proceeds through reaction of dissolved CO₂ with carbonate ions and therefore involves no O₂. Another difference is that marine photosynthesis and respiration can produce much larger changes in atmospheric O₂ than CO₂, especially on short time scales. Here the difference depends mainly on the fact that CO₂ exchange between the atmosphere and oceans proceeds much more slowly than O₂ exchange. CO₂ is exchanged slowly because most of carbon in the oceans is in the form of carbonate and bicarbonate ions which are not exchanged across the air-sea interface.

Two techniques are now available for measuring changes in atmospheric oxygen, one involving interferometry [Keeling, 1988; Keeling and Shertz, 1992], the other mass spectrometry [Bender *et al.*, 1993]. Both methods determine changes in atmospheric oxygen through changes in the O₂/N₂ ratio of air. Changes in the O₂/N₂ ratio are mainly caused by changes in O₂ because N₂ is constant to a very high level. Like isotopic ratios, the O₂/N₂ ratio is expressed as deviations from a reference

$$\delta(O_2/N_2) = \left(\frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1 \right) \quad (2)$$

The resulting deviations are multiplied by 10⁶ and the result is expressed in a new unit called a "per meg." In these units 1/0.2095 = 4.8 per meg is equivalent to

Table 2.

Process	Ratio of O ₂ Flux to CO ₂ Flux
Photosynthesis and Respiration on Land CO ₂ + H ₂ O ⇌ CH ₂ O + O ₂	-1.05 ^a
Burning Fossil Fuel CH _y + (1 + $\frac{y}{4}$) O ₂ ⇌ $\frac{y}{2}$ H ₂ O + CO ₂	-1.42 ^b
Oceanic Uptake of Excess CO ₂ H ₂ O + CO ₂ + CO ₃ ⁻ → 2HCO ₃ ⁻	0
Ocean Photosynthesis and Respiration 106CO ₂ + 16NO ₃ ⁻ + H ₂ PO ₄ ⁻ + 17H ⁺ ⇌ C ₁₀₆ H ₂₈₃ O ₁₁₀ N ₁₆ P + 138O ₂	-2 to -8 ^c

^a On average, the ratio for terrestrial organic matter is slightly more reduced than for carbohydrate, which yields a O₂:CO₂ ratio slightly higher than 1.0 [Keeling, 1988].

^b This is the global average ratio estimated for the year 1989 based on fuel production data [Marland and Boden, 1991], and using O₂:CO₂ ratios of different fuel types [Keeling, 1988].

^c Ocean photosynthesis adds O₂ to seawater and removes CO₂ from seawater in proportions of approximately -1.3:1 as determined by the composition of marine organic matter [Redfield *et al.*, 1963]. The relative fluxes across the air-sea interface also depend on the relative efficiencies of gas exchange and can vary depending on the time scale involved [Keeling and Severinghaus, 1993].

1 part-per-million by volume (ppmV) because O₂ comprises 20.95% of air by volume [Machta and Hughes, 1970].

Measurements on air samples collected at three sea-level sites using the interferometric technique were reported by Keeling and Shertz [1992], and are shown here in Figure 4. Significant seasonal variations in δ(O₂/N₂) are evident at all three sites. An interannual decrease in O₂/N₂ is clearly evident in the La Jolla data. Concurrent CO₂ data are also shown.

One process leading to seasonal variations in O₂/N₂ is the seasonal uptake and release of O₂ due to photosynthesis and respiration of terrestrial ecosystems. These exchanges of O₂ are closely tied to exchanges in CO₂ with an exchange ratio of approximately -1.05:1 (O₂:CO₂). The seasonal variations in CO₂ in the northern hemisphere are almost entirely caused by these terrestrial exchanges, and they can be used to correct for the effects of terrestrial exchange on the O₂/N₂ variations [Keeling and Shertz, 1992]. The residual variations in O₂/N₂ must be oceanic in origin. The oceanic component is especially pronounced in the southern hemisphere where the seasonal O₂/N₂ variations are accompanied by only very small variations in CO₂.

Oxygen is released to the atmosphere by the oceans at middle and high latitudes in the spring and summer when the net rate of photosynthesis in surface waters exceeds the rate of respiration. Oxygen is removed from the atmosphere in the fall and winter when marine photosynthesis rates are lower and when deeper water, undersaturated in oxygen, mixes upwards to the surface. These seasonal air-sea O₂ fluxes are linked to the rate at which organic material is produced and exported from the euphotic zone [Jenkins and Goldman, 1985; Keeling *et al.*, 1993] and they are linked to changes in dissolved inorganic carbon (DIC) in the water. Seasonal heating and cooling of the upper ocean also contributes to seasonal variations in atmospheric O₂/N₂ because of the solubility temperature dependence of O₂ and N₂ [Keeling and Shertz, 1992].

