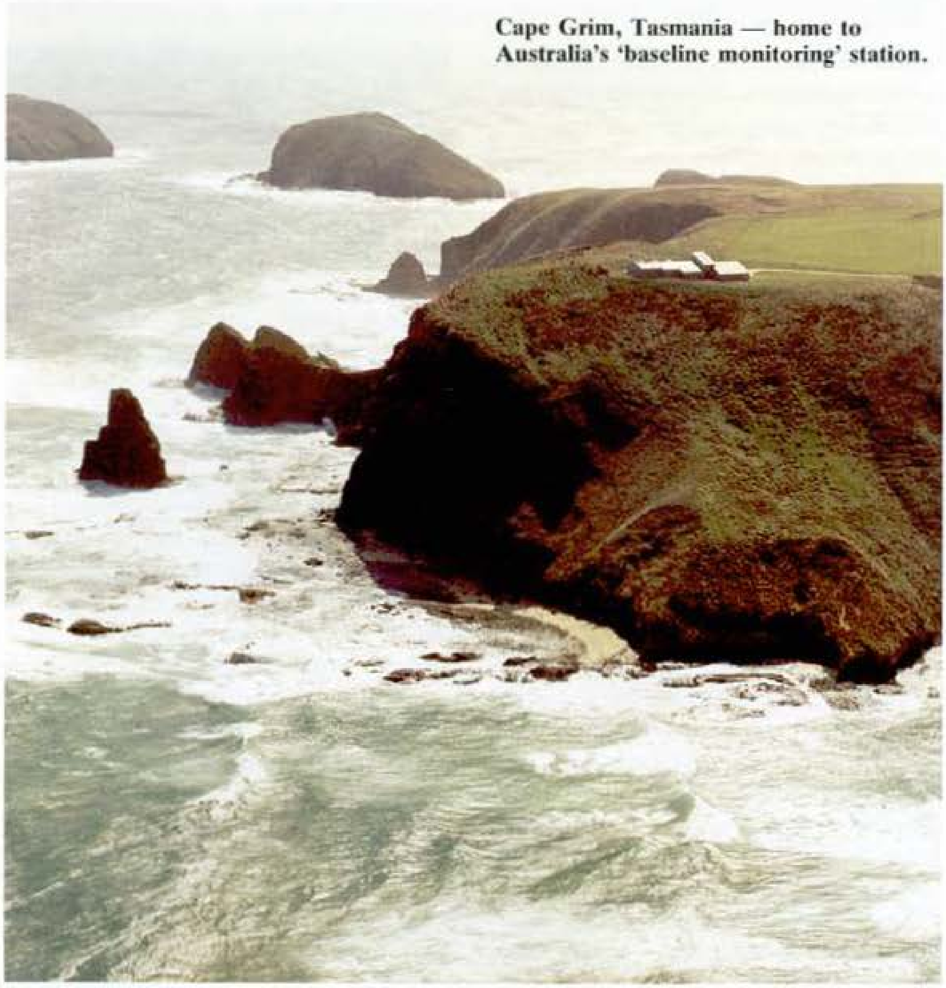
How plants alter the air's CO_2

The most careful analysis of air pumped into sampling flasks at 'baseline monitoring' stations around the world has shown a curious anomaly. One particular isotope of oxygen in carbon dioxide — oxygen-18 — is slightly less abundant in the Northern Hemisphere than in the Southern.


Cape Grim, Tasmania — home to Australia's 'baseline monitoring' station.

Oxygen in carbon dioxide comes in three forms — the common oxygen-16 variety (99·76% of the total) and the rarer oxygen-17 (0·04%) and oxygen-18 (0·20%) isotopes. Measurements by CSIRO scientists show that, for every 1000 molecules of carbon dioxide containing oxygen-18 in the south, we have only about 998 in the north. Although the difference is small, it has big implications.

