10.1.1 Introduction

The isotopic composition of a given element in living tissue depends on: (1) the source of that element (e.g., atmospheric CO$_2$ versus dissolved CO$_2$; seawater O$_2$ vs. meteoric water O$_2$), (2) the processes involved in initially fixing the element in organic matter (e.g., C$_3$ vs. C$_4$ photosynthesis), (3) subsequent fractionations as the organic matter passes up the food web. Besides these factors, the isotopic composition of fossil material will depend on any isotopic changes associated with diagenesis, including microbial decomposition. In this section, we will see how this may be inverted to provide insights into the food sources of fossil organisms, including man. This, in turn, provides evidence about the environment in which these organisms lived.

10.1.2 Isotopes and Diet: You are what you eat

In Chapter 8 we saw that isotope ratios of carbon and nitrogen are fractionated during primary production of organic matter. Terrestrial C$_3$ plants have $\delta^{13}$C values between -23 and -34‰, with an average of about -27‰. The C$_4$ pathway involves a much smaller fractionation, so that C$_4$ plants have $\delta^{13}$C between -9 and -17‰, with an average of about -13‰. Marine plants, which are all C$_3$, can utilize dissolved bicarbonate as well as dissolved CO$_2$. Seawater bicarbonate is about 8.5‰ heavier than atmospheric CO$_2$; as a result, marine plants average about 7.5‰ heavier than terrestrial C$_3$ plants. In contrast to the relatively (but not perfectly) uniform isotopic composition of atmospheric CO$_2$, the carbon isotopic composition of seawater carbonate varies due to biological processes. Because the source of the carbon they fix is more variable, the isotopic composition of marine plants is also more variable. Finally, marine cyanobacteria (blue-green algae) tend to fractionate carbon isotopes less during photosynthesis than do true algae, so they tend to average 2 to 3 ‰ higher in $\delta^{13}$C.

Nitrogen isotopes are, as we saw, also fractionated during primary uptake. Based on their source of nitrogen, plants may also be divided into two types: those that can utilize N$_2$ directly, and those utilize only “fixed” nitrogen as ammonia and nitrate. The former include the legumes (e.g., beans, peas, etc.) and marine cyanobacteria. The legumes, which are exclusively C$_3$ plants, utilize both N$_2$ (through symbiotic nitrogen-fixing bacteria in their roots) and fixed nitrogen, and have an average $\delta^{15}$N of +1‰, whereas modern nonleguminous plants average about +3‰. However, it seems likely that prehistoric nonleguminous plants were more positive, averaging perhaps +9‰, because the isotopic composition of present soil nitrogen has been affected by the use of chemical fertilizers. For both groups, there was
probably a range in $\delta^{15}\text{N}$ of $\pm 4$ or $5\%$, because the isotopic composition of soil nitrogen varies and there is some fractionation involved in uptake. Marine plants have $\delta^{15}\text{N}$ of $+7 \pm 5\%$, whereas marine cyanobacteria have $\delta^{15}\text{N}$ of $-1 \pm 3\%$. Figure 10.1 summarizes the isotopic composition of nitrogen and carbon in the various classes of photosynthetic organisms (autotrophs).

DeNiro and Epstein (1978) studied the relationship between the carbon isotopic composition of animals and their diet. (Most of the animals in this study were perhaps of little direct paleontological interest, being small and soft-bodied. DeNiro and Epstein studied small animals for a practical reason: they are easier to analyze than a large animal such as a horse.) Figure 10.2 shows that there is little further fractionation of carbon by animals and thus the carbon isotopic composition of animal tissue closely reflects that of their diet. DeNiro and Epstein (1978) estimated that carbon in animal tissue is on average about $1\%$ heavier than their diet. Mice, although not analyzed whole and not shown in Figure 10.2, were also included in the study. Various tissues from mice had $\delta^{13}\text{C}$ within $\pm 2\%$ of their diet, so the relationships in Figure 10.2 extend to vertebrates as well. DeNiro and Epstein found that the same species has a different isotopic composition when fed a different diet. Conversely, different species had similar isotopic compositions when fed the same diet. Thus diet seems to be the primary control on the isotopic composition of animals. Subsequent work by McCutchan et al. (2003) found an average shift in $\delta^{13}\text{C}$ of animals relative to their diet of $+0.5 \pm 0.13$.

The small fractionation between animal tissue and diet is a result of the slightly weaker bond formed by $^{12}\text{C}$ compared to $^{13}\text{C}$. The weaker bonds are more readily broken during respiration, and, not surprisingly, the $\text{CO}_2$ respired by most animals investigated was slightly lighter than their diet. Thus only a small fractionation in carbon isotopes occurs as organic carbon passes up the food chain, about $+1\%$ at each step in the chain. Terrestrial food chains are usually not more than 3 trophic levels long, implying a maximum further fractionation of $+3\%$. Marine food chains can have up to 7 trophic levels, implying a maximum carbon isotope difference between primary producers and top predators of $7\%$. These differences are smaller than the range observed in primary producers. In a simi-
lar study, DeNiro and Epstein (1981) found that $\delta^{15}N$ of animal tissue is related to the $\delta^{15}N$ of the animal’s diet, but is typically 3 to 4‰ higher than that of the diet (Figure 10.03). Thus in contrast to carbon, significant fractionation of nitrogen isotopes will occur as nitrogen passes up the food chain.

Schoeninger and DeNiro (1984) studied the carbon and nitrogen isotopic composition of bone collagen in animals. Their findings reflected just the relationships expected from the work of DeNiro and Epstein (1978, 1981): in primary herbivores, carbon in bone collagen was a few per mil heavier than the isotopic composition of plants, and $\delta^{15}N$ increased by about 3‰ at each trophic level. More recent work by McCutchan et al. (2003) found that the trophic shift in $\delta^{15}N$ was +1.4±0.21‰ for carnivores raised on invertebrates, +3.3±0.26‰ for carnivores raised on other high-protein diets and was +2.2±0.30‰ for herbivores. Marine vertebrates tend to have more positive $\delta^{15}N$ than do their terrestrial counterparts because they generally feed at a higher trophic level. The primary producers in the ocean are generally microscopic algae. Most marine herbivores are also small (zooplankton); there are very few marine vertebrate herbivores (anchovies are an example). As we noted, marine food chains are longer than terrestrial ones and since nitrogen isotope fractionation occurs at each level, the top marine predators have more positive $\delta^{15}N$ than terrestrial top predators. These relationships are summarized in Figure 10.4.

Apatite in bone appears to undergo isotopic exchange with meteoric water once it is buried, but bone collagen and tooth enamel appear to be robust and retain their original isotopic compositions. Tooth enamel, in which carbon is present as carbonate, however, is systematically 12 to 15‰ heavier than carbon in organic tissue. (Such a fractionation is, of course, expected, and consistent with the observation that carbonate is always heavier than organic carbon.) Collagen typically has carbon about 4‰ heavier than diet. These results mean that the nitrogen and carbon isotopic composition of fossil bones and teeth can be used to reconstruct the diet of fossil animals.

### 10.1.3 Carbon Isotopes and the Evolution of Horses and Grasslands

Horses (Family Equidae) have been around for 58 million years. Beginning in the early Miocene, a major radiation took place and the number of genera in North America increased from three at 25 Ma to twelve at 10 Ma. It subsequently fell at the end of the Miocene, and the last North American species became extinct in the Holocene. A major change in dental morphology, from low-crowned to high crowned, accompanied the Miocene radiation. For nearly 100 years, the standard textbook explanation of this dental change was that associated with a change in feeding from leaf browsing to grass grazing. Grasses contain enough silica to make them quite abrasive, thus a high crowned tooth would last...
longer in a grazing animal and would therefore be favored in horse’s evolution as it switched food sources. The change in horse diet was thought to reflect the evolution of grassland ecosystems (or biomes). This line of reasoning led to the conclusion that grasslands first became important biomes in the Miocene.

Carbon isotope ratios provide the first opportunity to test this hypothesis. Grasses of tropical and temperate regions are almost exclusively C₄ plants. C₃ grasslands occur only in high latitude regions. In the North American prairie, for example, C₃ grasslands become important only north of the US-Canadian border (Figure 10.5). The appearance of grasslands inferred from the evolution of horse teeth implies a change from a predominantly C₃ to a predominantly C₄ photosynthetic pathway and a corresponding shift in the δ¹³C of the biomass in these regions. Since the carbon isotopic composition of animals reflects that of their diet, and since the δ¹³C of dental enamel appears to record the δ¹³C of the animal, the change in horse dentition should also be reflected in a change in the carbon isotopic composition of those teeth if the change in dentition were related to a change in diet.

Wang et al. (1994) carried out such a test by analyzing the carbon isotopic composition of dental enamel from fossil horse teeth of Eocene through Pleistocene age. They found a sharp shift in the isotopic composition of the teeth consistent with a change in diet from C₃ to C₄ vegetation, but it occurred later than the change in dental morphology (Figure 10.6). The change in dental morphology begins in the mid-Miocene (about 18 Ma), while shift in δ¹³C occurs at around 7 Ma. This leads to an interesting dilemma. Which change, morphology or carbon isotopic composition, actually reflects the appearance of the grassland biome? It is possible that the change in dental morphology is unrelated to the evolution of grasslands? If that is the case, it is difficult to understand the change in dental morphology. Alterna-
tively, grasslands may have appeared in mid-Miocene and only subsequently become dominated by C₄ grasses.

If the latter interpretation is correct, it raises the question of what evolutionary pressure caused the change from C₃ to C₄ photosynthesis in tropical and temperate grasses. An important observation in that respect is that C₄ grasslands appear to have become important in both North America and Asia at about the same time (7 Ma). Indeed, the first evidence for a shift from C₃ dominant to C₄ dominant ecosystems came from an observed change in the δ¹³C of soil carbonate in Pakistan (Quade et al., 1989). Quade et al. (1989) first interpreted this as a response to the uplift of the Tibetan Plateau and the development of the Monsoon. However, other evidence, including oxygen isotope data from Pakistani soil carbonates, suggests the Monsoons developed about a million years earlier (at about 8 Ma). The synchronicity of the C₄ grass becoming dominant in the grasslands in Asia and North America (Figure 10.7) suggests a global cause, while the Monsoons are a regional phenomenon. Furthermore, subsequent ¹⁴C studies of the teeth of horses and other mammals revealed that, at least in Tibet, uplift of the plateau was associated with a shift from C₄ to C₃ vegetation (Wang et al., 2006).

Though there has been some speculation that the C₄ photosynthetic pathway may have evolved as early as the Cretaceous, the oldest direct fossil evidence for C₄ plants (plants with enlarged bundle-sheath cells) is late Miocene; i.e., the same age as the observed δ¹³C increase. Thus the isotopic shift may date the evolution of C₄ photosynthesis. C₄ photosynthesis involves only relatively minor modification of plant enzymes and structures and it occurs in diverse, distantly related families. It may, therefore, have evolved independently in many families (Ehleringer, et al. 1991). This also suggests some global environmental change that favored C₄ photosynthesis.

Several groups suggested that the appearance of C₄ grasses reflects a drop in the concentration of atmospheric CO₂ in the Miocene. In the C₃ photosynthetic pathway,
Rubisco can catalyze not only the fixation of carbon in phosphoglycerate, but also the reverse reaction where CO₂ is released, a process called photospiration. When concentrations of CO₂ are high, the forward reaction is favored and the C₃ pathway is more efficient overall than the C₄ pathway. At low CO₂ concentrations, however, the C₄ pathway, in which CO₂ is first transported into bundle-sheath cells, is more efficient, as the concentration in bundle-sheath cells is maintained at around 1000 ppm (Figure 10.08). Thus under present conditions, C₄ plants have a competitive advantage. At higher CO₂ conditions, C₃ plants are more efficient. There is some evidence that Eocene CO₂ concentrations were much higher than present (perhaps 800 ppm as opposed to 250 ppm pre-Industrial Revolution), and that concentrations dropped dramatically during the Miocene (however, other isotope evidence, which we will discuss in a subsequent section, suggests the drop in CO₂ concentrations occurred in the Eocene). Such a drop would give C₄ plants a competitive advantage. This would be particularly true in the warm climates where C₄ plants dominate because the rate of photospiration is temperature dependent.

An interesting epilogue to these studies is that of MacFadden et al., (1999) who analyzed both carbon isotopes and abrasion patterns of 6 species of early Pliocene (~ 5 Ma) horses from Florida. All six species bore the high-crowned dental hallmark of grazers. Some species grazed solely on C₄ grasses, but others, notably including D. mexicanus, a close relative of the modern horse, browsed C₃ shrubs and trees. The high crowned dental morphology had been inherited from their ancestors and when the species switched back to eating browse, its teeth did not change. This is an example that evolution is often “irreversible”.

### 10.1.3.2 Isotopes, Archeology, and Paleodiets

The differences in nitrogen and carbon isotopic composition of various foodstuffs and the preservation of these isotope ratios in bone collagen provides a means of determining what ancient peoples ate. The Tehuacan valley in the state of Puebla, Mexico contains a remarkable archeological record of human habitation going back nearly 10,000 years. Consequently, it had been the subject of classic studies on the origins of Western Hemisphere agriculture by R. S. MacNeish in the 1960’s. The first inhabitants, the Ajuerado phase, were small bands of nomadic hunter-gathers. The first evidence for plant cultivation came in the El Riego phase with evidence of experimentation with plantings of squash, chili, amaranth, and possibly wild maize (teosinte). DeNiro and Epstein (1981) analyzed the isotopic composition of bone collagen from human remains of Tehuacan inhabitants and found that maize (a C₄ plant) became an important part of their diet as early as 4000 BC, whereas archeological investigations had concluded maize did not become important in their diet until perhaps 1500 BC (Figure 10.9a). In addition, there seemed to be steady increase in the dependence on legumes (probably beans) from 6000 BC to 1000 AD and a more marked increase in legumes in the diet after 1000 AD (Figure 10.9b).

