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 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

\[ \delta = \left( \frac{^{18}O/^{16}O}_{\text{sample}} / \frac{^{18}O/^{16}O}_{\text{standard}} \right) - 1 \] (1)

where the δ value is customarily multiplied by 1000 and expressed in per mille (‰). Bottinig 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 Bottinig 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; Faurh 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 H₂¹⁸O evaporates preferentially relative to H₂¹⁶O. 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].
A global steady-state budget for $\delta^{18}O$ 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 seawater. One significant source of uncertainty here is the global average isotopic composition of chloroplast water. Logically, the $\delta^{18}O$ 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

![Diagram of atmospheric CO$_2$ cycle](image)

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 $10^{18}$ 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 $+5\%$, 34% come from soil water at an average of $-7\%$, and 21% come from seawater at an average of $1\%$. 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% less enriched in 18O compared to water at the evaporating surface [Yakir et al., 1993; Yakir et al., 1994]. The difference in δ18O between chloroplasts and evaporation sites probably varies significantly from species to species [Yakir et al., 1993].

A global model describing oxygen atom exchanges of CO2 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 Δf (see Table 1) against 18O on net uptake of CO2. The isotopic exchange flux between the atmosphere and leaves is thus obtained by multiplying Δf by net flux of CO2 into the leaves (basically equal to gross primary production, GPP). The factor Δf is not a true fractionation factor because it depends on the isotopic composition of atmospheric CO2. Δf is nevertheless useful because it can be measured in controlled experiments as well as modeled over the surface of the earth [Farquhar et al., 1983].

The latitudinal distribution of Δf as estimated by Farquhar et al. [1993], is shown in Figure 2. Also shown is the latitudinal variation of CO2 in equilibrium with surface seawater (δ*), the isotopic composition of CO2 returned to the atmosphere through soils (δf), the sum δf + Δf, and the annual mean surface values of δ18O of CO2. Changes with leaves and soils tend to drive the local δ18O of atmospheric CO2 towards the sum δf + Δf. This sum tends to decrease towards high latitudes in the northern hemisphere, following the depletion of 18O/16O of precipitation. The latitudinal gradient in δf + Δf can account qualitatively for the latitudinal gradient in 18O/16O of CO2 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 18O/16O ratio of CO2 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 18O/16O of CO2 during the warmer months when atmospheric CO2 exchanges most rapidly with leaf and soil reservoirs which are depleted in 18O/16O at middle and high northern latitudes. The ratio will tend to increase during other seasons as a result of transport of higher 18O/16O ratios from more southern latitudes. Other factors, such as seasonal variations in soil water 18O/16O ratios, in leaf water isotopic enrichment, and in the ratio of CO2 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 18O/16O ratios of CO2? Farquhar et al. [1993] propose using the measurements to distinguish between CO2 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 CO2 with Terrestrial Ecosystems

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_a</td>
<td>Atmospheric CO2 partial pressure (pCO2)</td>
</tr>
<tr>
<td>C_e</td>
<td>pCO2 in chloroplasts</td>
</tr>
<tr>
<td>C^18O_a</td>
<td>Atmospheric C^18O/16O partial pressure</td>
</tr>
<tr>
<td>R_a</td>
<td>18O/16O ratio of atmospheric CO2</td>
</tr>
<tr>
<td>R_c</td>
<td>18O/16O ratio of CO2 in equilibrium with chloroplast water</td>
</tr>
<tr>
<td>R_s</td>
<td>18O/16O ratio of CO2 in equilibrium with soil water</td>
</tr>
<tr>
<td>R_{PDB}</td>
<td>18O/16O ratio of CO2 derived from the carbonate standard Pee Dee Belemnite [see Friedman and O’Neil, 1977]</td>
</tr>
<tr>
<td>δ_a</td>
<td>(R_a - R_{PDB})/R_{PDB}</td>
</tr>
<tr>
<td>δ_e</td>
<td>(R_e - R_{PDB})/R_{PDB}</td>
</tr>
<tr>
<td>δ_c</td>
<td>(R_c - R_{PDB})/R_{PDB}</td>
</tr>
<tr>
<td>δ_f</td>
<td>δ_c + c_{soil}</td>
</tr>
<tr>
<td>F_{in}</td>
<td>Gross flux of CO2 into stomata</td>
</tr>
<tr>
<td>F_{out}</td>
<td>Gross flux of CO2 out of stomata</td>
</tr>
<tr>
<td>R</td>
<td>Flux of CO2 out of soil from root and soil respiration</td>
</tr>
<tr>
<td>α_{sof}</td>
<td>Fractionation factor of diffusion through stomata (same both directions)</td>
</tr>
<tr>
<td>α_{soil}</td>
<td>Fractionation factor for diffusion out of soil</td>
</tr>
<tr>
<td>c_{soil}</td>
<td>α_{soil} = 1</td>
</tr>
<tr>
<td>c_{soil}</td>
<td>α_{soil} = 1</td>
</tr>
<tr>
<td>A</td>
<td>Gross primary production (A = F_{in} - F_{out})</td>
</tr>
<tr>
<td>Δf</td>
<td>Effective discrimination against C^18O/16O relative to net CO2 assimilation [Farquhar et al., 1993]; Δf = (C_f/(C_f - C_e))(δ_e - δ_a)</td>
</tr>
<tr>
<td>M</td>
<td>Number of moles of air in the atmosphere</td>
</tr>
<tr>
<td>N</td>
<td>Net ecosystem production (N = F_{in} - F_{out} - R)</td>
</tr>
</tbody>
</table>

