Chapter 7

CARBON IN THE LOW-TEMPERATURE ENVIRONMENT

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Chapter 7

CARBON IN THE LOW-TEMPERATURE ENVIRONMENT

7.1 Introduction

Carbon dioxide has been called “the most important substance in the biosphere” (Revelle, 1985). It makes life on Earth possible and warms our planet to the habitable condition where H₂O is in the liquid state. Carbon is the foundation of the World’s major energy source, and as fossil fuels continue to be burned at an alarming rate of 10 gigatons of CO₂ emitted per year, we have come to recognize the serious effects of anthropogenic-induced global warming. The carbon cycle is a complex system of feedback mechanisms at many levels, and has been an intense disciple of geologic study. Stable carbon isotopes have played a critical role in this research, being used to constrain sizes and fluxes into and out of the various carbon reservoirs. Other applications include evaluating variations in temperature and productivity in the past, photosynthetic pathways, diets, metabolic pathways, evidence for early life on earth and variations in greenhouse gas abundances through time. In this chapter we will review the carbon cycle, discuss plant photosynthesis and carbonate formation as it relates to carbon isotopes, and provide several examples of application of carbon isotope geochemistry to geological processes.

Carbon exists in oxidized, elemental and reduced forms. Oxidized forms include CO₂ and carbonates, elemental forms include graphite and diamond, and reduced forms include methane and organic matter. As is the case for almost all compounds, the heavy isotope ¹³C is concentrated in the more oxidized forms¹. Metabolic reduction of carbon (i.e. formation of organic matter) is a non-equilibrium process where ¹²C is strongly partitioned into organic matter, leading to two major crustal reservoirs of carbon; a reduced low δ¹³C reservoir and an oxidized high δ¹³C reservoir. Assuming that most carbon in the surficial/crustal reservoir originated as volcanic CO₂ emissions with a near constant mantle value, the massive biologically-induced reduction of carbon over time led to a concomitant production of free oxygen (O₂ gas) critical to most life forms on Earth today.

7.2 The carbon cycle

The carbon cycle is complex and has been studied at many scales. The mantle reservoir, which swamps all others in size, is unimportant when considering changes in atmospheric p(CO₂) related to short-term anthropogenic contributions. Transfer to and from the mantle reservoir (the flux rate) is simply too slow. Likewise, the abundance of CO₂ in the atmosphere is miniscule compared to the major reservoirs, and can be ignored when concerned with the long-term carbon budget. On the other hand, transfer of CO₂ between reservoirs is often made via the atmosphere, making it an important flux. In addition to size, therefore, fluxes into and out of the different reservoirs are of critical importance.

¹ Rare exceptions include carbon monoxide (relative to graphite), nitric oxide and ammonium ion for the nitrogen system.
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The major reservoirs for carbon in the crust are sedimentary inorganic carbon in the form of carbonates (e.g., limestones, dolomites), organic carbon, and carbon hosted in crystalline rocks. Reservoirs, their abundance, fluxes, and their $\delta^{13}$C values are given in Table 1 and shown in Figures 7.1 and 7.2.

To a first approximation, we can assume that the carbon cycle is a balanced, steady-state system. Fluxes into and out of each reservoir equal each other, as seen in Figure 7.1. The exception, of course, is the anthropogenic flux of CO$_2$ from fossil fuel burning to the atmosphere, causing a minor, short-term ($10^3$ – $10^5$ y) imbalance. Although small in size, the fluxes involving atmospheric CO$_2$ are immense, so that equilibrium between oceans and terrestrial organic carbon is maintained at near steady-state. There is a huge annual incorporation of CO$_2$ during plant respiration ($122 \times 10^{15}$ g C/year), which is nearly balanced by decomposition of plants and organic carbon in soils. The other large flux is between the atmosphere and surface ocean, where CO$_2$ is transferred to dissolved bicarbonate and back again. Finally, the flux between the surface and deep oceans is large and nearly balanced. The fluxes between the other reservoirs – carbonates, mantle,
organic carbon in sedimentary rocks – are orders of magnitude slower, and have relevance only in studies of long term climate variation.


<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Mass/10^{15} g C</th>
<th>δ^{13}C ‰ (PDB) average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere (@ 290 PPM)</td>
<td>775</td>
<td>-6 to -7</td>
</tr>
<tr>
<td>Ocean (TDC)</td>
<td>35,000</td>
<td>0</td>
</tr>
<tr>
<td>(DOC)</td>
<td>1,000</td>
<td>-20</td>
</tr>
<tr>
<td>(POC)</td>
<td>3</td>
<td>-22</td>
</tr>
<tr>
<td>Land plants</td>
<td>1600</td>
<td>-25 (-12 for C₄ plants)</td>
</tr>
<tr>
<td>Soil humus</td>
<td>1000-3000</td>
<td>-25 (-12 for C₄ plants)</td>
</tr>
<tr>
<td>Sedimentary inorganic C</td>
<td>60,000,000</td>
<td>0 to 1</td>
</tr>
<tr>
<td>(carbonates)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>organic carbon</td>
<td>15,000,000</td>
<td>-23</td>
</tr>
<tr>
<td>continental silicic crust</td>
<td>7,000,000</td>
<td>-6</td>
</tr>
<tr>
<td>mantle</td>
<td>324,000,000</td>
<td>-5 to -6</td>
</tr>
</tbody>
</table>

7.2.1 Carbon isotope budget of the Earth

Fractionation between oxidized, inorganic carbon species is generally small. In contrast, the fractionation between inorganic (oxidized) and organic (reduced) carbon is very large. In fact, isotopically light carbon is a characteristic signature of life. The δ^{13}C values of 3.7 Ga carbonates from Greenland have been used to postulate a gradual buildup of organic matter through time (e.g., Schidlowski et al., 1979; Mojzsis et al., 1996). If all terrestrial carbon has come from the mantle with minimal fractionation, then the average δ^{13}C values of the terrestrial carbon reservoirs must equal those of the mantle. The two main terrestrial reservoirs, carbonate sedimentary rocks and organic carbon should equal to the assumed mantle value of -5.5‰ according to the equation

\[ x \left( \delta^{13}C \right)_{\text{carbonate}} + (1 - x)(\delta^{13}C)_{\text{organic carbon}} = -5.5‰ \] 7.1,

where \( x \) is the fraction of carbonate relative to total carbon in both reservoirs. Average carbonate and organic carbon reservoirs give a rough \( \Delta^{13}C \) (carbonate – organic carbon) value of 23‰ and an average δ^{13}C value of carbonates of 0‰, equation 7.1 becomes

\[ x \left( \delta^{13}C \right)_{\text{carbonate}} + (1 - x)(\delta^{13}C_{\text{carbonate}} - 23) = -5.5‰ \] 7.2,

resulting in a carbonate fraction of 0.76, in good agreement with the data in Table 1.

