THE CARBON CYCLE, ISOTOPES, AND CLIMATE

I

THE SHORT-TERM CARBON CYCLE AND ANTHROPOGENIC IMPACTS

There is considerable reason to believe that the Earth’s climate is linked to atmospheric CO$_2$ concentrations. There are several lines of evidence for this. First, and perhaps, most importantly, is the observation that CO$_2$ gas is transparent to visible radiation but strongly absorbs infrared radiation. Most of the energy the Earth receives from the Sun is the visible part of the spectrum. The Earth looses an equal amount of energy in the form of infrared radiation (if it did not, the Earth’s surface would continually get hotter). Atmospheric CO$_2$ absorbs this outgoing radiation and acts as an insulating layer, keeping the Earth warmer than it otherwise would be. In principle anyway, the higher the atmospheric CO$_2$ concentration, the warmer the Earth’s surface will be. This is the familiar greenhouse hypothesis, first proposed by Savant Ahrrenius in 1895 in a paper entitled “On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground”. No one thought much about this problem until Roger Revelle and Hans Suess warned in the 1950’s that the atmospheric CO$_2$ was increasing due to burning of fossil fuels, and that this could lead to warming of the Earth’s surface.

As Figure 37.1 indicates, carbon cycles rapidly between 5 reservoirs on the surface of the Earth. Of the total carbon in these 5 reservoirs, atmospheric CO$_2$ is only a small part. Roughly equal amounts of carbon are present in the terrestrial biosphere, the atmosphere, and the surface ocean, with somewhat more being present in soil carbon. The bulk of the surficial carbon, about 7 times as much as in the atmosphere, is dissolved in the deep ocean (mainly as HCO$_3^-$). The fluxes of carbon to and from the atmosphere are large relative to the amount of CO$_2$ in the atmosphere; indeed nearly 25% of the atmospheric CO$_2$ ‘turns over’ in a year. The balance of these fluxes controls the concentration of atmospheric

![Diagram of the Carbon Cycle]

Figure 38.1. The Carbon Cycle. Numbers in green show the amount of carbon (in 10$^{15}$ grams or gigatons, Gt) in the atmosphere, oceans, terrestrial biosphere, and soil (including litter, debris, etc.). Fluxes (red) between these reservoirs (arrows) are in Gt/yr. Also shown in the approximate isotopic composition of each reservoir. Magnitudes of reservoirs and fluxes are from Schlesinger (1991), isotopic compositions are from Heimann and Maier-Reimer (1996).
The isotopic composition varies between these reservoirs, primarily due to the fractionation during photosynthesis. In the last several hundred years, man has affected the carbon cycle through burning of fossil fuels and clearing of forests. Both these activities can be viewed as fluxes of carbon to the atmosphere, the former from sedimentary organic carbon, the latter from the terrestrial biosphere. The present fossil fuel flux is between 5 and 6 Gt per year, a reasonably well-known value, and is growing; the deforestation flux is uncertain, but 2 Gt per year is a commonly cited figure. This has resulted in a roughly 0.7% per year annual increase in the concentration of CO$_2$ in the atmosphere (Figure 38.2), as determined by a global system of monitoring stations, the first of which were installed by C. D. Keeling in the late 1950’s at Mauna Loa and the South Pole. This is equivalent to an increase in the mass of atmospheric CO$_2$ reservoir of about 3 Gt/year. This increase in atmospheric CO$_2$ is only about 58% of the fossil fuel flux and 43% of the total estimated anthropogenic carbon flux. Thus 3 or more Gt of carbon are “missing” in the sense they are going into some reservoir other than the atmosphere, presumably the ocean or terrestrial biosphere.

