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 39.1, 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 38.1 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 2.5-5 x 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), however, it is the fluxes to and from sediments and the mantle that control the atmospheric CO$_2$ concentration.

**Long Term Carbon Cycle**

**Figure 39.1.** 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.
TERTIARY CARBON ISOTOPE RATIOS AND EXTINCTIONS

Figure 39.2 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 $\delta^{13}$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 carbon has $\delta^{13}$C of -6, and consequently volcanism will drive the system to more negative values. The fractionation between dissolved carbonate and precipitated carbonate is fairly small, so
both erosion and burial of carbonate 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 39.2 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 bioproductivity, 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 $\delta^{18}O$ 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 foraminifera, 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 39.2 can be 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 an 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 be-
between the δ\textsuperscript{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\textsubscript{2}. At lower atmospheric CO\textsubscript{2} levels, we would expect plants to fix a greater proportion of the CO\textsubscript{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\textsubscript{4} plants in the late Miocene. However, 95% of the biomass is still C\textsubscript{3}, so this effect is likely to be small.

THE PHANEROZOIC
CARBON ISOTOPE RECORD
AND MODELS OF ATMOSPHERIC CO\textsubscript{2}

Figure 39.4 shows the Phanerozoic variation of δ\textsuperscript{13}C in carbonates and δ\textsuperscript{34}S in evaporites, both of which presumably record the isotopic composition of sea-water at the time of deposition. Perhaps the most notable features of this plot is the dramatic negative shift in δ\textsuperscript{13}C associated with the Permo-Triassic (the largest mass extinction event of all) and the large increase in δ\textsuperscript{13}C associated with the expansion of land plants and high rates of burial of organic carbon 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\textsubscript{2}, making sulfides more subject to oxidation. This mechanism may account for the shift to more positive δ\textsuperscript{13}C and more negative δ\textsuperscript{34}S in the Carboniferous apparent in Figure 39.4.

The sedimentary record of δ\textsuperscript{34}S and δ\textsuperscript{13}C have given rise to various attempts to model the variation of atmospheric CO\textsubscript{2} and O\textsubscript{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 39.5). 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 car-
bon 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:

\[ \delta_o F_{bc} + (\delta_o - \alpha_c) F_{bg} = \delta_o (F_{wc} + F_{mc}) + \delta_g (F_{wg} + F_{mg}) \]  

39.2

where the subscript o denotes the ocean and \( \alpha_c \) is the fractionation during photosynthesis. Because the isotopic composition of the oceans through time can be estimated from \( \delta^{13}C \) in carbonate (e.g., Figure 39.3), equation 39.2 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 \( (F_o(t)) \), biological activity \( (f_b(t)) \), a rate constant \( k_{wc} \), river runoff \( (f_d(t)) \), the mass of carbonate rock \( (C) \), and the \( CO_2 \) “weathering feedback function”, \( f_{CO_2}(t) \):

\[ F_{wc} = f_{CO_2}(t)f_{A}(t)f_{D}(t)f_{R}(t)k_{wg}C \]  

39.3

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 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):

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

39.4

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 35.8. 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:

\[ F_{wc} = f_{A}(t)f_{D}(t)f_{R}(t)k_{wg}G \]  

39.5

where \( f_b \) 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 \( (f_b(t)) f_{CO_2}(t) \) do not occur because weathering of sedimentary organic matter results simply from oxidation rather than attack by carbonic acid or bio-

Figure 39.5. Simple model of carbon flow considered by Berner (1991). Masses of carbon are given in units of \( 10^{18} \) moles. Fluxes are described in the text. After Berner (1991).

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logically 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 \( \text{CO}_2 \) 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:

\[
F_{mc} = f_G(t)f_C(t)k_{mc}C
\]

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

\[
F_{mg} = f_G(t)k_{mg}G
\]

Finally, the flux of carbon due to weathering of silicate rocks and consequent uptake of \( \text{CO}_2 \) and burial as carbonate \( (F_{ws}) \) is expressed as:

\[
F_{ws} = F_{bc} - F_{wc} = f_{CO_2}(t)f_A(t)f_D(t)f_R(t)f_E(t)F_{ws}(0)
\]

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 39.1 and 39.2, calculated the burial fluxes in 1 million year steps. From values of \( F_{wc} \) and \( F_{bc} \) he solved for \( f_{CO_2}(t) \) in equation 39.8 and then for \( \text{CO}_2(t) \). 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:

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

and

\[
\frac{d(\delta C)}{dt} = \delta_{c,f_{bc}} - \delta_{c}(F_{wm} + F_{mc})
\]

The results, with an error envelope based on the sensitivity of the method to various uncertainties in the input parameters, are shown in Figure 39.6. 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 \( \text{CO}_2 \) during warm periods of the early Paleozoic, low \( \text{CO}_2 \) (resulting from organic carbon burial, presumably a consequence of colonization of land by plants) associated with glaciation in the late Paleozoic, and high \( \text{CO}_2 \) (associated with volcanism, among other things) in the warm Cretaceous. Thus if the model is correct, it substantiates the widely held assumption that atmospheric \( \text{CO}_2 \) 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.
REFERENCES AND SUGGESTIONS FOR FURTHER READING


That’s all Folks!