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 CO_2. 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

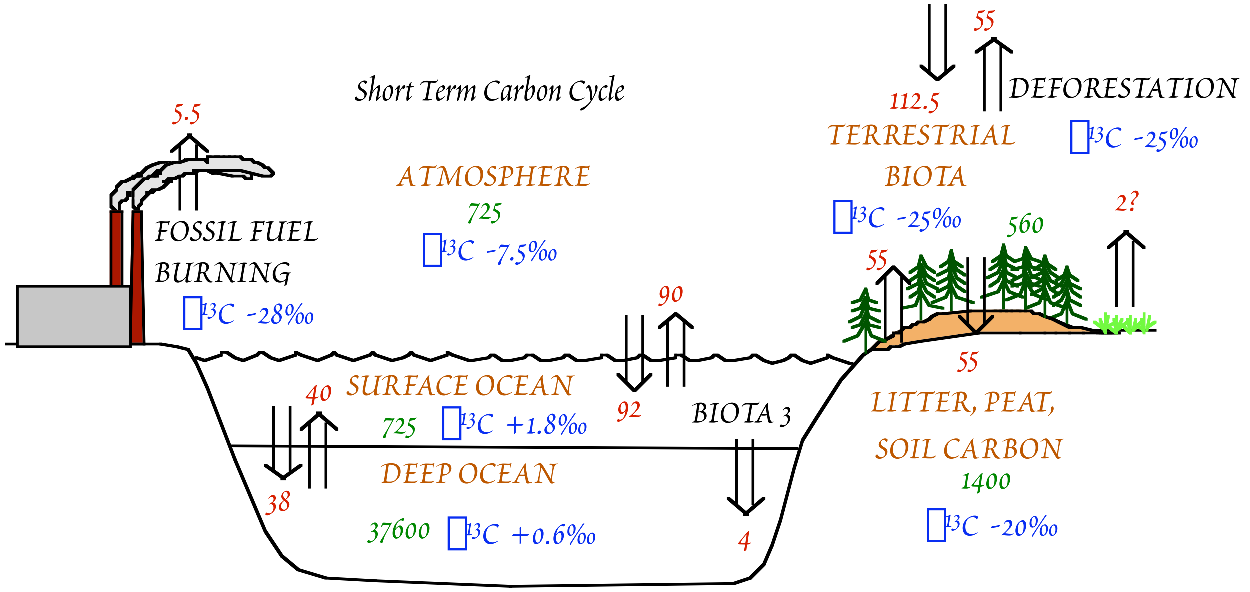

Figure 38.1. The Carbon Cycle. Numbers in green show the amount of carbon (in 10^{15} grams or gigatons, Gt) in the atmosphere, oceans, terrestrial biosphere, and soil (including litter, debris, etc.). Fluxes (red) between these reservoirs (arrows) are in Gt/yr. Also shown in the approximate isotopic composition of each reservoir. Magnitudes of reservoirs and fluxes are from Schlesinger (1991), isotopic compositions are from Heimann and Maier-Reimer (1996).