Measurements of seasonal variations in O₂/N₂ will be useful constraining estimates of the annual net photosynthetic production of organic carbon in the euphotic zone. To succeed this application also requires taking account of transport within the atmosphere and transport of O₂ between the euphotic zone and deeper waters. Atmospheric oxygen data may be especially helpful in determining productivities over large regions because the air mixes so rapidly.

Measurements of O₂/N₂ ratios will also be useful for determining the mechanisms by which excess carbon dioxide produced from fossil-fuel burning is being removed from the atmosphere. Over the long-term, we can represent the global budget for atmospheric CO₂ according to

$$\Delta\text{CO}_2 = F + C - O + B \quad (3)$$

where ΔCO₂ is the annual averaged change in atmospheric CO₂, *F* is the source of CO₂ from burning fossil fuels, *C* (virtually negligible) is the CO₂ source from ce-

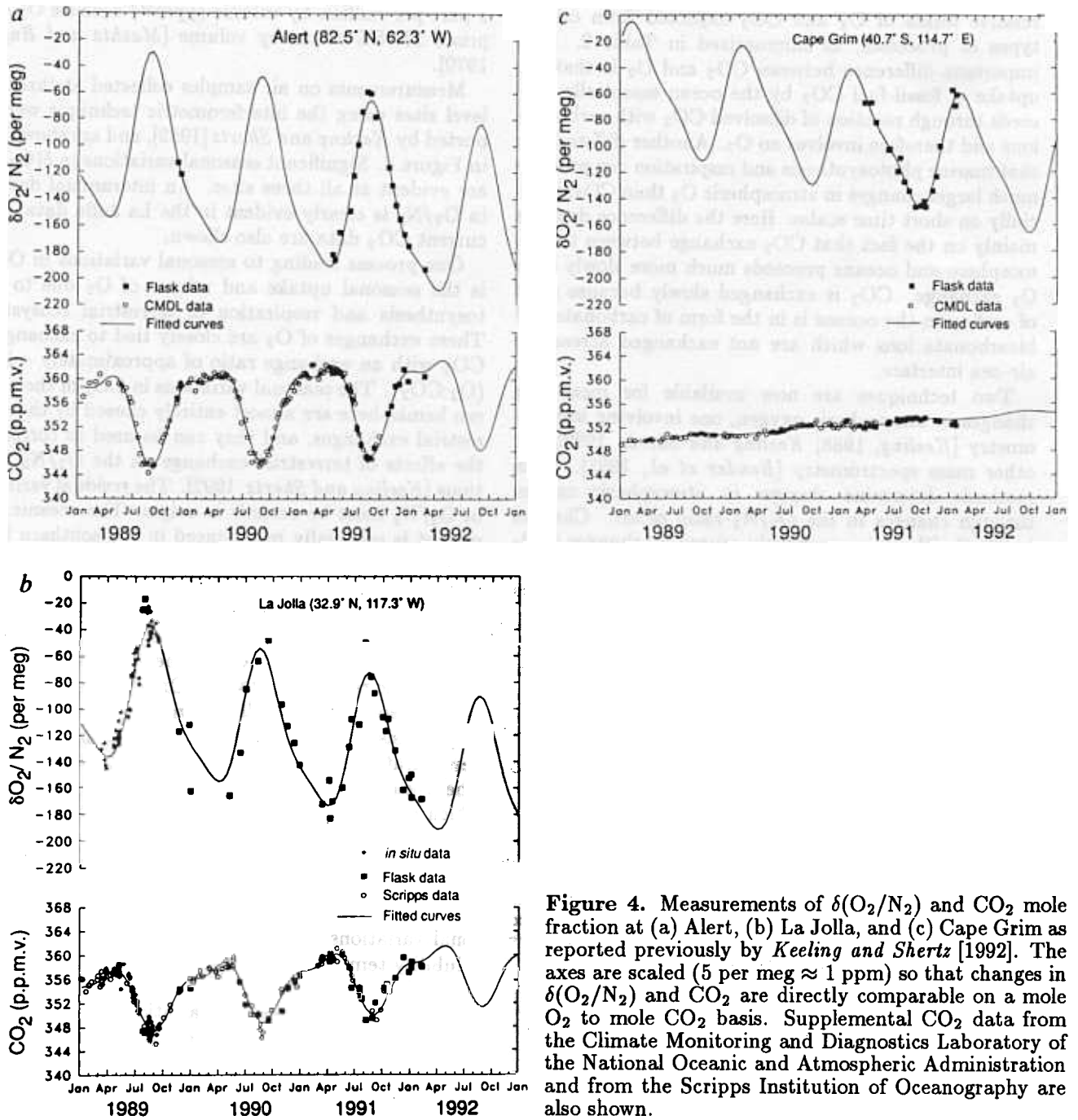


Figure 4. Measurements of $\delta(O_2/N_2)$ and CO_2 mole fraction at (a) Alert, (b) La Jolla, and (c) Cape Grim as reported previously by Keeling and Shertz [1992]. The axes are scaled (5 per meg \approx 1 ppm) so that changes in $\delta(O_2/N_2)$ and CO_2 are directly comparable on a mole O_2 to mole CO_2 basis. Supplemental CO_2 data from the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration and from the Scripps Institution of Oceanography are also shown.