Why are those two molecules missing? The most likely explanation the discoverers of the anomaly have come up with invokes the power of the earth's green plants, 90% of which grow in the Northern Hemisphere, where most of the world's land mass lies.

No, the plants aren't performing isotope-altering nuclear reactions. But Dr Roger Francey of the CSIRO Division of Atmospheric Research and his collaborator Dr Pieter Tans of the University of Colorado calculate that, to effect the transmutation and support a two-in-a-thousand excess in the Northern Hemisphere against vigorous atmospheric mixing, leafy plants must be doing a lot of work.

They must be pumping about 300 000 million tonnes of carbon, as carbon dioxide, into their stomata each year, dissolving it in leaf water, exchanging oxygen atoms from the carbon dioxide for oxygen atoms from the water, and releasing the (slightly altered) carbon dioxide again. The alteration comes from numbers of oxygen-16 atoms in the carbon dioxide getting exchanged for oxygen-18 ones from water, because isotope abundances in the two compounds differ somewhat.

That annual 300 gigatonnes is considerably greater than the mass of carbon (50 Gt) added to the world's vegetation each year (a quantity called net primary production). It also exceeds the annual gross primary production figure of roughly 150 Gt of carbon, which is the total amount of carbon dioxide that is fixed during photosynthesis (this allows for the 100 Gt that plants breathe out, mostly at night).

The gap can be met, say the researchers, by transitory stomatal 'visiting' of carbon dioxide — a process assumed but not normally measured by plant physiologists.

When plants open their stomata, molecules of carbon dioxide diffuse in, and many are captured by the photosynthetic machinery. However, not all are taken out of circulation in this way. In fact, only about one-third of the molecules are fixed and contribute to gross primary production; the rest of the visitors diffuse back out.

Although physiologists calculate that the length of stay inside a leaf is only about 1 second, the new isotope measurements suggest that some nifty tricks are performed in that time. Dr Francey and Dr Tans propose that the CO_2 molecule — between entering and leaving — has an encounter with a ubiquitous plant enzyme called carbonic anhydrase.

Carbonic anhydrase is a bit of an enigma: it's the second-most abundant protein in green plant tissue, but nobody knows what it's there for. Apparently it doesn't play any essential part in photosynthesis.

Nevertheless, the enzyme is extremely powerful in catalysing the binding of carbon dioxide with water. The time for hydrating a CO_2 molecule is cut about a million-fold by carbonic anhydrase, making this one of the fastest enzyme reactions known.

What the researchers are suggesting is that the enzyme enables atmospheric carbon dioxide to exchange one of its constituent oxygen atoms for an oxygen atom from one of the plant's water molecules. It then separates from the water molecule and leaves the plant — all in about a second.

In effect, plants are using their leaves to expose a very large surface area of water, derived from below the ground, to carbon dioxide. The enzyme very efficiently amplifies the exchange between the two.

Now a key fact is that the abundance of oxygen-18 in water, in general, differs from that in carbon dioxide, so whenever CO_2 dissolves in water the gas gradually becomes enriched or depleted in oxygen-18.

It so happens that, near the Poles, groundwater (like rain-water) has relatively fewer oxygen-18 molecules than near the Equator (the difference is due to the slightly different volatility of $H_2{}^{18}O$ and $H_2{}^{16}O$). Most of the world's plants reside in mid northern latitudes; here, then, exists the best opportunity for atmospheric carbon dioxide to exchange oxygen with oxygen-18-depleted water.

The CSIRO data carry significant implications for global carbon-cycle modelling. If the plant hypothesis proves right, it provides a new way of gauging the activity of the global biosphere, important in constructing models of how plants will respond to rising carbon dioxide levels and for predicting ultimate carbon dioxide concentrations.

In this connection, it's worth noting that the results of CSIRO's isotope-monitoring program at Cape Grim, Tasmania, show clear variations between years, with a maximum oxygen-18 content in the summer of 1983/84. The data also show a regular annual cycle, suggesting seasonal plant activity.