7.3 Carbon reservoirs

General ranges for δ^{13}C values of typical reservoirs are shown in Figure 7.2 and described in further detail in the following sub-sections.
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7.3.1 Mantle
Mantle carbon enters the crustal reservoir mainly from mid-ocean spreading ridges and rift systems. The $\delta^{13}C$ value of CO$_2$ from the mantle is ~6 to -5‰ (see Chapter 11). The $\delta^{13}C$ values of carbonatites and MORB are close to mantle value, with a minor light component (-22 to -26‰) for diamonds and MORB (Deines, 2002). The explanation for the low values may be related to subduction of organic carbon or degassing processes in the mantle (see Section 11.2.2 for more details).

Fig. 7.2. General range of $\delta^{13}C$ (and $\delta^{18}O$) values of selected carbon-bearing materials.
7.3.2 Plants

The formation of reduced organic carbon occurs by reduction of CO$_2$ during photosynthesis\(^2\). Other forms of reduced carbon, from petroleum to animals, to black shales, ultimately can trace their origin back to photosynthesis. Therefore, we begin by reviewing the mechanisms and isotopic fractionations that occur during photosynthesis. Terrestrial plants derive their carbon from photosynthetic fixation of atmospheric CO$_2$, as does marine plankton. Other aquatic plants fix carbon from dissolved HCO$_3^-$.

Photosynthetic organisms remove ~10% of the CO$_2$ in the atmosphere per year, which is balanced by the decomposition of plant material at a later stage. The simple glucose producing reaction involves the reduction of CO$_2$ and production of O$_2$ using water as a hydrogen donor:

$$6\text{CO}_2 + 12\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 6\text{O}_2$$  \[7.3\]

The overall reaction is divided into two separate mechanisms: the “Light reaction” and the “Dark reaction”. The Light reaction involves transfer of electrons from the donor molecule water to the acceptor molecule nicotinamide adenine dinucleotide phosphate (NADP), an important coenzyme in the plant cell. The Dark reaction uses NADPH and ATP to fix reduced C and transfer it into carbohydrates in the Calvin-Benson\(^3\) cycle (C$_3$ cycle). The important step in terms of stable isotope chemistry is carboxylation, which involves the addition of CO$_2$ to the acceptor molecule, ribulose bis-phosphate (RuBP), catalyzed by the enzyme ribulose bisphosphate carboxylase-oxygenase (Rubisco). It is the partial removal of CO$_2$ during carboxylation that leads to the major carbon isotope fractionation in plants.

An additional process that occurs in plants is photorespiration, where O$_2$ is taken-up and CO$_2$ is generated. In this process, Rubisco catalyzes the oxygenation of RuBP, ultimately releasing CO$_2$, an overall energy consuming process. Two other photosynthetic pathways called the C$_4$ dicarboxylic acid pathway (C$_4$ pathway) and Crassulacea Acid Metabolism (CAM) have evolved that limit the inefficiencies of C$_3$ photorespiration. In these processes, CO$_2$ is concentrated at the active site of Rubisco to enhance the efficiency of photosynthesis. Photorespiration is significantly reduced in plants using these photosynthetic pathways.

A model of the C$_4$ pathway was first published in 1965 and 1966 (Hatch and Slack, 1966), where $^{14}$CO$_2$ was used as an isotopic tracer to identify the products of photosynthesis in sugarcane. The first labeled products are 4-carbon acids (oxaloacetate and then malate), rather than the 3-carbon acid 3-phosphoglyceric acid (3PGA) in the C$_3$ pathway. Malate enters the bundle sheath cells and is decarboxylated, releasing CO$_2$ which is used by the Calvin cycle as in C$_3$ plants. By concentrating CO$_2$ at the site of carboxylation (Rubisco), C$_4$ (and CAM) minimize photorespiration, a benefit under conditions of low stomatal conductance\(^4\). Low stomatal conductance is beneficial in hot arid environments, where minimizing water loss is critical, and under conditions of low $p$(CO$_2$). The disadvantage is that C$_4$ photosynthesis is less efficient that C$_3$, so that there

\(^2\) Minor CO$_2$ reduction also occurs by chemotrophs, which utilize chemical energy rather than light energy.
\(^3\) Melvin Calvin won the Nobel prize in chemistry in 1961 for his work on assimilation of CO$_2$ by plants.
\(^4\) Stomata are the pore openings of the epidermal layer of plant tissue where transpiration occurs.
is a competition between plants that use one or the other pathway. The basic rules useful for paleoclimate reconstruction are the following (Ehleringer et al., 1997):

- **C₄ plants** do well under conditions of low $p$(CO$_2$)
- **C₄ plants** have high water efficiency, and so are tolerant to high temperatures and aridity. There is a nearly perfect correlation between % C₄ flora in a community and minimum growing-season temperature (Teeri and Stowe, 1976).

Only about 0.4% of angiosperms are C₄ plants, but they account for 18% of total global productivity. C₄ plants include important crops such as maize, sugarcane, sorghum, and tropical pasture grasses. The C₃ pathway is used by trees, most shrubs, herbs and cool weather grasses and aquatic plants. C₃ plants are favored in high latitudes, cooler climates, and, because C₄ plants are so successful in regions with summer rainfall, regions with more arid summers. Forests, woodlands and high latitude grasses are generally C₃.

The different photosynthetic pathways were first recognized by stable isotope geochemists on the basis of two distinct populations of $\delta^{13}$C values in plants (Bender, 1968; Smith and Epstein, 1970). The typical range of C₃ plants is -33 to -23‰, with an average of -27 to -26‰ (Fig. 7.3). The $\delta^{13}$C values of C₄ plants are about 13‰ higher than those of C₃ plants, ranging from -16 to -9, averaging -13 to -12‰. There is no evidence of C₄ plants prior to the Cenozoic (Cerling and Quade, 1993; Cerling et al., 1993). Interestingly, Craig (1954) identified C₄ plants in an elegant work of the carbon isotope fractionation of plants, but incorrectly postulated that the high $\delta^{13}$C values were related to uptake of dissolved carbonates.

