The Carbon Cycle, Isotopes, and Climate

The Short-Term Carbon Cycle and Anthropogenic Impacts

There is considerable reason to believe that the Earth’s climate is linked to atmospheric CO₂ concentrations. There are several lines of evidence for this. First, and perhaps, most importantly, is the observation that CO₂ 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 loses an equal amount of energy in the form of infrared radiation (if it did not, the Earth’s surface would continually get hotter). Atmospheric CO₂ 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 CO₂ 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 CO₂ was increasing due to burning of fossil fuels, and that this could lead to warming of the Earth’s surface.

As Figure 26.1 indicates, carbon cycles rapidly between 5 reservoirs on the surface of the Earth. Of the total carbon in these 5 reservoirs, atmospheric CO₂ 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 50 times as much as in the atmosphere, is dissolved in the deep ocean (mainly as HCO₃⁻). The fluxes of carbon to and from the atmosphere are large relative to the amount of CO₂ in the atmosphere; indeed nearly 25% of the atmospheric CO₂ ‘turns over’ in a year. The balance of these fluxes controls the concentration of atmospheric CO₂. The isotopic composition varies between these reservoirs, primarily due to the fractionation during photosynthesis.

![Diagram of the Carbon Cycle](image)

Figure 38.1. The Carbon Cycle. Numbers in green show the amount of carbon (in 10¹⁵ 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).
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 $\text{CO}_2$ in the atmosphere (Figure 26.2), 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 $\text{CO}_2$ reservoir of about 3 Gt/year. This increase in atmospheric $\text{CO}_2$ 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 $\delta^{13}\text{C}$ (the isotopic composition of fossil fuel burned has varied over time from $\delta^{13}\text{C} \approx -24\%o$ in 1850 to $\delta^{13}\text{C} \approx -27.3\%o$ in 1980 as coal has been partly replaced by oil and gas). Thus we might expect to see a decrease in the $\delta^{13}\text{C}$ of atmospheric $\text{CO}_2$. This is indeed observed. Based on measurements of $\delta^{13}\text{C}$ in tree rings and ice cores, the $\delta^{13}\text{C}$ of atmospheric $\text{CO}_2$ has declined by about 1.5‰ since 1800 (e.g., Figure 26.3). This is significantly greater (up to a factor of 2 greater) than that expected from
Figure 26.3. Variation is $\delta^{13}C$ in an ice core from Siple Station, Antarctica (open squares; Friedli et al., 1986) and direct atmospheric samples from the South Pole (crosses; Keeling et al., 1989). After Friedli et al. (1986).

The small concentration gradient between hemispheres (as indicated by the similar CO$_2$ concentrations at Mauna Loa and the South Pole) 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 most estimates of ocean uptake are around 2 Gt/yr but there is substantial uncertainty surrounding this number.

An 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.

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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 to 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 smectic uptake rate is apparently being taken up by the terrestrial biosphere. 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 most estimates of ocean uptake are around 2 Gt/yr but there is substantial uncertainty surrounding this number.

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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 20th 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 CO₂ 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 24, plants photosynthesize more efficiently at higher CO₂ concentrations, so increasing atmospheric CO₂ 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 CO₂, it is unclear whether such stimulation would actually occur. However, higher CO₂ concentrations may allow plants to close their stomata somewhat. Stomata, through which leaves exchange gas with the atmosphere, are pathways both for CO₂ into the leaf and for H₂O 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 into grasslands and grasslands into deserts.

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 CO₂ concentration might be one of these. Early evidence that atmospheric CO₂ concentration might vary between glacial and interglacial epochs came from carbon isotope studies of deep-sea cores. Shackleton found that seawater δ¹³C 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 CO₂ and perhaps provide the necessary feedback to amplify orbital forcing of climate change. Further evidence of varying atmospheric CO₂ came from the first measurement of CO₂ concentrations in ice cores in the late 1970’s and early 1980’s. These data suggested atmospheric CO₂ had fallen to levels as low as 200 ppm or less during glacial epochs.