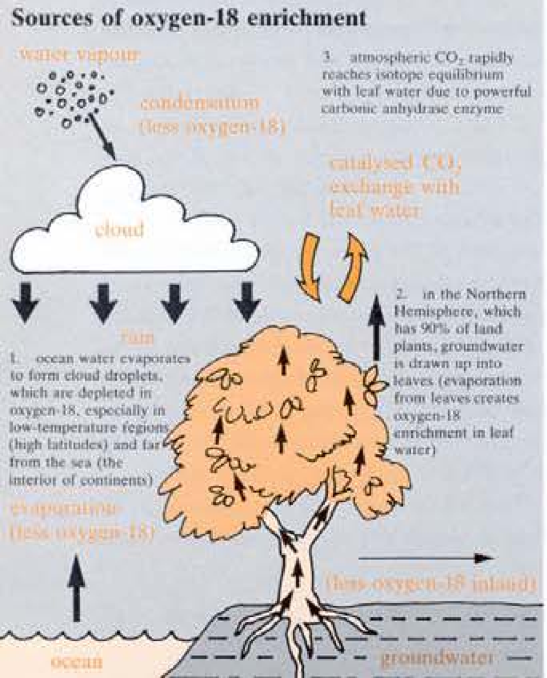
Up pops the latitude effect

Initially, collecting oxygen-18 and oxygen-16 data was incidental to the main business at hand — making measurements of carbon isotope abundances in carbon dioxide sampled at the Cape Grim Baseline Air Pollution Station (jointly operated by the Bureau of Meteorology and the CSIRO Division of Atmospheric Research).

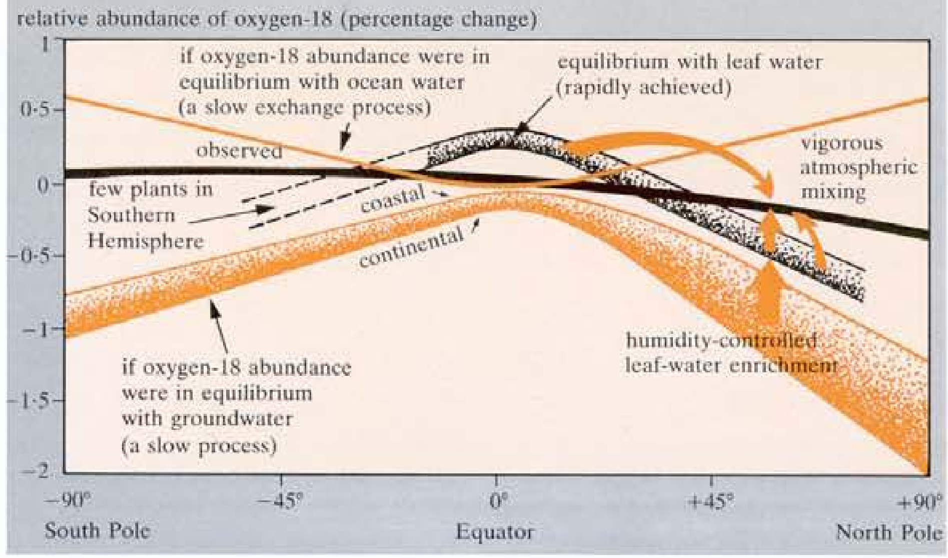
This work involves on-site extraction of the carbon dioxide for a 2-hour period by first cooling an air stream to −70°C to remove water vapour, then cooling to −196°C to trap the CO_2, which is sent to CSIRO laboratories at Aspendale (Melbourne) for analysis. The method is unique, and produces isotope data of superior quality (in terms of accuracy and repeatability) compared with overseas programs.