Both sources of the anthropogenic carbon flux, biospheric carbon and sedimentary organic carbon, have highly negative $\delta^{13}$C (the isotopic composition of fossil fuel burned has varied over time from $\delta^{13}$C $\approx -24\%$ in 1850 to $\delta^{13}$C $\approx -27.3\%$ in 1980 as coal has been partly replaced by oil and gas). Thus we might expect to see a decrease in the $\delta^{13}$C of atmospheric CO$_2$. This is indeed observed. Based on measurements of $\delta^{13}$C in tree rings and ice cores, the $\delta^{13}$C of atmospheric CO$_2$ has declined by about 1.5% since 1980.
1800 (e.g., Figure 38.3). This is significantly greater (up to a factor of 2 greater) than that expected from burning of fossil fuel alone, which is one line of evidence that there is has been a significant destruction of the terrestrial biosphere over the last 200 years.

To what degree the “missing” CO$_2$ (i.e., that fraction of CO$_2$ produced by burning fossil fuel and terrestrial biosphere destruction that has not accumulated in the atmosphere) has been taken up by the oceans or by terrestrial reservoirs remains a debated question. Accurate predictions of future increases in atmospheric CO$_2$ require an answer, because storage of carbon in these two reservoirs is quite different. Once stored in the oceans, most carbon is unlikely to re-enter the atmosphere soon. However, increases in the terrestrial biomass or detritus and soil carbon may be unique, short-lived phenomena and, furthermore, may be susceptible to continued human intervention and climate change.

Several teams of investigators have attempted use to $\delta^{13}$C changes in the atmosphere and ocean to determine what has happened to the balance of the anthropogenic carbon. Unfortunately, the uncertainties involved are such that several of these teams have arrived at somewhat different conclusions. The small concentration gradient between hemispheres (as indicated by the similar CO$_2$ concentrations at Mauna Loa and the South Pole in Figure 38.2) requires that much of the anthropogenic CO$_2$ be taken up in the northern hemisphere. Based on global isotopic measurements of $\delta^{13}$C in the atmosphere, Keeling et al. (1989) concluded that the uptake by the oceans was 2.2 Gt/year in 1980. In their model, the hemispheric gradient is explained by a large northern hemisphere oceanic sink (the North Atlantic?). Quay et al. (1992) concluded based on measurement of the depth-integrated change of $\delta^{13}$C in the oceans from 1970 to 1990 that the oceanic uptake rate was about 2.1 Gt/year. Tans et al. (1993) used the isotopic disequilibrium between the atmosphere and surface ocean to estimate an oceanic uptake rate of less than 1 Gt/year. By comparing seasonal and latitudinal variations in atmospheric $\delta^{13}$C, Ciais et al. (1995) concluded that the terrestrial biosphere north of 30°N took up 3.6 Gt/yr in 1992-1993, while the global ocean took up only 1.82 Gt/yr in these years. They concluded that there was a net flux of 1.7 Gt/yr from the tropical terrestrial biosphere (30°S to 30°N) to the atmosphere in these years, presumably because of deforestation. Heimann and Maier-Reimer (1996) also used the rate of $\delta^{13}$C change in the ocean to estimate an oceanic uptake rate of 2.1±0.9 Gt/yr. They also pointed out the importance of the riverine carbon flux to the ocean, which previous workers had neglected. Thus there is a range in estimates of the oceanic uptake of from 1 to 2.2 Gt/yr and a clear answer as to whether the ocean or the terrestrial biosphere is the predominate sink of the “missing” anthropogenic CO$_2$ remains elusive.

Even allowing for a generous ocean uptake of 2 Gt per year leaves at least additional 3 Gt per year, more than the deforestation flux, that is apparently being taken up by the terrestrial biosphere. Ciais et al. (1995) concluded most of this occurs in northern hemisphere temperate and polar regions. This also consistent with the hemispheric gradient in atmospheric CO$_2$. Since most of the fossil fuel burning occurs in the northern hemisphere, we would expect the concentration of CO$_2$ to be slightly higher at Mauna Loa than at the South Pole. This is indeed the case; however, the hemispheric gradient in less
than that predicted by most models of atmospheric CO$_2$ transport, indicating much of the missing CO$_2$ must be taken up in the northern hemisphere.