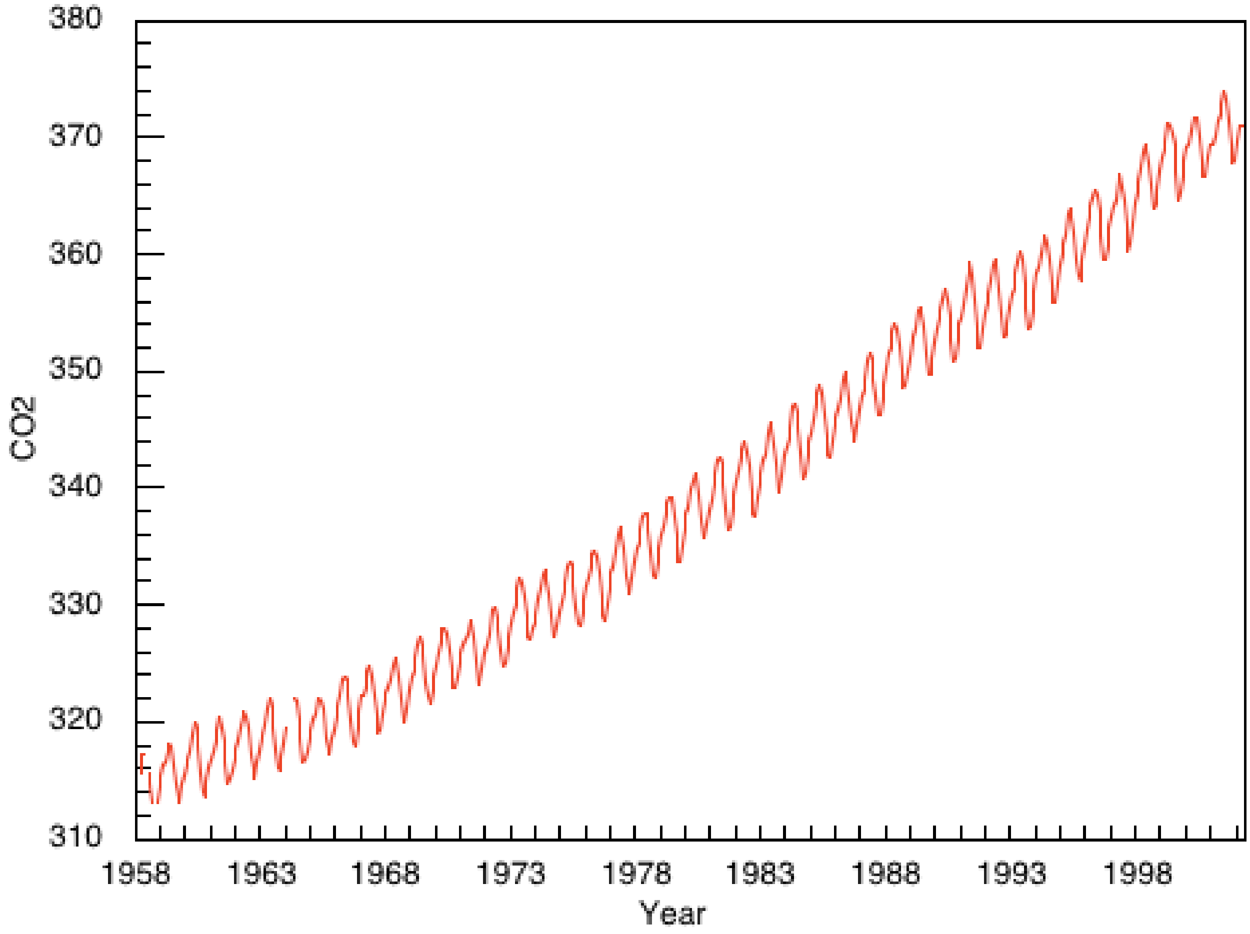

Figure 37.2. Atmospheric CO_2 concentrations (ppm volume) measured by C. D. Keeling from 1958 to 2001 at Mauna Loa (Hawaii). Annual cycles reflect the effects of seasonal changes in photosynthesis.

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 (Figure37.2), 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 1800 (e.g., Figure 37.3). 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.

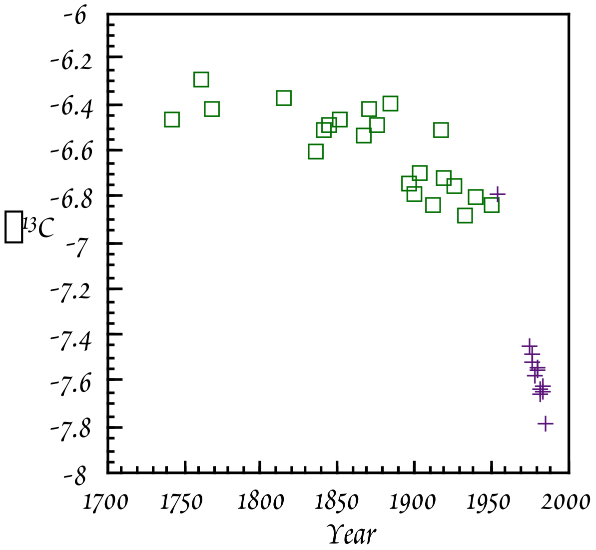

Figure 37.3. Variation is $\delta^{13}C$ in an ice core from Sipple Station, Antarctica (open squares; Friedli et al., 1986) and direct atmospheric samples from the South Pole (crosses; Keeling et al., 1989). After Friedli et al. (1986).

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 37.2) 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 (Figure 37.2); 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 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 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 34, 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_2O 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

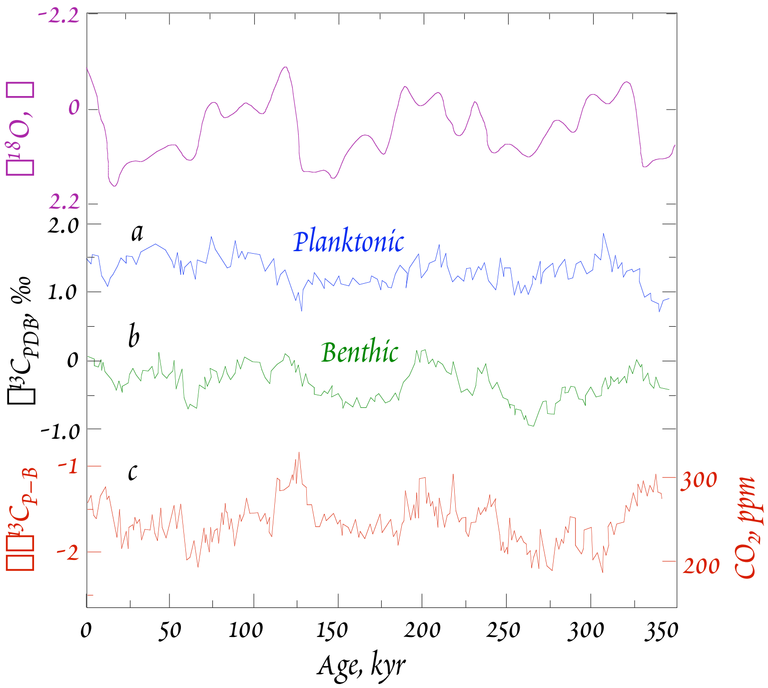

Figure 37.4. Variations in $\delta^{13}C$ in (a) planktonic foraminifera, (b) benthic foraminifera, and the difference between planktonic and benthic foraminifera ($\Delta\delta^{13}C_{P-B}$) in core V19-30 (Shackleton and Pisias, 1985) compared with the composite $\delta^{18}O$ record of Imbrie et al. (1984). Scale on the right shows the modeled change in atmospheric CO_2 concentration resulting from changing biological productivity of the oceans.

