

## 8.6 Diagenetic transformation of organic material

Mud deposited on the ocean floor normally contains enough dead organic matter to provide food for a burrowing fauna of fish, worms, and mollusks. Even so, almost all these creatures depend on oxygen being available in the interstitial water. Only the top few centimeters of the mud, known as the bioturbated layer, will provide such an oxygenated environment. This layer is recognizable from its burrows and its chaotic character. The top part of the oxygenated sediment is thus mixed to the extent that the finer sedimentary structures disappear. Imagine for a moment that we are observers on the sea floor, resisting burial, and living long enough to observe the sediment sinking beneath our feet. We would see the bioturbated layer acting like a moving average on the sedimentary record (electronics aficionados might liken it to a low-pass filter). If, however, the bottom water is particularly poor in oxygen, usually because of a great abundance of organic matter, burrowing animals cannot breathe, bioturbation is impossible, and the sedimentary record conserves even the finest details down to the infra-millimetric scale (the rocks are then often referred to as laminites).

Below the bioturbated layer, the dissolved oxygen of the interstitial water is fully used up. Other organisms, microbes, take over. To maintain their metabolism they are able to oxidize organic matter by reducing other dissolved components, such as nitrates to nitrogen (denitrification), solid  $\text{MnO}_2$  and  $\text{Fe}(\text{OH})_3$  to soluble  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ , and sulfates to hydrogen sulfide. These reactions are also known as dissimilatory reactions because they do not involve assimilation of their products by cellular material. These biochemical reactions occur in the space of a few tens of centimeters below the water–sediment interface. The sequence of early diagenetic reactions in the uppermost layers below the sediment–water interface is controlled by the redox potential of the possible diagenetic reactions. We are going to assume that dead organic matter is represented for simplicity by  $\text{CH}_2\text{O}$  (formaldehyde), a very simple compound which could be a precursor of sugars and which is oxidized into  $\text{HCO}_3^-$ , the stable form of carbon in solution. Another form of “food” is the acetate ion released by acetogenic bacteria, probably the most abundant organic substrate in oxygen-poor sediments. The dominance plot of the different redox species is shown in Fig. 8.8 for a  $\text{pH} \approx 7$ : it indicates the sequence of reduction reactions, which is simply that of decreasing  $\text{pe}$ . Right below the interface, the oxic layer is well ventilated by the bioturbation and organisms use normal respiratory oxidative mechanisms to turn organic matter into carbon dioxide plus water, but also ammonium into nitrites followed by nitrates, a process known as nitrification. When all the dissolved oxygen is used up and cannot any longer be replenished by burrowing animals, bacteria turn to increasingly stable electron acceptors, nitrate,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{SO}_4^{2-}$  to oxidize organic matter. The sequence of the most important dissimilatory reactions is shown in Fig. 8.9 and is determined by the energy they liberate. It can be seen from this sequence how interstitial solutions become increasingly reducing with depth. Under these conditions, nitrate is reduced to nitrogen (denitrification), which is lost to the ocean through pore waters, while ferric iron and manganese accumulated on the sea floor as hydroxides are progressively reduced and dissolved. Most of the reduced  $\text{Mn}^{2+}$  is also returned to bottom seawater