It would appear then that expansion of the northern hemisphere terrestrial biosphere at least balances, and likely exceeds, deforestation, which now occurs mainly in the tropics. There are several possible explanations for this. These are as follows.

1. As agriculture became more efficient in the 20$^{th}$ century, land cleared for agriculture in Europe and North America in previous centuries has been abandoned and is returning to forest.
2. Average global temperature has increased by over 0.5°C over the last century, perhaps as a result of rising atmospheric CO$_2$ concentrations. This temperature increase may be producing an expansion of boreal forests.
3. Pollution, particularly by nitrates emitted when fossil fuel is burned, may be fertilizing and enhancing growth of the biosphere.
4. As we saw in Lecture 35, plants photosynthesize more efficiently at higher CO$_2$ concentrations, so increasing atmospheric CO$_2$ concentrations can, in principle, stimulate plant growth. Since most plant growth is generally limited by availability of nutrients such as phosphate and nitrate rather than CO$_2$, it is unclear whether such stimulation would actually occur. However, higher CO$_2$ concentrations may allow plants to close their stomata somewhat. Stomata, through which leaves exchange gas with the atmosphere, are pathways both for CO$_2$ into the leaf and for H$_2$O out of the leaf. Closing the stomata somewhat would reduce water loss and therefore may allow plants to survive in drier climates, leading to an expansion of forests and grasslands.

**THE QUATERNARY CARBON ISOTOPE RECORD AND GLACIAL CYCLES**

In our discussion of Quaternary climate cycles, we noted the need for feedback mechanisms to amplify the Milankovitch signal and mentioned that atmospheric CO$_2$ concentration might be one of these. Early evidence that atmospheric CO$_2$ concentration might vary between glacial and interglacial epochs came from carbon isotope studies of deep-sea cores. Shackleton found that seawater $\delta^{13}$C increased during glacial times. He attributed this isotopic change to an increase in the terrestrial biomass that would occur as a result of, among other things, increasing land area due to falling sea level (there is more biological productivity per square meter on land than in the ocean). This would draw down atmospheric CO$_2$ and perhaps provide the necessary feedback to amplify orbital forcing of climate change. Further evidence of varying atmospheric CO$_2$ came from the first measurement of CO$_2$ concentrations in ice cores in the late 1970’s and early 1980’s. These data suggested atmospheric CO$_2$ had fallen to levels as low as 200 ppm or less during glacial epochs.

The data also suggested CO$_2$ had risen quite rapidly at the end of the last glaciation. The rapid changes suggested to Broecker (1982) that the ocean must somehow be involved, since it is a much larger carbon reservoir and exchanges relatively quickly with the atmosphere. He noted that one obvious mechanism, changing the solubility of CO$_2$ in the ocean due to changing temperature (solubility of CO$_2$ increases with decreasing temperature), would produce only about a 20 ppm decrease in atmospheric CO$_2$ during glacial times, and about half this would be offset by decreasing volume of the oceans. Broecker suggested the changes in atmospheric CO$_2$ resulted from changing biological productivity in the oceans, in other words, the effectiveness of the biological pump. He suggested that as sea level rose, phosphorus was removed by biological processes from the ocean and deposited on continental shelves. Because the water column is short above continental shelves, there is less opportunity for falling organic matter to be recycled before being incorporated in the sediment. He supposed that phosphorus is the limiting nutrient in the oceans; lowering its concentration would decrease marine biological productivity and thereby allow the concentration of CO$_2$ in the atmosphere to rise. He also suggested a test of the idea. If his hypothesis were correct, the difference in $\delta^{13}$C between surface and deep water should decrease during interglacial epochs, since this difference is a result of $^{12}$C depletion.
by photosynthesis in surface waters. The test could be carried out by analyzing the carbon isotopic composition of benthic and planktonic forams.