A dependence of C₄ vegetation, or on herbivores that fed on it, is certainly not new in human history. Carbon isotopic studies have shown that human ancestors Australopithecus africanus and Homo ergaster had diets of which was on average 25% derived from C₄ plants (van der Merve et al., 2003, Lee-Thorp et al., 2000). The fraction of diet derived from C₄ plants was highly variable: from nearly 0 to 50% for dif-
different individuals. The dependence of C₄-derived nutrition is consistent with the idea that human evolution involved, in part, leaving the forests (which are composed entirely of C₃ plants) and moving out into the savannah, which is dominated by C₄ grasses. δ¹³C of both plant biomarkers (organic chemicals that can be associated with a specific biological source) in Gulf of Aden sediments and soil increased over the last 3 Ma, indicating an expansion of East African grasslands. DeMenocal (2011) points out that there is a particularly rapid change in these δ¹³C values occurs around 2.6 Ma, which coincides with the appearance of the genus Homo and the extinction of Australopithecus afarensis (“Lucy”).

Mashed grain and vegetable charred onto potsherds provides an additional record of the diets of ancient peoples. DeNiro and Hasdorf (1985) found that vegetable matter subjected to conditions similar to burial in soil underwent large shifts in δ¹⁵N and δ¹³C but did not undergo such shifts if the vegetable matter was burned or charred. The carbonization (charring, burning) process itself produced only small (2 or 3‰) fractionations. Since these fractionations are smaller than the range of isotopic compositions in various plant groups, they are of little significance. In the process of cooking, plant remains can become charred onto the pots in which they are cooked. Since potsherds are among the most common artifacts recovered in archeological sites, this provides a second value means of reconstructing the diets of ancient peoples.

Figure 10.9 summarizes the results obtained in a number of studies of bone collagen and pot sherds (DeNiro, 1987). Studies of several historical populations, including Eskimos and the Tlingit Indians of the Northwest US, were made as a control. The isotope data show that the diet of Neolithic Europeans consisted entirely of C₃ plants and herbivores feeding on them, in contrast to the Tehuacan Indians, who depended mainly on C₄ plants. Prehistoric peoples of the Bahamas and Denmark depended both on fish and on agriculture. In the case of Mesolithic Denmark, other evidence indicates the crops were C₃, and the isotope data bear this out. Although there is no corroborating evidence, the isotope data suggest the Bahamians also depended on C₃ rather than C₄ plants. The Bahamians had lower δ¹⁵N because the marine component of their diet came mainly from coral reefs. Nitrogen fixation is particularly intense on coral reefs, which leads to ¹⁵N depletion of the water, and consequently, of reef organisms. A limitation of this approach, however, is that animals derive their nitrogen from proteins they consume. Protein-poor foods, such as potatoes, which can provide a significant proportion of dietary calories, are effectively invisible to nitrogen isotope analysis.
A taste for “seafood”, including freshwater fish, seems to be one way in which the earliest fully modern human of Europe differed from Neanderthals. The former arrived in Europe about 40,000 years ago, and rapidly displaced the Neanderthals, who had been there for the previous 100,000 years or more. Carbon and nitrogen isotopic compositions of Neanderthal bone collagen over that time suggests they hunted herbivores who fed on C₃ plants (there were no edible C₄ plants in Europe). Bone collagen of Paleolithic modern humans from Europe has higher δ¹⁵N and lower δ¹³C than that of Neanderthals they displaced. Comparison of human isotopic compositions with those of possible prey species, such as bison, ibex, and red deer, led Richards and Trinkaus (2009) to conclude that humans must have included significant amounts of aquatic or marine foods in their diet. This is particularly true of bones found at Pečstra cu Oase, Romania, which at 40,000 years, are the oldest dated modern human remains found in Europe to date.

Oxygen in combination with strontium isotope ratios have also proved useful in archeological research. An excellent example is the case of the “Iceman”, the remains of a copper age human that had been frozen and mummified in an Alpine glacier for 5200 years before his discovery in 1991. The body was discovered by Austrian hikers near the crest of the Alps and Austrian authorities took custody of it, but it actually had been found just across the border in Italy. Consequently, there were questions as to whether the Iceman was Austrian or Italian, as well as a jurisdictional dispute between the Austrian and the Italians. Müller et al. (2003) analyzed oxygen, carbon and strontium, and lead isotope ratios in the Iceman’s bones and teeth. The isotopic composition of tooth enamel is fixed in childhood, whereas bone material is renewed continually and hence its isotopic composition reflects the environment over the last several years of life. Rain falling on the Italian side of the Alps is derived from the relatively warm Mediterranean and is isotopically heavier than the rain in Austria, derived from the relatively cold North Atlantic. The Iceman’s tooth enamel and bones had δ¹⁸O close to -11, implying he grew up and lived most of his adulthood in the Eisack/Isarco, Rienz, Hohlen, or Non valleys of the Italian side. Comparison of Sr and Pb isotopic compositions of the Iceman’s bones with rocks outcropping in the region confirm his Italian origin and suggest that the Feldthurns archeological site in the Eisack valley was most likely his home.

Figure 10.10. δ¹³C and δ¹⁵N of food stuffs and diets reconstructed from bone collagen and vegetable matter charred onto pots by DeNiro and colleagues. The Huanca people were from the Upper Mantaro Valley of Peru. Data from pot sherds of the Huanca I period (AD 1000-1200) suggest both C₃ and C₄ plants were cooked in pots, but on C₃ plants during the Huanca II period (AD 1200-1470). Also shown in the average bone collagen 13 Neanderthals from Europe and a 40,000 year old modern human from Pečstra cu Oase, Romania (Richards and Trinkaus, 2009). Modified from DeNiro (1987).
10.1.5 Carbon Isotopes and the Earliest Life

We saw in Chapter 8 that carbon fixation, whether through chemosynthesis or photosynthesis, produces a large negative isotopic fractionation of carbon. This large fractionation occurs in the Benson-Calvin cycle that is common to all autotrophs. Consequently, \( \delta^{13}C \) values of -20‰ or less in reduced carbon compounds are generally interpreted as evidence of biologic origin of those compounds. Schidlowski (1988) first reported \( \delta^{13}C \) as low as -26‰ in samples from Godthåbsfjord region of West Greenland that are ostensibly older than 3.5 Ga. In 1996, Mojzsis and others reported \( \delta^{13}C \) between -20 to -50‰ in graphite inclusions in grains of apatite in 3.85 Ga in banded-iron formations (BIFs) from Akilia Island in that same area of West Greenland. In 1999, Røsing reported \( \delta^{13}C \) of -19‰ from graphite in tubiditic and pelagic metasedimentary rocks from the Isua greenstone belt in the same area (Figure 10.11). These rocks are thought to be older than 3.7 Ga.

Schidlowski (1988), Mojzsis et al. (1996), and Røsing (1999) all interpreted these negative \( \delta^{13}C \) as evidence of a biogenic origin of the carbon, and therefore that life existed on Earth at this time. This is older that the earliest physical fossil evidence of life, which occurs in rocks 3.5 Ga old. Furthermore, the earliest part of this time coincides with the late heavy bombardment of the Moon, and a similar asteroid bombardment is thought to have affected the Earth at this time – presumably, making life difficult for any organisms that did exist. Perhaps not surprisingly then, the interpretation of life older than 3.7 Ga has been controversial.

There are several reasons for the controversy, but all ultimately relate to the extremely complex geological history of the area. The geology of the Godthåbsfjord region includes not only the early Archean Isua greenstone belt and Itsaq gneiss complex, but also rocks of middle and late Archean age as well. Most rocks are multiply and highly deformed and metamorphosed and the exact nature, relationships, and structure of the precursor rocks are difficult to decipher.

Rosing et al. (1996) demonstrated that at least some of the carbonates sampled by Schidlowski (1988) cross-cut pre-existing lamination and argued that they are veins deposited by metamorphic fluid flow. Van Zuilen et al. (2003) argue that the graphite originated by thermal decomposition of siderite, in reactions such as:

\[
3 \text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}
\]

followed by disproportionation of the CO:
The difference in δ13C they observed between the graphite and carbonate phases, roughly 5 to 10‰, is consistent with equilibrium fractionation in the range of 300-600°C.

On Akilia Island, the locality studied by Mojzsis et al. (1996), the predominant Amitsoq gneisses are metamorphosed dioritic to granitic plutons that surround fragments of metasedimentary rocks that include conglomerates, BIFs, metacherts, and felsic metasediments with graded bedding. The precursors are thought to have been deposited in a shallow marine environment; they were subsequently metamorphosed to nearly granulite facies. Both the ortho- and paragneisses were intruded by the mafic Amerilik dikes, which are now amphibolites. The region was again deformed, folded and metamorphosed in the late Archean. Structural relationships are unclear and although some dates are as old as 3.87 Ga, the age of the metasediments is far less clear. Indeed, the apatites themselves have Pb-Pb ages of 1.5 Ga, but it is unclear whether this is a crystallization or metamorphic age. Even if this is a recrystallization age, it is possible that (1) the depositional age of the metasediments is as young as 3.6 or 3.7 Ga and (2) the apatites and their graphite inclusions are secondary and grew during the early Archean metamorphism.

Samples studied by Røsing (1999) come from some of the least deformed rocks in the region. The rocks have been metamorphosed only to schist facies and original sedimentary structures are apparent. The δ13C in these rocks is fairly uniform, and distinctly more negative than δ13C of graphite (-11‰) and carbonate (-2.5‰) from carbonate veins in the region. Røsing argues that not only that the negative δ13C of graphite is evidence of a biogenic origin of the carbon, but, from sedimentological considerations, that source of the carbon was photosynthetic planktonic organisms. Røsing (1999) reported a Sm-Nd age of 3.78±0.81 Ga for the sediments and the volcanic rocks upon which they were deposited, although the scatter in the isochron is relatively large. Cross-cutting intrusive rocks, however, are well dated at 3.71 Ga and provide a minimum age.

While Røsing’s data do perhaps reflect the best case for life from the Isua area, this age remains 160 Ma younger than the age claimed by Mojzsis et al. (1996). Furthermore, δ13C values are not as negative as the data of Mojzsis (1996) and it remains unclear whether the fractionation of ~16.5‰ between the graphite and local carbonate might have resulted from abiologic processes.

**10.1.6 Tracing Methane Contamination in Drinking Water**

While rarely abundant, methane is ubiquitous at the surface of the Earth. It is present in the atmosphere (present concentration: 1.8 ppm) where it is an important greenhouse gas. As we noted in Chapter 8, biogenic methane is produced naturally by methanogens in reducing environments such as swamps and anoxic marine sediments, as well as in land fills, rice paddies, and in the guts of animals by fermentation and reduction of CO2. Thermogenic methane, which is the main component of natural gas, is produced in buried organic-rich sediments by thermal cracking of hydrocarbons. The latter represents an increasingly important resource for an energy-hungry world. Natural gas has the advantage of producing significantly less CO2 and far fewer pollutants such as nitrogen and sulfur oxides, hydrocarbons, particulates, etc. that cause, acid rain, smog, that have adverse effects on human health. In this sense, it is a clean fuel. In the past, natural gas has been recovered (“produced” in industrial jargon) from porous reservoir rocks from which it can readily be pumped, often as a by-product of petroleum production. New technologies including horizontal drilling and hydrofracturing (in which water and sand is forced into the formation at high pressure to increase porosity), however, have enabled production of natural gas from impermeable source rocks, typically shales, where it has been trapped for millions or hundreds of millions of years. Whereas in the conventional petroleum and natural gas production, a limited number of wells are concentrated atop natural subsurface reservoirs where gas and petroleum has concentrated in “traps”, “shale gas” is recovered by drilling many wells over broad areas. Hydrofracturing combined with this broad dispersal of wells has raised a number of environmental concerns, particularly in relatively densely populated areas, such as the northeastern U.S.
One of these concerns is the presence of methane in drinking water. Methane is not toxic in the usual sense, but it is a potential explosion and asphyxiation hazard. Residents have complained of methane in their drinking water (and indeed, there are anecdotal reports of residents igniting water flowing from their faucets) and filed lawsuits against the gas companies. Gas companies respond that methane occurs naturally in soil and rocks through which groundwater flows and that therefore methane in drinking water is not necessarily a result of drilling operations. Osborne et al. (2011) sampled water from 60 residential water wells in New York and Pennsylvania. They found measurable methane was present in 85% of these wells. However, in water wells more 1 km distant from a natural gas well, methane concentrations averaged 1.1 mg/L whereas concentrations averaged 19.3 mg/L in water wells within 1 km of a natural gas well. More significantly, in water wells near natural gas wells, $\delta^{13}$C of methane averaged $-37\%$ whereas in those not near natural gas wells $\delta^{13}$C averaged $-54\%$. Figure 10.12 compares the carbon and hydrogen isotopic compositions in these samples with fields for methane from various sources (Figure 8.22). Water samples taken near natural gas wells fall within the field of thermogenic methane while those from other wells generally fall within the biogenic field. Clearly, thermogenic methane from natural gas wells is contaminating water in nearby wells. It should be pointed out, however, that (1) in many wells where the presence of thermogenic methane could be documented from isotopic compositions, methane concentrations were not elevated above background levels, and (2) the study showed that in a few wells with elevated methane, the methane was of biogenic origin and not due to contamination by natural gas drilling.