Aquatic photosynthetic organisms derive their carbon from dissolved carbon in water. The $\delta^{13}$C values of algae range from -22 to -10‰, plankton from -31 to -18‰, kelp from < -20 to -10‰. Most warm-water plankton have a $\delta^{13}$C value of -22 to -17‰. It has been proposed that there is a temperature-dependent fractionation of the $\delta^{13}$C value of plankton (Sackett et al., 1965; Degens et al., 1968). As plankton get a significant portion of their carbon from dissolved CO$_2$ as opposed to bicarbonate, the temperature dependence is a function of availability. There is no need to postulate temperature-sensitive enzymatic reactions to explain observed fractionations with change in water temperature. When molecular CO$_2$ is sufficiently abundant, there is constant fractionation of about 19‰ between CO$_2$ and cells over all reasonable temperatures. The average $\delta^{13}$C value of marine plants is ~ -20‰.

The carbon isotope fractionation attending photosynthesis was first outlined by Park and Epstein (1960) who noted that two particular steps involved significant fractionation. These were 1) the preferential uptake of $^{12}$C from air CO$_2$ and 2) the conversion of dissolved CO$_2$ by Rubisco to reduced carbon. A simple expression relating $\delta^{13}$C value of a C₃ plant to that of CO$_2$ in air is given by (Farquhar et al., 1989):

$$\Delta^{13}C_{(\text{CO}_2 \text{ in air - plant})} = a \frac{p_a - p_i}{p_a} + b \frac{p_i}{p_a}$$

where $\Delta^{13}$C is the overall discrimination during C assimilation, $a$ (4.4‰) is the discrimination associated with gas phase diffusion in air and $b$ (29‰) is the discrimination associated with carboxylation (mainly by Rubisco). The variables $p_a$ and
\( p_i \) are the partial pressures of CO\(_2\) in the bulk air and intercellular air spaces, respectively. If we take \( p_i = 0.7p_a \) as a typical ratio, then \( \Delta = 21.6 \). For a \( \delta^{13}C \) value of air is -7.9‰\(^5\), plants will form with a \( \delta^{13}C \) value of -28.9‰, in good agreement with typical values for modern \( C_3 \) plants. With lower internal pressure, the discrimination in the carboxylation step is reduced, and the overall fractionation associated with photosynthesis decreases.

It is worthwhile to view equation 7.4 under extreme variations in \( p_i \) and \( p_a \). If \( p_i \) equals \( p_a \) (as might be the case in very low light), then there is no fractionation associated with diffusion of CO\(_2\) into the stomata or cell because there is no CO\(_2\) pressure gradient. The first part of equation 7.4 equals 0 (\( p_a - p_i = 0 \)) and only the fractionation associated with discrimination during intake of carbon by carboxylation. The second part of equation 7.4 reaches its largest possible value (when \( p_i/p_a = 1 \)) which is really quite intuitive. If there is lots of CO\(_2\) in the cell, then the carboxylation step can easily discriminate in favor of the light isotope. Under these conditions the \( \Delta^{13}C_{(CO_2 \text{ in air - plant})} \) reaches a maximum value of 29‰.

At the other extreme consider what happens when a plant is water stressed. The stomata close to minimize water loss, so that there is a large difference in \( p_i \) and \( p_a \). Only a very small amount of CO\(_2\) is admitted into the plant, and that which does make it into the cell is completely consumed in the carboxylation step. As \( p_i \) approaches 0, then the first part of equation 7.4 approaches a value of 4.4‰ and the second part (discrimination

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\(^5\) The Holocene, pre-industrial value was –6.5‰. The modern value is -8.5‰.
unique to C₄ plants). θ is the fraction of carbon fixed by PEP carboxylation that ultimately leaks out of the bundle sheath cells, and contributes to the discrimination at Rubisco. If θ = 0, all carbon fixed by PEP carboxylation is refixed by Rubisco, so that the Rubisco discrimination (b3θ) equals zero. Typical values of ρ in C₄ plants are in the range of 0.3 to 0.4, and θ = 0.3, giving an Δ value of 4‰, or a δ¹³C value of -11.9‰ for the plant, in good agreement with measured values. Note that when \( b_4 + b_3 \theta = a \), Δ = a and is independent of \( \rho(\text{CO}_2) \), as has been observed in experimental studies (Fig. 7.4).

The sensitivity of C₃ plants to \( \rho(\text{CO}_2) \) has led researchers to propose using δ¹³C of plants as a proxy for \( \rho(\text{CO}_2) \) variations in the recent past (e.g., Marino and McElroy, 1991; Feng and Epstein, 1995). Similarly, δ¹³C values of marine phytoplankton have been used to estimate paleo- \( \rho(\text{CO}_2) \) levels (Popp et al., 1989; Freeman and Hayes, 1992).

Local carbon isotope variations occur in dense forest canopies, where plants preferentially incorporate \(^{12}\text{C}\), whereas decay of leaf litter re-releases the \(^{12}\text{C}\) enriched \( \text{CO}_2 \). The net ‘canopy effect’ causes biomass formed close to the forest floor to have δ¹³C values that are approximately 5‰ less than at the canopy top (Cerling et al., 2004).

7.3.3 Organic carbon in sediments

Soil and sedimentary organic carbon reflects the biogenic source. This is clearly evident when considering that coal and disseminated kerogen (i.e., the insoluble organic matter in sediments) have δ¹³C values that overlap the range defined by pre-industrial C₃ plants. Soils in sugar cane fields have δ¹³C values that are consistent with a C₄ plant community. The isotopic range of most petroleum deposits is -30 to -27‰ compared to coal (-26 to -23‰); the difference is consistent with petroleum having a marine sediment
origin (Deines, 1980). Keep in mind that modern marine and terrestrial biomass have distinct isotopic ranges.

There are only minor isotopic shifts associated with preferential oxidation of different components of organic matter. The δ\(^{13}\)C value of soil CO\(_2\) generally matches that of the soil organic matter, indicating little isotopic fractionation during decay. Increasing diagenesis (and catagenesis at higher temperatures) leads to the loss of CO\(_2\), H\(_2\)O, and CH\(_4\). H/C ratios decrease with increasing thermal maturity\(^6\) until a value of zero is reached for graphite, the ultimate product of metamorphism. Inorganic thermal breakdown of the macromolecular carbon skeleton of kerogens favors the breaking of slightly weaker \(^{12}\)C-\(^{12}\)C bonds, thereby liberating \(^{13}\)C-depleted smaller molecules (e.g., methane and CO\(_2\)), such that \(^{13}\)C is slightly concentrated in the residual kerogen.