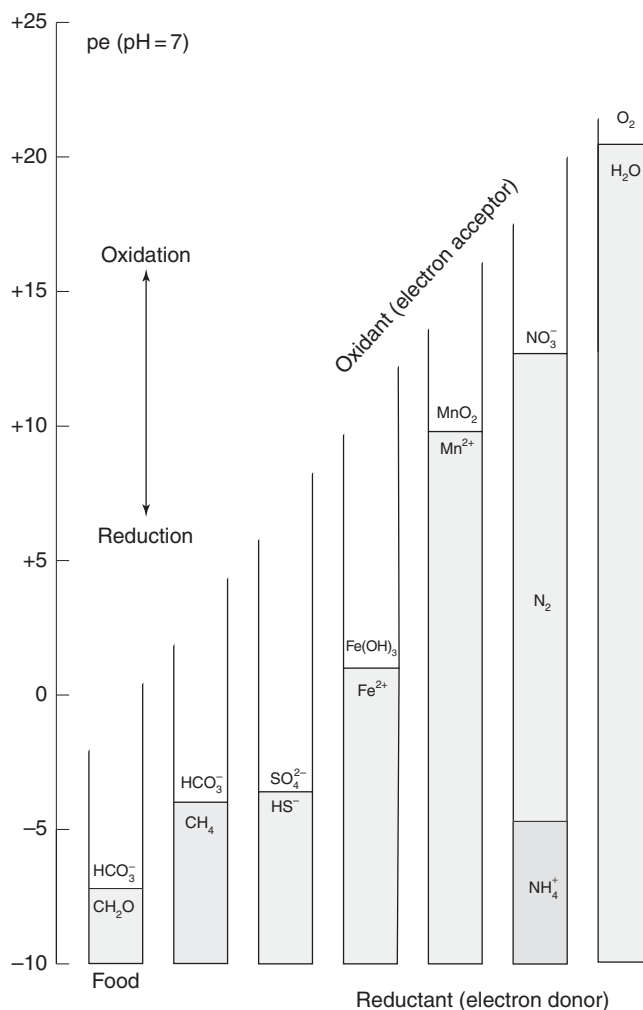


Figure 8.8

Dominance plot of the major species present in sediments and pore waters and which can act as either electron donor (reductant) or acceptor (oxidant). Low-pe organic matter  $\text{CH}_2\text{O}$  (food) is supposed to be present in excess. The energy driving its oxidation (upward) into  $\text{HCO}_3^-$ , is obtained from the dissimilatory reduction (downward) of the oxidants shown at the high-pe end of each bar.

with pore water where, upon re-oxidation, it contributes to the small diagenetic component of polymetallic nodules. In contrast, ferrous iron reacts with the sulfur liberated by the dissimilatory reduction of sulfate and precipitates as pyrite  $\text{FeS}_2$ , a particularly common diagenetic mineral in sedimentary rocks with a high organic matter content. At even greater depth and if temperature is adequate, leftover organic material may be reduced to methane. All these reactions are biologically mediated. Overall, pore waters seeping out from sediments rich in organic matter and nitrogen are not only highly reduced but also rich in metals. Because porous flow is largely controlled by the rate of burial, this is certainly an important control factor of these processes.

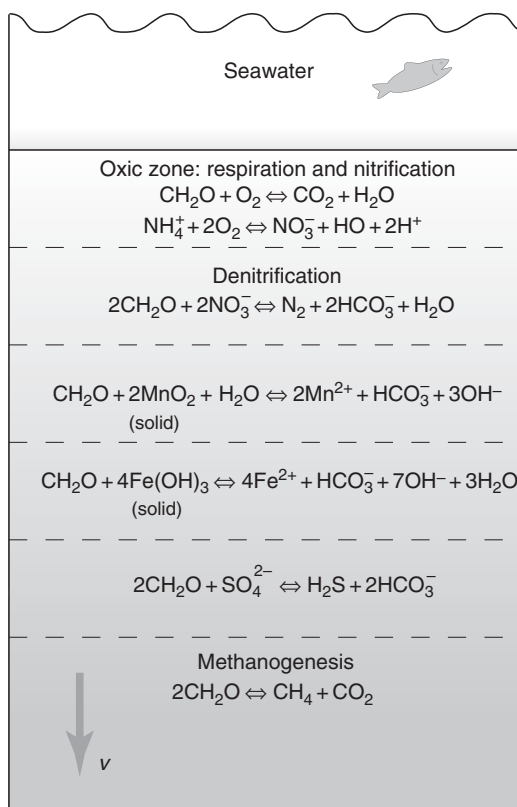


Figure 8.9

The successive reactions of early diagenesis below the sediment–water interface. Interstitial water from the upper layer is ventilated by burrowing animals. Bacteria use the dissimilatory reduction of nitrate, solid  $\text{MnO}_2$ , and  $\text{Fe}(\text{OH})_3$ , then sulfate still present in interstitial water to oxidize dead organic material, here represented by the molecule  $\text{CH}_2\text{O}$ . The inception of methanogenesis requires that the sediments were originally rich in organic material. The section represents only a few tens of cm but the whole pile is moving downwards at the rate of sedimentation.

Denitrification is associated with progressive loss of  $\text{N}_2$ , sulfate reduction with progressive sulfide precipitation, and methanogenesis with methane seeping: Rayleigh distillation amplifies isotopic fractionation between the reduced and the oxidized reservoirs of N, S, and C with respect to equilibrium values and leads to major isotopic shifts in the residue. Most of the methane produced by methanogene, however, is converted back into organic matter by methanotrophic archaea and never reaches the sediment–water interface. Methanotrophs are often associated with acetogenic bacteria which release acetate as an end-product of fermentation. Such associations in which a species utilizes the poisonous by-product of another are known as consortia.

