

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 37.1, 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 36.1 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 500 ppm CO_2 in mantle, which implies a total inventory of 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), however, it is the fluxes to and from sediments and the mantle that control the atmospheric CO_2 concentration.

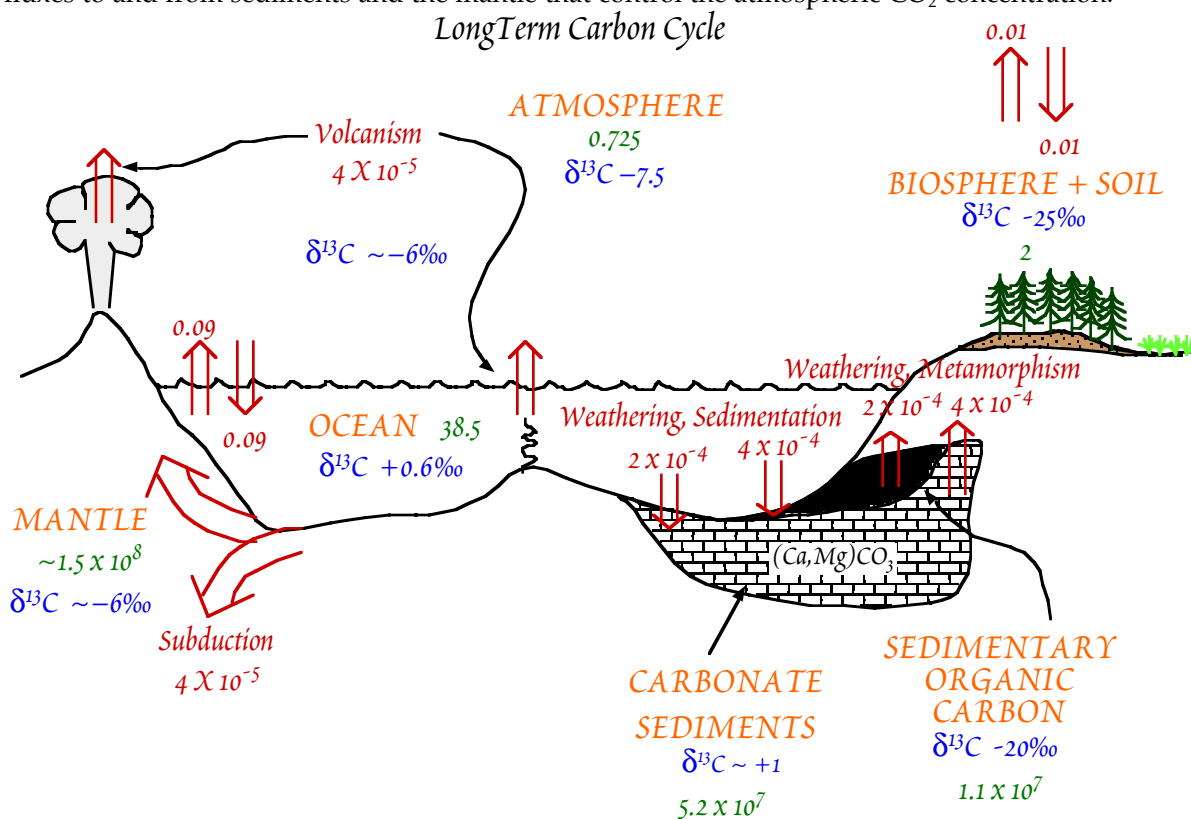


Figure 37.1. The Carbon Cycle. Green numbers show the amount of carbon (in 10^{18} grams) in the reservoirs. Fluxes between these reservoirs (arrows) are shown in italics in units of 10^{18} g/yr (in red). Masses and fluxes refer to the pre-Industrial Revolution state of the system. Uncertainties on many of the masses and fluxes are large. Also shown are estimates of the carbon isotopic composition.