Results on the relative proportions of carbon-12 and carbon-13 can provide the scientists with valuable information on the size of the global carbon pool and how this

Sources of oxygen-18 enrichment



How (and why) abundance of oxygen-18 in atmospheric CO_2 varies



If the atmosphere were still, we would observe in the Northern Hemisphere an oxygen-18 abundance in atmospheric carbon dioxide the same as that in the CO_2 given out by plants. In the Southern, with much fewer plants, an abundance between the figures for groundwater and ocean-water would be seen. However, because of vigorous atmospheric mixing, carbon dioxide from widespread latitudes comes together, and we get the result shown by the solid black curve.

Secrets from a Pharaoh's tomb

Last year, a team of new-breed archeologists carefully drilled a hole through a 1·6-m-thick limestone slab that ancient Egyptians had used to seal a funeral pit belonging to their Pharaoh, Cheops, at the base of his Great Pyramid.

The modern intruders, under the direction of the United States National Geographic Society and the Egyptian Antiquities Organization, encased their drill within a special air lock. They took little: some litres of the enclosed air, and some photographs (obtained by inserting a miniature cameras through the 8-cm-diameter hole). Then they sealed the hole and were gone, respectfully leaving the 4600-year-old pit to its intended solitude.

The photographs showed a disintegrated wooden boat, perhaps intended for the Pharaoh's journey to immortality.

And what of the air samples? For one thing, they will tell archeologists something about the chemistry of decay processes, and suggest ways of preserving antiquities.

There is also a strong environmental interest — if the pit's seal had been hermetic, and the air proved very old, then scientists would get a figure for the carbon dioxide content of the air back then — long before humans began altering natural levels by burning fossil fuel and clearing forests. Atmospheric scientists have some data from air bubbles trapped in polar ice (see *Ecos* 47), but readings from a different source would provide extra confidence in that vital 'baseline' quantity.

The air was decanted and sent to a number of selected laboratories for accurate analysis of a wide range of atmospheric constituents. Ten litres of recovered air were sent to Dr Francey at the Division of Atmospheric Research for measurement of the stable carbon isotopes.

The age of the air was determined by the presence or absence of modern chemicals (such as chlorofluorocarbons, or CFCs) and by radiocarbon dating of the carbon dioxide. The CFC content proved that air as modern as that over Cairo had found its way in — unfortunately the tomb's seal wasn't very good.

Nevertheless, the carbon dioxide content was twice that outside. Measurement of the carbon isotopes confirmed that this was due to decay of the ancient cedar boat. Abundances of the stable and radioactive isotopes both point to an effective age of the enclosed carbon dioxide of about 1900 years — that is, a mixture of the old (4600 years) and the new.

Finding a Pharaoh's funeral bark. F. El-Baz. *National Geographic*, 1988, **173**, 512–33.

Inside the Cape Grim laboratory, Dr Francey extracts carbon dioxide from air piped down from the rooftop.

is affected by plants and burning fossil fuel (see *Ecos* 28, page 6). However, the mass spectrometer the scientists use to measure relative abundances cannot distinguish $^{12}C^{16}O^{17}O$ from $^{13}C^{16}O^{16}O$ (they have the same mass), so the ^{18}O : ^{16}O ratio provides a way of correcting for this (by assuming a constant ratio between the ^{17}O and ^{18}O abundances). It also proves useful as a cross-check on the integrity of the carbon-isotope data.

A few years ago, Dr Francey noticed that the oxygen-isotope data from Cape Grim showed yearly variations, and he wondered why. At the time, Dr Tans was on an exchange visit at the Division, and Dr Francey sought his help in explaining this puzzle.

The research pair quickly found other data were scarce and very 'noisy'. Where indications of yearly variations were noted, the suggested explanations were, by their calculations, untenable.

Dr Francey and Dr Tans presume that other people's data lose precision on oxygen-18 abundance in CO_2 because of a failure to pre-dry their air samples. Whenever carbon dioxide comes in contact with a film of water (perhaps on the inside of the sampling flask), it tends to dissolve in the water. Chemical experiments show that, in solution, it takes on average some 27 seconds (at 25°C) for the oxygen in a carbon dioxide molecule to exchange with the oxygen in a water molecule.