Dead organisms and fecal pellets are highly unstable and prone to utilization as biological fuel by other organisms. Hydrolysis of the phosphate groups and oxidation of the amino group take place very rapidly during decay, while most carbohydrates such as cellulose disappear during fermentation. At low temperature, the most resistant part of the original organic components are (a) the long aliphatic chains of lipids, saturated (no double

C–C bond) or unsaturated, derived from membrane material and (b) the aromatic compounds derived from the phenol rings of lignin. On land, this forms the base of humic substances, notably humic and fulvic acids, which are heterogeneous mixtures of amino acids, sugars, proteins, and aliphatic compounds. Fulvic acids are soluble in water under all conditions, humic acids are insoluble at  $\text{pH} < 2$ .

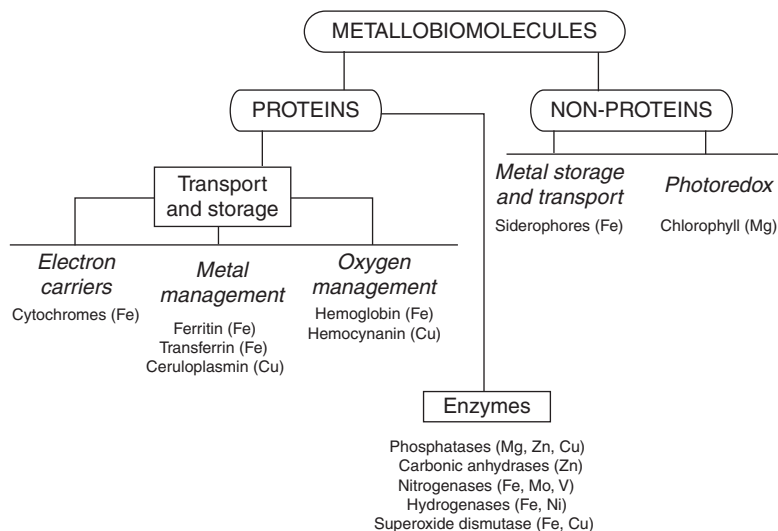
During diagenesis, humic compounds evolve into kerogen which, upon heating between 50 and 120 °C evolves into the hydrocarbons of crude oil. Oil is normally preserved when it seeps out from its primary site of formation towards a porous reservoir. Further heating induces the cracking of hydrocarbon chains with loss of methane (natural gas) and eventually, at temperatures in excess of 300 °C, leaves pure carbon as graphite (coal or anthracite) in the rock. Since methane ( $\text{CH}_4$ ) has the highest possible hydrogen/carbon ratio, two convenient maturation indices of organic products are the O/C and H/C ratios (Fig. 8.1). Normally the terms used are: gas, for  $\text{C}_2$  to  $\text{C}_4$  hydrocarbons; light oil, for  $\text{C}_4$  to  $\text{C}_{14}$ ; and oil, beyond that point.

## 8.7 Biomarkers

Easily degradable organic matter, such as proteins and carbohydrates, is unlikely to fare well with recycling and diagenesis. The fate of insoluble molecules is certainly more promising. Among those, some fatty acids, long-chain alkanes and alkenes, and terpenes often pass diagenesis largely unharmed even if they lose some of their functional groups. These geochemical fossils can be matched with existing organisms or their ancestors, and used to interpret ancient microbial ecosystems. They can also have been left by unknown organisms and reveal long-gone creatures and metabolic pathways. Biomarkers can be used to reconstruct the evolutionary tree of a particular group of microbes. Occasionally, the discovery of new biomarkers has led to the discovery of unsuspected organisms and metabolic processes, such as the “anammox” bacteria capable of combining ammonia with nitrites into  $\text{N}_2$ . There is, however, much ambiguity in interpreting these complex molecules since more than one group of bacteria or algae may produce similar substances.