C/N ratios can be used to distinguish algal and land-plant origins of organic matter. The lower C/N ratios in aqueous plants are related to the absence of cellulose and lignin, in contrast to land plants where lignocellulosic structural biopolymers are needed to fight the effects of gravity. In combination with δ\(^{13}\)C values, different sources for organic matter in lake sediments can be unambiguously identified (Fig. 7.5).

The power of using C/N ratios and δ\(^{13}\)C values in lake sediments to determine origin is illustrated in a core from Lake Baikal, southern Siberia. Lake Baikal is extremely deep, and has a record of over 9000 years of continuous sedimentation. Sediment type, C/N ratios and δ\(^{13}\)C values all change dramatically at ~6.8 thousands years before present (Fig. 7.6). The low C/N ratios in the younger sediments and δ\(^{13}\)C values averaging ~28‰ indicate a very high component of lacustrine algae with a minor vascular plant material component. Older sediments have a much larger land plant component, indicating lower productivity in the lake. The higher δ\(^{13}\)C values suggest a significant C\(_4\) component (Qui et al., 1993).

\(^6\) In a straight chain n-alkane hydrocarbon molecule, the H/C ratio is \(2 + 2/C\). In the extreme case of graphite, the H/C ratio is 0.
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The use of organic carbon in sedimentary sequences for chemostratigraphic reconstruction is complicated by the wide range of source material and preferential breakdown of certain components. One way of isolating unique organic components is with compound-specific gas chromatography techniques. Hayes et al. (1989) found that by analyzing only the geoporphyrin fraction, they were able to discriminate primary carbon of marine photosynthetic origin from that derived from non-photosynthetic sources. The geoporphyrin fractions were consistently depleted in $^{13}$C relative to total organic carbon by up to 7‰, and provided far more information than bulk organic carbon alone. Additional works have shown that the organic carbon (as well as biogenic carbonates) could be used to evaluate differences in productivity in the past (e.g., Popp et al., 1989).

The $\delta^{13}$C value of POC (particulate organic carbon) transferred by rivers is determined by its source. Values for C$_3$-based catchments are in the range of -25 to -30‰ (Sackett and Thompson, 1963; Strain and Tan, 1979; Spiker, 1981). POC derived from a high percentage of C$_4$ plants obviously has a higher value than that derived from a mainly C$_3$ source.

The $\delta^{13}$C values of TDC (total dissolved carbon) as opposed to particulate organic matter may also have significant contributions from dissolved carbonate rocks, in addition to oxidation of organic material. Rivers draining carbonate-poor catchments typically have $\delta^{13}$C values around -20‰, while carbonate-rich drainages have $\delta^{13}$C values closer to -10 to -11‰. Under cool conditions, less organic matter is oxidized, and the $\delta^{13}$C value of river waters reflects a larger contribution of dissolved carbonate. Estimated average global TDC values range from -6 to -9‰ (Anderson and Arthur, 1983) to ~-5‰ (Kump, 1991), a number that is used in considering the global carbon cycle (section 7.4).

7.3.4 Methane

The $\delta^{13}$C values of methane are invariably far lower than their source (Rosenfeld and Silverman, 1959). Depending on the mechanism of methane formation, $\delta^{13}$C values of methane can be as low as -100‰ (Fig. 7.7) and form organic matter via methanotrophic organisms with similarly low $\delta^{13}$C values (Kaplan and Nissenbaum, 1966). Oxidation of light methane generates CO$_2$ and ultimately carbonates with anomalously low $\delta^{13}$C values (Irwin et al., 1977). In freshwater systems, CH$_4$ is formed by acetate fermentation (e.g., CH$_3$COOH $\rightarrow$ CH$_4$ + CO$_2$) where the carbon in methane is derived from the methyl group of acetate. In saline environments, methane is produced by reduction of CO$_2$ (e.g. CO$_2$ + 8(H) $\rightarrow$ CH$_4$ + 2H$_2$O). In the first case, carbon isotope
fractionation between acetate and newly-formed CH$_4$ is small. In contrast, there is a large fractionation between CO$_2$ and methane evolved during CO$_2$ reduction, so that methane formed by this mechanism has much lower $\delta^{13}$C values (Whiticar et al., 1986; Whiticar, 1999). Fig. 7.7 shows the profound differences in the $\delta$D values of methane produced by different mechanisms. Bacterial fermentation can produce $\delta$D values lower than -400°C.

7.3.5 Atmospheric CO$_2$

The average global $\delta^{13}$C value of CO$_2$ in the atmosphere has changed from -6.7‰ in 1956 to -7.9‰ in 1982 (Keeling et al., 1979), to less than -8.3‰ today as a result of fossil fuel burning. (The change is commonly referred to as the Suess Effect, although this term originally was used in the context of changing $\Delta^{14}$C values due to the burning of ‘dead’ $^{14}$C fossil fuels). Variations in the $\delta^{13}$C values of the atmospheric CO$_2$ before Keeling’s work at Mona Loa have been measured using C$_4$ plants$^7$ (Drake et al., 2016) and particularly ice cores (Fig. 7.8). Ancient variations in atmospheric $\delta^{13}$C are more difficult to determine, but can be estimated from marine carbonates. The global atmospheric $\delta^{13}$C value is related to the overall global carbon cycle, where different sources and sinks and their respective fluxes will lead to a quasi steady-state system (Affek and Yakir, 2014).

There are also variations associated with fossil fuel burning near large industrial-populated areas. Diurnal, seasonal and regional variations (N. Hemisphere vs. S.

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$^7$ The $\delta^{13}$C value of C$_4$ plants is relatively insensitive to $p$(CO$_2$) as seen in Fig. 7.4.
Hemisphere) are also found to exist due to different natural sources and sinks of CO₂ (e.g., Ciais et al., 1995; Clark-Thorne and Yapp, 2003). The δ¹³C value of atmospheric CO₂ changes by more than 1‰ on an annual timescale due to summer-winter changes in productivity. See Affek and Yakir (2014) for a detailed review.

