

# Heavy carbon dioxide

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THE isotopes of oxygen in atmospheric carbon dioxide have long suffered from neglect — as one veteran of the business has put it, “figuring out the carbon isotopes was enough work without having to bother about the oxygen isotopes as well”. Well, people are finally starting to bother. And as Farquhar *et al.* now show (on page 439 of this issue<sup>1</sup>), the oxygen isotopes should provide valuable information on exchanges of carbon between the Earth’s atmosphere, oceans and terrestrial biota.

Globally, there is much more oxygen in water and oxygen gas than in CO<sub>2</sub>. Oxygen atoms in CO<sub>2</sub> are not exchanged with water vapour or oxygen gas; rather, such exchange takes place only when CO<sub>2</sub> is dissolved in liquid water and only when the dissolved CO<sub>2</sub> is hydrolysed as carbonic acid. The hydrolysis reaction is so slow that a CO<sub>2</sub> molecule must remain dissolved in water for at least 20 seconds to have much chance of exchanging oxygen atoms with the water. In general, allowing for kinetic and equilibrium fractionation, the ratio of oxygen isotopes (<sup>18</sup>O and <sup>16</sup>O)

in atmospheric CO<sub>2</sub> should follow the <sup>18</sup>O/<sup>16</sup>O ratio of the liquid water reservoirs with which the atmosphere makes most frequent and prolonged contact.

Those ratios vary considerably. Cloud water, rain water and soil water are depleted in H<sub>2</sub><sup>18</sup>O relative to sea water because fractional distillation in the atmosphere produces lower <sup>18</sup>O/<sup>16</sup>O in precipitation at higher latitudes. Leaf water is enriched relative to soil water by evapotranspiration because H<sub>2</sub><sup>18</sup>O evaporates less readily than H<sub>2</sub><sup>16</sup>O.

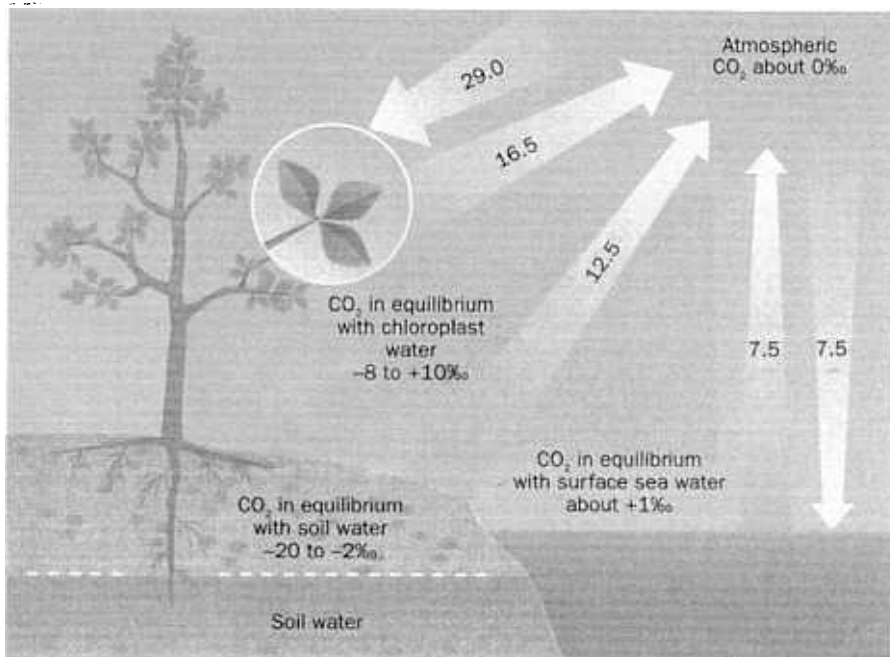
Previously, the oceans were believed to be the primary reservoir for exchange of oxygen atoms in CO<sub>2</sub> because early measurements showed that the <sup>18</sup>O/<sup>16</sup>O ratio of atmospheric CO<sub>2</sub> was very close to the value expected for equilibrium with surface sea water<sup>2,3</sup>. Subsequent measurements, however, revealed large-scale patterns in <sup>18</sup>O/<sup>16</sup>O of CO<sub>2</sub> that were out of sync with what would be expected from calculations based on the temperature variations at the sea surface<sup>4-6</sup>. Particularly interesting was the observation by

Francey and Tans<sup>6</sup> that the ratio of <sup>18</sup>O to <sup>16</sup>O in CO<sub>2</sub> is much lower at high latitudes in the Northern Hemisphere. Maintenance of this deficit in spite of vigorous atmospheric mixing means that the turnover time of oxygen atoms in CO<sub>2</sub> must be as short as two years. This is much less than the exchange time for CO<sub>2</sub> with the oceans (about 10 years) and, in fact, is shorter than the exchange time for carbon atoms in CO<sub>2</sub> with any reservoir.