Among the most successful findings, let us quote archeol as a compound produced by methanogenic archaea and crocetane produced by methanotroph archaea, which were essential in understanding the consortia built around methanogens and methanotrophs. Aromatic carotenoids are pigments which betray the presence of bacteria selectively catching light at particular wavelengths to achieve the phototrophic oxidation of sulfides. Some forms of terpenes, known as hopanes, have only recently been related to cyanobacteria. Other well-identified but orphan compounds remain without a known progenitor. Alkenones are produced by coccolithophores to regulate cytoplasm viscosity and the relative abundance of related varieties is commonly used to infer ancient sea-surface temperatures and pressures of atmospheric carbon dioxide.

Because of their remarkable preservation, biomarkers are also used for isotopic analysis: the  $\delta^{13}\text{C}$  of alkenones is believed to be a very sensitive, and unfortunately unique, indicator of the carbonate speciation in the surface ocean and therefore of the  $\text{CO}_2$  pressure in the atmosphere.



**Figure 8.10** Some biological molecules containing metals and their biological functions (after Fenton, 1995).

## 8.8 Metals in organic matter

Metallic deposits of probable biological origin are known, such as the Precambrian banded iron formations (BIF). It is suspected that this is not an isolated case and the emerging field of the stable isotope geochemistry of metals may soon be able to come up with biomarkers of its own. Among the trace metals that contribute to different functions in the cell, some may contribute to the sedimentary record. For example:

1. Iron enters multiple molecules such as porphyrin, a ring of nitrogen-bearing chelates. Porphyrin groups are present for electron transfer in cytochrome and for dioxygen transport in hemoglobin. Proteins containing both S and N (ferredoxin) perform more specialized functions such as photophosphorylation during photosynthesis.
2. Because of its property of super-acidity, Zn is one of the most prevalent trace elements of life and has been found in over 600 proteins, notably associated with the immune system. It is found in carbonic anhydrase, which dramatically increases the rate of conversion of  $\text{CO}_2$  into  $\text{HCO}_3^-$ .
3. Copper is present in cytochrome oxidase for electron transfer in the energy cycle and replaces iron in hemocyanin for dioxygen transport in some species.
4. Magnesium concentration in the cytoplasm is in the percent range. It is the core cation of chlorophylls.
5. Potassium is used to maintain gradients and controls transfers across the cell membranes (biological pumps).

Some metallobiomolecules are listed in [Fig. 8.10](#).

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## References

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A major achievement of low-temperature geochemistry is its ability to provide estimates of variables such as ocean temperature, atmospheric composition and pressure, erosion intensity, and biological productivity. These estimates come through geochemical observables, known as proxies, which can be related with some confidence to a variety of parameters of our environment. The understanding of ancient climates, oceans, atmospheres, and biological activity would be very poor in the absence of these proxies and would remain qualitative and highly speculative. The derived environmental information, however uncertain it may be, can always be tested against predictions and with the help of improved observations can be continuously improved.

Let us first briefly review some of the most important environmental proxies for modern environments (< 65 Ma).

1. As shown by Dansgaard in 1964, mean annual air temperature can be determined (or estimated) from the mean  $\delta D$  or  $\delta^{18}O$  value of the local precipitation (rain or snow).
2. The amount of ice locked up in polar regions is derived from the average  $\delta^{18}O$  value of seawater.
3. The temperature of deep oceanic water can be obtained from the  $\delta^{18}O$  values of benthic foraminifera.
4. The surface ocean  $\delta^{18}O$  is perturbed by evaporation, precipitation, and continental run-off. The sea-surface temperature (SST) can instead be obtained from the Mg/Ca and Sr/Ca ratios in the carbonates produced by organisms living in the photic zone, typically corals, pelagic foraminifera, and coccolithophores. The  $\delta^{18}O$  values of fish

tooth enamel (phosphate), which is more resistant to diagenetic modification than carbonates, are a useful temperature proxy. Sea-surface temperature is also obtained from the relative abundances of alkenones extracted from sediments.