10.2 STABLE ISOTOPES IN PALEOClimatology

10.2.1 Introduction

At least since the classic work of Louis Agassiz in 1840, geologists have contemplated the question of how the Earth’s climate might have varied in the past. But until 1947, they had no means of quantifying paleotemperature changes. In that year, two papers were published, one by Jacob Bigeliesen and Maria Meyer, entitled “Calculation of equilibrium constants for isotopic exchange reactions” and one by Harold Urey entitled “The thermodynamic properties of isotopic substances”, which effectively initiated the field of stable isotope geochemistry. Urey calculated the temperature dependence of oxygen isotope fractionation between calcium carbonate and water and proposed that the isotopic composition of carbonates could be used as a paleothermometer (Urey, 1947). Urey’s postdoctoral associate Samuel Epstein and
several students tested Urey’s idea by growing molluscs in water of various temperatures (Epstein et al., 1953). They found the following empirical relationship:

\[ \Delta = \delta^{18}O_{\text{cal}} - \delta^{18}O_{\text{water}} = 15.36 - 2.673 (16.52 + T)^{0.5} \]

This equation was in good, though not exact, agreement with the theoretical prediction of Urey (Figure 10.13). The field of paleothermometry began with a paper based on these principles by J. M. McCrae (1950).

10.2.2 The Record of Climate Change in Deep Sea Sediments

It is perhaps ironic that while glaciers are a continental phenomenon, our best record of them is from the oceans. In part, this is because each period of continental glaciation largely destroys the record of the previous one. In contrast, deep-sea sediments are generally not disturbed by glaciation. Thus while much was learned by studying the effects of Pleistocene glaciation in Europe and North America, much was left unresolved: questions such as the precise chronology, cause, temperatures, and ice volumes (ice area could of course be determined, but this is only part of the problem). The questions of temperature chronology was largely resolved through isotopic studies of deep-sea biogenic sediments. Dating of coral reefs provided the best estimates of ice volume. These, as we shall see, provided the essential clue as to cause. While that question too has been largely resolved, the details are still being worked out.

The principles involved in paleoclimatology are simple. As Urey formulated it, the isotopic composition of calcite secreted by organisms should provide a record of paleo-ocean temperatures because the fractionation of oxygen isotopes between carbonate and water is temperature dependent. In actual practice, the problem is somewhat more complex because the isotopic composition of the shell, or test, of an organism will depend not only on temperature, but also on the isotopic composition of water in which the organism grew, vital effects (i.e., different species may fractionate oxygen isotopes somewhat differently), and post-burial isotopic exchange with sediment pore water. As it turns out, the latter two are usually not very important for carbonates, at least for late Tertiary/Quaternary sediments, but the former is.

10.2.3 The Quaternary $\delta^{18}$O Record

The first isotopic work on deep-sea sediment cores with the goal of reconstructing the temperature history of Pleistocene glaciations was by Emiliani (1955), who was then a student of Urey at the University of Chicago. Emiliani analyzed $\delta^{18}$O in foraminifera from piston cores from the world ocean. Remarkably, many of Emiliani’s findings are still valid today, albeit in modified form. He concluded that the last glacial cycle had ended about 16,000 years ago, and found that temperature increased steadily between that time and about 6000 years ago. He also recognized 14 other glacial–interglacial cycles over the last 600,000 years (we now recognize only about 6 major glacial intervals over this time), and found that these were global events, with notable cooling even in low latitudes. He concluded that bottom water in the Atlantic was 2° C cooler, but that...
bottom water in the Pacific was only 0.8°C cooler during glacial periods. He also concluded that the fundamental driving force for Quaternary climate cycles was variations in the Earth’s orbital parameters.

Emiliani had the field of oxygen isotope paleoclimatology virtually to himself until about 1970. In retrospect, it is remarkable how much Emiliani got right. By that time, others saw the value of this approach and got into the act. Their work resulted in significant modifications to some of Emiliani’s conclusions. One of the main improvements was simply refining the time scale using paleomagnetic stratigraphy and, later, some of the geochronological tools we discussed earlier in this book ($^{10}$Be, Th isotopes, etc.). In his initial work, Emiliani had only $^{14}$C dating available to him, and he dated older sections simply by extrapolating sedimentation rates based on $^{13}$C dating.

Another important modification to Emiliani’s work was a revision of the magnitude of temperature variations. Emiliani realized that the isotopic composition of the ocean would vary between glacial and interglacial times as isotopically light water was stored in glaciers, thus enriching the oceans in $^{18}$O. Assuming a $\delta^{18}$O value of about $-15‰$ for glacial ice, Emiliani estimated that this factor accounted for about 20% of the observed variations. The remainder he attributed to the effect of temperature on isotope fractionation. However, Shackleton and Opdyke (1973) argued that storage of isotopically light water in glacial ice was actually the main effect causing oxygen isotopic variations in biogenic carbonates, and that the temperature effect was only secondary. Their argument was based on the observation that nearly the same isotopic variations occurred in both planktonic (surface-dwelling) and benthic (bottom dwelling) foraminifera. Because of the way in which the deep water of the ocean is formed and circulates, Shackleton and Opdyke argued that deep-water temperature should not vary much between glacial and interglacial cycles. Analyzing tests of both benthic and planktonic organisms allowed a better calculation of temperature changes. The isotopic composition of tests of benthic organisms, i.e., those growing in deep water, could be used to determine the change in seawater isotopic composition. This would allow a more precise calculation of surface water temperature change from the isotopic composition of planktonic tests (shells of organisms growing in surface water).

Nevertheless, the question of just how much of the variation is deep-sea carbonate sediments is due to ice build-up and how much is due to the effect of temperature on fractionation continued to be debated. After Shackleton and Opdyke’s work, climate modeling suggested deep-water temperatures might indeed vary, though probably not as much as Emiliani had calculated. It is now clear that the average $\delta^{18}$O of glacial ice is less than $-15‰$, as Emiliani had assumed. Typical values for Greenland ice are $-30$ to $-40‰$ (relative to SMOW) and as much as $-50‰$ for Antarctic ice.

If the exact isotopic composition of ice and the ice volume were known, it would be a straightforward exercise to calculate the effect of continental ice build up on ocean isotopic composition. For example, the present volume of continental ice is

![Figure 10.14. Cartoon illustrating how $\delta^{18}$O of the ocean changes between glacial and interglacial periods.](image)
27.5 × 10^6 km^3, while the volume of the oceans is 1350 × 10^6 km^3. Assuming glacial ice has a mean δ^18O of ~30‰ relative to SMOW, we can calculate the δ^18O of the hydrosphere as ~0.6‰ (neglecting freshwater reservoirs, which are small). At the height of the Wisconsin Glaciation, the volume of glacial ice is thought to have increased by 42 × 10^6 km^3, corresponding to a lowering of sea level by 125 m. If the δ^18O of ice was the same then as now (~-30‰), we can readily calculate that the δ^18O of the ocean would have increased by 1.59‰. This is illustrated in Figure 10.14.

To see how much this affects estimated temperature changes, we can use Craig’s* (1965) revision of the Epstein calcite-water geothermometer:

\[ T°C = 16.9 - 4.2 \Delta_{\text{cal-water}} + 0.13(\Delta_{\text{cal-water}})^2 \]  

According to this equation, the fractionation should be 33‰ at 20°C. At 14°C, the fractionation is 31.5‰. If a glacial foram shell were 2‰ lighter, Emiliani would have made a correction of 0.5‰ for the change in oxygen isotopic composition of seawater and attributed the remainder of the difference, 1.5‰, to temperature. He would have concluded that the ocean was 6°C cooler. However, if the change in the isotopic composition of seawater is actually 1.5‰, leaving only a 0.5‰ difference due to temperature, the calculated temperature difference is only about 2°C. Thus the question of the volume of glacial ice, and its isotopic composition needed to be resolved before δ^18O in deep-sea carbonates could be used to calculate paleotemperatures. It is now generally assumed that the δ^18O of the ocean changed by 1.5‰ between glacial and interglacial periods, but second order local variations also occur (due to evaporation and precipitation), leaving some uncertainty in exact temperatures. Comparison of sealevel curves derived from dating of terraces and coral reefs indicate that each 0.011‰ variation in δ^18O represents a 1 m change in sealevel.

By now, thousands of deep-sea cores have been analyzed for oxygen isotope ratios. Though most reveal the same general picture, the δ^18O curve varies from core to core. In addition to the changing isotopic composition of the ocean, the δ^18O in a given core will depend on several other factors. (1) The temperature in which the organisms grew. (2) The faunal assemblage, as the exact fractionation will vary from organism to organism. For this reason, δ^18O analyses are often performed on a single species. However, these “vital effects” are usually small, at least for planktonic foraminifera. (3) Local variations in water isotopic composition. This is important in the Gulf of Mexico, for example. Melt-water released at the end (termination) of glacial stages flooded the surface of the Gulf of Mexico with enough isotopically light melt-water to significantly change

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* Harmon Craig was also a student of Harold Urey.
its isotopic composition relative to the ocean as a whole. (4) Sedimentation rate varies from core to core, so that δ¹⁸O as a function of depth in the core will differ between cores. Changes in sedimentation rate at a given locality will distort the appearance of the δ¹⁸O curve. (5) Bioturbation, i.e., burrowing activity of seafloor animals, which may smear the record.

10.2.4 The Cause of Quaternary Glaciations

For these reasons, correlating from core to core and can sometimes be difficult and constructing a "standard" δ¹⁸O record is a non-trivial task. Nevertheless, it is the first step in understanding the global climate change signal. Figure 10.15 shows the global δ¹⁸O record constructed by averaging 5 cores (Imbrie, et al., 1984). A cursory examination of the global curve shows a periodicity of approximately 100,000 years. The same periodicity was apparent in Emiliani's initial work and led him to conclude that the glacial-interglacial cycles were due to variations in the Earth's orbital parameters. These are often referred to as the Milankovitch cycles, after M. Milankovitch, a Serbian astronomer who argued they caused the ice ages in the early part of the twentieth century†.

Three parameters describe these variations: $e$: eccentricity, $\varepsilon$: obliquity (tilt), and precession: $e \sin \omega$, where $\omega$ is the longitude of perihelion (perihelion is the Earth's closest approach to the Sun). The eccentricity (i.e., the degree to which the orbit differs from circular) of the Earth's orbit about the Sun, and the degree of tilt, or obliquity, of the Earth's rotational axis vary slightly. Precession refers to the change in the direction in which the Earth's rotational axis tilts when it is closest to the Sun (perihelion). These variations, which are illustrated in Figure 10.16, affect the pattern of solar radiation, or insolation, that the Earth receives. Changes in these parameters have negligible effect on the total insolation, but they do affect the pattern of insolation. For example, tilt of the rotational axis determines seasonality, and the latitudinal gradient of insolation. It is this gradient that drives atmospheric and oceanic circulation. If the tilt is small, seasonality will be reduced (cooler summers, warmer winters). Precession relative to the eccentricity of the Earth's orbit also affects seasonality. For example, the Earth presently is closest to the Sun in January. As a result, northern hemisphere winters (and southern hemisphere summers) are somewhat milder than they would be otherwise. For a given latitude and season, precession will result in a ±5% difference in insolation. While the Earth's orbit is only slightly elliptical, and variations in eccentricity are small, these variations are magnified because insolation varies with the inverse square of the Earth-Sun distance. These variations can change the insolation and the average annual equator-to-pole gradient.

Variation in tilt approximates a simple sinusoidal function with a period of 41,000 yrs. Variations in eccentricity can be approximately described with characteristic period of 100,000 years. In actuality variation in eccentricity is more complex, and is more ac-

† While Milankovitch was a strong and early proponent of the idea that variations in the Earth's orbit caused ice ages, he was not the first to suggest it. J. Croll of Britain first suggested it in 1864, and published several subsequent papers on the subject.
curately described with periods of 400,000, 123,000, 85,000, and 58,000 yrs. Similarly, variation in precession has characteristic periods of 23,000 and 19,000 yrs.

While Emiliani suspected $\delta^{18}\text{O}$ variations were related to variations these “Milankovitch” parameters, the first quantitative approach to the problem was that of Hayes et al. (1976). They applied Fourier analysis to the $\delta^{18}\text{O}$ curve, a mathematical tool that transforms a complex variation such as that in Figure 10.15 to the sum of a series of simple sine functions. Hayes et al. then used spectral analysis to show that much of the spectral power of the $\delta^{18}\text{O}$ curve occurred at frequencies similar to those of the Milankovitch parameters. The most elegant and convincing treatment, however, was that of Imbrie (1985). Imbrie’s treatment involved several refinements and extension of the earlier work of Hayes et al. (1976). First, he used improved values for Milankovitch frequencies. Second, he noted these Milankovitch parameters might vary with time, as might the climate system’s response to them. The Earth’s orbit and tilt are affected by the gravitational field of the Moon and other planets. In addition, other astronomical events, such as bolide impacts, can affect them. Thus Imbrie treated the first and second 400,000 years of Figure 10.15 separately. The power spectrum for these two parts of the $\delta^{18}\text{O}$ curve is shown in Figure 10.17.