The data also suggested CO₂ 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 CO₂ in the ocean due to changing temperature (solubility of CO₂ increases with decreasing temperature), would produce only about a 20 ppm decrease in atmospheric CO₂ during glacial times, and about half this would be offset by decreasing volume of the oceans. Broecker suggested the changes in atmospheric CO₂ 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 CO₂ in the atmosphere to rise. He also suggested a test of the idea. If his hypothesis were correct, the difference in δ¹³C between surface and deep water should decrease during interglacial epochs, since this difference is a result of ¹³C 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 (Δδ_{18}C_{P,B}) that correlated with δ^{18}O and therefore implied differences between deep and surface water δ^{13}C (Figure 26.4). 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 Δδ^{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 δ^{13}C data and the Δδ^{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 δ^{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 δ^{13}C variations relative to those of δ^{18}O, Shackleton and Pisias found that changes in Δδ^{13}C_{P,B} led those of δ^{18}O, suggesting ice volume was responding to CO_{2} concentrations, and not visa versa. Indeed, the calculated changes in CO_{2} are in phase with the Milankovitch-driven insolation, but they lead ice volume. In other words, it appears Milankovitch changes drive CO_{2} changes, which then changes ice volume. 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 26.5. 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. 26.4), 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 δ$^{13}$C during glacial periods could help to resolve this question. Looking at Figure 26.1, we can see that since the terrestrial biosphere has lower δ$^{13}$C than the atmosphere, storage of carbon in the biosphere should raise atmospheric δ$^{13}$C. On the other hand, since the oceans have higher δ$^{13}$C than the atmosphere, transfer of carbon from the atmosphere to the ocean should lower atmospheric δ$^{13}$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 δ$^{13}$C was 0.3±0.2‰ 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.

δ$^{13}$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 δ¹³C̄ of marine phytoplankton and the concentration of dissolved inorganic CO₂ (Degens et al., 1968; Degens, 1969). The method is illustrated in Figure 26.6: there is an observed inverse correlation between dissolved CO₂ and δ¹³C̄ of phytoplankton. We found in Lecture 20 that the fractionation of carbon isotopes during photosynthesis is related to CO₂ concentrations (Figure 20.10). 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, [CO₂(aq)] can be estimated from measurements δ¹³C̄. [CO₂(aq)] 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 26.7 shows an example from Rau (1994) of the calculated [CO₂(aq)] in surface ocean water over the last 140,000 years using the correlation in Figure 26.6. δ¹³C̄ 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 [CO₂(aq)] predicted from the observed variations in CO₂ in the Vostok core (Figure 26.5) 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 δ¹³C̄ in estimating past variations in P̄CO₂. 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 (δ¹³C(DIC)). We expect, for example, an inverse relationship between

![Figure 26.6](image-url)

*Figure 26.6. Estimation of atmospheric CO₂ concentration from the observed δ¹³C̄. Graph a shows the observed correlation between the [CO₂(aq)] in seawater and δ¹³C̄ in modern marine phytoplankton; b shows the dependence of [CO₂(aq)] on partial pressure of CO₂ and temperature. Using the observed correlation, the partial pressure of atmospheric CO₂ can be estimated from the measured δ¹³C̄ if temperature is known and equilibration between the ocean and atmosphere is assumed. From Rau (1994).*
δ\textsuperscript{13}C\textsubscript{DIC} and [CO\textsubscript{2aq}] in ocean water simply because of the effects of photosynthesis and respiration, and we know δ\textsuperscript{13}C\textsubscript{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 δ\textsuperscript{13}C\textsubscript{DIC} by measuring δ\textsuperscript{13}C in carbonate from the same sediment fraction in which the δ\textsuperscript{13}C\textsubscript{org} is measured. This was done, for example, by Jasper and Hayes (1994). Beyond this, diagenetic processes in the sediment might modify the δ\textsuperscript{13}C\textsubscript{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 δ\textsuperscript{13}C in a specific organic molecule (C\textsubscript{34} alkenone, 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 20, the isotopic fractionation during photosynthesis depends on the ratio of concentration of CO\textsubscript{2} in the atmosphere to that in the cell interior:

\[ \Delta = a + (c/c_a)(b - a) \quad (20.12) \]

where \( a \) is the fractionation due to diffusion, \( c_i \) is the CO\textsubscript{2} concentration in the cell interior, \( c_a \) is the ambient CO\textsubscript{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 CO\textsubscript{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:

\[ r = k_1c_a - k_2c_i \quad 26.1 \]

where \( r \) is the growth rate and \( k_1 \) and \( k_2 \) are two constants. Rearranging and substituting into 20.12, we have:

\[ \Delta = a + (b - a)(k_1 - r/c_a)/k_2 \quad 26.2 \]