ment manufacturing, O is the oceanic CO_2 sink, and B is the net source of CO_2 from terrestrial ecosystems (B can be positive or negative), all in units of moles yr^{-1} . Likewise, we can represent the budget for atmospheric oxygen according to

$$\Delta O_2 = -F - H - \alpha_B B \quad (4)$$

where ΔO_2 is the change in atmospheric oxygen, H is the O_2 sink owing to the oxidation of elements other than carbon (predominately hydrogen) in fossil fuels, and α_B represents the $O_2:C$ exchange ratio for terrestrial biomass.

Adding Eqs. (3) and (4), and solving for O yields

$$O = -(\Delta O_2 + H) - (\Delta CO_2 - C) - (\alpha_B - 1)B \quad (5)$$

The last term on the right-hand side of Eq. (5) can be evaluated by solving Eq. (4) for B , although this term is virtually negligible since $\alpha_B \approx 1$. Solving Eq. (4) for B yields

$$B = -(1/\alpha_B)(\Delta O_2 + F + H) \quad (6)$$

These equations show how observations of the change in atmospheric oxygen combined with estimates of fossil-fuel CO_2 production and O_2 consumption can be used to directly calculate the net exchange of CO_2 with the oceans and with the land biosphere.

Using preliminary estimates of the O_2 trend based on the data shown in Figure 4, Keeling and Shertz [1992] derive an oceanic uptake of 3.0 ± 2.0 gT C/yr ($1 \text{ gT} = 10^{15} \text{ g}$) and a net terrestrial carbon sink of 0.2 ± 2.0 gT C/yr for the 1989–1991 period. This estimate is clearly preliminary, and the uncertainties are too large to make these results very useful in constraining CO_2 sinks. The primary source of uncertainty comes from uncertainty in the O_2 trend, and this uncertainty should decrease as longer records are obtained.

Bender *et al.* [1994b] have extended our knowledge of variations in atmospheric O_2/N_2 ratio back over the past decade by measurements on air samples extracted from glacial firn at Vostok Station, Antarctica. The detected O_2/N_2 variations imply that the terrestrial biosphere was neither a large source nor sink of CO_2 over this longer period, agreeing with Keeling and Shertz [1992], although the uncertainties in this preliminary work are again quite large. Attempts to extend the records even further into the past from air extracted from bubbles in the glacial ice have so far been frustrated by processes which fractionate O_2 relative to N_2 in the ice bubbles or during the extraction process [Craig *et al.*, 1988; Sowers *et al.*, 1989; Bender *et al.*, 1995].

Although uptake of anthropogenic CO_2 by the oceans has no effect on atmospheric O_2 , it is possible that natural variability in the oceans could lead to net O_2 exchange with the oceans on interannual time scales. This possibility, which was neglected in Eq. (4), would complicate the use of O_2/N_2 data for discriminating between terrestrial and oceanic sinks for CO_2 . Such air-sea exchanges are especially likely on the 3 to 6 year time scale of the El Niño phenomenon [Keeling and Severinghaus, 1994] which means that the O_2/N_2 records will probably need to span several El Niño events before the data can be used to place firm constraints on the sources and sinks of anthropogenic CO_2 .

Conclusions

This review has discussed the controls of the oxygen isotope ratios in atmospheric CO_2 and O_2 and in the O_2/N_2 ratio and how measurements of these quantities can be used to study the material exchanges with biota over large areas. Measurements of the $^{18}O/^{16}O$ ratio of atmospheric CO_2 can provide information on stomatal conductance and gross primary production of terrestrial ecosystems. Measurements of variations in the $^{18}O/^{16}O$ ratio of atmospheric O_2 can provide information on variations in the isotopic composition of globally averaged metabolic water, which is linked to the ratio of gross primary production on land versus the ocean. Measurements of the O_2/N_2 ratio can provide information on net rates of carbon storage or release from the terrestrial biosphere and on rates of carbon fixation in the ocean.

Acknowledgments. I thank Joe Berry for first articulating to me the idea of using $\delta^{18}O$ in CO_2 for constrain-

ing GPP and stomatal conductances. This work has been supported by the Environmental Protection Agency Global Change Research Program, IAG#DW49935603-01-2, and the National Science Foundation under grant ATM-9309765.

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(Received July 12, 1994; accepted November 22, 1994.)