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.

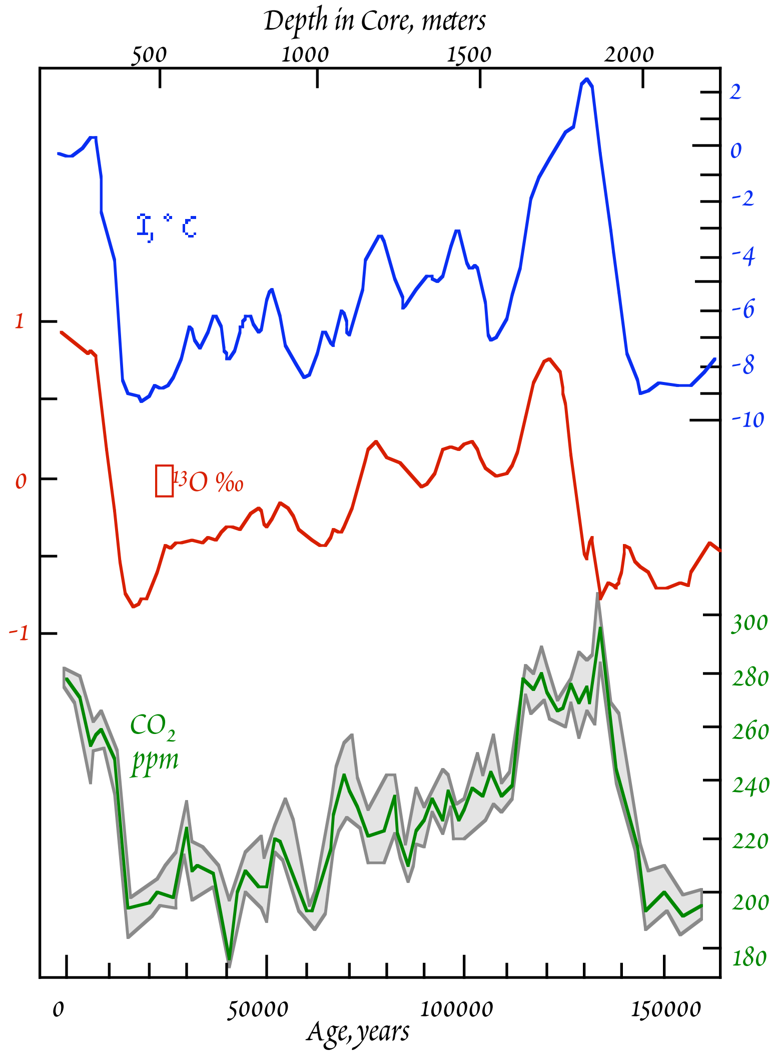

Figure 37.5. Comparison of CO_2 in bubbles (gray shows analytical uncertainties) in the Vostok ice core with temperatures calculated from δD and the marine $\delta^{18}O$ record. From Barnola et al. (1987).

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 ($\Delta\delta^{13}C_{P-B}$) that correlated with $\delta^{18}O$ and therefore implied differences between deep and surface water $\delta^{13}C$ (Figure 37.4). 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 $\Delta\delta^{13}C_{P-B}$ 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 $\Delta\delta^{13}C_{P-B}$ 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 $\Delta\delta^{13}C_{P-B}$ 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 37.5. 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. 37.4), 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 37.1, we can see that since the terrestrial biosphere has lower $\delta^{13}C$ than the atmosphere,