### 7.4 δ¹³C values of carbonates

#### 7.4.1 Introduction

Most marine carbonates form in near-equilibrium with dissolved inorganic carbon, primarily HCO₃⁻. Disequilibrium, related to vital effects (see section 7.4.3), can be corrected for, and with proper characterization, do not limit the information that is available from carbon isotope data from carbonates. The fractionation during carbonate precipitation is small and relatively insensitive to temperature (unlike the oxygen isotope fractionation), so that δ¹³C values of ancient marine carbonates reflect the δ¹³C value of dissolved inorganic carbon from which they formed. Locally, and on relatively short time scales, the δ¹³C value of dissolved inorganic carbon will be related to productivity, ocean circulation, weathering, and other factors such as rapid input of exotic carbon sources. Over the 10-100 million year scale, the global δ¹³C value of dissolved inorganic carbon varies in relation to the relative proportions of the two major carbon reservoirs, organic carbon and carbonate in the crust. And, because the residence time of dissolved inorganic carbon in the ocean is sufficiently long, major carbon isotope variations in marine sequences can be correlated over a wide geographic scale (Scholle and Arthur, 1980).

These ideas were, in part, formulated by Keith and Weber (1964) and Weber et al. (1965) 50 years ago. The use of carbon isotope geochemistry in reconstruction of paleoclimate is without doubt, one of the most important tools in the paleoclimatologist’s modern arsenal.

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![Fig. 7.8. Variations in δ¹³C value of atmospheric CO₂ as a function of age. Data are from direct measurements of atmospheric CO₂, measured δ¹³C values of maize (a C₄ plant) and ice core air inclusions. After (Marino and McElroy, 1991).](image-url)
7.4.2 General characterization of carbonates

A certain number of basic rules apply to carbonates.

1. The source of the carbon for marine limestones is dissolved bicarbonate, with a Δ^{13}C_{carbonate-dissolved} bicarbonate of 1 to 2‰. Average ocean TDC (predominantly HCO_{3}^{-}) for the bulk ocean has a δ^{13}C value of ~1‰ (Fig. 5.5). Δ^{13}C values of TDC in the shallow oceans are higher than the overall ocean by about 1 to 2‰ due to the actions of the biological pump (Box 7.1).

2. The average δ^{18}O and δ^{13}C values of unaltered marine carbonates are close to 0‰ (on the PDB scale). The δ^{13}C value of carbonates in equilibrium with modern surface waters is 2-4‰. Lower values are related to vital effects and diagenesis. Deep water limestones have slightly positive δ^{18}O values because they form under cold conditions where the fractionation between carbonates and water is larger.

3. Terrestrial carbonates have low δ^{18}O values because they form in equilibrium with meteoric water. Tuffs and freshwater limestones incorporate a combination of dissolved inorganic carbon and atmospheric CO_{2}. If the dissolved inorganic carbon comes from the dissolution of marine carbonates, δ^{13}C value will be near zero. In contrast, dissolved inorganic carbon sourced by oxidation of organic matter will lead to strongly negative δ^{13}C values of precipitating carbonates. In general, freshwater limestones have negative δ^{13}C values, depending on the contribution from organic carbon.

4. The δ^{13}C value of soil carbonates is controlled by CO_{2} respired from soil biota, as well as from decaying organic litter and soil organic carbon, so that the δ^{13}C values of soil carbonates (paleosols) are an indicator of the type of plant (C_{3} vs. C_{4}) living at the time of carbonate formation. Soils formed in the presence of C_{4} plants have δ^{13}C values 12 to 13‰ higher than those formed in predominantly C_{3} plant communities (see section 7.5). The δ^{18}O value is a function of local meteoric water, with minor secondary evaporation effects.

5. Diagenesis almost always lowers the δ^{18}O values of marine carbonates (O’Neil, 1987). δ^{13}C values also tend to become lower during diagenesis as well, but the effect is often far less pronounced. This is a logical outcome of the fact that most diagenetic aqueous fluids contain only trace amounts of dissolved carbon (see Fig. 6.8). Much larger fluid/rock ratios are needed to alter the δ^{13}C than δ^{18}O value. In rare cases, δ^{13}C values of diagenetically altered marine carbonates will increase by reaction with residual CO_{2} following methanogenesis (removal of light carbon).

7.4.3 The vital effect

Certain organisms consistently deposit their carbonate shells out of carbon and/or oxygen isotope equilibrium with ambient fluids, the so-called vital effect. Vital effects have been explained by either metabolic processes or by a combination of metabolic and kinetic processes (McConnaughey, 1989a, b). Stable isotope relations observed in biogenic
Box 7.1. The biological pump. There is a steady-state, non-equilibrium carbon isotope fractionation between TDC in the shallow and deep ocean due to high biological activity in the near-surface photic zone of the ocean. Photosynthesizing organisms incorporate carbon and nutrients during their growth in the shallow ocean. In doing so, they preferentially incorporate \(^{12}\text{C}\) in their tissues, causing a \(^{13}\text{C}\) enrichment in the remaining TDC of the shallow ocean. Upon their death, the remains of organisms sink into the deep ocean where they are oxidized, releasing light carbon back to the ocean. The continuous removal of light carbon from the shallow ocean in essence acts as a CO\(_2\) pump, transferring light carbon from shallow to deep levels in the ocean, and causing a 1 to 2‰ fractionation between the two ocean reservoirs. In times of reduced productivity, the intensity of the biological pump decreases, and the shallow oceans will reequilibrate with the larger deep ocean TDC reservoir. The transfer of carbonates from the shallow to deep ocean has a negligible effect because the \(\delta^{13}\text{C}\) value of carbonates differ only slightly from that of TDC.

Carbonates have fascinated isotope geochemists and biologists alike since the inception of the discipline. With appropriate caveats, it is reasonable to state that biogenic carbonate is commonly deposited in or near oxygen isotope equilibrium with ambient waters. And, when disequilibrium is the rule for a given organism, the departure from equilibrium is often fairly constant and the temperature sensitivity of the disequilibrium fractionation is nearly the same as that of equilibrium fractionations. Thus relative temperatures can often be determined with a good degree of confidence in these cases. Facts like these explain in part the success of the oxygen isotope paleotemperature method (Watkins et al., 2013).

In stark contrast to the oxygen isotope case, biogenic carbonate is rarely deposited in carbon isotope equilibrium with dissolved carbon in environmental waters. In addition, the overall magnitude of carbon isotope disequilibrium is greater than for oxygen because the carbon reservoir (HCO\(_3^-\)) in these systems is vastly smaller than the oxygen reservoir (H\(_2\)O). In all but a few cases, the direction of disequilibrium is such that \(^{12}\text{C}\) is preferentially incorporated into the shells so that \(\delta^{13}\text{C}\) values are more negative than equilibrium values. Departures from equilibrium precipitation are shown for many extant organisms in Figure 7.9.