Imbrie observed that climate does not respond instantaneously to forcing. For example, maximum temperatures are not reached in Ithaca until mid or late July, 3 to 4 weeks after the maximum insolation, which occurs on June 21. Thus there is a phase difference between the forcing function (insolation) and climatic response (temperature). Imbrie also pointed out that the climate might respond differently to different forcing functions. As an example, he used temperature variations in the Indian Ocean, which respond both to annual changes in insolation and to semiannual changes in ocean upwelling. The response to these two forcing functions differs in different localities. The extent to which climate responds to a particular forcing function is the gain. The phase lag may also differ from locality to locality. Mathematically, the climatic response can be expressed as:

$$y = g_1(x_1 - \phi_1) + g_2(x_2 - \phi_2)$$  \hspace{1cm} (10.3)

where $y$ is the climatic response (temperature) $x_1$ and $x_2$ are the two forcing functions (insolation and upwelling), $g_1$ and $g_2$ are the gains associated with them and $\phi_1$ and $\phi_2$ are the phase lags).

Imbrie (1985) constructed a model for response of global climate (as measured by the $\delta^{18}\text{O}$ curve) in which each of the 6 Milankovitch forcing functions was associated with a different gain and phase. The values of gain and phase for each parameter were found statistically by minimizing the residuals of the power spectrum (Figure 10.17). Table 10.1 gives the essential parameters of the model. $\sigma_i$ is the strength of each forcing function, and $\sigma_0$ is the strength of the response (given in meters of sealevel reduction), $k$ is the coefficient of coherency, $g$ is the gain ($\sigma_i/\sigma_0$), and $\phi$ is the phase difference between input function and the climatic response. The resulting model is shown in comparison with the data for the past 400,000 years and the next
25,000 years in Figure 10.18. The model has a correlation coefficient, $r$, of 0.88 with the data. Thus about $r^2$, or 77%, of the variation in $\delta^{18}O$, and therefore presumably in ice volume, can be explained Imbrie’s Milankovitch model. The correlation for the period 400,000–782,000 yrs is somewhat poorer, around 0.80, but nevertheless impressive. Imbrie’s work has, of course, not been the last word on this and models of this type have become more sophisticated in succeeding decades (summarized, for example, in reviews by A. L., Berger, 1991, Ruddiman, 2006, and W. H. Berger, 2013).

Since variations in the Earth’s orbital parameters do not affect the average annual insolation the Earth receives, but only its pattern in space and time, one might ask how this could cause glaciation. The key factor seems to be the insolation received during summer by high northern latitudes. This is, of course, the area where large continental ice sheets develop. The southern hemisphere, except for Antarctica, is largely ocean, and therefore not subject to glaciation. Glaciers apparently develop when summers are not warm enough to melt the winter’s accumulation of snow.

Nevertheless, the total variation in insolation is small, and not enough by itself to cause the climatic variations observed. Apparently, there are feedback mechanisms at work that serve to amplify the fundamental Milankovitch forcing function. One of these feedback mechanisms was identified by Agassiz, and that is ice albedo, or reflectance. Snow and ice reflect much of the incoming sunlight back into space. Thus as glaciers advance, they cause further cooling. Any additional accumulation of ice in Antarctica, however, does not result in increased albedo, because the continent is fully ice covered even in non-glacial time, hence the dominant role of northern hemisphere insolation in driving climate cycles. Establishing the role of other feedback mechanisms is a matter of much current research. Isotope geochemistry provides some interesting insights into tow of these, ocean circulation and carbon dioxide, and we discuss them in the subsequent sections.

### 10.2.5 Carbon Isotopes, Ocean Circulation, and Climate

As we noted, the Milankovitch variations change only the distribution of solar energy received by the Earth, not the total amount. If this were the only factor in climate change, we would expect that the gla-
The role of surface ocean in climate is well understood: for example, the south-flowing California Current keeps the West Coast of the U.S. relatively dry and maintains more moderate temperatures in coastal regions than they would otherwise be. The role of the deep, or thermohaline, circulation of the oceans is less obvious, but perhaps no less important. Whereas the surface ocean circulation is wind-driven, the deep circulation is driven by density, which is in turn controlled by temperature and salinity.

In the present ocean, most deep ocean water masses “form” in high latitudes. Once these deep-water masses form, they do not return to the surface for nearly a thousand years. The principal site of deep-water formation today is the Southern Ocean where the Antarctic Intermediate Water (AAIW) is formed in the Antarctic Convergence and Antarctic Bottom Water (AABW), the densest of ocean water masses, is formed near the coast of Antarctica, particularly in the Weddell Sea. A lesser amount of deep water is also formed in the Labrador, Greenland, and Norwegian Seas of the far northern Atlantic when warm, salty water from the Gulf of Mexico and the Mediterranean is strongly cooled during winter; this water mass is called North Atlantic Deep Water (NADW). After formation, this water sinks to the bottom of the ocean an flows southward. Today, it is the deepest and densest water mass in the North Atlantic. In the South Atlantic, the somewhat cold and denser AABW flows northward beneath the NADW, which is in turn overlain by AAIW.

Formation of deep water thus involves loss of thermal energy by the ocean to the atmosphere and the present thermohaline circulation of the oceans keeps high latitude climates milder than they would otherwise be. In particular, energy extracted from the Atlantic Ocean water in the formation of NADW keeps the European climate relatively mild.

We saw in Chapter 8 that $\delta^{13}C$ is lower in deep water than in surface water (Figure 8.18). This results from biological cycling: photosynthesis in the surface waters discriminates against $^{13}C$, leaving the dissolved inorganic carbon of surface waters with high $\delta^{13}C$, while oxidation of falling organic particles rich in $^{12}C$ lowers $\delta^{13}C$ in deep water: in effect, $^{12}C$ is “pumped” from surface to deep water more efficiently than $^{13}C$. $\delta^{13}C$ values in the deep water are not uniform, varying with the “age” of the deep water: the longer the time since the water was at the surface, the more enriched it becomes in $^{12}C$ and the lower the $\delta^{13}C$. Since this is also true of total inorganic carbon and nutrients such as $PO_4$ and $NO_3$, $\delta^{13}C$ correlates negatively with nutrient and $\Sigma CO_2$ concentrations. NADW has high $\delta^{13}C$ because it contains water that was recently at the surface (and hence depleted in $^{13}C$ by photosynthesis). Deep water is not formed in either the Pacific or the Indian Oceans; all deep waters in those
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Oceans; all deep waters in those oceans flow in from the Southern Ocean. Hence deep water in the Pacific, being rather “old” has low δ13C. AABW is a mixture of young NADW, which therefore has comparably high δ13C, and recirculated Pacific deep water and hence has lower δ13C than NADW. Thus these water masses can be distinguished on the basis of δ13C.

Examining δ13C in benthic foraminifera in cores from a variety of locations, Oppo and Fairbanks (1987) concluded that production of NADW was lower during the last glacial maximum and increased to present levels in the interval between 15000 and 5000 years ago. Figure 10.19 shows an example of data from core RC13-229, located in the South Atlantic. δ13C values decrease as δ18O increases. As we saw in the previous sections, δ18O in marine carbonates is a measure of glacial ice volume and climate. As the climate warmed at the end of the last glacial interval, δ13C values in bottom water in the South Atlantic increased, reflecting an increase in the proportion of NADW relative to AABW in this region.

From δ13C variations in Mediterranean and Central Atlantic cores, Oppo and Fairbanks (1987) also concluded that the production of MIW was greater during the last glacial maximum. Thus the mode of ocean circulation apparently changes between glacial and interglacial times; this change may well amplify the Milankovitch signal.

Subsequent carbon isotope studies of benthic foraminifera have established that deep circulation in the Atlantic was much different that it is today (Figure 10.20). Rather than formation of cold, dense NADW (characterized by heavy carbon) in the far northern Atlantic, a less dense water mass called “Glacial North Atlantic Intermediate Water” or GNAIW formed further south in the Atlantic. Rather than sinking to the bottom of the North Atlantic, it sunk only to depths of 1500 m or so and flowed southward above the north-flowing glacial AABW, characterized by light carbon, which penetrated all the way into the North Atlantic. Today, production of NADW releases heat to the atmosphere, warming it. In the absence of NADW production in glacial times, the North Atlantic

Figure 10.20. Cross-section of δ13C the North Atlantic today and during glacial times. As discussed in the text, different water masses have different δ13C signatures. From Curry and Oppo (2005).
region, and Europe in particular, would have been much colder. This is further evidence that NADW production in an important positive feedback amplifying the primary “Milankovitch” signal.

10.2.6 The Tertiary Marine $\delta^{18}O$ Record

Imbrie’s (1985) analysis suggests that the climate system’s response to Milankovitch forcing has changed significantly even over the last 800,000 years. The present glacial-interglacial cycles began only 2 million years ago, yet the orbital variations responsible for Milankovitch forcing should be more or less stable over 10’s of millions of years. They should provide a steady and, hence, predictable pacing of climate change. Indeed, this pattern can be seen in high-resolution marine isotopic records, such as Figure 10.21. The amplitude of the isotopic variations, however, have not been constant, but rather have increased with time, particularly since the beginning of the Pliocene (about 5 million years ago). Interestingly, the important of eccentricity and obliquity in forcing climate appears to have changed over time. During the Pliocene and early Pleistocene the 41,000 yr obliquity component appears to be dominant, and this appears to be the case in the early Oligocene (~30-35 Ma) as well (Zachos et al., 2001). In the last half of the Pleistocene the 100,000 yr component of eccentricity appears to be dominant. These differences do not reflect differences in the strength of the Mi-

Figure 10.21. Variation in $\delta^{18}O$ in benthic foraminifera in the Tertiary. Data are from Ocean Drilling Program Sites 659 in the eastern equatorial Atlantic, 588 in the southwest Pacific, 929 in the western equatorial Atlantic, 522 in the South Atlantic, and 659 in the Southern Ocean. The upper curves in (A) and (C) represent Gaussian band-pass filters designed to isolate variance associated with the 400- (red) and 100-ky eccentricity cycles. Note that $\delta^{18}O$ is relative to PDB, rather than SMOW. This is conventional for carbonates. From Zachos et al. (2001).
lankovitch signal, but rather global climate’s sensitivity to it. In addition to the Milankovitch-related wiggles, one also sees a clear trend toward higher δ¹⁸O with time, suggesting general global cooling.

Longer-term changes in Tertiary climate resulted from factors other than astronomical forcing. Some of these changes were driven by plate tectonics and include widening of the North Atlantic, opening and widening of the Tasmanian and Drake Passages, allowing for winds and currents in the Southern Ocean to circle the globe unrestricted; collision of India with Asia and subsequent uplift of the Himalayas and Tibetan Plateau; uplift of Panama and closure of the Central American Seaway. Two other factors are the growth of polar ice sheets, which did not exist when the Tertiary began and a decline in atmospheric CO₂, which we will discuss in a subsequent section.

Superimposed on the general increase in δ¹⁸O are some important “events” in which δ¹⁸O changes more rapidly. Going backward through time, these include the shifts that mark the onset of Pleistocene glaciation, the rapid increase in δ¹⁸O from mid-Miocene through Pliocene, a brief (~200 ky) excursion, referred to as Mi-1, to more positive δ¹⁸O that coincided with the Oligocene/Miocene boundary (~23 Ma) and is thought due to a brief expansion of Antarctic ice volume. This event was followed by a series of intermittent but smaller glaciations. Another sharp change, referred to as Oi-1, occurred just above the Eocene/Oligocene boundary (34.0 Ma) and reflects the sudden appearance of large continental ice sheets on Antarctica. This in turn may have been due to reorganization of the oceanic and atmospheric circulation as evidenced by global wide shifts in the distribution of marine biogenic sediments.

Studies of spatially distributed cores suggest that global temperatures were some 2° C warmer during the Eocene that at present. Perhaps more significantly, the latitudinal gradient in temperature may have been only half the present one. This suggests oceanic and atmospheric circulation was different from the present, and on the whole much more efficient at transporting heat from equator to poles. Why this was so remains unclear.

The Eocene-Oligocene shift is thought to represent the beginning of present system where temperature variations dominate thermohaline circulation in the oceans, and initiation of extensive East Antarctic glaciation. As we found in the previous section, deep ocean water masses are formed at high latitudes and are dense mainly because they are cold. Typically deep water today has a temperature between 2° and −2° C. Before the Eocene, deep water appears to have been much warmer, and thermohaline circulation may have been dominated by salinity differences. (The formation of Mediterranean Intermediate Water, which forms as a result of evaporative increase in salinity, can be viewed as a remnant of this salinity-dominated circulation.) It was probably not until late Miocene that the present thermohaline circulation was completely established. Even subsequent to that time, important variations may have occurred, as we have seen.

The mid-Miocene increase in δ¹⁸O probably represents the expansion of the Antarctic ice sheets to cover West Antarctica. This interpretation is supported by δD analyses of sediment pore water. Even though pore water exchanges with sediment, water dominates the deuterium budget so that δD values are approximately conservative (diffusion also affects δD, but this effect can be corrected for). An increase of about 10‰, δD occurs between mid and late Miocene, which is thought to reflect the accumulation of deuterium-depleted water in Antarctic ice sheets.

10.2.7 Continental Isotopic Records

Climate change has left an isotopic record on the continents as well as in the deep sea. As with the deep-sea records, it is the isotopic composition of H₂O that is the paleoclimatic indicator. The record may be left directly in ice, in carbonate precipitated from water, or in clays equilibrated with water. We will consider examples of all of these in this section.