Assuming the other terms are constant, this equation predicts the fractionation is proportional to ratio of the growth rate to ambient CO\textsubscript{2} concentration. This is exactly the relationship observed by Laws et al. (1995) in experiments (Figure 26.8). Thus a determination of P\textsubscript{CO\textsubscript{2}} from δ\textsuperscript{13}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 20.10 and reflects in part, the dependence of the speciation of dissolved CO\textsubscript{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 δ\textsuperscript{13}C of particulate
organic matter and [CO\textsubscript{2aq}] in the modern ocean. Thus it remains to be seen whether $\delta^{13}C$ in organic matter can reliably be used to estimate paleo-P\textsubscript{CO\textsubscript{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-P\textsubscript{CO\textsubscript{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 P\textsubscript{CO\textsubscript{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 P\textsubscript{CO\textsubscript{2}} and global climate. Thus these results, if correct, suggest the role of atmospheric CO\textsubscript{2} is far less than most paleoclimate models believe.

**The Long-Term Carbon Cycle**

On geologic timescales, the carbon cycle model must be augmented by 3 reservoirs, sedimentary carbonate, sedimentary organic carbon, and the mantle, as well as fluxes between these reservoirs and the oceans and atmosphere. Such a long-term model is shown in Figure 26.9, where anthropogenic perturbations have been removed. The most important thing to notice is that there is much more carbon in the carbonate and sedimentary organic carbon reservoirs than in all the reservoirs in Figure 26.1 combined. However, the fluxes to and from the sedimentary reservoirs are small, so they play little role in short-term (< 1 Ma) atmospheric CO\textsubscript{2} variations (at least in natural ones; we could properly consider fossil fuel burning as a flux from sedimentary organic carbon to the atmosphere). We should also point out that only a small fraction of the sedimentary organic carbon is recoverable fuel; most is present as minor amounts (typically 0.5% or less) of kerogen and other refractory organic compounds in sediments. Even greater amounts of carbon are probably stored in the mantle, though the precise amount is difficult to estimate. An order of magnitude figure might be 125-500 ppm CO\textsubscript{2} in mantle, which implies a total inventory of $1.3-5 \times 10^9$ Gt, or nearly $10^9$ times the amount in the atmosphere. Again, the flux from the mantle to the atmosphere, which results from volcanism, is small, so the mantle plays no role in short-term atmospheric CO\textsubscript{2} variations. On long time scales (>>10^9 yr), however, it is the fluxes to and from sediments and the mantle that control the atmospheric CO\textsubscript{2} concentration.
TERTIARY CARBON ISOTOPE RATIOS AND EXTINCTIONS

Figure 26.10 shows $\delta^{13}C$ and $\delta^{18}O$ in benthic forams from 40 DSDP and ODP drill cores selected to represent, as best as possible, global means. On these time scales, the main influences on $\delta^{13}C$ are changes in biological productivity and ocean circulation, burial and erosion of carbon in sediments, and the volcanic flux. Recall that organic carbon has strongly negative $\delta^{13}C$ – burial of organic carbon will drive the marine system toward more positive values, erosion of organic carbon will drive it to negative values. Volcanic $CO_2$ has $\delta^{13}C$ of -6, very similar to the atmospheric value, so changes in the volcanic flux will have a minimal effect on the system. The fractionation between dissolved carbonate and precipitated carbonate is fairly small, so both erosion and burial of carbonate also have only a small effect on $\delta^{13}C$ of the system. There are a number of interesting features of this record. Let’s consider these in chronological sequence.