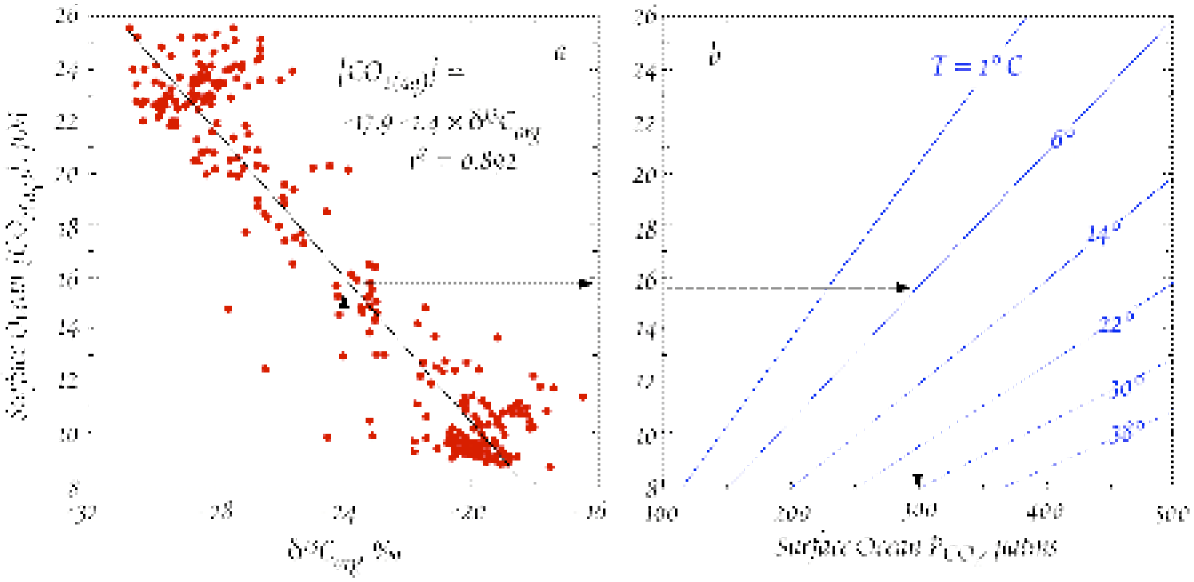

Figure 37.6. Estimation of atmospheric CO_2 concentration from the observed $\delta^{13}C_{org}$. Graph a shows the observed correlation between the $[CO_{2aq}]$ in seawater and $\delta^{13}C_{org}$ in modern marine phytoplankton; b shows the dependence of $[CO_{2aq}]$ on partial pressure of CO_2 and temperature. Using the observed correlation, the partial pressure of atmospheric CO_2 can be estimated from the measured $\delta^{13}C_{org}$ if temperature is known and equilibration between the ocean and atmosphere is assumed. From Rau (1994).

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±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.

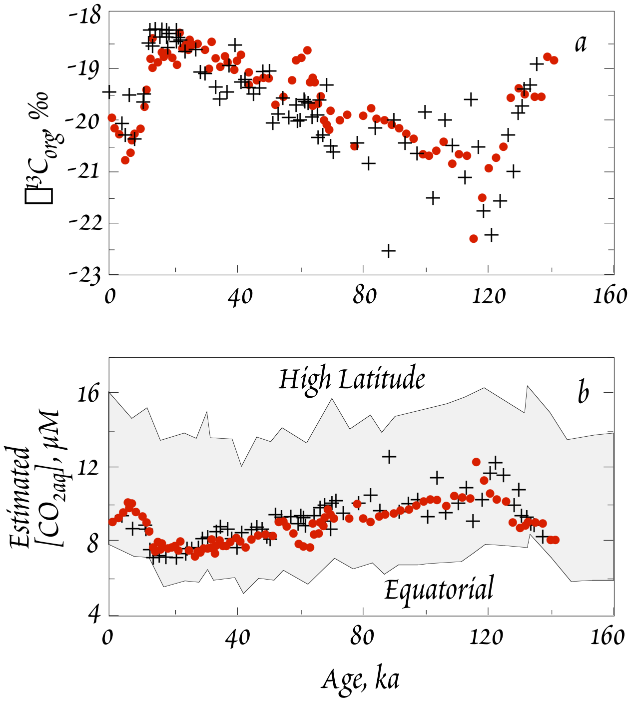

Figure 37.7. a. Variation in $\delta^{13}C_{org}$ in core 12392-1 from 25°N in the North Atlantic (Muller et al., 1983) and MD 77-169 (Fontugne and Duplessy, 1986). b. Variation in $[CO_{2aq}]$ calculated by Rau (1994) from the data in (a) using the correlation shown in Figure 37.6. This is compared with the variation in $[CO_{2aq}]$ calculated from the variations in CO_2 in bubbles in Vostok ice and estimates of surface water temperatures. From Rau (1994).

$\delta^{13}C$ IN ORGANIC CARBON AND ATMOSPHERIC CO_2 CONCENTRATION

Ice cores will be able provide information on atmospheric CO_2 concentrations for at best the last several hundred 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 CO_2 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 CO_2 resulting from continued burning of fossil fuels.

One possible method of determining paleo-CO_2 concentrations arises from an observed relationship between $\delta^{13}C_{org}$ of marine phytoplankton and the concentration of dissolved inorganic CO_2 (Degens et al., 1968; Degens, 1969). The method is illustrated in Figure 37.6: there is an observed inverse correlation between dissolved CO_2 and $\delta^{13}C_{org}$ of phyoplankton. We found in Lecture 28 that the fractionation of carbon isotopes during photosynthesis is related to CO_2 concentrations (Figure 28.4). The reason for this, in simple terms, is that when more CO_2 is available, plants can afford to be more selective and therefore show a greater preference for ^{12}C. Thus in principle at least, $[CO_{2aq}]$ can be estimated from measurements $\delta^{13}C_{org}$. $[CO_{2aq}]$ in equilibrium with the atmosphere depends on the partial pressure of atmospheric CO_2 and temperature; hence if temperature is known, the partial pressure of CO_2 can also be estimated.

Figure 37.7 shows an example from Rau (1994) of the calculated $[CO_{2aq}]$ in surface ocean water over the last 140,000 years using the correlation in Figure 37.6. $\delta^{13}C_{rorg}$ 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 $[CO_{2aq}]$ predicted from the observed variations in CO_2 in the Vostok core (Figure 37.5) 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 $\delta^{13}C_{org}$ in estimating past variations in P_{CO_2}. 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 $\delta^{13}C$ in dissolved inorganic carbon ($\delta^{13}C_{DIC}$). We expect, for example, an inverse relationship between $\delta^{13}C_{DIC}$ and $[CO_{2aq}]$ in ocean water simply because of the effects of photosynthesis and respiration, and we know $\delta^{13}C_{DIC}$ has varied in the past (though the glacial-interglacial variations appear to have been small). It is possible to take account of variations in $\delta^{13}C_{DIC}$ by measuring $\delta^{13}C$ in carbonate from the same sediment fraction in which the $\delta^{13}C_{org}$ is measured. This was done, for example, by Jasper and Hayes (1994). Beyond this, diagenetic processes in the sediment might modify the $\delta^{13}C_{org}$, 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 $\delta^{13}C$ in a specific organic molecule (C_{37} alkadienone, a lipid) known to be produced by phytoplankton.