Shackleton and Pisias (1985) carried out this test by analyzing the carbon isotopic composition of a core from the Panama Basin, an area with sufficiently high sedimentation rate to clearly show the changes. They found that there were indeed variations in the difference in isotopic composition between benthic and planktonic foraminifera ($\Delta^{13}C_{P,B}$) that correlated with $\delta^{18}O$ and therefore implied differences between deep and surface water $\delta^{13}C$ (Figure 38.4). These differences in turn implied differences in the biological productivity in the ocean sufficient to cause changes the atmospheric CO$_2$. Indeed, assuming biological activity removes organic carbon and carbonate in a constant ratio, the differences in the $\Delta^{13}C_{P,B}$ suggested changes in the concentration of atmospheric CO$_2$ of over 100 ppm, similar to the range observed in ice cores.

Shackleton and Pisias (1985) also performed a spectral analysis on the $\delta^{13}C$ data and the $\Delta^{13}C_{P,B}$ parameter. The results showed there were important spectral components at periods of 100 kyr, 40 kyr, and 23 kyr, the now familiar Milankovitch periods. Thus $\delta^{13}C$ and atmospheric CO$_2$ are clearly related to climate. From this analysis, however, it is unclear what is cause and what is effect. Looking at the phase of the $\delta^{13}C$ variations relative to those of $\delta^{18}O$, Shackleton and Pisias found that changes in $\Delta^{13}C_{P,B}$ led those of $\delta^{18}O$, suggesting ice volume was responding to CO$_2$ concentrations, and not visa versa. This is an interesting result, but one that is inconsistent with the mechanisms of CO$_2$ change envisioned by both Shackleton and Broecker.

The best record of late Quaternary atmospheric CO$_2$ is that provided air bubbles preserved in the Vostok ice core and analyzed by Barnola et al. (1987), shown in Figure 38.5. Although the details of the record differ somewhat from that predicted by Shackleton and Pisias, the range in concentrations is rather similar to that predicted (Fig. 38.4), showing the general validity of using differences in carbon isotopes as an indicator of atmospheric CO$_2$. In the Vostok record, an increase in CO$_2$ appears to lead an increase temperature by about 1000 years when glacial epochs end. At the end of the last interglacial, however, CO$_2$ appears to lag temperature by as much as 10,000 years, suggesting a complex relationship between CO$_2$, ice volume, and climate.

The exact mechanism by which atmospheric CO$_2$ concentrations change in glacial cycles remains uncertain. As we noted above, a roughly 20ppm decrease in atmospheric CO$_2$ concentration during glacial times would be expected...
from the cooling of the oceans. The exact change will depend on how much ocean cooling occurs, however, and there is now evidence this has been underestimated (continental paleoclimatic records suggest a greater variation in temperatures in the tropics than inferred from marine carbonate records). A roughly $10$ ppm increase in atmospheric CO$_2$ should occur during glacial times because of the decrease in ocean volume. Hence these two effects should produce a net $10$ ppm change, only about $10\%$ of the change actually observed. Changes in the terrestrial biosphere, high latitude peat deposits and soil carbon, the efficiency of the oceanic biological pump, and the vertical circulation of the oceans, may also be important. As we saw in the previous lecture, there is indeed evidence that the deep circulation of the ocean differs between glacial and interglacial periods. These changes potentially affect nutrient levels in the surface water, which in turn could affect the efficiency of the biological pump. Ocean circulation changes may also affect atmosphere-ocean exchange as well as the residence time of carbon in the deep ocean.

Measurement of atmospheric $\delta^{13}$C during glacial periods could help to resolve this question. Looking at Figure 38.1, we can see that since the terrestrial biosphere has lower $\delta^{13}$C than the atmosphere, storage of carbon in the biosphere should raise atmospheric $\delta^{13}$C. On the other hand, since the oceans have higher $\delta^{13}$C than the atmosphere, transfer of carbon from the atmosphere to the ocean should lower atmospheric $\delta^{13}$C, though the effect would be smaller. Thus far there are only sparse data available on the isotopic composition of the CO$_2$ in ice bubbles. These measurements are difficult to make because of the limited amount of CO$_2$ present in the ice. Leuenberger et al. (1992) found that atmospheric $\delta^{13}$C was $0.3\pm0.2\%o$ lower during the last glacial period than at present. The data then are consistent with idea that the oceans are the principal reservoir in which CO$_2$ is stored during glacial periods.