As we noted with the deep-sea carbonate record, the preserved isotopic signal can be a function of several variables. Continental records tend to be even more difficult to interpret than marine ones. All the isotopic records we will consider record in some fashion the isotopic composition of precipitation in a given region. The isotopic composition of precipitation depends on a host of factors:
(1) The isotopic composition of the oceans (the ice volume effect).
(2) The isotopic composition of water in the source area (the $\delta^{18}O$ of surface water in the ocean varies by a per mil or more because of evaporation, precipitation and freezing and is correlated with salinity).
(3) Temperature and isotopic fractionation in the source area (when water evaporates a temperature dependence isotopic fraction occurs; kinetic affects will also occur, and will depend on the vigor of mixing of water at the sea surface; higher wind speeds and more turbulent mixing will reduce the kinetic fractionation).
(4) Atmospheric and oceanic circulation patterns (as we saw in Chapter 8, the isotopic composition of water vapor is a function of the fraction of vapor remaining, which is not necessarily a simple function of temperature; changes in atmospheric and oceanic circulation may also result in changes in the source of precipitation in a given region).
(5) Temperature in the area where the precipitation falls, as this determines the fractionation between vapor and water.
(6) Seasonal temperature and precipitation patterns. The isotopic record might reflect water falling during only part of the year, and the temperature recorded may therefore be that of only a single season rather than an annual average. For example, even in a wet area such as Ithaca, NY, recharge of ground water occurs mainly in winter; during summer, evaporation usually exceeds precipitation.
(7) Evaporation of water or sublimation of ice. The isotopic record might be that of water remaining after some has evaporated. Since evaporation involves isotopic fractionation, the preserved isotopic record will not necessarily be that of the precipitation that falls.

All of these are climatic factors and are subject to change between glacial and interglacial periods. Changes in these factors do not mean that the stable isotope record in a given region is not recording climatic changes, but they do mean that the climatic changes recorded might not be global ones.

10.2.8 Vostok and EPICA Antarctic Ice Cores

Climatologists recognized early on that continental ice preserves a stratigraphic record of climate change. Some of the first ice cores recovered for the purpose of examining the climatic record and analyzed for stable isotopes were taken from Greenland in the 1960’s (e.g., Camp Century Ice Core). Subsequent cores have been taken from Greenland, Antarctica, and various alpine glaciers. The alpine glaciers generally give isotopic records of only a few thousand years, but are nevertheless useful, recording events such as the Little Ice Age. The Greenland and Antarctic cores provide a much longer record. Very long ice cores that covered 150,000 years were first recovered by the Russians from the Vostok station in Antarctica in the 1980’s (e.g., Jouzel, et al., 1987) and were deepened over the next 20 years, eventually reaching back 400,000 years. Drilling was halted in 2003 out of concern for intersecting and contaminating the body of water beneath the ice, known as Lake Vostok. Attention then shifted to the EPICA (European Project for Ice Coring in Antarctica) project, which recovered 3270 meters of ice core, extending back through 8 glacial cycles and more than 800,000 years.

Hydrogen isotopes show a much larger range and much greater temperature-dependent fractionation that oxygen, so in ice, interest centers of $\delta^2D$. Figure 10.22 compares the EPICA $\delta^2D$ record with the marine $\delta^18O$ record. As may be seen, there is good agreement between the marine $\delta^18O$ record and the EPICA $\delta^2D$ record back to ~800 ky B.P. The lowermost 60 meters of ice, however, appear to have been deformed and do not provide a reliable record. The core also provides a record of atmospheric CO$_2$, O$_2$, N$_2$ and $\delta^18O$$_2$ from gas trapped in bubbles and we will return to this in a subsequent section.

Jouzel et al. (2007) converted $\delta^2D$ to temperature variations based on a 6.2‰/°C relationship between $\delta^2D$ and temperature in Antarctic snow and on simulations using Global Circulations Models that incorporate water isotopes using simple Rayleigh fractionation models of the sort we considered in Chapter 8. Their results are shown in Figure 10.23.
Spectral analysis of the Vostok and EPICA isotope records shows strong peaks in variance at 41 kyr (the obliquity frequency) and at the 23 kyr precessional frequency. Thus the ice core data appear to confirm the importance of Milankovitch climatic forcing. It is interesting and significant that even in this core, taken at 78° S, it is primarily insolation at 65° N that is the controlling influence. There are, however, some differences between the ice record and the marine record, and we will consider these further in a subsequent section.

10.2.9 Ice Records from Greenland: GRIP, GISP, and NGRIP

To complement the remarkable record of the Antarctic ice cores, drilling was begun in the late 1980’s on two deep ice cores at the summit of the Greenland ice cap. A core drilled by a European consortium project, called GRIP (Greenland Ice Core Project), was located exactly on the ice divide; a core by a U.S. consortium, called GISP2 (Greenland Ice Sheet Project), was drilled 28 km to the west of the GRIP site. Flow and deformation of ice in the lower parts of these cores compromised the climate beyond 110,000 yrs BP. Consequently, in 2003 a second core was completed by the European consortium, located several hundred km to the northwest of the GRIP site, called NGRIP, penetrated over 3000 m and successfully recovered a record of the entire last glacial cycle. Because snowfall rates are higher in Greenland than they are in central Antarctica, so the record covers less time. On the other hand, they provide more detailed climate records of the Holocene and the last glacial cycle. They also provide a record of climate in the northern hemisphere, and in the North Atlantic, the region that undoubtedly holds the key to Quaternary glacial cycles. Over roughly to the past 120,000 years, there is an good correlation between the NGRIP record and marine δ18O and Antarctic ice records.

Records are most detailed for the last glacial interval, spanning the period from roughly 110,000 years ago to 14,000 years ago. This time was also much more variable during in addition to being colder on average. In particular, there are cold periods that end with rapid warming on time scales of a few decades. The transition back to cold episodes was much slower. These rapid fluctuations in climate are known as Dansgaard-Oeschager events and can be correlated to δ18O variations in high-resolution (i.e., high sedimentation rate) sediment cores from the North Atlantic. As may be seen in Figure 10.23, the
warming events correlate with isotopic (temperature) maxima in Antarctica, suggesting coupling of climate between the two hemispheres. The causes of these events are still unclear, but changes in the North Atlantic ocean circulation, perhaps triggered by an influx of fresh water, are suspected.

A number of other chemical and physical parameters are being or have been measured in the Greenland ice cores. One of the more important finding to date is that cold periods were also dusty periods (again, this had previously been suspected from marine records). Ice formed in glacial intervals has higher concentrations of ions such as Ca\(^{2+}\) and Na\(^{+}\) derived from sea salt and calcite and other minerals in soils in arid regions, indicating higher atmospheric dust transport during glacial periods, reflecting conditions that were both dustier and windier. Windier conditions could well result if thermohaline circulation was reduced, as the pole to equator temperature gradient would increase. Atmospheric dust may be an important feedback in the climate cycle: dust can act as nuclei for water condensation, increasing cloud cover and cooling the climate (Walker, 1995). It may also serve as a feedback in another way. In parts of the ocean far from continents wind blown dust is a significant source of Fe, whose abundance locally limits biological productivity. Increased winds during the last glacial period may

Figure 10.23. Antarctic temperature variation calculated from the EPICA ice core compared to the \(\delta^{18}O\) record from the GRIP ice core from Greenland. From Jouzel et al., (2007).
have fertilized the ocean with Fe, effectively turning up the biological pump and drawing down atmospheric CO$_2$. On the negative side, the abundance of dust and aerosols compromises the record of atmosphere gases such as CO$_2$ that trapped air bubbles provide in the much cleaner Antarctic ice. It's easy to understand why, particularly for CO$_2$. CaCO$_3$ will react with aerosols in the ice such as H$_2$SO$_4$ and HNO$_3$ (produced from SO$_2$ and NO$_2$ released by volcanic eruptions and other natural processes) to produce CO$_2$. Thus the Greenland ice cores have not been useful in reconstructing changes in atmospheric CO$_2$.

10.2.10 Devil’s Hole Vein Calcite Record

Another remarkable isotopic record is that of vein calcite in Devil’s Hole in Nevada. Devil’s Hole is an open fault zone near a major groundwater discharge area in the southern basin and range in southwest Nevada (Devil’s Hole is located in the next basin east from Death Valley). The fissure is lined with calcite that has precipitated from supersaturated ground water over the past 500,000 years. A 36 cm long core was recovered by SCUBA divers and analyzed by Winograd, et al. (1992). The results are compared with the Vostok and SPECMAP records in Figure 10.24. Ages of the Devil’s Hole core are based 22 U-Th ages determined by mass spectrometry.

Though the Devil’s Hole record is strongly similar to the SPECMAP record, there are some significant differences. In particular, Winograd et al. (1992) noted that Termination II, the end of the second to the last glacial epoch, in the Devil’s Hole and Vostok records precedes that seen in the SPEC MAP record by about 13 kyr (140 kyr vs. 127 kyr). This is an important point because Termination II in the SPECMAP record corresponds with a peak in northern hemisphere summer insolation. Since Termination II in the Devil’s Hole record, which is much better dated than the other two, appears to precede the peak in summer insolation, Winograd et al. argued that the Milankovitch theory must be wrong, i.e., that insolation variations due to orbital changes cannot be driving glacial cycles.

The subtle differences between the Vostok, Devil’s Hole, and SPECMAP records were considered by Grootes (1993). He noted that the age control on the SPECMAP record were weak. Ages on this record were adjusted to correlate with sea level changes as determined by dating of coral reefs and terraces and “tuned” to Milankovitch cycles. Recent high precision mass spectrometric U-Th dates on coral terraces from Barbados and New Guinea are in fact about 7 thousand years older than earlier alpha counting dates, which were used to adjust the SPECMAP time scale. Thus the age of Termination II in the marine carbonate record needed to be revised upward from 127 kyr to 135 kyr. Once this revision is made, Grootes noted that the completion of the glacial-interglacial change coincides in the 3 records (at

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* The ends of glacial epochs are called Terminations. They are quantitatively defined as the mid-point in the δ¹⁸O rise and are numbered successively backward in time.
about 130-132 kyr), but the beginnings differ.

Grootes (1993) argued that all 3 records may be correct but may be recording different aspects of climate change. These differences may provide some insight into the exact manner in which glacial epochs end. The onset of the $\delta^{18}O$ increase in the Vostok record, which occurs at 145 kyr, significantly precedes the northern hemisphere increase in insolation, but it does coincide well with an increase in southern hemisphere summer insolation. The Vostok temperature increase may well reflect this increased southern hemisphere insolation. This is consistent with an earlier inference that melting of what were probably quite substantial ice shelves around Antarctica preceded melting of the northern hemisphere ice cap and caused the initial increase in $\delta^{18}O$ in the ocean. Southern hemisphere insolation waned at about 138 kyr, and subsequent warming and sea level drive would have been driven by northern hemisphere warming and interhemispheric coupling by ocean currents and CO$_2$.

Grootes (1993) was also able to explain much of the remaining discrepancy between the Devil’s Hole and SPECMAP records. The isotopic variations in Devil’s Hole are due local temperature changes, changes in ocean isotopic composition, and all the other factors we discussed above. Grootes (1993) first corrected the Devil’s Hole record for changing oceanic $\delta^{18}O$. The effect of this is to make the residual $\delta^{18}O$ variations greater than the uncorrected ones. He suggested that differences in temperature at the site of evaporation and increased wind velocity during the glacial maxima just before Termination II would reduce the fractionation recorded in the Devil’s Hole area. The increase in Devil’s Hole $\delta^{18}O$ may reflect this reduced fractionation. A change in ocean-atmosphere circulation patterns may have effectively blocked cold Arctic air from reaching the Devil’s Hole area and moderated temperatures there. The controversy surrounding the Devil’s Hole record emphasized the complexity of factors influencing continental isotopic records and the difficulty in their interpretation.

10.2.11 Soils and Paleosols

The concentration of CO$_2$ dissolved in soil solutions is very much higher than in the atmosphere, reaching 1% by volume. As a result, soil water can become supersaturated with respect to carbonates. In soils where evaporation exceeds precipitation, soil carbonates form. The carbonates

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† Both the increased equator-to-pole temperature gradient and increased concentration of dust in ice cores indicate higher wind speeds at glacial maxima.
kaolinite and montmorillonite form in approximate equilibrium with meteoric water so that their δ18O values are systematically shifted by +27 ‰ relative to the local meteoric water, while δD are shifted by about 30‰. Thus kaolinites and montmorillonites define a line parallel to the meteoric water line (Figure 10.27), the so-called kaolinite line. From this observation, Lawrence and Taylor (1972) and Taylor (1974) reasoned that one should be able to deduce the isotopic composition of rain at the time ancient kaolinites formed from their δD values. Since the isotopic composition of precipitation is climate dependent, as we have seen, ancient kaolinites provide another continental paleoclimatic record.

Lawrence and Meaux (1993) conclude, however, that most ancient kaolinites have exchanged hydrogen subsequent to their formation, and therefore not a good paleoclimatic indicator (this conclusion is, however, controversial). On the other hand, they conclude that oxygen in kaolinite does preserve the original δ18O, and that can, with some caution, be used as a paleoclimatic indicator. Figure 10.28 compares the δ18O of ancient Cretaceous North American kaolinites with the isotopic composition of mod-
ern precipitation. If the Cretaceous climate were the same as the present one, the kaolinites should be systematically 27‰ heavier than modern precipitation. For the southeastern US, this is approximately true, but the difference is generally less than 27‰ for other kaolinites, and the difference decreases northward. This indicates these kaolinites formed in a warmer environment than the present one. Overall, the picture provided by Cretaceous kaolinites confirm what has otherwise be deduced about Cretaceous climate: the Cretaceous climate was generally warmer, and the equator to pole temperature gradient was lower.