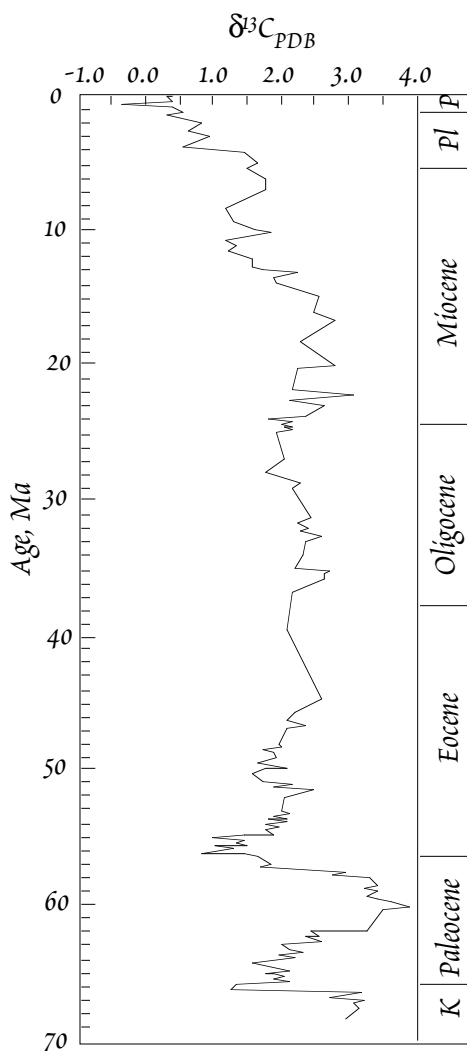


Figure 37.2. $\delta^{13}\text{C}$ in the Tertiary as recorded by bulk carbonate in South Atlantic DSDP cores. From Shackleton (1987).

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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ (Figure 37.3).

THE PHANEROZOIC CARBON ISOTOPE RECORD AND MODELS OF ATMOSPHERIC CO_2

Figure 37.3 shows the variation of $\delta^{13}\text{C}$ in carbonates and $\delta^{34}\text{S}$ in evaporites, both of which presumably record the isotopic composition of seawater at the time of deposition, through the Phanerozoic. 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

TERTIARY CARBON ISOTOPE RATIOS AND EXTINCTIONS

Figure 37.2 shows $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ record does not tell us what caused these extinctions, but it does suggest the

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 37.3.

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). 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. 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:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg} \quad 37.1$$

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 37.1 states that the rate of release of carbon in 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:

$$\delta_o F_{bc} + (\delta_o - \alpha_c) F_{bg} = \delta_o (F_{wc} + F_{mc}) + \delta_g (F_{wg} + F_{mg}) \quad 37.2$$

where the subscript o denotes the ocean and α_c is the fractionation during photosynthesis. 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 atmospheric CO_2 concentration ($f_{CO_2}(t)$) and the mass of carbonate rock (C):

$$F_{wc} = f_{CO_2}(t) f_A(t) f_D(t) f_E(t) k_{wc} C \quad 37.3$$

Similarly for organic sediment weathering:

$$F_{wg} = f_A(t) f_D(t) f_R(t) k_{wg} G \quad 37.4$$

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.

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 volcanism rate (f_G) and the ratio ($f_C(t)$) of platform carbonate to deep sea carbonate (the latter being more commonly subducted), so:

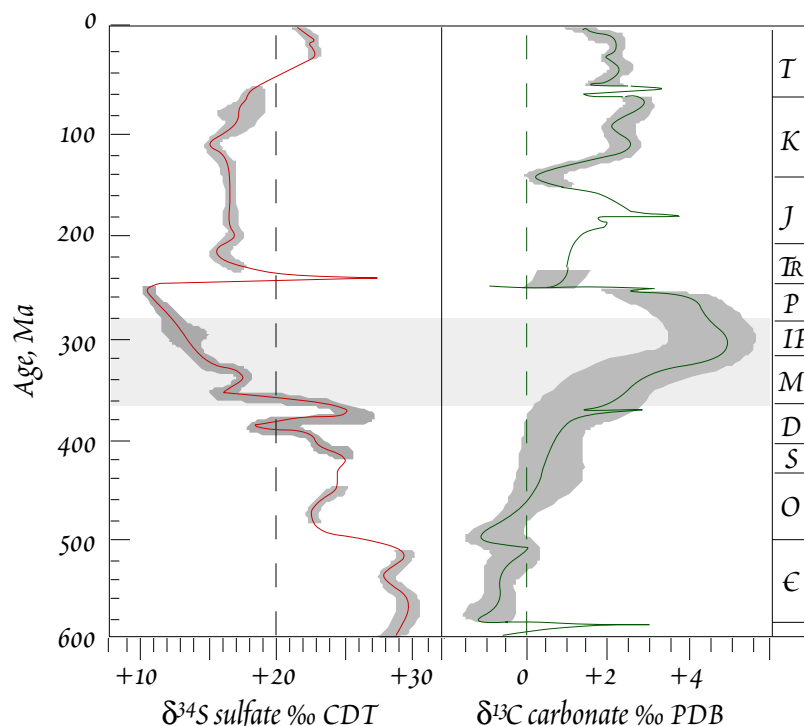


Figure 37.3. Isotopic compositions of carbon and sulfur in the oceans through Phanerozoic time. After Holser (1984).

