Geol. 656 Isotope Geochemistry

lecture 38 Spring 2003

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 2.5-5 □ 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),

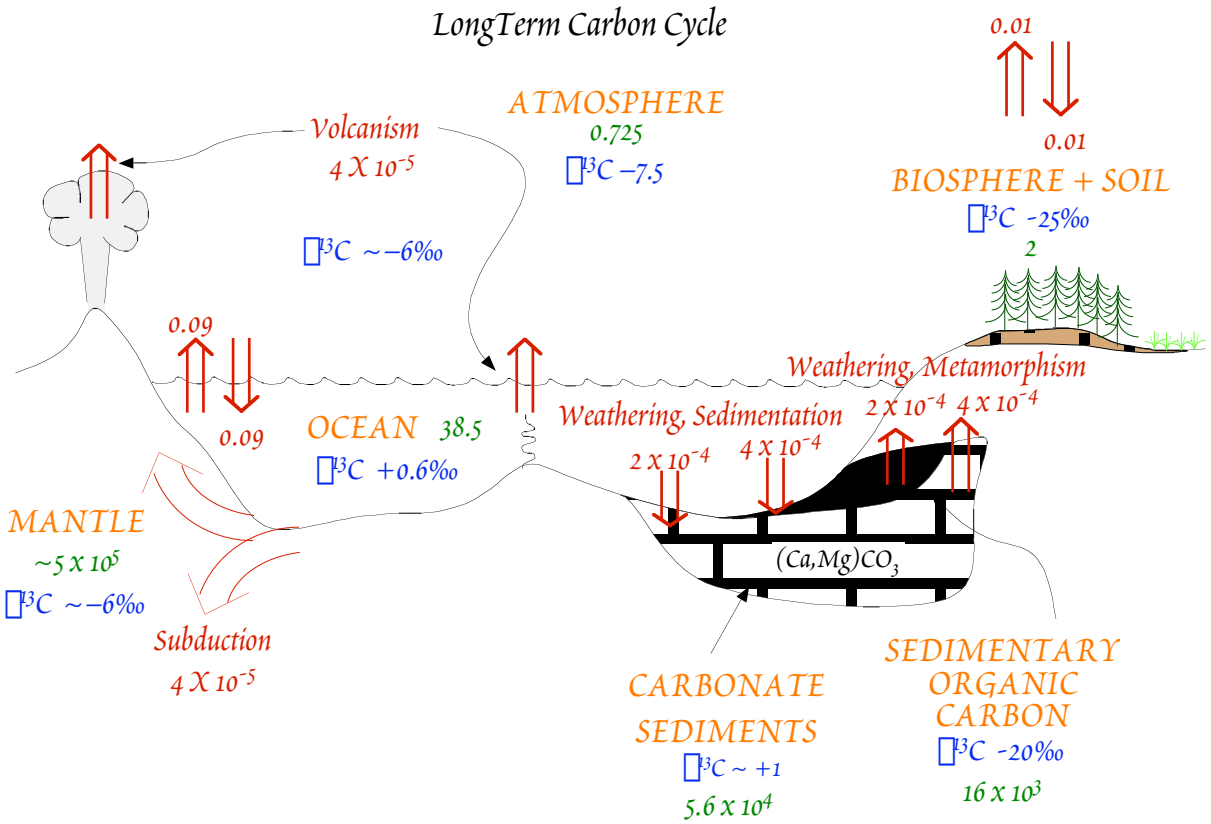


Figure 38.1. The Carbon Cycle. Green numbers show the amount of carbon (in 10^{18} grams) in the reservoirs. Fluxes between these reservoirs (arrows) are shown in italics in units of 10^{18} g/yr (in red). Masses and fluxes refer to the pre-Industrial Revolution state of the system. Uncertainties on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

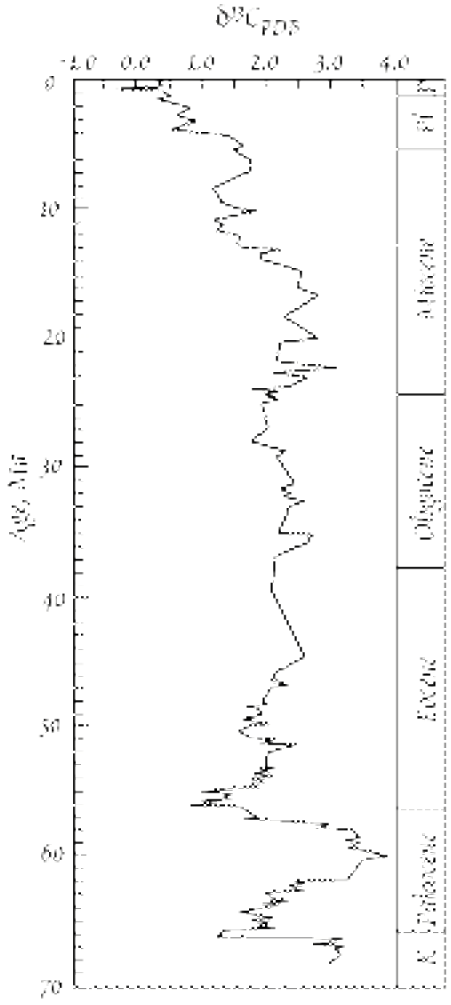


Figure 38.2. $\delta^{13}C$ in the Tertiary as recorded by bulk carbonate in South Atlantic DSDP cores. From Shackleton (1987).