### Equations:

1. **Mass balance of atmospheric CO2:**
   \[
   M \frac{dC_a}{dt} = F_{out} - F_{in} + R
   \]
   \[\text{(A)}\]

2. **Mass balance of atmospheric C^18O/16O:**
   \[
   M \frac{d(R_a C_a)}{dt} = \alpha_{soil} R_c F_{out} - \alpha_{soil} R_a F_{in} + \alpha_{soil} R_c R_e R
   \]
   \[\text{(B)}\]

3. **Flux/gradient proportionality:**
   \[
   F_{out}/(F_{in} - F_{out}) = C_f/(C_f - C_e)
   \]
   \[\text{(C)}\]

4. **Combining (A) and (B):**
   \[
   M \frac{dR_a}{dt} = \alpha_{soil} (R_c - R_a) F_{out} - R_a (\alpha_{soil} - 1)(F_{in} - F_{out}) + (\alpha_{soil} R_c - R_a) R
   \]
   \[\text{(D)}\]

5. **Rearranging (D):**
   \[
   M \frac{dR_a}{dt} = \alpha_{soil} (R_c - R_a) F_{out} + (\alpha_{soil} - 1)(R_c - R_a) R + F_{out}
   \]
   \[\text{(E)}\]

6. **FORMULATION 1 (results from converting (D) to δ notation):**
   \[
   M C_a \frac{d\delta_a}{dt} = (\delta_e - \delta_a) F_{out} + (\delta_e - c_{soil}) R - c_{soil} N
   \]
   \[\text{(F)}\]

7. **FORMULATION 2 (combining (C) and (D), and converting to δ notation):**
   \[
   M C_a \frac{d\delta_a}{dt} = A \Delta f + (\delta_e - \delta_a) R
   \]
   \[\text{(G)}\]

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1. See Tans et al., 1993, for example of approximations used.
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/oo [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 \( H_2O \), while respiration preferentially removes \( ^{16}O \) 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 $O_2$ 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 $O_2$ utilization depletes a significant fraction of the $O_2$ originally present in the water. If total depletion occurred, then the effective fractionation for respiration in the deep sea would be zero because the $^{18}O/^{16}O$ ratio of the removed $O_2$ would be equal to the $^{18}O/^{16}O$ ratio of the $O_2$ originally dissolved in the water. In the case where $O_2$ is only partially depleted, the effective respiratory fractionation factor can be calculated based on the percentage $O_2$ 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], Keddon et al. [1993], and Bender [1990], and using estimates of the global $O_2$ 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

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**Figure 3.** The global steady-state budget for the oxygen isotopes of atmospheric $O_2$ per Bender et al. [1994]. Fluxes are in units of $10^{15}$ moles $O_2$ yr$^{-1}$. The $^{18}O$ 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 $O_2$ flux from leaves thus exceeds the net $O_2$ production by leaves, i.e., the $O_2$ 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%/o adopted from Farquhar et al. [1993] for average chloroplast water. A value of 8.7%/o 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 18O/16O of CO2 would be out of balance. One possible way of reconciling both the CO2 and O2 isotope budgets might be by increasing the 18O of chloroplast water and decreasing the 18O of CO2 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 O2 and CO2 budgets depend on different weighted averages of chloroplast water. For the O2 budget, the average needs to be weighted by GPP plus photosynthesis, while for CO2 the average needs to be weighted by the flux of CO2 out of stomata, which is equal to the gross flux of CO2 into stomata minus GPP. In any case more work is needed to construct mutually consistent budgets for 18O in both atmospheric O2 and CO2.