Several basic rules apply. Slowly precipitating carbonates are most likely to be in equilibrium. There are many shells that appear to precipitate carbonates in equilibrium with water, but others that are lighter than equilibrium values by 4 and 14‰ for oxygen and carbon isotope ratios, respectively. Photosynthesis has no apparent effect on the \(\delta^{18}\text{O}\) value of newly-forming carbonate material, but can lead to higher \(\delta^{13}\text{C}\) values because organic matter formed during photosynthesis preferentially incorporates \(^{12}\text{C}\), leaving the inorganic carbon reservoir with higher \(\delta^{13}\text{C}\) values.

The kinetic aspect of vital effects concerns the relative rates of both diffusion and chemical reactions of different isotopologues of dissolved carbonate species in the body fluids. Light isotopologues (both carbon and oxygen isotopes) diffuse faster than heavy isotopologues and react with other substances faster. As a consequence, \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) values of biogenic carbonate secreted rapidly with a kinetic isotope effect (1) are more negative than equilibrium values and (2) covary (Fig. 7.10). The word rapidly is emphasized because organisms whose isotopic ratios reflect a kinetic process must
precipitate their carbonate almost immediately after some key reaction because the normally rapid oxygen isotope exchange between HCO$_3^-$ and H$_2$O has not taken place. Information like this is helpful to marine biologists and biochemists attempting to understand physical and chemical controls on skeletogenesis in a variety of species. The difference between $\delta^{18}$O/$\delta^{13}$C relations governed by both kinetic and metabolic effects and kinetic effects alone are shown nicely for two species of coral in Figure 7.10.

Metabolic processes have little effect on oxygen isotope ratios, but they can have a strong effect on carbon isotope ratios of dissolved inorganic carbon (DIC) in the internal pool of body fluids that are used for calcification. The processes of interest cause removal of light CO$_2$ from this pool during photosynthesis and addition of light CO$_2$ to the pool from respired CO$_2$. Photosynthetic organisms like algae preferentially use isotopically light ($\text{CO}_2$)$_{\text{aq}}$ to synthesize organic matter in soft tissues thereby leaving behind isotopically heavy carbon in the internal DIC pool. Thus if photosynthesis is a viable
control on $^{13}$C/$^{12}$C ratios in these systems, $\delta^{13}$C values of skeletal parts of photosynthetic organisms should be more positive than those of non-photosynthetic organisms living in similar environments. In fact $\delta^{13}$C values of shells of hermatypic corals (those containing symbiont zooxanthellae) are usually higher than those of ahermatypic corals. In addition, the higher the rate of photosynthesis or growth rate (e.g. at higher illumination), the higher are the $\delta^{13}$C values of certain corals. But just the reverse effect has been noted for large foraminifera in natural settings – the greater the growth rate, the lower the $\delta^{13}$C if shell carbonate. The effects are clearly complicated.

Respired CO$_2$ has lower $\delta^{13}$C values than that of ambient DIC and can become a constituent of the internal carbon pool in some organisms. For example, Lee and Carpenter (2001) provided good evidence that carbon from respired CO$_2$ is incorporated into biogenic carbonate by certain taxa of marine calcareous algae. When metabolic factors dominate the vital effect of a population of organisms, $\delta^{13}$C values can vary widely while $\delta^{18}$O values remain relatively constant.

### 7.4.4 Carbonate speciation effects

In addition to vital effects related to kinetic and metabolic effects, isotope fractionations can be controlled by speciation effects. Through laboratory culturing experiments, Spero et al. (1997) showed that pH dependent variations in carbonate speciation in seawater can bear significantly on carbon and oxygen isotope ratios of shells secreted by certain foraminifera and presumably, other organisms as well. With increasing pH and concomitant increase in [CO$_3^{2-}$]$_9$, both $\delta^{18}$O and $\delta^{13}$C values steadily decrease below values predicted by equilibrium relations. The magnitude of the effect is sufficient to lower $\delta^{18}$O and $\delta^{13}$C values of *O. universa* shells by 0.2 and 0.6‰, respectively, with an increase of only 0.2 pH units.

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8 CO$_2$ and H$_2$O are usually in approximate oxygen isotope equilibrium in body fluids due to the presence of the carbonic anhydrase enzyme which catalyzes the exchange reaction.

9 [CO$_3^{2-}$] increases almost linearly with pH from a normal seawater pH value of 8.0 to a value of 8.6.
Zeeb (1999) explained these effects for oxygen by considering equilibrium oxygen isotope fractionation factors between the various species involved in carbonate precipitation. The oxygen isotope fractionation between HCO₃⁻ and CO₃²⁻ is an astonishingly high 16‰¹⁰. With increase in pH, the CO₃²⁻/HCO₃⁻ ratio increases such that, if the carbonate species are taken up by the organism in proportion to their relative abundance, the slope of the δ¹⁸O-[CO₃²⁻] theoretical relation is ~0.0024, a value that is indistinguishable from the value of ~0.0022 observed in the laboratory for O. universa.

The speciation effect becomes particularly important when oxygen isotope analyses of foraminifera are used to reconstruct seawater temperatures during glacial periods. Several lines of evidence indicate that glacial oceans were more alkaline than modern oceans. If p(CO₂) of the atmosphere was significantly lower in peak glacial times than during interglacial periods, as chemical analyses of inclusions in ice cores would suggest, the concentration of CO₃²⁻ might have increased enough to induce significant lowering of δ¹⁸O of shell carbonate that could be incorrectly attributed to an increase in ocean temperature.

7.4.5 Controls on the δ¹³C value of marine carbonates over long time scales

In spite of the complicating vital effects discussed above, to a first approximation, the δ¹³C values of precipitating marine carbonates are determined by the value of total dissolved inorganic carbon (TDC, mainly HCO₃⁻). The average δ¹³C_{TDC} of whole-ocean is 0-1‰. The calcite-bicarbonate carbon isotope fractionation is small and relatively insensitive to temperature (Fig. 7.11), so that measured δ¹³C values of marine carbonates directly reflect the δ¹³C value of TDC. The near-surface TDC has a δ¹³C value that is 1 to 2‰ higher than the overall ocean due to the effects of the biological pump (box 7.1). The positive δ¹³C values of the near-surface water about 9‰ higher than atmospheric CO₂, in excellent agreement with estimates for equilibrium fractionation between the two reservoirs (Mook et al., 1974).