10.3 The Carbon Cycle, Isotopes, and Climate

10.3.1 The Short-Term Carbon Cycle and Anthropogenic Impacts

There is considerable reason to believe that the Earth’s climate is linked to atmospheric CO₂ concentrations. There are several lines of evidence for this. First, and perhaps, most importantly, is the observation that CO₂ gas is transparent to visible radiation but strongly absorbs infrared radiation. Most of the energy the Earth receives from the Sun is the visible part of the spectrum. The Earth looses an equal amount of energy in the form of infrared radiation (if it did not, the Earth’s surface would continually get hotter). Atmospheric CO₂ absorbs this outgoing radiation and acts as an insulating layer, keeping the Earth warmer than it otherwise would be. In principle anyway, the higher the atmospheric CO₂ concentration, the warmer the Earth’s surface will be. This is the familiar greenhouse hypothesis, first proposed by Savant Ahrrenius in 1896 in a paper entitled “On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground”. At that time, there were neither the temperature records nor data on changes in atmospheric CO₂ concentration. Consequently, no one paid much attention to this until oceanographer Roger Revelle and physicist Hans Suess of Scripps Institution of Oceanography became interested in the problem in the 1950’s and convinced their colleague Charles Keeling to begin making regular measurements of atmospheric CO₂ concentration.

As Figure 10.29 indicates, carbon cycles rapidly between 5 reservoirs on the surface of the Earth. Of the total carbon in these 5 reservoirs, atmospheric CO₂ is only a small part. Roughly equal amounts of

![Figure 10.29. The Carbon Cycle. Numbers in black italic show the amount of carbon (in 10¹⁵ grams or gigatons, Gt) in the atmosphere, oceans, terrestrial biosphere, and soil (including litter, debris, etc.). Fluxes (red) between these reservoirs (arrows) are in 10¹⁵ g C/yr. Also shown in the approximate isotopic composition of each reservoir. Magnitudes of reservoirs and fluxes are principally from Siegenthaler and Sarimeto (1993) and Falkowski et al. (2000), isotopic compositions are from Heimann and Maier-Reimer (1996).](image-url)
carbon are present in the terrestrial biosphere, the atmosphere, and the surface ocean, with somewhat more being present in soil carbon. The bulk of the surficial carbon, about 50 times as much as in the atmosphere, is dissolved in the deep ocean (mainly as HCO$_3^-$). The fluxes of carbon to and from the atmosphere are large relative to the amount of CO$_2$ in the atmosphere; indeed nearly 25% of the atmospheric CO$_2$ ‘turns over’ in a year. The balance of these fluxes controls the concentration of atmospheric CO$_2$. The isotopic composition varies between these reservoirs, primarily due to the fractionation during photosynthesis.

In the last several hundred years, man has affected the carbon cycle through burning of fossil fuels and clearing of forests. Both these activities can be viewed as fluxes of carbon to the atmosphere, the former from sedimentary organic carbon, the latter from the terrestrial biosphere. The carbon flux from fossil fuel burning increased significantly over the 20th century and is presently around 7 Gt per year, a reasonably well-known value, and is growing; the deforestation flux is uncertain, but 2 Gt per year is a commonly cited figure. This has resulted in a roughly 0.5% per year annual increase in the concentration of CO$_2$ in the atmosphere (Figure 10.30), as determined by a global system of monitoring stations (the first of which were installed by Charles Keeling in the late 1950’s at Mauna Loa and the South Pole). This is equivalent to an average increase in the mass of atmospheric CO$_2$ reservoir of about 3 Pg/yr* since 1960. This increase in atmospheric CO$_2$ is only about 60% of the fossil fuel flux and 49% of the total estimated anthropogenic carbon flux. Thus roughly 3 to 5 Pg of carbon are “missing” in the

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*Pg = pentagrams or $10^{15}$g. This is also referred to as a gigatons; 1 Pg = 1 gigaton.
sense they are going into some reservoir other than the atmosphere, presumably the ocean or terrestrial biosphere.

Both sources of the anthropogenic carbon flux, biospheric carbon released by deforestation and sedimentary organic carbon released by burning fossil fuels, have highly negative $\delta^{13}\text{C}$ (the isotopic composition of fossil fuel burned has varied over time from $\delta^{13}\text{C} = -24\%$ in 1850 to $\delta^{13}\text{C} = -28\%$ at present as coal has been partly replaced by oil and gas). Thus we might expect to see a decrease in the $\delta^{13}\text{C}$ of atmospheric CO$_2$ with time. This is indeed observed. First, Figure 10.31 shows the $\delta^{13}\text{C}$ of atmospheric CO$_2$ measured at Mauna Loa over the period 1990-2013. There is a clear decrease in $\delta^{13}\text{C}$ over time. Superimposed on the temporal decrease are seasonal variations reflecting uptake a light carbon (making atmospheric carbon heavier) in the spring as photosynthesis increases and release of light carbon the fall as respiration becomes dominant over photosynthesis. On a longer time scale, measurements of $\delta^{13}\text{C}$ in ice cores, compliment the direct measurements (Figure 10.32) and show that $\delta^{13}\text{C}$ of atmospheric CO$_2$ was approximately constant over the first half of the last millennium, increased slightly around 1600 (perhaps related to the little ice age), then began to decline around the time of the industrial revolution. The decline is greater (up to a factor of 2 greater) than that expected from burning of fossil fuel alone, which is one line of evidence that there is has been a significant destruction of the terrestrial biosphere over the last 200 years.

To what degree the “missing” CO$_2$ (i.e., that fraction of CO$_2$ produced by burning fossil fuel and terrestrial biosphere destruction that has not accumulated in the atmosphere) has been taken up by the oceans or by terrestrial reservoirs remains an incompletely resolved question. Accurate predictions of future increases in atmospheric CO$_2$ require an answer, because storage of carbon in these two reservoirs is quite different. Once stored in the oceans, most carbon is unlikely to re-enter the atmosphere soon. However, increases in the terrestrial biomass or detritus and soil carbon may be unique, short-lived phenomena and, furthermore, may be susceptible to continued human intervention and climate change.

Several teams of investigators have attempted use to $\delta^{13}\text{C}$ changes in the atmosphere and ocean to determine what has happened to the balance of the anthropogenic carbon. Because of the rapid decline of $\delta^{13}\text{C}$ in atmospheric CO$_2$, the oceans and atmosphere are out of isotopic equilibrium. The extent of this disequilibrium depends on the rate of air-ocean exchange of CO$_2$ and can be used to estimate the rate of ocean uptake. Another approach is to example the depth-integrated changes in $\delta^{13}\text{C}$ over time. Figure 10.33 shows the change in $\delta^{13}\text{C}$ with depth in the North Atlantic between 1993 and

Figure 10.31. Monthly variation in carbon isotopic composition of atmospheric CO$_2$ measured at Mauna Loa, Hawaii between 1990 and 2013. Data from the NOAA-ESRL Global Monitoring System.
2003. The anthropogenic signal has penetrated to the base of the water column in this region (the North Atlantic is unusual in this respect because of the sinking of NADW; the anthropogenic signal is not observed at depth in the Pacific or Indian Oceans). Based on observations such as these, Quay et al. (2007) estimated that the North Atlantic was taking up 0.32 Pg C/yr.

Other approaches have been aimed at estimating the total ocean uptake. The small concentration gradient between hemispheres (as indicated by the similar CO$_2$ concentrations at Mauna Loa and the South Pole) requires that much of the anthropogenic CO$_2$ be taken up in the northern hemisphere. Based on global isotopic measurements of $\delta^{13}$C in the atmosphere, Keeling et al. (1989) concluded that the uptake by the oceans was 2.2 Gt/year in 1980. In their model, the hemispheric gradient is explained by a large northern hemisphere oceanic sink. By comparing seasonal and latitudinal variations in atmospheric $\delta^{13}$C, Ciais et al. (1995) concluded that the terrestrial biosphere north of 30°N took up 3.6 Gt/yr in 1992-1993, while the global ocean took up only 1.82 Gt/yr in these years. Heimann and Maier-Reimer (1996) also used the rate of $\delta^{13}$C change in the ocean to estimate an oceanic uptake rate of 2.1±0.9 Gt/yr. They also pointed out the importance of the riverine carbon flux to the ocean, which previous workers had neglected. Using a box diffusion ocean model to match both the observed $\delta^{13}$C and nuclear bomb-related $^{14}$C changes, Quay et al. (2003) estimated an oceanic CO$_2$ uptake rate of 1.7 ± 0.2 Pg C/yr between 1970 and

Figure 10.32. Variation is $\delta^{13}$C in an ice from the Law Ice Dome, Antarctica (filled diamonds) and air samples from Cape Grim, Tasmania (open circles). Data from Francey et al. (1999).

Figure 10.33. $\delta^{13}$C as a function of water depth in the North Atlantic as sampled in 1993 and again in 2003. After Quay et al., (2007).
1990. Joos et al. (1999) used atmospheric CO$_2$ and $\delta^{13}$C records over the last millennium to reconstruct temporal variability in the terrestrial and oceanic carbon sink. They concluded that there was considerably interannual variability in oceanic CO$_2$ uptake, which correlates with El Niño-Southern Oscillation cycles (during El Niño conditions ocean uptake is higher). They found that interannual variations in the oceanic sink for the 1980-1996 period were around $\pm$1 Gt C/yr and currently averages around 2 Gt C/yr. The variability of ocean and biosphere uptake might explain why there is so much uncertainty in the estimates of these fluxes. Summarizing a variety of studies and approaches, Gruber et al. (2009) estimated the ocean uptake at 2.2$\pm$0.3 Gt/yr.

An ocean uptake of 2 Gt per year leaves at least additional 3 Gt per year, more than the deforestation flux, that is apparently being taken up by the terrestrial biosphere. Ciais et al. (1995) concluded most of this occurs in northern hemisphere temperate and polar regions. Since most of the fossil fuel burning occurs in the northern hemisphere, we would expect the concentration of CO$_2$ to be slightly higher at Mauna Loa than at the South Pole. This is indeed the case; however, Ciais et al. found that the hemispheric gradient was less than that predicted by most models of atmospheric CO$_2$ transport, indicating much of the missing CO$_2$ must be taken up in the northern hemisphere.

It would appear then that expansion of the northern hemisphere terrestrial biosphere at least balances, and likely exceeds, deforestation, which now occurs mainly in the tropics. There are several possible explanations for this. These are as follows.

1. As agriculture became more efficient in the 20th century, land cleared for agriculture in Europe and North America in previous centuries has been abandoned and is returning to forest.
2. Average global temperature has increased by over 0.5°C over the last century, perhaps as a result of rising atmospheric CO$_2$ concentrations. This temperature increase may be producing an expansion of boreal forests.
3. Pollution, particularly by nitrates emitted when fossil fuel is burned, may be fertilizing and enhancing growth of the biosphere.
4. As we saw in Chapter 8, plants photosynthesize more efficiently at higher CO$_2$ concentrations, so increasing atmospheric CO$_2$ concentrations can, in principle, stimulate plant growth. Since most plant growth is generally limited by availability of nutrients such as phosphate and nitrate rather than CO$_2$, it is unclear whether such stimulation would actually occur. However, higher CO$_2$ concentrations may allow plants to close their stomata somewhat. Stomata, through which leaves exchange gas with the atmosphere, are pathways both for CO$_2$ into the leaf and for H$_2$O out of the leaf. Closing the stomata somewhat would reduce water loss and therefore may allow plants to survive in drier climates, leading to an expansion of forests into grasslands and grasslands into deserts.

10.3.2 The Quaternary Carbon Isotope Record and Glacial Cycles

In our discussion of Quaternary climate cycles, we noted the need for feedback mechanisms to amplify the Milankovitch signal and mentioned that atmospheric CO$_2$ concentration might be one of these. Early evidence that atmospheric CO$_2$ concentration might vary between glacial and interglacial epochs came from carbon isotope studies of deep-sea cores. Shackleton (1977) found that seawater $\delta^{13}$C increased during glacial times. He attributed this isotopic change to an increase in the terrestrial biomass that would occur as a result of, among other things, increasing land area due to falling sea level (there is more biological productivity per square meter on land than in the ocean). This would draw down atmospheric CO$_2$ and perhaps provide the necessary feedback to amplify orbital forcing of climate change. Further evidence of varying atmospheric CO$_2$ came from the first measurement of CO$_2$ concentrations in air bubbles in ice cores beginning in the late 1970’s and early 1980’s. The best of these records have come from the Antarctic ice cores from the Vostok and EPICA ice cores. The most recent of these efforts is shown in Figure 10.34. There is a remarkable similarity between temperatures deduced from $\delta$D of the ice and the measured CO$_2$ in the bubbles. Also interesting is that over the past 450,000 years, CO$_2$ in each interglacial interval reaches about the same 280-300 ppm level as in the recent, pre-
industrial ancient past. Interglacial CO₂ levels appear to be lower in the 450,000-750,000 year interval. During cold intervals, atmospheric CO₂ decreases by 100 ppm, or more than 35%, to 180 ppm than during interglacial periods. In the Antarctic ice records, air temperatures appear to rise several hundred years before CO₂ rises when glacial epochs end (i.e., at “terminations”), implying that climate change is somehow forcing CO₂.