What process could exchange the oxygen atoms but not the carbon atoms in atmospheric CO<sub>2</sub>? Francey and Tans speculated that a large fraction of the CO<sub>2</sub> that enters leaf cells was leaking back out to the atmosphere after exchanging oxygen atoms with leaf water. Although the typical residence time for a CO<sub>2</sub> molecule in leaf water is less than one second, oxygen atom exchange could occur with the help of the enzyme carbonic anhydrase, which is present in the chloroplasts of leaf cells and dramatically speeds up the hydrolysis reaction.

Farquhar *et al.* now show that water in the chloroplasts, where oxygen exchange occurs, has effectively the same isotopic composition as water at the evaporating sites in the leaves. This allows them to quantify the ideas of Francey and Tans with the use of a relatively simple model relating the isotope exchanges to the gross primary production of plants. Even so, the model necessarily requires keeping track of a large number of variables — the isotopic composition of water in the soil and air, leaf temperature, water vapour pressure in the air, the fraction of CO<sub>2</sub> that diffuses back out of the leaf, and gross primary production — and producing maps of these variables over the surface of the Earth. Farquhar *et al.* test their model by showing that it produces the correct <sup>18</sup>O/<sup>16</sup>O ratio for bulk atmospheric CO<sub>2</sub> (see figure), and then use the model to show qualitatively how the deficit in <sup>18</sup>O/<sup>16</sup>O of CO<sub>2</sub> at northern high latitudes arises from the decrease in <sup>18</sup>O/<sup>16</sup>O of soil and leaf water at these latitudes.

The logical next step for the authors is to combine their model with numerical simulations of large-scale air motions so they can test the predictions against observed variations in <sup>18</sup>O/<sup>16</sup>O of CO<sub>2</sub>. One area needing more work is the iso-



The global cycle for oxygen isotopes of atmospheric CO<sub>2</sub>. Some 55% of the CO<sub>2</sub> that diffuses into the chloroplasts of leaf cells diffuses back out to the atmosphere after exchanging oxygen atoms with the water in the chloroplasts. This exchange drives the <sup>18</sup>O/<sup>16</sup>O ratio of atmospheric CO<sub>2</sub> towards the value expected from equilibrium with chloroplast water. The remaining 45% of CO<sub>2</sub> is taken up by photosynthesis, and eventually returns to the atmosphere through respiration or decomposition in the soil. This fraction, known as gross primary production, drives the <sup>18</sup>O/<sup>16</sup>O ratio of atmospheric CO<sub>2</sub> towards equilibrium with soil water. (Note that the kinetic isotope fractionations caused by diffusion into leaves and out through soil tend to cancel.) Roughly 45% of the oxygen atoms in atmospheric CO<sub>2</sub> comes from chloroplast water at an average isotopic composition of +5‰, 34% come from soil water at an average of -7‰, and 21% come from sea water at +1‰. This combination yields atmospheric CO<sub>2</sub> at 0‰. The annual CO<sub>2</sub> fluxes shown are in units of 10<sup>15</sup> moles of carbon. The <sup>18</sup>O/<sup>16</sup>O ratios of CO<sub>2</sub> are expressed as deviations ( $\delta = (^{18}\text{O}/^{16}\text{O}) / (^{18}\text{O}/^{16}\text{O})_{\text{PDB}} - 1$ ) from the ratio of the carbonate standard Pee-Dee Belemnite (PDB). The deviations are multiplied by 1,000 and expressed in per mil (‰).

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topic composition of chloroplast water because some studies have indicated that chloroplast water is not always as enriched in  $^{18}\text{O}$  as the water at the evaporating sites in leaves<sup>7,8</sup>. Eventually, the aim is to use  $^{18}\text{O}/^{16}\text{O}$  data to tie down uncertainties in the exchange of  $\text{CO}_2$  and water with terrestrial ecosystems.

One such application proposed by Farquhar *et al.* is to use the data to constrain estimates of net uptake or release of carbon from terrestrial ecosystems.

This is likely to prove difficult because such net fluxes produce only small variations in  $^{18}\text{O}/^{16}\text{O}$  which will probably be masked by larger variations caused by other processes. The unique value of the oxygen isotopes is their sensitivity to rates of gross primary production and rates of diffusion through stomata, as these exchanges can produce large variations in the isotopes without producing detectable changes in the carbon isotopes or the total concentration of  $\text{CO}_2$  (refs 6, 7).

Perhaps the most remarkable outcome of this work is the confirmation that the minuscule amount of water in chloroplasts actually dominates the isotopic signature of oxygen atoms in atmospheric  $\text{CO}_2$ . Score another point for those who argue that biology rules the chemistry of the Earth. □

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