It is worthwhile to consider how all of the surface reservoirs interact. If we accept a +1‰ for the δ¹³C value of the deep ocean (Fig. 5.5) then the shallow ocean is 1 to 2‰ heavier than this, assuming that the biological pump is active. That puts the shallow ocean at 2-3‰. Carbonates precipitating in the shallow ocean will be still higher, reaching δ¹³C values as high as 4‰. From Fig. 7.11, we see that atmospheric CO₂ should be about 9‰ lighter than the dissolved shallow water bicarbonate, or -6 to -7‰, in excellent agreement with the pre-anthropogenic δ¹³C value of the atmosphere as measured in glacial ice. Finally, we

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¹⁰There is also a large oxygen isotope fractionation of about 8 per mil between the analogous H₃PO₄ and PO₄³⁻. Large fractionations between such similar species are not well understood.

Fig 7.11. Carbon isotope fractionation curves for calcite, bicarbonate and CO₂ gas. Data from Emrich et al. (1970).
consider plants. The average $\delta^{13}C$ value of C$_3$ plants is -26‰, suggesting a $\Delta^{13}C_{CO_2-C_3}$ plants value of 20‰. From equation 7.4, a fractionation of 20‰ is achieved when $p_i = 0.65 p_a$, in agreement with measured data. Not surprising then, all of the shallow carbon reservoirs are in near equilibrium or in a condition of steady-state disequilibrium (deep and shallow ocean). So it might seem worthwhile to ask which reservoirs control the $\delta^{13}C$ value of the whole system. The answer is that it depends very much on the timescale that one is considering. On the sub-annual time scale, the $\delta^{13}C$ value of the atmosphere will change due to different seasonal rates of photosynthesis and oxidation of organic matter. On a yearly to decadal timescale, the atmosphere will be controlled by exchange with the shallow ocean and plants. On a longer timescale, the activity of the biological pump will control the fractionation between the shallow and deep ocean, which in turn would affect the $\delta^{13}C$ value of the plant communities. And on a still longer timescale, the overall $\delta^{13}C$ value of the near surface system will be dictated by the proportions of carbon delivered to the oceans by the large organic and inorganic carbon reservoirs (Fig. 7.1).

Fig. 7.12 is a secular curve of the $\delta^{13}C$ value of marine carbonates on a million year time scale. The $\delta^{13}C$ value of precipitating carbonates is controlled by the value of the total dissolved carbon in the ocean and the TDC composition is related to proportions of inorganic and organic carbon by equation 7.2. Variations in Fig. 7.12 are related to tectonic activity, particularly erosion and/or deposition of organic-rich material and changing degrees of productivity. Note that formation or dissolution of carbonates will not affect the $\delta^{13}C$ value of TDC because the carbon isotope composition of the two reservoirs are almost the same. During the Carboniferous period when extremely high amounts of organic carbon were buried, the $\delta^{13}C$ values of inorganic carbon and TDC of the oceans reached their highest level in the Phanerozoic, and this is reflected in the carbonate record, where $\delta^{13}C$ values of carbonates reach over +4‰.

Because reduction of inorganic carbon releases oxygen, the $p(O_2)$ of the atmosphere is closely tied to the amount of carbon in the reduced form$^{11}$. Photosynthetic reduction of CO$_2$ releases O$_2$, thereby raising the $p(O_2)$ of the atmosphere (Berner, 1987).

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$^{11}$ Oxygen stored in sulfate can be re-released as O$_2$ during sulfate reduction. Removal of organic carbon by subduction also acts to shift the balance between $\delta^{13}C$ value and $p(O_2)$. 

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Accordingly, we see a close relationship between the long term $\delta^{13}C$ value of marine carbonates and atmospheric $p(O_2)$ (Fig. 7.13).

The most extreme carbon isotope variations are found in Proterozoic carbonates (Fig. 7.14). Carbon isotope values in marine carbonates range from less than -4‰ to over 10‰. Changes in the Archean are related to increased biological fractionation as a result of methanotrophic\textsuperscript{12} recycling (Krissansen-Totton et al., 2015). Large excursions in the Proterozoic have been explained in terms of large transfers of carbon between the inorganic and organic reservoirs, and concomitant fluctuations in atmospheric $p(O_2)$ (Des Marais, 2001). It is almost certain that the long-term deviations from isotopic steady-state conditions were caused by radical global changes in (i) the ability of biota to reduce vast amounts of carbon and (ii) Earth’s dynamic processes that can temporarily shield reduced organic carbon from re-oxidation. Note that the global $\delta^{13}C$ values of organic carbon change far more than that of carbonates, due to their different reservoir sizes.

7.4.6 Variations in the $\delta^{13}C$ values of marine carbonates at short time scales

Short term ‘spikes’ in $\delta^{13}C$ values of carbonates are related to catastrophic changes in ocean productivity or inputs of light

\textsuperscript{12} Methanotrophs are prokaryotes that metabolize methane.
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carbon. Over 60 such worldwide events have been recognized (Holser et al., 1996). We must be sure to clearly distinguish between a local and worldwide event. Isolated shallow marine basins can locally exhibit sharp carbon isotope excursions due to local geographic effects, such as changing circulation, overturn, changes in access to the open ocean etc. These do not have global significance. Because the residence time of TDC is long (1.8 ka and 55 ka for the shallow and deep oceans, respectively), complete homogenization on the worldwide scale should occur if an event affects the entire planet. To be sure that a carbon isotope excursion is truly of global significance, the event must be identified in geographically distinct carbonate sections throughout the world.

There are several mechanisms that can cause rapid global-wide changes to the $\delta^{13}C$ value of TDC. The first of these is a sudden loss of productivity due to a catastrophic event, such as the large impact at the K/T boundary, intense volcanic activity or rapid change in oceanic circulation. The sudden loss of productivity has been termed the ‘Strangelove Ocean’ (Hsü and McKenzie, 1985), after the Stanley Kubrick classic film Dr. Strangelove. Loss of productivity shuts down the biological pump, and the shallow ocean quickly equilibrates with the deep ocean on a 100 year time scale (Fig. 7.15). The shallow ocean thus acquires the $\delta^{13}C$ values of the much larger deep ocean reservoir. Recovery and restart of the biological pump occurs on much longer time scales, ranging from 0.5 to 1 Ma depending on the rapidity with which biological productivity once again resumes. The Cretaceous-Tertiary boundary is the classic example of perturbation of the biological pump, where all of the features expected by catastrophic productivity loss are observed (Zachos and Arthur, 1986). Certainly one of the best-refined examples of a global carbon isotope shift is that which occurs at the Paleocene/Eocene boundary (Fig. 7.16). Kennett and Stott (1991) recognized that there was a marked decrease in the $\delta^{13}C$ values for both shallow and deep water foraminifera