Bender et al. [1994a] estimate that the Dole effect which would result from exchanges with the oceans alone is around 2 to 3%/o lower than that which would result from terrestrial exchanges alone (see Figure 3). This difference would be even larger if a 18O value higher than 4.4%/o 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 18O/16O of O2 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 18O/16O ratio of atmospheric O2 has closely followed the 18O/16O 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 18O/16O ratio between atmospheric O2 and surface seawater, has been constant to around ±0.5%/o 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 18O variations in ice core O2 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 18O of atmospheric O2 must lag behind variations of 18O in surface seawater by the turnover time of atmospheric O2 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 18O of atmospheric O2 on shorter time scales? Temporal and spatial surveys [Dole et al., 1984; Kroopnick and Craig, 1972] showed that 18O in the present atmosphere is constant to at least 0.25%/o. More recent tropospheric measurements indicate that 18O is constant to at least 0.03%/o (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 18O to be lower in summer than in winter in both northern and southern hemispheres by about 0.02%/o. This estimate is based on assuming that the 0.01% seasonal increase in the atmospheric O2/N2 ratio (see next section) is driven by the input of photosynthetic O2 that is 20%/o lower in 18O than atmospheric O2. 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 18O. Detecting such small changes may eventually be feasible with very precise mass spectrometric measurements.

In summary, our knowledge of variations in 18O of atmospheric O2 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 O2/N2 Ratio**

The atmospheric reservoirs of O2 and CO2 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 O2 abundance. These reactions also produce and destroy CO2, but the chemistry of atmospheric CO2 is further complicated by reactions with seawater. In seawater, CO2 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 O2 and CO2 can be quantified in terms of the
relative fluxes of O\text{2} and CO\text{2} expected from certain types of processes, as summarized in Table 2. One important difference between CO\text{2} and O\text{2} is that the uptake of fossil-fuel CO\text{2} by the ocean essentially proceeds through reaction of dissolved CO\text{2} with carbonate ions and therefore involves no O\text{2}. Another difference is that marine photosynthesis and respiration can produce much larger changes in atmospheric O\text{2} than CO\text{2}, especially on short time scales. Here the difference depends mainly on the fact that CO\text{2} exchange between the atmosphere and oceans proceeds much more slowly than O\text{2} exchange. CO\text{2} 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 O\text{2}/N\text{2} ratio of air. Changes in the O\text{2}/N\text{2} ratio are mainly caused by changes in O\text{2} because N\text{2} is constant to a very high level. Like isotopic ratios, the O\text{2}/N\text{2} ratio is expressed as deviations from a reference

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

(2)

The resulting deviations are multiplied by $10^4$ 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 1 part-per-million by volume (ppmV) because O\text{2} comprises 20.95% of air by volume [Machta and Hughes, 1970].

Measurements on air samples collected at three seal-level sites using the interferometric technique were reported by Keeling and Shertz [1992], and are shown here in Figure 4. Significant seasonal variations in $\delta(O_2/N_2)$ are evident at all three sites. An interannual decrease in O\text{2}/N\text{2} is clearly evident in the La Jolla data. Concurrent CO\text{2} data are also shown.

One process leading to seasonal variations in O\text{2}/N\text{2} is the seasonal uptake and release of O\text{2} due to photosynthesis and respiration of terrestrial ecosystems. These exchanges of O\text{2} are closely tied to exchanges in CO\text{2} with an exchange ratio of approximately $-1.05:1$ (O\text{2}:CO\text{2}). The seasonal variations in CO\text{2} in the northern hemisphere are almost entirely caused by these terrestrial exchanges, and they can be used to correct for the effects of seasonal exchange on the O\text{2}/N\text{2} variations [Keeling and Shertz, 1992]. The residual variations in O\text{2}/N\text{2} must be oceanic in origin. The oceanic component is especially pronounced in the southern hemisphere where the seasonal O\text{2}/N\text{2} variations are accompanied by only very small variations in CO\text{2}.