First, there is a decline in $\delta^{13}C$ around the Cretaceous-Tertiary boundary. This is not well shown in Figure 26.10 because the curve has been smoothed, but does show up well in detailed studies, such as that of d’Hondt et al. (1998). Figure 39.3 shows $\delta^{13}C$ values in carbonate from DSDP site 528. The data show a sharp drop in $\delta^{13}C$ at the K-T boundary. This is consistent with a strong reduction in biopro-
ductivity, and consequently, a drop in the burial rate of organic carbon. The marine system appears to have partially recovered within a million years, and completely recovered within 3 million years.

The next notable event is the so-called Late Paleocene Thermal Maximum at 55 Ma. A sharp drop (3‰) in $\delta^{13}C$ coincides with an increase in $\delta^{18}O$ that corresponds to an increase in deep ocean temperature of 5-6°C that occurred within 10,000 years. Recovery occurred over 200,000 years. The event is also characterized by widespread dissolution of seafloor carbonate, mass extinction of benthic fora-
minifera, and emergence and dispersal of species both on land and in the sea. There are a variety of hypotheses as to the cause of this event, but perhaps the most interesting and provocative is that warming of ocean deep water (which in Figure 26.10 can seen to be occurring through the late Paleocene) eventually destabilized methane hydrates in shelf sediments. The resulting release of methane to the atmosphere both drove ocean-atmosphere \( \delta^{13}C \) to lighter mean values and, as a consequence of methane’s strong greenhouse effect, dramatically increased global temperatures.

The next events are the Oi-1 and Mi-1 glaciations both of which reflect brief extremes in Antarctic ice-volume and temperature. The positive shifts in \( \delta^{18}O \) are indicative of global cooling, while the positive shift in \( \delta^{13}C \) suggests a increase in burial of organic carbon or a decrease in its erosion, either of which would have decreased \( CO_2 \) in the ocean-atmosphere system and thereby contributed to the cooling.

The final interesting feature is a roughly 1‰ decrease in \( \delta^{13}C \) in the late Miocene. This could result from either a decrease in organic carbon burial, an increase in organic carbon erosion, or an increase in volcanism. There is no evidence of the latter; furthermore, all of these should have resulted in an increase in atmospheric \( CO_2 \). However, there is independent evidence from boron isotopes (Pearson and Palmer, 2001) and \( \delta^{13}C \) in alkenones from marine phytoplankton (Pagani, et al, 1999) that atmospheric \( CO_2 \) concentrations have been fairly stable at 200-300 ppm since the late Oligocene (this contrasts with much higher concentrations prior to 40 Ma). Derry and France-Lanord (1996) proposed this decrease reflects a decrease in the fractionation between organic and inorganic carbon, i.e., a decrease in the fractionation during photosynthesis. There is independent evidence of this in decreasing difference between the \( \delta^{13}C \) of organic and carbonate fractions of sediments through the Tertiary. Derry and France-Lanord hypothesized that this ultimately results from decreasing levels of atmospheric \( CO_2 \). At lower atmospheric \( CO_2 \) levels, we would expect plants to fix a greater proportion of the \( CO_2 \) in their cell interiors and the net fractionation should consequently fall. Further contributing to the overall decrease in fractionation between organic and inorganic carbon would be the evolution of \( C_4 \) plants in the late Miocene. However, 95% of the biomass is still \( C_3 \), so this effect is likely to be small.

**THE PHANEROZOIC CARBON ISOTOPE RECORD AND MODELS OF ATMOSPHERIC \( CO_2 \)**

Figure 26.12 shows the Phanerozoic variation of \( \delta^{13}C \) in carbonates and \( \delta^{34}S \) in evaporites, both of which presumably record the isotopic composition of seawater at the time of deposition. Perhaps the most notable features of this plot is the dramatic negative shift in \( \delta^{13}C \) associated with the Permo-
Triassic (the largest mass extinction event of all) and the large increase in $\delta^{13}C$ associated with the expansion of land plants and high rates of burial of organic carbonic in the Carboniferous.

The isotopic composition of carbon and sulfur should be linked. The linkage occurs because burial and erosion of reduced sediment (organic carbon and sulfide) affect the concentration of atmospheric oxygen. Thus for example, high rates of burial of organic carbon in the Carboniferous may have increased atmospheric $O_2$, making sulfides more subject to oxidation. This mechanism may account for the shift to more positive $\delta^{13}C$ and more negative $\delta^{34}S$ in the Carboniferous apparent in Figure 26.12.