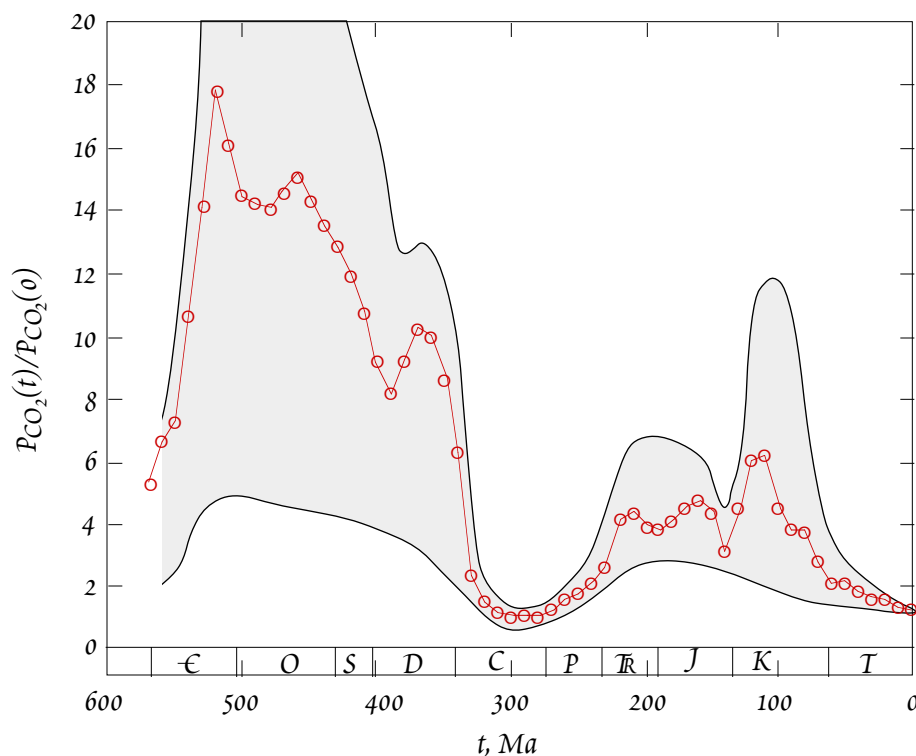


Figure 37.4. Ratio of atmospheric CO₂ concentration to present atmospheric CO₂ in the model of Berner (1991).

$$F_{mc} = f_G(t)f_C(t)k_{mc}C \quad 37.5$$

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

$$F_{mg} = f_G(t)k_{mg}G \quad 37.6$$

Finally, the flux of carbon due to weathering of silicate rocks and consequent uptake of CO₂ and burial as carbonate (F_{ws}) is expressed as:

$$F_{ws} = F_{bc} - F_{wc} = f_{CO_2}(t)f_A(t)f_D(t)f_R(t)f_E(t)F_{ws}(0) \quad 37.7$$

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

Berner estimated the various values of these parameters from information in the geological literature, and solved for $f_{CO_2}(t)$ in equation 37.7 and then for CO₂ in 1 million year steps. The results, with an error envelope based on the sensitivity of the method to various uncertainties in the input parameters, are shown in Figure 37.4. The show generally high CO₂ during warm periods of the early Paleozoic, low CO₂ (resulting from organic carbon burial) associated with glaciation in the late Paleozoic, and high CO₂ (associated with volcanism, among other things) in the warm Cretaceous. Of course, this is simply a model, and many question its validity. While the results are certainly interesting, just how accurate these estimates are remains to be seen.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

- Berner, R. A., A. C. Lasaga and R. M. Garrels, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci.*, 1983, 641-683, 1983.
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That's all Folks!