It is clear that CO₂ is following climate at acting as a positive feedback. But what is the mechanism by which atmospheric CO₂ concentrations change in glacial cycles? Changes in seawater temperature (CO₂ is more soluble in water at lower temperature), changes in ocean volume, changes the terrestrial biosphere as Shackleton suggested, high latitude peat deposits and soil carbon, the efficiency of the oceanic biological pump, and the vertical circulation, or “ventilation”, of the oceans have all been suspected as being part of the feedback system. Research over the last 30 years, including carbon isotope studies, suggests that changes in ocean circulation linked to climate-related changes in atmospheric circulation may be the most important of these effects.

Even from the early data, it was apparent that CO₂ had risen quite rapidly at the end of the last glaciation. The rapid changes in both atmospheric CO₂ and the larger difference in δ¹³C between ocean and atmosphere during glacial periods suggested to Broecker (1982) that the ocean must somehow be involved since it is a much larger carbon reservoir and exchanges relatively quickly with the atmosphere. He noted that one obvious mechanism, changing the solubility of CO₂ in the ocean due to changing temperature (solubility of CO₂ increases with decreasing temperature), would produce only about a 20 ppm decrease in atmospheric CO₂ during glacial times, and about half this would be offset by decreasing volume of the oceans. Broecker suggested the changes in atmospheric CO₂ resulted from changing biological productivity in the oceans, in other words, the effectiveness of the biological pump. He suggested that as sea level rose, phosphorus was removed by biological processes from the ocean and de-
posited on continental shelves. Because the water column is short above continental shelves, there is less opportunity for falling organic matter to be recycled before being incorporated in the sediment. He supposed that phosphorus is the limiting nutrient in the oceans; lowering its concentration would decrease marine biological productivity and thereby allow the concentration of CO₂ in the atmosphere to rise.

Boyle (1988) proposed a different mechanism for changing atmospheric CO₂ but one that nevertheless involved the oceans. In his model, the primary driving factor is a redistribution of nutrients and metabolic CO₂ in the ocean so that they are concentrated in deep rather than in intermediate waters as in the present ocean. As the concentrations of CO₂ in the bottom water increase, pH drops and calcium carbonate sediment on the deep ocean floor dissolves. This, in turn, increases pH and ocean alkalinity, allowing it to dissolve more CO₂ from the atmosphere. Following on this idea, Toggweiler (1999) and Toggweiler et al., (2006) suggests that this redistribution of CO₂ reflects differences in ocean circulation in the Southern Ocean as well as the North Atlantic. Toggweiler (1999) suggested that reduced ventilation of deep water reduced atmospheric CO₂ by 21 ppm, that an additional 36 ppm reduction occurs due to the consequent carbonate dissolution and increase in ocean alkalinity, and that cold water temperatures further reduced atmospheric CO₂ by 23 ppm (CO₂ is more soluble in water at lower temperatures). Toggweiler et al. (2006) suggested specifically the ocean circulation changes result from a climate-driven migration of the westerly winds in the Southern Ocean. In the present interglacial climate, these most intense Westerlies are located south of the Antarctic polar front. As a result of a phenomenon called Ekman transport, these winds drive water away from Antarctica, and as a result, water rises, or “upwells” from depth (Figure 10.35a). This upwelling allows CO₂ built-up by respiration in the deep ocean to vent to the atmosphere, keeping atmospheric CO₂ concentrations high. As climate cools in glacial periods, these winds migrate northward where they produce considerable less upwelling. The result is that water in the “Southern Circuit” (Figure 10.35b) circulates slowly during

Figure 10.35. a. Map showing the position of the strongest Westerlies today and at the Last Glacial Maximum in relation to the Antarctic Circumpolar Current (ACC). The Westerlies are pushed to these limits by the positive feedback between atmospheric temperature and CO₂. The threshold, which extends into the Indian and Atlantic, is the northernmost zone where the Westerlies can induce strong upwelling. b. Schematic diagram of simplified deep circulation of the ocean. Respired CO₂ accumulates during glacial periods in the deep southern domain because the southern circulation was inactive or very weak. The box labeled “DP/ACC” depicts the ocean’s main upwelling zone along the southern flank of the ACC in the latitude band of Drake Passage (DP). After Toggweiler et al. (2006).
glacial periods, allowing respired CO₂ to accumulate.

Many of the mechanisms by which climate could drive changes in CO₂ involve biology, i.e., photosynthesis and respiration. Because of the large fractionation of carbon isotopes associated with photosynthesis, these mechanisms predict changes in δ¹³C in the oceans and atmosphere. For example, looking at Figure 10.29, we can see that since the terrestrial biosphere has lower δ¹³C than the atmosphere, storage of carbon in the biosphere should raise atmospheric δ¹³C. On the other hand, since the oceans have higher δ¹³C than the atmosphere, transfer of carbon from the atmosphere to the ocean should lower atmospheric δ¹³C, though the effect would be smaller. Slow ventilation of deep water, as proposed by Toggweiler (1999) should not only increase CO₂ in deep water, is should lower its δ¹³C. Hodell et al. (2003) demonstrated sharp gradients in ocean water δ¹³C between 2100 and 2700 m depth during glacial periods over the last 1.1 Ma from analysis of benthic foraminifera (Figure 10.36). The gradient in δ¹³C reflects much greater accumulation and storage of respired CO₂ in the deep and intermediate waters of the Southern Ocean and is consistent with the proposals of Toggweiler (1999) and Toggweiler et al. (2006). Hodell et al. (2001) also found that the carbonate compensation depth (CCD), the depth below which carbonate sediment is not found in the ocean because it dissolves faster than it builds up, rose and fell in a manner consistent with the proposals of Boyle (1988) and Toggweiler (1999).

δ¹³C of atmospheric CO₂ for the past 22,000 years has been measured in bubbles in the EPICA ice core by Elsig et al. (2009) and Lourantou et al. (2010) and is shown in Figure 10.37. Over the last 6000 years, atmospheric CO₂ concentrations increased by 10 ppm or so while δ¹³C decreased slightly. Elsig et al. (2010) suggested this was due to a combination of desertification of the Sahara plus anthropogenic land-use change (i.e., development of agriculture). In the interval from about 10,000 years ago to about 7500 years ago, CO₂ decreased slightly while δ¹³C increased relatively rapidly. The principle effect here was most likely expansion of the terrestrial biosphere to previously glaciated areas and storage of isotopically light carbon in peat and soil at high latitudes. Changes in carbonate compensation and growth of coral reefs (to keep up with rising sealevel) likely also had an influence. Coral reef growth, perhaps counter-intuitively, has the effect of increasing atmospheric CO₂. Reef organisms effectively precipitate calcite through the reaction:

\[ \text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+ \]

Consequently, reef growth decreases ocean alkalinity and pH, allowing the oceans to dissolve less CO₂.

Prior to 11,000 years ago, the variation in δ¹³C is more complex. Over this period, δ¹³C correlates with the slope of the atmospheric CO₂ curve rather than its value, such that δ¹³C is low when CO₂ concentration is rising rapidly. An initial increase in atmospheric CO₂ and decrease in δ¹³C marks the end of the last glacial maximum around the time of Henrich Event 1 (Henrich events, first identified as layers of ice-rafted debris in sediment cores from the North Atlantic, are now understood to be events where the North

![Figure 10.36. Comparison of modern and glacial period in δ¹³C in shells of the benthic forams of the Cibicidoides genus recovered from cores from the South Atlantic. After Hodell et al. (2003).](image-url)
American ice sheet destabilized and sent great flotillas of icebergs into the North Atlantic. The is followed by a period when $\delta^{13}C$ increased and atmospheric $CO_2$ concentrations stabilized during the Bølling-Allerød period, a time recognized from pollen records of Europe as one of rapidly moderating climate and ice sheet retreat. Following this, $\delta^{13}C$ again decreased and atmospheric $CO_2$ increased in the Younger Dryas period, a time recognized from European pollen records as a return to cold, almost glacial, conditions. Laurantou et al. (2010) concluded from this record that changes in Southern Ocean ventilation played the dominant role changing atmospheric $CO_2$, but changes in marine productivity, North Atlantic circulation, and the terrestrial biosphere were involved as well. The initial increase in atmospheric $CO_2$ is likely due to more rapid ventilation of the Southern Ocean in a poleward shift in Westerlies as suggested by Tuggweiler et al. (2006), but reduced ocean productivity also played a role. During the Bølling-Allerød, production of North Atlantic Deep Water intensified, enhancing warming in the North Atlantic region. In response, expansion of the northern hemisphere terrestrial biosphere to higher latitudes and consequent build up of carbon and peat eventually caused $\delta^{13}C$ to decrease and the increase in atmospheric $CO_2$ to stall. Meltwater from retreating glaciers flooded the North Atlantic in the Younger Dryas shut down NADW production, producing locally cooler conditions but resulting in more vigorous Southern Ocean overturn, driving up atmospheric $CO_2$ and increasing its $\delta^{13}C$.

10.3.3 The Long-Term Carbon Cycle

On geologic timescales, our 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. This long-term model is shown in Figure 10.38, 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 10.29 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 125-500 ppm CO$_2$ in mantle, which implies a total inventory of 1.3-5 x 10$^8$ Gt, or nearly 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.

10.3.3.1 The Tertiary Carbon Isotope Record of Cooling and Extinction

Figure 10.39 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 CO$_2$ has $\delta^{13}$C of -6, very similar to the atmospheric value, so changes in the volcanic flux will have a minimal effect on the isotopic composition of system. The fractionation between dissolved carbonate and precipitated carbonate is fairly small, so both erosion and burial of carbonate also 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 10.39 because the curve has been smoothed, but does show up well in detailed studies, such as that of d’Hondt et al. (1998). Figure 10.40 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 (~2.5‰) in $\delta^{13}$C 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 500,000 years. 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 deepwater (which in Figure 10.39 can seen to be occurring through the late Paleocene) eventually destabilized methane hydrates in continental shelf sediments. The resulting release of methane to the atmosphere both drove ocean-atmosphere $\delta^{13}$C to lighter mean values and dramatically increased global temperatures as a consequence of the strong greenhouse effect of methane and its oxidation product, CO$_2$. The oceans became significantly more acidic at this time as evidenced by a

![Figure 10.39. $\delta^{13}$C and $\delta^{18}$O in marine benthic foraminifera. Data are a compilation from many cores. In the Late Miocene, $\delta^{13}$C of Pacific and Atlantic bottom waters diverge, and these are shown as separate curves. Also shown are significant climatic, tectonic, and biologic events Modified from Zachos et al. (2001).]
much shallower carbonate compensation depth, which strongly suggests higher atmospheric CO$_2$. This event was accompanied by shifts in the diversity and distribution of fauna and flora, notably including a migration of warm-climate mammals to high latitudes. At the same time, up to 50% of species of deep-sea benthic foraminifera species became extinct, even though they had survived previous crises such as the K-T impact without significant extinction.

The next events are the Oi-1 and Mi-1 glaciations both of which that 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 a 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, which we will consider in the following chapter, and $\delta^{13}$C in alkenones from marine phytoplankton, which we’ll discuss in the following section, 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 35 Ma). Derry and France-Lanord (1996) proposed this decrease reflects a decrease in the fractionation between organic and inorganic carbon due lower atmospheric CO$_2$ levels. As we found in Chapter 8, if plants should fix a greater proportion of the CO$_2$ in their cell interiors, as they might at low atmospheric CO$_2$ then net fractionation should decrease. Again, however, other evidence suggests that atmospheric CO$_2$ concentration was more or less constant through the Miocene.

**10.3.3.2 Estimating Paleo-atmospheric CO$_2$ Concentrations from $\delta^{13}$C in Organic Carbon**

Ice cores provide information on atmospheric CO$_2$ concentrations back nearly a million years. But what role has atmospheric CO$_2$ concentrations played in climate variations in the Tertiary and earlier periods? What part of early Tertiary warmth can be attributed to higher atmospheric CO$_2$? The need to predict the climatic consequences of fossil fuel burning and build-up of atmospheric CO$_2$ make these questions important.

One method of determining paleo-CO$_2$ concentrations arises from an observed relationship between $\delta^{13}$C$_{org}$ of marine phytoplankton and the concentration of dissolved inorganic CO$_2$ (Degens et al., 1968; Degens, 1969). We saw in Chapter 8 that the fractionation of carbon isotopes during photosynthesis is related to CO$_2$ concentrations (e.g., Figure 8.17). The reason for this, in simple terms, is that when more...
CO$_2$ is available, plants are more selective and therefore show a greater preference for $^{12}$C. Thus in principle at least, [CO$_{aq}$] can be estimated from measurements $\delta^{13}$C$_{org}$. Atmospheric CO$_2$ can then be calculated from the equilibrium between CO$_{aq}$ and CO$_{g}$, that equilibrium depends on temperature, which must also be estimated. There are other complications, however, and a variety of studies contributed to developing a useful proxy for atmospheric CO$_2$ concentrations from $\delta^{13}$C of marine organic matter over the next few decades, including Rau (1994) and Jasper and Hayes (1994). These efforts culminated in the work of Pagani et al. (1999).