Around this time, CSIRO was setting up a global air-sampling network. Funded by the National Energy Research, Development and Demonstration Council, Dr Francey and colleagues began monthly collections of clean, pressurised air in 5-L glass flasks from five stations, ranging from Alaska to the South Pole (a further five stations now participate). Unlike comparable flask networks, the CSIRO program takes considerable care to pre-dry the air.

The researchers began to see that the dissolution of carbon dioxide in water, and

Dimensions of the CO_2 picture

The Division of Atmospheric Research's major study of the global carbon cycle was initiated in 1972 by Dr Graeme Pearman. Since then, CSIRO researchers have made high-quality observations of CO_2 concentrations from aircraft over south-eastern Australia, from the Cape Grim (Tasmania) Baseline Air Pollution Station, and from Antarctic stations.

In recent years, the scientists have focused their attention on measuring the isotopic composition of CO_2, for this allows them to pinpoint the sources of variations — over time and from place to place — in CO_2 concentrations. It also allows a more accurate description of the exchange mechanisms simulated in computer models.

The major isotopic ratio they're after is carbon-13 : carbon-12. The size of this ratio depends on how much atmospheric CO_2 ends up in the oceans and how much in land plants.

They are also interested in the carbon-14 : carbon-12 ratio in CO_2 because this gives a radiocarbon 'dating' for it (as carbon-14 undergoes slow radioactive decay). Old CO_2 (from fossil-fuel combustion or from deep-ocean upwelling) has less carbon-14 than modern CO_2 (live plants and surface waters). Carbon-14 analyses of Cape Grim samples are done by collaborating laboratories in Australia and overseas.

The promise of the oxygen-18 : oxygen-16 measurements is that they will provide, for the first time, figures for gross — rather than net — fluxes of CO_2.

A crucial parameter in the prediction of future levels of atmospheric CO_2 is a knowledge of the level prior to the large change brought about over the last 100–200 years by widespread land-use changes and industrialisation.

On this front, most success has come from an analysis of air trapped in Antarctic ice cores (see *Ecos* 47). The faint breath of air liberated from the ice tells us that CO_2 levels in 1850 were about 285 p.p.m. (by volume), compared with current levels of near 350 p.p.m.

Other sources of vintage air may also provide valuable cross-checks, and this is why hopes were held for the air from the Cheops pyramid. Scientists overseas have analysed air bubbles trapped in extremely ancient amber — with mixed and uncertain results — and recently New Zealand scientists sent Dr Francey some air recovered from compressed-air cylinders used 40 years ago to crank flying-boat engines.

Dr Francey's earlier attempt to derive figures for bygone CO_2 levels from measuring the ratio of carbon-13 to carbon-12 in Tasmanian tree rings was complicated by the discovery that the trees' physiology changes in response to increasing atmospheric CO_2, thus modifying the isotopic ratios. (This phenomenon is, however, likely to prove useful in measuring the direct influences of changing atmospheric composition on plants.)

On the theoretical side, the CSIRO scientists have been building, testing, and operating computer models of global carbon transport and exchange. Basically, two types of models have evolved:

- ▷ one-dimensional models (using only horizontal layers in the atmosphere and ocean) for studies of long-term response of the global atmosphere–biosphere–ocean system to changes in atmospheric CO_2 levels (for example, due to fossil-fuel combustion)
- ▷ two-dimensional models (employing horizontal layers and zones of latitude) that reflect the spatial distribution and short-term (seasonal) variations in sources and sinks of atmospheric CO_2

The CSIRO group is now attempting to integrate newly acquired data (in particular, the isotopic data) with the models. They are working with the Centre for Mathematical Analysis at the Australian National University in this exercise. Estimates of important figures such as rates of tropical rainforest destruction, mid latitude reforestation, and biological productivity of the Antarctic oceans are starting to emerge.