![Fig 7.15. Variations in the $\delta^{13}C$ value of shallow-water foraminifera– red (P. petaloidea) and deep-water foraminifera– blue (R. rotundata) across the K/T boundary. Convergence of the shallow- and deep-water foraminifera data indicate a loss of productivity and shut-down of the biological pump. Lines show theoretical changes in carbonate $\delta^{13}C$ values across a catastrophic extinction boundary. Solid line = shallow-level carbonate trend with return to full recovery; dashed line, same with organic burial rate = 0.9 of the pre-event value; dotted line is the predicted deep-water carbonates. See (Zachos et al., 1989; Kump, 1991).](image-url)
that occurred in just a few thousand years. This is a marked difference to the observations of K/T boundary sections. In the K/T sections, the $\delta^{13}C$ values of shallow and heavy carbon converge to a common value. The shifts can be explained in terms of reduction in productivity and shutting down the biological pump. In the case of the Paleocene/Eocene boundary sections, there is a lowering of both planktic and benthic foraminifera $\delta^{13}C$ values. These data cannot simply be explained by mixing of shallow and deep ocean. To explain Fig. 7.16 requires massive input of a $^{13}C$-poor carbon source. Initial explanations for the isotopic anomaly at the Paleocene/Eocene were only partially satisfactory. Then in 1995, Dickens et al. (1995) proposed that dissociation of oceanic methane hydrate could explain both the low $\delta^{13}C$ values seen in Figure 7.16 as well as changes in the oxygen isotope ratios. Release of unstable methane hydrates (with $\delta^{13}C$ values averaging -65‰) related to changing ocean circulation patterns would cause a rapid lowering in the $\delta^{13}C$ values of the surface ocean and a more gradual change in the deep ocean as light CO$_2$ generated by the oxidation of methane was transferred through the thermocline. Similarly, the sharp decrease in $\delta^{18}O$ values in the planktic foraminifera data indicate a rapid warming of the surface ocean due to the increase in greenhouse gases, whereas the deep ocean took longer to respond.

As is so often the case, additional information – this time from boron isotope data – have led to a different interpretation for the Paleocene-Eocene boundary carbon excursion. Gutjahr et al. (2017) use boron isotopes as a proxy for shallow ocean pH and suggest that the Paleocene-Eocene excursion is more likely related to an enormous release of CO$_2$ during volcanism from the North Atlantic Igneous Province.

![Fig. 7.16. $\delta^{13}C$ and $\delta^{18}O$ values of benthic and planktic foraminifera across the Paleocene-Eocene boundary. Changes in $\delta^{18}O$ values indicate a warming of 5-8°C over a few thousand years. The abrupt lowering of $\delta^{13}C$ values indicates a switching off of the biological pump and incorporation of light carbon, presumably from methane gas hydrates. Reprinted from Jenkyns (2003), with permission from the Royal Society of London.](image-url)
7.5 \(\delta^{13}C\) studies of terrestrial carbonates

Just about every type of carbonate precipitated on the land surface has been analyzed in order to extract climatological and paleoclimatological information (e.g., Swart et al., 1993). Studies aimed at elucidating information about modern conditions include the source of CO\(_2\) for deposition of travertines (Turi, 1986), and information on rainfall and evaporation from oxygen isotope ratios of calcrites (Rossinsky and Swart, 1993). Breecker et al. (2009) identified a seasonal bias in the precipitation of soil carbonates on the basis of combined carbon and oxygen isotope ratios of soil CO\(_2\). Chronological information can be obtained from speleothems (Schwarcz et al., 1976; Baskaran and Krishnamurthy, 1993), stromatolites (Casanova and Hillaire, 1993), ostracods, soil carbonates (Cerling and Quade, 1993), and varved lake deposits (McKenzie, 1985), just to name a few.

The \(\delta^{13}C\) value of pedogenic carbonate is dominated by the vegetation isotopic signal, with significant differences due to varying proportions of C\(_3\) and C\(_4\) plants (Cerling and Quade, 1993). Soil carbonates, fossil tooth enamel and sediments in the Bengal Fan both show a remarkable increase of 10 to 12‰ between 7 and 5 Million years ago (Quade et al., 1989) that have been since recognized as a global feature (Cerling et al., 1993; France-Lanord and Derry, 1994). The shift in the Bengal Fan sediments (Fig. 7.17) reflects the global expansion of C\(_4\) biomass over a previously dominant C\(_3\) plant community, due to a drop in atmospheric CO\(_2\) levels. The cause of this global effect may be related to initiation of the Asian monsoon system.

![Fig. 7.17. Carbon isotope shift related to a global shift from a C\(_3\) to C\(_4\) dominated plant community. The increased success of C\(_4\) plants beginning \(-7\) Ma is related to a decrease in the atmospheric p(CO\(_2\)). Isotope data are from paleosol carbonates from Pakistan. Similar trends are found in North and South America from tooth enamel, demonstrating that the trend is global. From Cerling et al. (1993).](image-url)
7.5.1 Paleo-p(CO$_2$) estimates from soil carbonates

It has been demonstrated that the $\delta^{13}$C value of soil carbonates is directly related to the partial pressure of CO$_2$ in the atmosphere (Cerling, 1991; Cerling, 1992). The concept is based on the idea that soil-derived CO$_2$ and atmospheric CO$_2$ have very different $\delta^{13}$C values. The $\delta^{13}$C value of the soil CO$_2$ close to the soil-air interface is strongly affected by the partial pressure of CO$_2$ in the atmosphere. Because soil carbonates precipitate in equilibrium with the ambient soil CO$_2$, their $\delta^{13}$C values will be closely tied to the $p$(CO$_2$) of the atmosphere. Fig. 7.18 shows the compilation of atmospheric $p$(CO$_2$) over the Phanerozoic. What is striking is that while variations are large, the highest $p$(CO$_2$) values over the last 400 million years are no higher than what is projected for the end of the century due to fossil fuel burning.

![Fig. 7.18. Compilation of atmospheric $p$(CO$_2$) estimates for the Phanerozoic based on the $\delta^{13}$C values of soil carbonates. Blue line represents 10 Ma bin average. Also shown are average values based on other proxies (grey curve). The highest $p$(CO$_2$) values over the last 400 million years are no greater than what is predicted from fossil fuel burning if left unchecked. Modified from Breecker et al. (2010).](image-url)
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