Complicating factors including diagenetic effects on the organic matter and a dependence of the fractionation on species, cell geometry, and growth rate. Some of these problems can be overcome by focusing on a single organic compound such as the C$_{37}$ alkadienone, as suggested by Jasper and Hayes (1994). This molecule, a 37-long hydrocarbon chain including a ketone bond and two unsaturated (i.e., doubly bonded) carbons, is particularly resistant to diagenetic change (indeed, it survives in petroleum). It is produced by a specific group of haptophyte algae (e.g., coccolithophoroids such as Emiliania huxleyi) whose cell physiology and geometry is rather similar, and which live in the upper 100 m of the water column, which should be in near-equilibrium with atmospheric CO$_2$. According to the photosynthesis model of Farquhar (1982), which we presented in Chapter 8, the isotopic fractionation during photosynthesis depends on the ratio of concentration of CO$_2$ in the atmosphere to that in the cell interior. We might expect that this ratio will depend on the photosynthetic rate: at high rates, there will be a draw down of CO$_2$ in the cell interior. Pagani et al. (1999) assumed that the carbon fractionation during photosynthesis obeyed the following simple relationship:

$$\Delta = a - b \frac{[CO_2]_{aq}}{[CO_2]}$$

where $b$ depends on physiological factors affecting fractionation, particularly growth rate. Experiments by Bidigare et al. (1997, 1999) determined the value of $a$ and showed that $b$ correlated strongly with diagenetic effects.
solved phosphate concentration; the latter is not surprising since photosynthesis rates in marine phytoplankton are well known to be limited by nutrient availability in most areas. The problem, of course, is nutrient levels in the geologic past are not directly known. Pagani et al. (1999) essentially finessed this issue by focusing on samples in oligotrophic (i.e., nutrient limited) areas of the ocean, such as DSDP site 588 in the Coral Sea.

The other thing that must be known in order to determine $\Delta$ is the carbon isotopic composition of dissolved CO$_2$; Pagani et al. (1999) determined this from the isotopic composition of planktonic foraminifera shells in the same layer. Combining paleotemperature estimates based on $\delta^{18}O$ discussed in the previous section with estimated [CO$_2$]$_{aq}$ estimated using equation 10.4, they estimated atmospheric CO$_2$ through most of the Miocene and late Oligocene (Figure 10.41). The results were surprising because they showed that CO$_2$ has been near its pre-industrial modern level throughout most of the Miocene. Thus the cooling that occurred in the late Miocene seen in Figure 10.39 was not due to decreasing atmospheric CO$_2$ as was widely suspected. $P_{CO_2}$ does appear to declined sharply at the Oligocene-Miocene boundary, coinciding with a known glacial event, but otherwise there is relationship to apparent climate change over this period. As we shall see in the next chapter, boron isotopic measurements largely confirm these results.

We should also caution that these results do not negate the now well-established control that CO$_2$ exerts on climate. We have seen that atmospheric CO$_2$ correlates strongly with temperature through the Pleistocene climate extremes. And, as we shall see, atmospheric CO$_2$ was higher in the early Tertiary and Cretaceous when climate was warm. As of 2013, atmospheric CO$_2$ stood at over 397 ppmv. That this is higher than it has been at any time over the last 25 million years is very much reason for concern.

10.3.3.3 The Phanerozoic Carbon Isotope Record and Models of Atmospheric CO$_2$

Figure 10.42 shows the Phanerzoic variation of $\delta^{13}C$ in and $\delta^{34}S$ in marine carbonates, both of which presumably record the isotopic composition of seawater at the time of deposition. (This long-term record misses some short-term events, such as dramatic negative shifts in $\delta^{13}C$ associated with the Permo-Triassic and Cretaceous-Tertiary extinctions that are captured by detailed sampling such as that shown in Figure 10.40.) The record does reveal a gradual increase in $\delta^{13}C$ and decrease in $\delta^{34}S$ through much of the Paleozoic and a more dramatic increase in $\delta^{13}C$ (and decrease in $\delta^{34}S$) associated with the expansion of land plants and high rates of burial of organic carbonic in the Carboniferous.

![Isotopic compositions of carbon and sulfur in the oceans through Phanerzoic time](image_url)
We expect the isotopic compositions of carbon and sulfur to be linked because burial and erosion of reduced sediment (organic carbon and sulfide) affect the concentration of atmospheric oxygen. As a simple consequence of mass balance, photosynthesis and subsequent burial of organic carbon increases $\delta^{13}$C in the ocean-atmosphere system and also increases atmospheric O$_2$ concentration. The latter enhances sulfide oxidation. Sulfide (and other forms of reduced sulfur) is isotopically light, so when it is oxidized to sulfate and added to the ocean, it lowers seawater $\delta^{34}$S. This mechanism accounts for the shift to more positive $\delta^{13}$C and more negative $\delta^{34}$S in the Carboniferous, when the terrestrial biota rapidly expanded and organic carbon (later to become coal) accumulated in vast swamps in what would become North America and parts of Europe and Asia.

The sedimentary record of $\delta^{34}$S and $\delta^{13}$C has given rise to various attempts to model the variation of atmospheric CO$_2$ and O$_2$ through geologic time. Berner, Lasaga and Garrels (1983, 1985) developed these ideas further in the GEOCARB model and its subsequent versions (e.g., Berner and Kothavala, 2001; Berner, 2006a; Berner, 2006b). We’ll consider only the gross aspects of this complex model here. The following is based mainly on Berner (2006).

Berner considered the fluxes between the ocean-atmosphere, carbonate, and organic carbon reservoirs (Figure 10.43). 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:

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

Figure 10.43. 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).

where $F$ is a flux, subscript $w$ denotes weathering, subscript $m$ magmatic or metamorphic release of carbon, subscript $b$ burial, subscript $c$ the carbonate reservoir, and subscript $g$ denotes organic sediments. Equation 10.5 states the steady-state condition that the rate of release of carbon from organic or carbonate sediment through metamorphism, magmatism, and weathering equals the rate burial of organic carbon and carbonate sediment. The isotopic composition of the oceans and atmosphere depends on these fluxes:

$$\delta_k F_{bc} + (\delta_o - \alpha) F_{bg} = \delta_o (F_{wc} + F_{mc}) + \delta_g (F_{wg} + F_{mg})$$

where the subscript $\delta_k$ denotes the ocean and $\alpha$ is the fractionation during photosynthesis. Because the isotopic composition of the oceans ($\delta^{13}$C$_o$) through time can be estimated from $\delta^{13}$C in carbonate (e.g., Figure 10.42), equation 10.6 provides a constraint on these fluxes.

Berner and Kothavala (2006) expressed rate of uptake of CO$_2$ via the weathering of Ca and Mg silicates over time ($F_{wg}$) as:
where \( f_b \) is the feedback factor for silicates expressing the dependence of weathering on temperature and on \( \text{CO}_2 \), \( f_m \) is the mountain uplift factor (ratio of land relief at time \( t \) to present relief), \( f_b \) is a factor expressing the dependence of weathering on soil biological activity due to land plants (\( = 1 \) at present), \( f_{AD} \) is the change in the ratio river discharge at time \( t \) to present river discharge due to change in paleogeography (a function of change in both land area and river runoff; the power of 0.65 reflects dilution of dissolved load at high runoff), and \( F_{\text{wsi}}(0) \) is the present weathering uptake of \( \text{CO}_2 \).

The weathering feedback works in two ways (Volk, 1987). First of all, global surface temperatures should correlate with atmospheric \( \text{CO}_2 \) concentrations. Since weathering reaction rates are, in principle, temperature dependent, Berner reasoned that weathering would be more rapid when temperatures, and hence atmospheric \( \text{CO}_2 \) concentrations, are higher (these same assumptions are present in the BLAG model). Second, Berner assumes that higher atmospheric \( \text{CO}_2 \) 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 \( \text{CO}_2 \) might directly speed weathering since protons generated by dissociation of carbonic acid plays a key role in weathering. However, the dissolved \( \text{CO}_2 \) in groundwater comes primarily from respiration by soil organisms rather than the atmosphere. Hence increasing atmospheric \( \text{CO}_2 \) would not directly affect weathering rates.) The weathering feedback function can be formulated as the product of these two factors:

\[
\frac{f_b(T, \text{CO}_2)}{f_b(T)} = \frac{f(T)}{f(T)} \quad 10.8
\]

The temperature dependence is contained in the usual Arrhenius exponential relationship:

\[
f(T) = e^{E/RT(T) + E/RT(0)} \times [1 - \rho(T(t) - T(0))]^{0.65} \quad 10.9
\]

where \( R \) is the gas constant, \( E \) is the activation energy for the weathering reaction, and \( \rho \) is the coefficient expressing the effect of temperature on global river runoff. The temperature difference is in turn dependent of atmospheric \( \text{CO}_2 \) levels, solar irradiation \( W_j \), and the effect of changes in paleogeography on temperature \( \lambda \):

\[
T(t) - T(0) = \gamma \ln \left( \frac{CO_2(t)}{CO_2(0)} \right) - W_s(t) + \lambda(t) \quad 10.10
\]

where \( \gamma \) is the ‘greenhouse’ coefficient and is computed from atmospheric global circulation models. \( f_{\text{CO}_2} \) is expressed as:

\[
f(\text{CO}_2) = \left[ \frac{CO_2(t)}{CO_2(0)} \right]^{0.5} \quad 10.11
\]

before vascular plants (which first appeared in the mid-Silurian about 425 Ma but only became important in the Devonian), and after vascular plants as:

\[
f(\text{CO}_2) = \left[ \frac{CO_2(t) / CO_2(0)}{1 + CO_2(t) / CO_2(0)} \right]^{\phi} \quad 10.12
\]

where \( \phi \) is a fertilization factor that expresses the dependency of photosynthesis rates on with \( \text{CO}_2 \) concentration and has a value near 0.4 (e.g., Figure 10.8).

Other fluxes in equations 10.5 through 10.7 are complex function of geological and biological history (e.g., volcanism, continental land area, biological productivity and evolution) and much of the work in constructing this model comes from estimating how these have varied from the geologic record. Berner then calculated the magmatic and weathering fluxes, and substituting these into equations 10.5 and 10.6, calculated the burial fluxes in 1 million year steps. From values of \( F_{\text{wsi}} \) and \( F_{\text{co}} \) he solved for \( f_{\text{CO}_2}(t) \)

* As was pointed out in Chapter 1, the Sun has grown about 30% brighter over geologic time.
in equation 10.7 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 mass balance equations such as:

\[
\frac{dC}{dt} = F_{bg} - (F_{wc} + F_{mc}) \tag{10.13}
\]

and

\[
\frac{d(\delta C)}{dt} = \delta F_{bc} - \delta (F_{wm} + F_{mc}) \tag{10.14}
\]

The results of the latest version of the model (Berner, 2006b), which distinguishes weathering of volcanic and non-volcanic rocks (the former are richer in Ca and Mg and hence more effective at removing atmospheric CO$_2$) shown in Figure 10.44. 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 early Paleozoic warm implies a significantly greater greenhouse effect than as present because the Sun was some 5% less bright then. 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 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 in the Carboniferous) associated with

Figure 10.44. Concentration of atmospheric carbon dioxide over the Phanerozoic. Open red circles with solid line is the GEOCARBULF model of Berner (2006b). Errors on the model are shown as gray and are take from Berner and Kothavala (2001).
glaciation in the late Paleozoic, and high CO₂ (associated with volcanism, among other things) in the warm Cretaceous. Thus if the model is correct, it substantiates the widely held assumption that atmospheric CO₂ concentrations strongly influence global temperature. The model has undoubtedly grown more realistic and accurate of its two decades of development, but just how accurate these estimates are remains to be seen. It would be far preferable to have CO₂ proxies, such as the δ¹³C of alkenones discussed in the previous section and boron isotopes discussed in the next chapter, for pre-Tertiary times.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


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Chapter 10 Stable Isotope Geochemistry


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Problems

1. Assuming that in a certain species of C₃ plant the fractionation of carbon isotopes during carboxylation is -29.4‰, the fractionation due to diffusion of CO₂ into the plant is -4.4‰, and the concentration of CO₂ in the interior of the cell is 150 ppm, what will the fractionation, Δ, be for exterior CO₂ concentrations of 150 ppm, 250 ppm, 360 ppm, and 600 ppm?

2. How does equation 10.4 compare to equation 8.9? What physical assumptions and mathematical manipulations need be made to reconcile the two?

6. Do a search of the scientific literature (using a tool such as Google Scholar, Scopus, or Web of Science) and find a recent paper where light stable isotopes have been used in an archeological or paleontological study. Describe the study and the role of isotope geochemistry in it.

3. Glaciers presently constitute about 2.1% of the water at the surface of the Earth and have a δ¹⁸OₓSMOW of ≈ -30. The oceans (δ¹⁸OₓSMOW = 0) contain essentially all remaining water. If the mass of glaciers were to increase by 50%, how would the isotopic composition of the ocean change (assuming the isotopic composition of ice remains constant)?

4. The mass of the oceans is 1.4 x 10²¹ g, that of the atmosphere is 5.1 x 10¹⁸ kg. During Pleistocene interglacial periods atmospheric CO₂ concentration was typically 290 ppmv (parts per million by volume) and a typical glacial atmospheric CO₂ concentration was 180 ppmv. If the interglacial concentration of dissolved CO₂ in the ocean was 2100 mmoles/kg, how much would the glacial concentration of dissolved CO₂ in the ocean have to be if all the CO₂ missing from the atmosphere had dissolved in the ocean? Assume a molecular weight for the atmosphere of 28.9.

5. The data in Figure 10.37 indicates that at the end of the last glacial period, atmospheric CO₂ rose from 190 ppm to 270 ppmv in 7000 years. Assuming all this CO₂ was derived from the ocean, how much greater must the ocean-to-atmosphere flux have been during this period than the present flux of about 92 Gt C/yr? (Assume a molecular weight for the atmosphere of 28.9 and note that the present flux is in gigatons of carbon rather than CO₂).