5. As shown in [Chapter 7](#), the pH of the ocean may be constrained by boron isotopes in carbonates. Again, the pH of surface waters also varies with evaporation, precipitation, and continental run-off. Deriving oceanic pH values from the rare deep-sea corals holds much promise.
6. The pressure of carbon dioxide is fairly difficult to constrain. It has been suggested recently that the  $\delta^{13}\text{C}$  of alkenones is a reliable proxy of  $P_{\text{CO}_2}$ .
7. Recent sea-level fluctuations can be tracked by dating corals that live right beneath the surface of the ocean. Dating is most precisely obtained from  $^{230}\text{Th}$  disequilibrium.
8. Local biological productivity can be constrained by the difference in  $\delta^{13}\text{C}$  between pelagic and benthic organisms. If diagenesis is not too severe,  $\delta^{15}\text{N}$  can also be useful. Productivity has also been estimated using the concentrations of biolimited elements, notably Cd.
9. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of marine carbonates is an excellent proxy of erosion rates and alkalinity fluxes: today, abundant radiogenic Sr from the old basement of the Himalayas is carried to the ocean by the powerful rivers from south and southeast Asia.
10. The isotope compositions of neodymium contrast between the Atlantic and the Pacific oceans because the most important rivers flow into the Atlantic. Neodymium (Nd) isotopes can be used to trace mixing between Atlantic and Pacific waters, whereas exchange between seawater and mid-ocean ridges and alteration of young volcanic rocks are particularly active in the Pacific.
11. Sulfur isotopes are fractionated by about 20 per mil between sulfate and sulfide. The values of  $\delta^{34}\text{S}$  therefore are a useful indicator of the relative amount of evaporites and iron sulfide locked up at a given time in the sedimentary mass.
12. We will see in [Chapter 12](#) why the Earth's mantle and crust are seriously depleted in platinum-group elements, and in particular in iridium (Ir). Nearly all meteorites are very rich in these elements. Large meteorite impacts are best fingerprinted by the presence in sediments of a thin layer of material rich in iridium corresponding to the time of impact.

This list is certainly not exhaustive but already gives a good feeling for what geochemistry can do about past environments and how much work is involved in understanding the modern climatic fluctuations and the major events that shaped the composition of the atmosphere and the oceans over geological time.

## 9.1 Phanerozoic climates

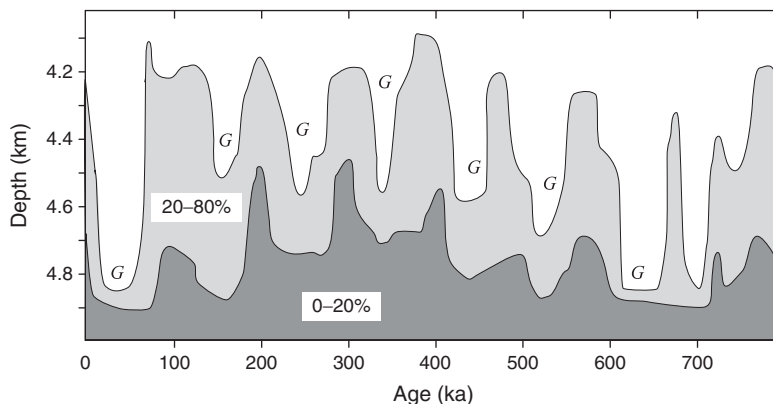
Atmospheric carbon dioxide is a greenhouse gas. When the Sun's rays strike the ground, they are reflected but, because the Earth is much cooler than the Sun, at longer wavelengths, in the infrared. We can feel this radiation when we walk along a paved road at night after



a sunny summer's day. Homonuclear diatomic molecules such as  $N_2$  and  $O_2$  do not absorb infrared, visible, or ultraviolet solar radiation because they remain symmetrical with a zero electric dipole, no matter how hard they are hit by photons. Such collisions are described as elastic. Nitrogen and oxygen therefore do not block the sunlight, they are optically transparent over most of the solar electromagnetic spectrum, and do not contribute to warming. In contrast, the symmetry of  $H_2O$ ,  $CO_2$ ,  $CH_4$ , and  $O_3$  vibrations changes when photons collide with these molecules: new vibrational and rotational patterns reflect absorption of electromagnetic radiation and the whole gas phase warms up, at least as long as atmospheric pressure is strong enough for frequent molecular collisions. The reflected radiation is therefore absorbed by  $H_2O$ ,  $CO_2$ ,  $CH_4$ , and ozone and warms up the atmosphere. This is the greenhouse effect. The history of the Earth's climate is therefore for a large part that of its atmospheric  $CO_2$ .