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 O\text{2} 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 O\text{2}/N\text{2} because of the solubility temperature dependence of O\text{2} and N\text{2} [Keeling and Shertz, 1992].

Measurements of seasonal variations in O\text{2}/N\text{2} 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 O\text{2} between the euphotic zone and deeper waters. Atmospheric oxygen data may be especially helpful in determining productivities over large regions because the air mixage so rapidly.

Measurements of O\text{2}/N\text{2} 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 CO\text{2} according to

$$\Delta CO_2 = F + C - O + B$$

(3)

where $\Delta CO_2$ is the annual averaged change in atmospheric CO\text{2}, $F$ is the source of CO\text{2} from burning fossil fuels, $C$ (virtually negligible) is the CO\text{2} source from ce-
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

\[
\Delta O_2 = -F - H - \alpha_B B \tag{4}
\]

where \( \Delta O_2 \) 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 \( \alpha_B \) represents the \( O_2:CO_2 \) exchange ratio for terrestrial biomass.

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

\[
O = -(\Delta O_2 + H) - (\Delta CO_2 - C) - (\alpha_B - 1)B \tag{5}
\]

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

\[
B = -(1/\alpha_B)(\Delta O_2 + F + H) \tag{6}
\]

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 \( \text{O}_2 \) trend based on the data shown in Figure 4, Keeling and Shertz [1992] derive an oceanic uptake of \( 3.0 \pm 2.0 \text{ gT C/yr} \) (1 \text{ gT} = 10^{12} \text{ g}) and a net terrestrial carbon sink of \( 0.2 \pm 2.0 \text{ gT C/yr} \) for the 1980–1991 period. This estimate is clearly preliminary, and the uncertainties are too large to make these results very useful in constraining \( \text{CO}_2 \) sinks. The primary source of uncertainty comes from uncertainty in the \( \text{O}_2 \) trend, and this uncertainty should decrease as longer records are obtained.

Bender et al. [1994b] have extended our knowledge of variations in atmospheric \( \text{O}_2/\text{N}_2 \) ratio back over the past decade by measurements on air samples extracted from glacial firn at Vostok Station, Antarctica. The detected \( \text{O}_2/\text{N}_2 \) variations imply that the terrestrial biosphere was neither a large source nor sink of \( \text{CO}_2 \) 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 glacier ice have so far been frustrated by processes which fractionate \( \text{O}_2 \) relative to \( \text{N}_2 \) in the ice bubbles or during the extraction process [Craik et al., 1988; Sowers et al., 1989; Bender et al., 1995].

Although uptake of anthropogenic \( \text{CO}_2 \) by the oceans has no effect on atmospheric \( \text{O}_2 \), it is possible that natural variability in the oceans could lead to net \( \text{O}_2 \) exchange with the oceans on interannual time scales. This possibility, which was neglected in Eq. (4), would complicate the use of \( \text{O}_2/\text{N}_2 \) data for discriminating between terrestrial and oceanic sinks for \( \text{CO}_2 \). Such air–sea exchanges are especially likely on the 3 to 6 year time scale of the El Nino phenomenon [Keeling and Severinghaus, 1994] which means that the \( \text{O}_2/\text{N}_2 \) records will probably need to span several El Nino events before the data can be used to place firm constraints on the sources and sinks of anthropogenic \( \text{CO}_2 \).

Conclusions

This review has discussed the controls of the oxygen isotope ratios in atmospheric \( \text{CO}_2 \) and \( \text{O}_2 \) and in the \( \text{O}_2/\text{N}_2 \) ratio and how measurements of these quantities can be used to study the material exchanges with biota over large areas. Measurements of the \( ^{18}\text{O}/^{16}\text{O} \) ratio of atmospheric \( \text{CO}_2 \) can provide information on stomatal conductance and gross primary production of terrestrial ecosystems. Measurements of variations in the \( ^{18}\text{O}/^{16}\text{O} \) ratio of atmospheric \( \text{O}_2 \) 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 \( \text{O}_2/\text{N}_2 \) 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.

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