The sedimentary record of $\delta^{34}S$ and $\delta^{13}C$ have given rise to various attempts to model the variation of atmospheric $CO_2$ and $O_2$ through geologic time. The classic work in this regard is that of Berner, Lasaga and Garrels (1983, 1985), which is often referred to as the BLAG model. A somewhat simpler approach was used by Berner (1991), and we shall follow that one. Berner considered the fluxes between the ocean-atmosphere, carbonate, and organic carbon reservoirs (Figure 26.13). He assumed that the system was in steady-state at any given time, an assumption justified by the small size of the atmosphere-ocean reservoir compared to the sedimentary ones. Thus one can write the following equation:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg}$$

where $F$ is a flux, the subscript $w$ denotes weathering, the subscript $m$ denotes magmatic or metamorphic release of carbon, the subscript $b$ denotes burial, the subscript $c$ denotes the carbonate reservoir and the subscript $g$ denotes organic sediments. Thus equation 39.1 states that the rate of release of carbon from organic or carbonate sediment through metamorphism or magmatism and weathering equals the rate burial of organic and carbonate sediment. The isotopic composition of the oceans and atmosphere depends on these fluxes:

$$\delta_0 F_{bc} + (\delta_0 - \alpha_c) F_{bg} = \delta_0 (F_{wc} + F_{mc}) + \delta_g (F_{wg} + F_{mg})$$

where the subscript $o$ denotes the ocean and $\alpha_c$ is the fractionation during photosynthesis. Because the isotopic composition of the oceans ($\delta^{13}C_o$) through time can be estimated from $\delta^{13}C$ in carbonate (e.g., Figure 26.12), equation 26.4 provides a constraint on these fluxes.

Berner assumed that the rate of weathering of carbonate at any time depends on the ratio of land area to ocean area ($f_{\text{land}}(t)$), biological activity ($f_b(t)$), a rate constant $k_{\text{wco}}$, river runoff ($f_r(t)$), the mass of carbonate rock (C), and the CO$_2$ “weathering feedback function”, $f_{\text{CO}_2}(t)$:
The “weathering feedback function” works in two ways. First of all, global surface temperatures should correlate with atmospheric CO$_2$ concentrations. Since weathering reaction rates are, in principle, temperature dependent, Berner reasoned that weathering would be more rapid when temperatures, and hence atmospheric CO$_2$ concentrations, are higher (these same assumptions are present in the BLAG model; Berner et al., 1983). Second, Berner assumes that higher atmospheric CO$_2$ leads to greater rates of photosynthesis and biological activity. This enhances weathering through greater production of biological acids and nutrient uptake. One might also speculate that atmospheric CO$_2$ might directly speed weathering since protons generated by dissociation of carbonic acid plays a key role in weathering. However, the dissolved CO$_2$ in groundwater comes primarily from respiration by soil organisms rather than the atmosphere. Hence increasing atmospheric CO$_2$ would not directly affect weathering rates.

Berner assumed the dependence of the weathering feedback function is related to atmospheric CO$_2$ by the following equation of Volk (1987):

$$ f_{CO_2} = \left[ \frac{2R_{CO_2}}{1 + R_{CO_2}} \right]^{0.4} \times 0.4 \times R_{CO_2}^{0.22} $$  \hspace{1cm} 26.6

where $R_{CO_2}$ is the ratio of atmospheric CO$_2$ concentration at the time of interest to the present concentration. The first term reflects the dependence of photosynthesis rate on CO$_2$ concentration of the form seen in Figure 24.8. The 0.4 exponent represents an acknowledgement that biological productivity is often limited by factors other than CO$_2$ availability. The second term reflects the temperature feedback as first formulated by Berner et al. (1983). For the period before the emergence of land plants (before 350 Ma), the first term is not present. Other evolutionary changes were accounted for in the biological activity function ($f_b(t)$).