**$\delta^{13}$C in Organic Carbon and Atmospheric CO$_2$ Concentration**

Ice cores are able provide information on atmospheric CO$_2$ concentrations for at best the last several hun-
dred thousand years. There is, however, reason to believe that climate has undergone even more dramatic changes earlier in Earth’s history (for example, the Tertiary variations we considered in the previous lecture). What role has atmospheric CO₂ concentrations played in these climatic variations? An answer is important because of the need to predict the climatic consequences of possible future increases in atmospheric CO₂ resulting from continued burning of fossil fuels.

One possible method of determining paleo-CO₂ concentrations arises from an observed relationship between δ¹³Corg of marine phytoplankton and the concentration of dissolved inorganic CO₂ (Degens et al., 1968; Degens, 1969). The method is illustrated in Figure 38.6: there is an observed inverse correlation between dissolved CO₂ and δ¹³Corg of phytoplankton. We found in Lecture 29 that the fractionation of carbon isotopes during photosynthesis is related to CO₂ concentrations (Figure 29.4). The reason for this, in simple terms, is that when more CO₂ is available, plants are more selective and therefore show a greater preference for ¹²C. Thus in principle at least, [CO₂aq] can be estimated from measurements δ¹³Corg, [CO₂aq] in equilibrium with the atmosphere depends on the partial pressure of atmospheric CO₂ and temperature; hence if temperature is known, the partial pressure of CO₂ can also be estimated.

Figure 38.7 shows an example from Rau (1994) of the calculated [CO₂aq] in surface ocean water over the last 140,000 years using the correlation in Figure 38.6. δ¹³Corg data are from two piston cores, one from the Indian Ocean at 10°N, the other from the Atlantic Ocean at 25°N. These are compared with changes in [CO₂aq] predicted from the observed variations in CO₂ in the Vostok core (Figure 38.5) and estimated changes in ocean surface water temperature at the equator and at high latitudes. The total temperature glacial-interglacial variation in equatorial surface is estimated at less than 2° C (as noted above, this may be an underestimate), while that at high latitudes varies by about 5°C.

There are, however, a number of complicating factors that may limit the usefulness of δ¹³Corg in estimating past variations in PCO₂. For one thing, the fractionation during photosynthesis will depend on temperature. For another, the procedure of Rau (1994) makes no effort to correct for any variations in δ¹³C in dissolved inorganic carbon (δ¹³CDIC). We expect, for example, an inverse relationship between

![Figure 38.6](image-url)

**Figure 38.6.** Estimation of atmospheric CO₂ concentration from the observed δ¹³Corg. Graph a shows the observed correlation between the [CO₂aq] in seawater and δ¹³Corg in modern marine phytoplankton; b shows the dependence of [CO₂aq] on partial pressure of CO₂ and temperature. Using the observed correlation, the partial pressure of atmospheric CO₂ can be estimated from the measured δ¹³Corg if temperature is known and equilibration between the ocean and atmosphere is assumed. From Rau (1994).
\( \delta^{13} \text{C}_{\text{DIC}} \) and \([\text{CO}_2\text{aq}]\) in ocean water simply because of the effects of photosynthesis and respiration, and we know \( \delta^{13} \text{C}_{\text{DIC}} \) has varied in the past (though the glacial-interglacial variations appear to have been small). It is possible to take account of variations in \( \delta^{13} \text{C}_{\text{DIC}} \) by measuring \( \delta^{13} \text{C} \) in carbonate from the same sediment fraction in which the \( \delta^{13} \text{C}_{\text{org}} \) is measured. This was done, for example, by Jasper and Hayes (1994). Beyond this, diagenetic processes in the sediment might modify the \( \delta^{13} \text{C}_{\text{org}} \) and furthermore, sedimentary inorganic carbon can be a mixture from a variety of sources and will not necessarily be representative of that in phytoplankton. To avoid this problem, Jasper and Hayes (1994) analyzed \( \delta^{13} \text{C} \) in a specific organic molecule (\( \text{C}_{37} \) alkadienone, a lipid) known to be produced by phytoplankton.