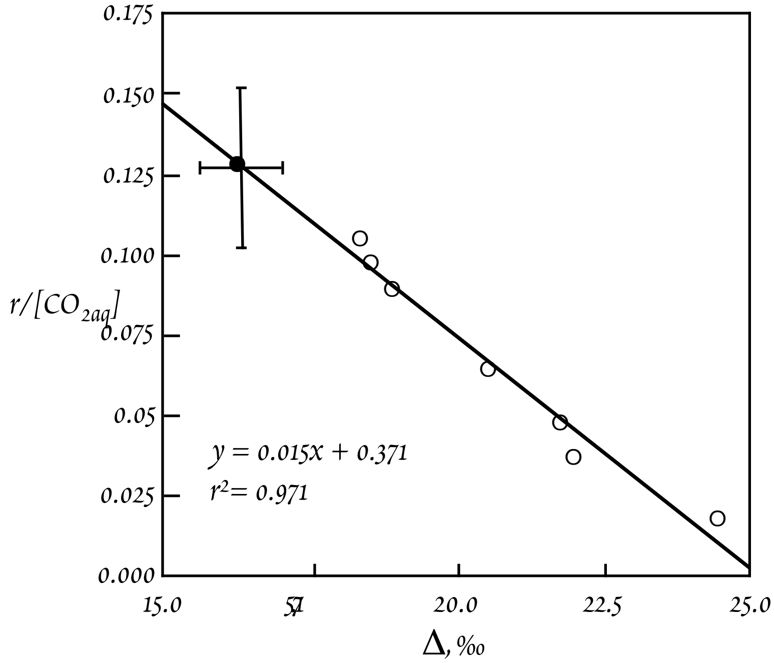

Figure 37.8. Variation in the ratio of growth rate (r) to $[CO_{2aq}\}$ with the fractionation of carbon isotopes during photosynthesis. Open symbols are laboratory experiments, closed symbol with error bar is range of growth rates, $[CO_{2aq}]$, and Δ observed in the equatorial Pacific.

There are however, other potential problems. According to the photosynthesis model of Farquhar (1982), which we presented in Lecture 28, the isotopic fractionation during photosythesis depends on the ratio of concentration of CO_2 in the atmosphere to that in the cell interior:

$$\Delta = a + (c_i/c_a)\,(b - a) \qquad (28.1)$$

where a is the fractionation due to diffusion, c_i is the CO_2 concentration in the cell interior, c_a is the ambient 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 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:

$$r = k_1c_a - k_2c_i \qquad 37.1$$

where r is the growth rate and k_1 and k_2 are two constants. Rearranging and substituting into 28.1, we have:

$$\Delta = a + (b - a)(k_1 - r/c_a)/k_2 \qquad 37.2$$

Assuming the other terms are constant, this equation predicts the fractionation is proportional to ratio of the growth rate to ambient CO_2 concentration. This is exactly the relationship observed by Laws et al. (1995) in experiments (Figure 37.8). Thus a determination of P_{CO_2} from $\delta^{13}C$ 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 27.4 and reflects in part, the dependence of the speciation of dissolved 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 $\delta^{13}C$ of particulate organic matter and $[CO_{2aq}]$ 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_{CO_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_{CO_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_{CO_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. P_{CO_2} then recovered to 220 ppmv by 9 Ma. Overall, they found little correlation between their estimate of atmospheric P_{CO_2} and global climate. Thus these results, if correct, suggest the role of atmospheric CO_2 is far less than most paleoclimate models believe.

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THE CARBON CYCLE, ISOTOPES, AND CLIMATE II

THE LONG-TERM CARBON CYCLE

On geologic times scales, 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 38.1, where the 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 37.1 combined. However, the fluxes to and from the sedimentary reservoirs are small, so they play little role in short-term (< 1 Ma) atmospheric CO_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 250-500 ppm CO_2 in mantle, which implies a total inventory of $2.5\text{-}5 \times 10^8$ Gt, or about 10^6 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_2 variations. On long time scales ($>10^6$ yr),