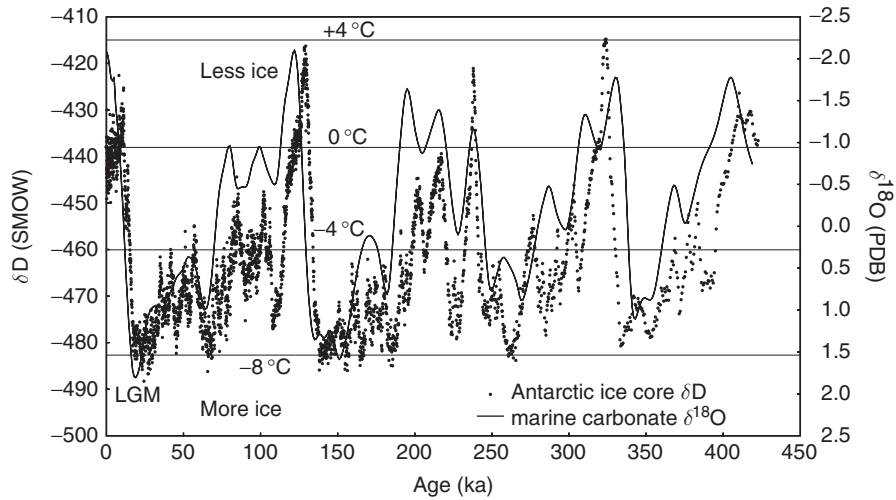
### 9.1.1 Quaternary climates

This effect can be seen clearly in the composition of Quaternary sediments where the extent of carbonate preservation varies with the depth of deposition in keeping with the pattern of glaciations (Fig. 9.1) that recur every  $\approx 100\,000$  years. Carbonate preservation clearly decreases and CCD rises during the high- $CO_2$  peaks of interglacial periods. This pattern is similar to the pattern of fluctuations in marine oxygen isotopes as recorded by the  $\delta^{18}O$  of the calcite of deep-water foraminifera. During glacial times, a greater quantity of ice with very negative  $\delta^{18}O$  values is stored in the polar ice caps and seawater oxygen is enriched in  $^{18}O$  (Fig. 9.2). Because the enrichment of  $^{18}O$  in rain and snow is stronger during cold periods, the glacial  $\delta^{18}O$  maxima in seawater and the carbonates in isotopic equilibrium with it (maximum ice volume) are the mirror image of  $\delta^{18}O$  minima in ice cores.



**Figure 9.1**

Preservation of carbonates in Quaternary sediments at various depths. The different shades of grey refer to the percentages of carbonate preservation shown. The zone between the two curves mainly depicts the transition of the carbonate compensation depth (CCD). During glacial periods (G), the  $CO_2$  content of the atmosphere was lower, the ocean less acidic, the CCD sank, and the calcareous fraction of sediments increased (after Farrell and Prell, 1989).



**Figure 9.2** Fluctuation of  $\delta^{18}\text{O}$  (relative to PDB standard) in the carbonate of benthic foraminifera (SPECMAP database). Increased storage of water in polar ice during glacial periods increases the  $^{18}\text{O}$  isotope concentration of the ocean. The  $\delta^{18}\text{O}$  curve follows (although with a small time lag) the temperature curve deduced from the  $\delta\text{D}$  values measured in the Vostok ice core in Antarctica (Petit *et al.*, 1999). The horizontal lines show the temperature shifts in the polar region deduced from the  $\delta\text{D}$  values in ice. LGM = last glacial maximum. The periodic aspect of fluctuations is caused by astronomical forcing (Milankovic cycles).

Lower average temperatures during the ice ages are explained by the astronomical modulation of insolation and its amplification by a lower level of  $\text{CO}_2$  in the atmosphere, and therefore a weaker greenhouse effect. Plotting  $P_{\text{CO}_2}$  vs.  $\Sigma\text{CO}_2$  for different pH values for seawater saturated in calcite as given by (7.39) and (7.40), we can see the effect of changing  $P_{\text{CO}_2}$  on the precipitation or dissolution of calcium carbonate (Fig. 9.3). A reduced  $P_{\text{CO}_2}$  decreases  $\Sigma\text{CO}_2$ , makes the ocean less acidic and therefore enhances carbonate preservation, which is reflected by a deepening of the CCD. The intervals during which limestone is abundant at great depths are cold periods.

The short-term variability in the isotopic composition of oxygen recorded by foraminifera is essentially indicative of the abundance of polar ice: temperatures at high latitudes vary periodically with orbital forcing, especially the precession of the equinoxes (19 000 and 23 000 years), the variation in the inclination (obliquity) of the Earth's axis of rotation on the ecliptic (41 000 years), and the eccentricity of the Earth's orbit around the Sun (100 000 years). These are the famous Milankovic cycles regulating the alternating pattern of Quaternary glacials and interglacials (Fig. 9.2).