There are, however, still other potential problems. According to the photosynthesis model of Farquhar (1982), which we presented in Lecture 29, the isotopic fractionation during photosynthesis depends on the ratio of concentration of \( \text{CO}_2 \) in the atmosphere to that in the cell interior:

\[
\Delta = a + (c/c_a)(b - a) \quad (29.1)
\]

where \( a \) is the fractionation due to diffusion, \( c_i \) is the \( \text{CO}_2 \) concentration in the cell interior, \( c_a \) is the ambient \( \text{CO}_2 \) concentration, and \( b \) is the fractionation during actual photosynthetic fixation. We might expect, however, that the ratio \( c_i/c_a \) will depend on the photosynthetic rate: at high rates, there will be a draw down of \( \text{CO}_2 \) in the cell interior. Laws et al. (1995) suggested the interior and exterior concentrations would be related to the photosynthetic rate (or growth rate of the cells) as:

\[
r = k_1 c_a - k_2 c_i \quad (38.1)
\]

where \( r \) is the growth rate and \( k_1 \) and \( k_2 \) are two constants. Rearranging and substituting into 29.1, we have:

\[
\Delta = a + (b - a)(k_1 - r/c_a)/k_2 \quad (38.2)
\]

Assuming the other terms are constant, this equation predicts the fractionation is proportional to ratio of the growth rate to ambient \( \text{CO}_2 \) concentration. This is exactly the relationship observed by Laws et al. (1995) in experiments (Figure 38.8). Thus a determination of \( \text{PCO}_2 \) from \( \delta^{13} \text{C} \) in organic carbon would appear to require a knowledge of growth rates, or the assumption that they do not vary significantly.

There appear to be other complications as well. Hinga et al. (1994) found that the fractionation during photosynthesis in culture experiments depended on pH and, furthermore, varied between species. The pH dependence may be seen in Figure 28.4 and reflects in part, the dependence of the speciation of dissolved \( \text{CO}_2 \) on pH. They found no dependence on growth rate, but the range in growth rate in their experiments was small. Consistent with these observations, Goericke and Fry (1994) observed almost no correlation between the fractionation due to photosynthesis calculated from \( \delta^{13} \text{C} \) of particulate or-
ganic matter and $[\text{CO}_2]_{aq}$ in the modern ocean. Thus it remains to be seen whether $\delta^{13} C$ in organic matter can reliably be used to estimate paleo-$PCO_2$.

In a more recent attempt at this, Arthur et al. (1998) used the difference in $\delta^{13} C$ between calcite and a specific class of organic molecules, di-unsaturated alkenones, in cores from the Pacific, Atlantic, and Indian oceans to estimate paleo-$PCO_2$ from the latest Oligocene through the Late Miocene (25 to 8 Ma). Alkenones are diagenetically resistant lipids produced only by a restricted class of marine algae. They found that $PCO_2$ declined sharply at the Oligocene-Miocene boundary, which coincides with a known glacial event, and continued to decline through an episode of global warming in the mid-Miocene (about 15 Ma), reaching a low of 170 ppmv by 9 Ma. Overall, they found little correlation between their estimate of atmospheric $PCO_2$ and global climate. Thus these results, if correct, suggest the role of atmospheric $CO_2$ is far less than most paleoclimate models believe.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


Broecker, W. S., Glacial to Interglacial changes in ocean chemistry, Prog. Oceanog., 11, 151-197, 1982.