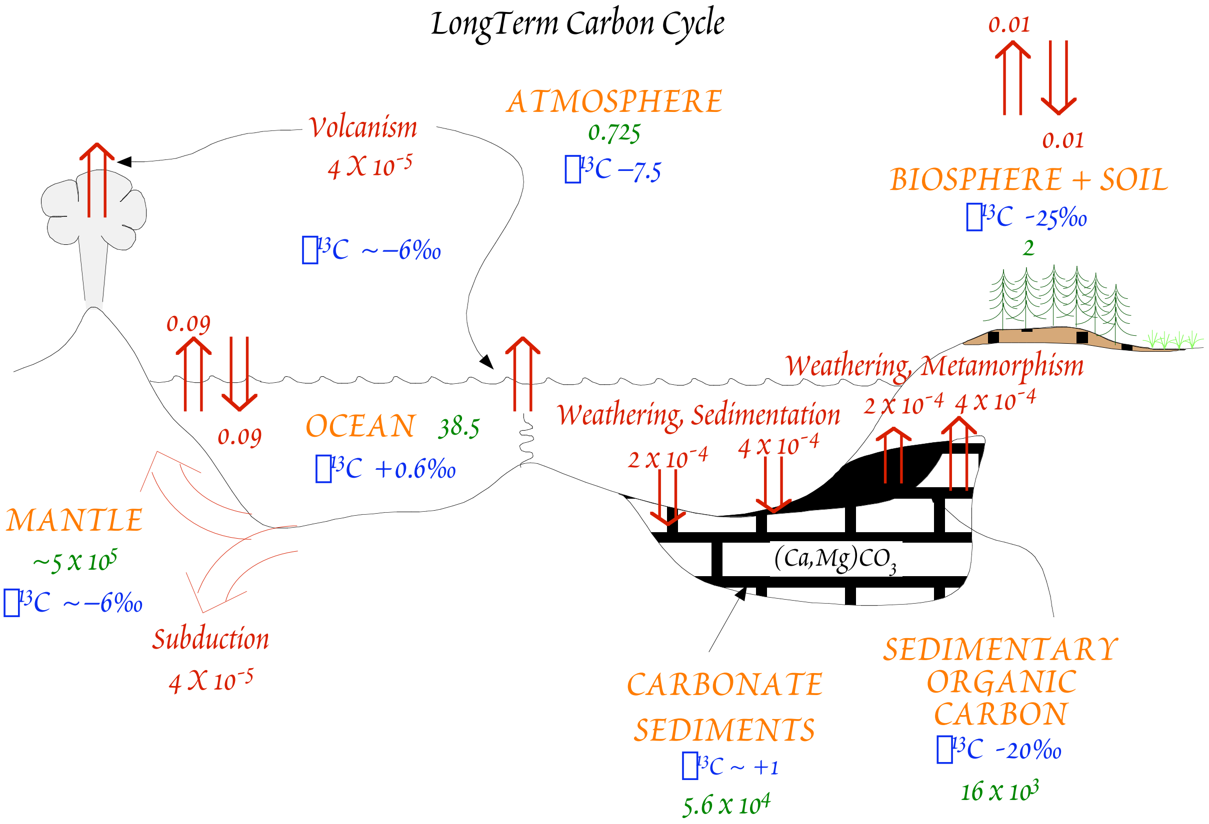


Figure 38.1. The Carbon Cycle. Green numbers show the amount of carbon (in 10^{18} grams) in the reservoirs. Fluxes between these reservoirs (arrows) are shown in italics in units of 10^{18} g/yr (in red). Masses and fluxes refer to the pre-Industrial Revolution state of the system. Uncertainties on many of the masses and fluxes are large. Also shown are estimates of the carbon isotopic composition.

however, it is the fluxes to and from sediments and the mantle that control the atmospheric CO_2 concentration.

TERTIARY CARBON ISOTOPE RATIOS AND EXTINCTIONS

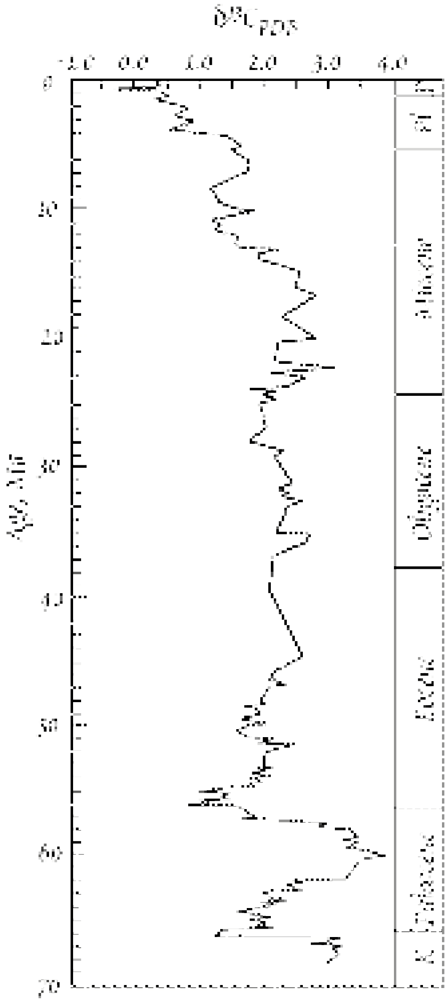


Figure 38.2. $\delta^{13}C$ in the Tertiary as recorded by bulk carbonate in South Atlantic DSDP cores. From Shackleton (1987).

Figure 38.2 shows $\delta^{13}C$ in bulk sediment from DSDP cores from the South Atlantic. On this time scale, burial and erosion of carbonate and organic sediments and the volcanic flux become important influences on $\delta^{13}C$ in the ocean atmosphere system, in addition to biological productivity and ocean circulation. There are a number of interesting features of this record. First is a general decline through the Tertiary, which accelerates in late Miocene. The cause is not clear, but in addition to changes in ocean circulation, two factors may be important. First is the appearance of planktonic foraminifera in the Cretaceous. The appearance of these calcite-secreting single-celled organisms may have increased the flux to the carbonate sediment reservoir, shifting the $\delta^{13}C$ of the ocean-atmosphere system to more negative values, and drawing down CO_2 concentrations in the process. The decrease since the late Miocene could be related to the evolution of C_4 plants. To understand why, imagine that the flux to and from organic sediments is constant. The appearance of C_4 plants shifts the isotopic composition of the flux *to* organic sediment from C_3 values (-25‰) toward C_4 values (–13‰). Yet the flux *from* organic sediment, which results from erosion and oxidation of carbon anciently reduced by photosynthesis, still has an isotopic composition of -25‰. Thus more ^{13}C goes in the organic carbon reservoir than what comes out, so the $\delta^{13}C$ in the ocean and atmosphere decreases. However, 95% of the biomass is still C_3, so this effect is likely to be small.