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

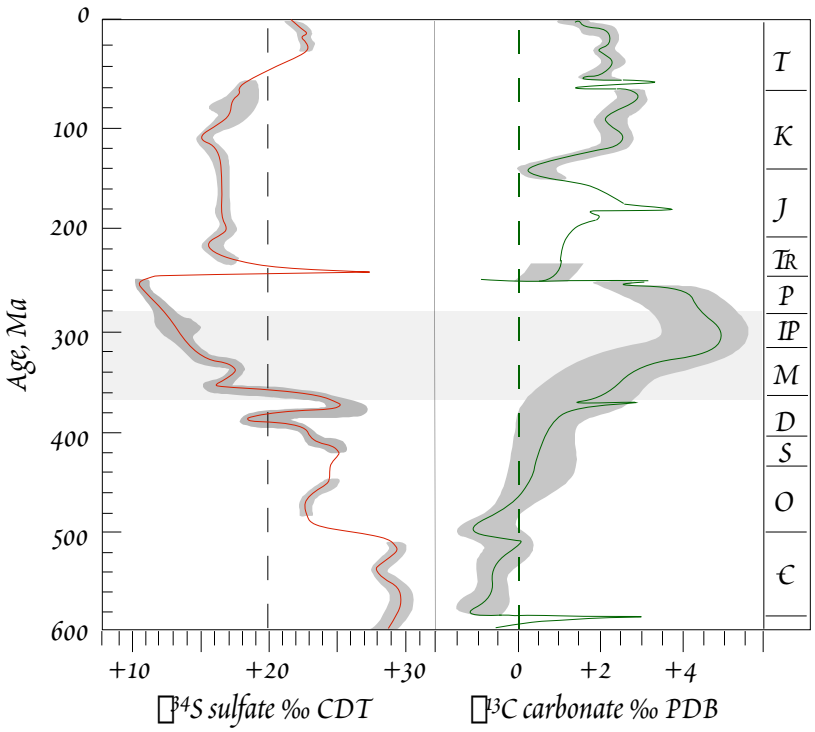


Figure 38.3. Isotopic compositions of carbon and sulfur in the oceans through Phanerozoic time. After Holser (1984).

The sedimentary record of $\delta^{34}S$ and $\delta^{13}C$ 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:

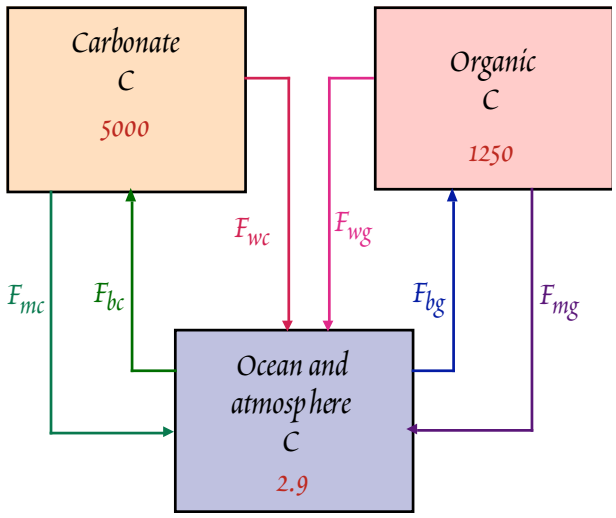
$$\delta_o F_{bc} + (\delta_o - \delta_c)F_{bg} = \delta_o(F_{wc} + F_{mc}) + \delta_g(F_{wg} + F_{mg}) \qquad 38.2$$

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 $\delta^{13}C$ 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.

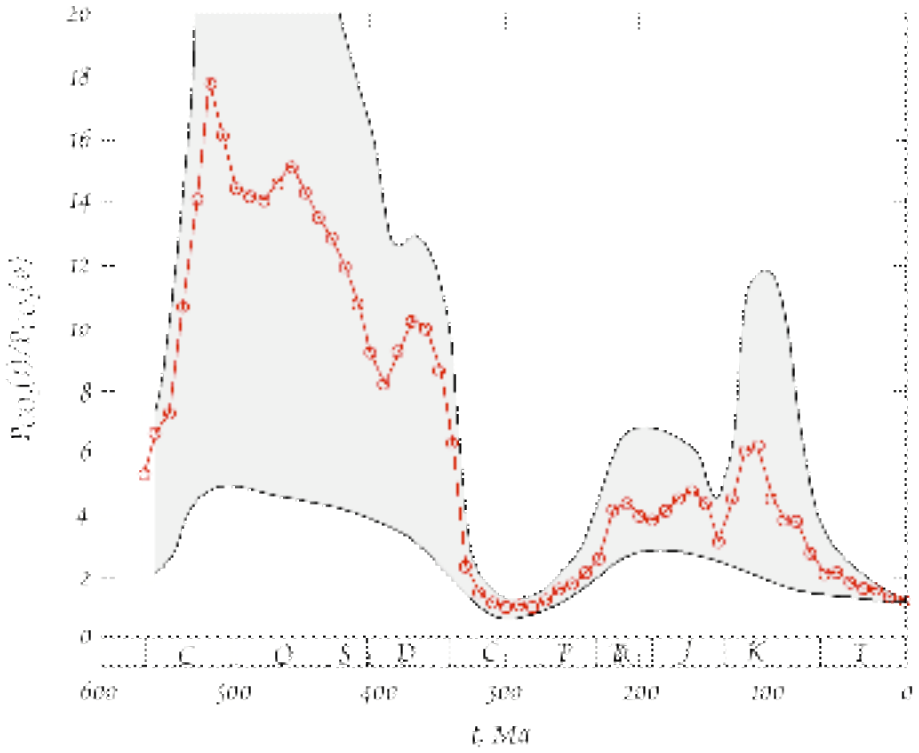


Figure 38.5. Ratio of atmospheric CO_2 concentration to present atmospheric CO_2 in the model of Berner (1991).

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

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

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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