The rate of organic sediment weathering is given by:

$$ F_{wc} = f_A(t)f_D(t)f_R(t)k_{wg}G $$  \hspace{1cm} 26.7

where $f_k$ is a factor that depends on mean land elevation, $k_{wg}$ is a rate constant, and $G$ is the mass of buried organic carbon. The terms for biological activity ($f_b(t)$) do not occur because weathering of sedimentary organic matter results simply from oxidation rather than attack by carbonic acid or biologically produced acids. On the other hand $f_b(t)$ is omitted from the expression for weathering of carbonate because their weathering shows little dependence on elevation.

Berner assumes that carbon is also deeply recycled through subduction of oceanic sediment. The metamorphic or magmatic release of CO$_2$ from carbonate rock depends on the ratio ($f_c(t)$) of platform carbonate to deep-sea carbonate (the latter being more commonly subducted) and the volcanism rate ($f_v$), so:

$$ F_{mc} = f_A(t)f_c(t)k_{mc}C $$  \hspace{1cm} 26.8

where $k_{mc}$ is a rate constant. Metamorphic or magmatic release of organic carbon is expressed as:
Finally, the flux of carbon due to weathering of silicate rocks and consequent uptake of CO$_2$ and burial as carbonate ($F_{ws}$) is expressed as:

$$F_{ws} = F_{bc} - F_{wc} = f_{CO_2}(t)f_{A}(t)f_{D}(t)f_{R}(t)f_{E}(t)F_{ws}(0)$$  \[26.10\]

where $F_{ws}(0)$ is the present flux.

Berner estimated the values of the various $f$ and $k$ parameters in these equations, as well as initial (at 570 Ma) values for the sizes and isotopic composition of the three reservoirs from information in the geological literature. For example, he assumed the volcanism rate was proportional to the rate of sea-floor spreading. Factors such as mean elevation and the ratio of land to ocean area are can be estimated from geologic information. He then calculated the magmatic and weathering fluxes, and substituting these into equations 26.3 and 26.4, calculated the burial fluxes in 1 million year steps. From values of $F_{wc}$ and $F_{wc}$, he solved for $f_{CO_2}(t)$ in equation 26.10 and then for CO$_2(t)$. This new value of $f_{CO_2}(t)$ was then used to iterate the calculation until a constant $f_{CO_2}(t)$ was obtained.

From this, new values for the mass of the reservoirs and their isotopic composition were calculated using mass balance equations such as:

$$\frac{dC}{dt} = F_{bg} - (F_{wc} + F_{mc})$$  \[26.11\]

and

$$\frac{d(\delta_c C)}{dt} = \delta_{c_{bc}} F_{bc} - \delta_{c}(F_{wm} + F_{mc})$$  \[26.12\]

The results, with an error envelope based on the sensitivity of the method to various uncertainties in the input parameters, are shown in Figure 26.14. The results correspond more or less with what is known from the geologic record about temperature changes during the Phanerozoic. To begin with, the Early Paleozoic was warm compared with the late Precambrian, which was a time of several major glaciations. The late Paleozoic, on the other hand, was cool, and the time of the last major glacial epoch

![Figure 26.14. Ratio of atmospheric CO$_2$ concentration to present atmospheric CO$_2$ in the model of Berner (1991).]
before the late Tertiary/Quaternary glaciation. The Cretaceous is well known as a remarkably warm period. Berner’s model shows generally high CO₂ during warm periods of the early Paleozoic, low CO₂ (resulting from organic carbon burial, presumably a consequence of colonization of land by plants) associated with glaciation in the late Paleozoic, and high CO₂ (associated with volcanism, among other things) in the warm Cretaceous. Thus if the model is correct, it substantiates the widely held assumption that atmospheric CO₂ concentrations strongly influence global temperature.

This is simply a model, however, and many question its validity. In particular, John Edmond has argued that although weathering reaction rates, like all reaction rates, are temperature dependent, this dependence is not important in nature because other factors limit reaction rates. He argues that the most important factor limiting weathering is the abundance of fresh rock, which is in turn controlled by tectonism. He points to the Orinoco drainage as an example (Edmond et al., 1995). Although temperatures are high, weathering is slow because a deep layer of thoroughly weathered soil inhibits water from reaching fresh rock. While Berner’s results are certainly interesting, just how accurate these estimates are remains to be seen.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


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