Also important in the Tertiary $\delta^{13}C$ record are several sharp excursions to negative values, most notably at the Cretaceous-Tertiary boundary and the Paleocene-Eocene boundary. These boundaries are, of course, defined by rapid faunal change, so it is not surprising they are associated with mass extinctions. The $\delta^{13}C$ record does not tell us what caused these extinctions, but it does suggest the extinctions were associated with drastic drops in biological productivity. Thus at least some extinctions are associated with severe biological crises, and perhaps with mass mortality. It is interesting that the recovery in $\delta^{13}C$ in each instance was relatively slow, suggesting that ecological niches left open by extinctions were not immediately filled. The greatest extinction event of all, the Permo-Triassic event, is associated with an even more dramatic negative shift in $\delta^{13}C$ (Figure 38.3).

THE PHANEROZOIC CARBON ISOTOPE RECORD AND MODELS OF ATMOSPHERIC CO_2

Figure 38.3 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. 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 δ^{13}C and more negative δ^{34}S in the Carboniferous apparent in Figure 38.3.

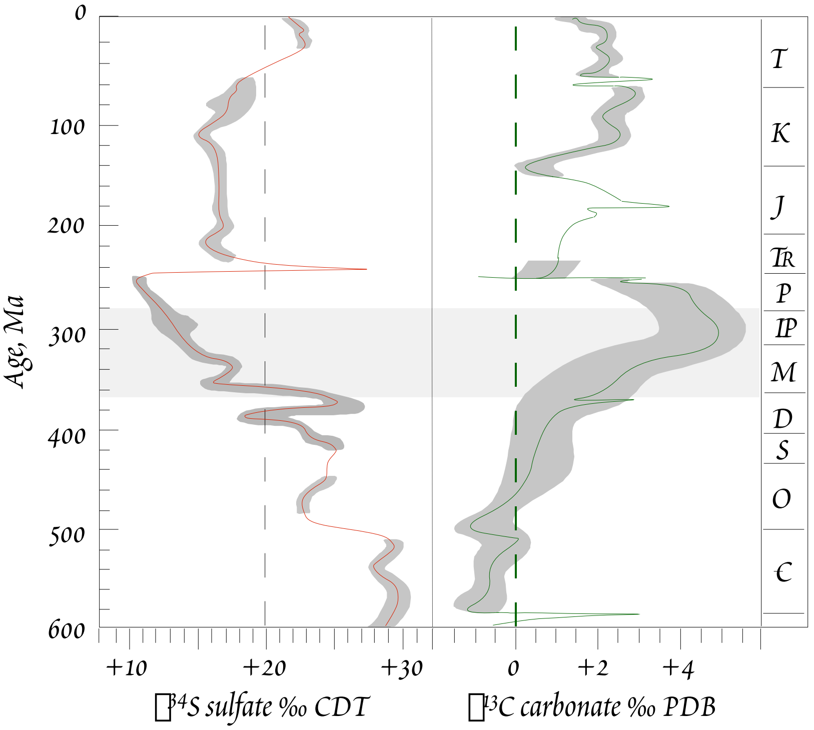


Figure 38.3. Isotopic compositions of carbon and sulfur in the oceans through Phanerozoic time. After Holser (1984).

The sedimentary record of δ^{34}S and δ^{13}C have given rise to various attempts to model the variation of atmospheric CO_2 and O_2 though 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 38.4). 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:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg} \qquad 38.1$$

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 38.1 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:

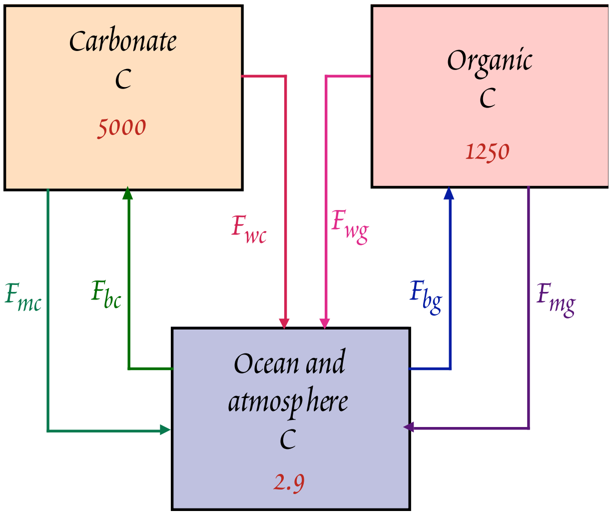
$$\delta_o F_{bc} + (\delta_o - \Delta_c)F_{bg} = \delta_o(F_{wc} + F_{mc}) + \delta_g(F_{wg} + F_{mg}) \qquad 38.2$$

where the subscript *o* denotes the ocean and Δ_c is the fractionation during photosynthesis. Because the isotopic composition of the oceans through time can be estimated from δ^{13}C in carbonate (e.g., Figure 38.3), equation 38.2 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_A(t)), biological activity (f_E(t)), a rate constant k_{wc}, river runoff (f_D(t)), the mass of carbonate rock (C), and the CO_2 "weathering feedback function", f_{CO2}(t):

$$F_{wc} = f_{CO2}(t) f_A(t) f_D(t) f_E(t) k_{wc} C \qquad 38.3$$

The "weathering feedback function" works in two ways. First of all, global surface temperatures should correlated 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* effect weathering rates.