Greenhouse impact — new book

'Greenhouse: Planning for Climate Change' is the title of a major new book that explores how climate change induced by the build-up of 'greenhouse gases' may affect Australia.

Edited by Dr Graeme Pearman of the CSIRO Division of Atmospheric Research, it examines possible impacts on Australia's coasts, hydrology and water resources, natural environment, agriculture, and society.

The 760-page book is the proceedings of the conference Greenhouse 87: Planning for Climate Change, held in Melbourne late last year. Copies are available for $70 each from CSIRO Publications, 314 Albert St, East Melbourne, Vic. 3002.

Helen Goodman uses a mass spectrometer to measure carbon dioxide isotopes.

its subsequent hydration, appeared to be essential steps in the control of the oxygen-isotope ratio of atmospheric carbon dioxide. And so they started looking at oxygen-18 abundances in various bodies of water, searching for clues that might explain the observed variations, in particular a clear effect of latitude revealed by the global flask network.

An early suggestion was that equilibrium with the oceans (which are enriched in the heavier oxygen-18 because of preferential evaporation of oxygen-16) could explain the observations. However, the rate of exchange of carbon dioxide with the oceans (about 90 Gt a year) is too slow to account for the observed differences in oxygen-16 : oxygen-18 ratios in the Northern and Southern Hemispheres and, in any case, would lead to a minimum at the Equator (where evaporation is greatest).

No, not quite empty. Flasks of air, shipped from across the world, arrive at the Division of Atmospheric Resarch, Melbourne, for analysis.

Dr Francey and Dr Tans have ruled out two other possible explanations for the different oxygen ratios in atmospheric carbon dioxide in the two Hemispheres — exchange of carbon dioxide with water vapour and with cloud droplets. Both are far too slow and don't lean towards the observed latitudinal pattern anyway.

The combustion of fossil fuel (enriched in oxygen-18) fits the pattern, in that most occurs, with the release of carbon dioxide, in the Northern Hemisphere. However, the amount burnt — about 5 Gt a year — is not nearly enough to account for the observations.

Just as the evaporation of oxygen-18 is slower than that of oxygen-16, so the heavier isotope condenses more slowly than its lighter sibling. Hence cloud droplets are depleted in oxygen-18 compared with ocean-water. Because these steps depend strongly on temperature, a clear latitude effect shows up.

Most of the oxygen-18-depleted water ends up in the ground, out of touch with the atmosphere. But then plants suck up the water through their roots and evaporate some of it to the air; because of the rapid catalysed exchange, this in turn leads to oxygen-18 enrichment of atmospheric carbon dioxide with respect to groundwater (but depleted compared with sea-water). Therein, say the researchers, lies the answer to the original puzzle.

Their one slight reservation concerns a possible small contribution from direct exchange with soil moisture. An uncatalysed exchange would be minute, but it's possible that some catalytic agent in soil accelerates the soil's contribution. However, the researchers have found virtually no data on catalysts in soils to enable them to investigate this effect further.

That plants are the major influence is suggested by another interesting feature of their isotope data. That is, at each sampling site, the carbon dioxide was 0·2% richer in oxygen-18 than the local rain- and groundwater. When Dr Francey and Dr Tans derived a model for this isotopic enrichment (a similar expression has been derived independently by Dr Graham Farquhar of the Australian National University), it predicted a humidity effect on oxygen-18 abundance. This humidity factor should be kept in mind when trying to interpret any year-to-year variations.

And so it seems that plants quietly go about their business of intimately linking the earth with the air. Only now, with isotopic analysis, have we come to appreciate how huge an undertaking that is.

Andrew Bell

More about the topic

Latitudinal variation in oxygen-18 of atmospheric CO_2. R.J. Francey and P.P. Tans. *Nature*, 1987, **327**, 495–7.