Berner assumed the dependence of the weathering feedback function is related to atmospheric CO_2 by the following equation of Volk (1987):

$$\square_{CO_2} = \left(\frac{2R_{CO_2}}{1+R_{CO_2}} \right)^{0.4} \square 0.4 \square R_{CO_2}^{0.22} \qquad 38.4$$

where $R_{CO@}$ 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 34.8. 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 ($f_E(t)$).

The rate of organic sediment weathering is given by:

$$F_{wc} = f_A(t) f_D(t) f_R(t) k_{wg} G \qquad 38.5$$

where f_R 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 ($f_E(t)$) $f_{CO2}(t)$ 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 $f_R(t)$ 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_G), so:

$$F_{mc} = f_G(t) f_C(t) k_{mc} C \qquad 38.6$$

where k_{mc} is a rate constant. Metamorphic or magmatic release of organic carbon is expressed as:

$$F_{mg} = f_G(t) k_{mg} G \qquad 38.7$$

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:

$$F_{ws} = F_{bc} - F_{wc} = f_{CO2}(t) f_A(t) f_D(t) f_R(t) f_E(t) F_{ws}(0) \qquad 38.8$$

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 seafloor 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 38.1 and 38.2, calculated the burial fluxes in 1 million year steps.

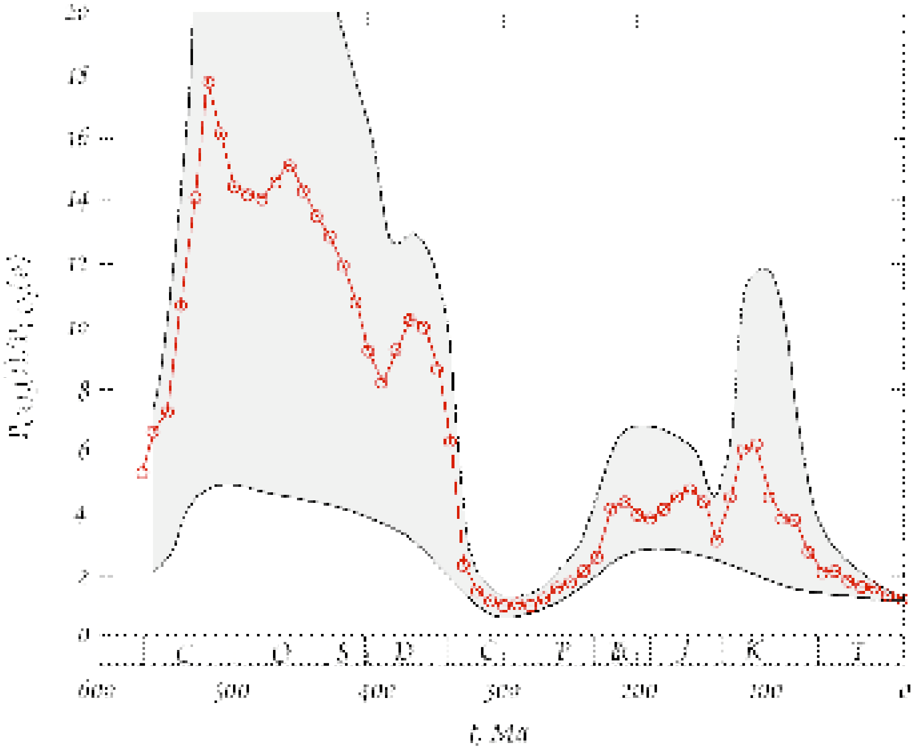


Figure 38.5. Ratio of atmospheric CO_2 concentration to present atmospheric CO_2 in the model of Berner (1991).

From values of F_{wc} and F_{bc}, he solved for $f_{CO_2}(t)$ in equation 38.8 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 the following mass balance equations such as:

$$dC/dt = F_{bg} - (F_{wc} + F_{mc}) \qquad 38.9$$

and

$$d(\delta_c C)/dt = \delta_o F_{bc} - \delta_c(F_{wm} + F_{mc}) \qquad 38.10$$

The results, with an error envelope based on the sensitivity of the method to various uncertainties in the input parameters, are shown in Figure 38.5. 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 before the late Tertiary/Quaternary glaciation. The Cretaceous, on hand, is well known as a remarkably warm period. Berner's model shows generally high CO_2 during warm periods of the early Paleozoic, low CO_2 (resulting from organic carbon burial, presumably a consequence of colonization of land by plants) associated with glaciation in the late Paleozoic, and high CO_2 (associated with volcanism, among other things) in the warm Cretaceous. Thus if the model is correct, it substantiates the widely held assumption that atmospheric CO_2 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.

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That s all Folks!