### 9.1.2 Mesozoic and Cenozoic climatic trends

In contrast, the long-term variability of oxygen isotopes in benthic (deep-sea) foraminifera reveals the secular cooling of the deep ocean waters. The temperatures recorded by the  $\delta^{18}\text{O}$  values fell by some 10–12 °C since the Paleocene optimum (55 Ma) (Fig. 9.4).

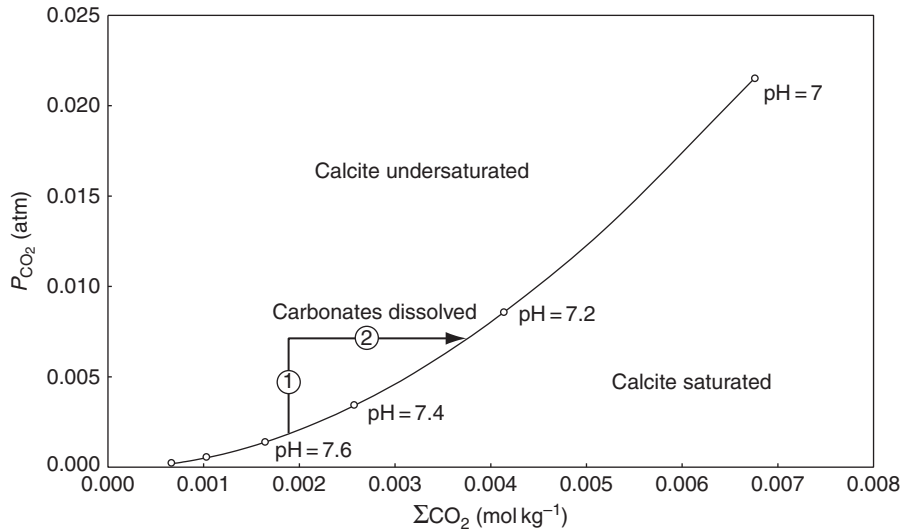


Figure 9.3

Effect of a change in the  $P_{\text{CO}_2}$  on the dissolution and precipitation of carbonates. The curve represents the pressure of carbon dioxide in the atmosphere above a solution saturated in calcite at different values of  $\Sigma\text{CO}_2$ . ① Sudden  $P_{\text{CO}_2}$  increase. ② Reaction of the excess dissolved  $\text{CO}_2$  with carbonate sediments. The opposite effect (precipitation of carbonates) would be obtained for a drop in  $P_{\text{CO}_2}$ .

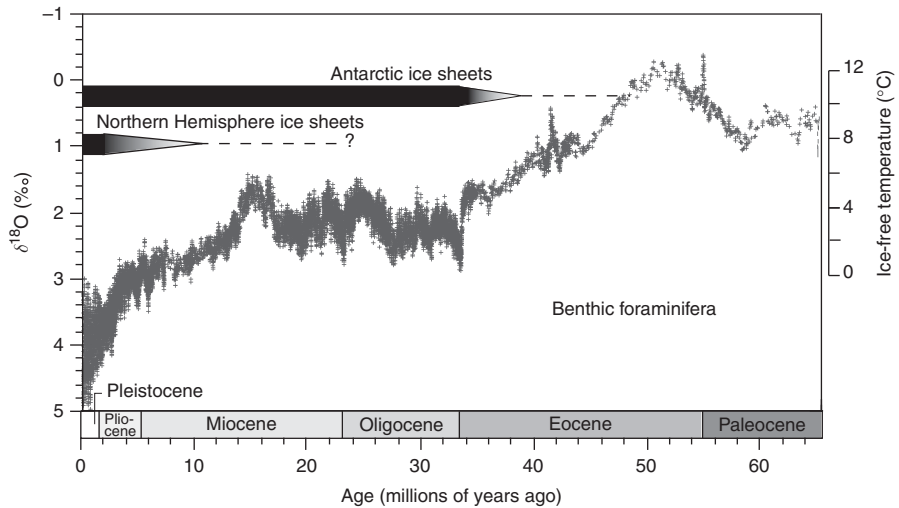


Figure 9.4

The cooling of deep water since the Paleocene ( $\approx 55$  Ma) optimum is recorded by the  $\delta^{18}\text{O}$  value (here reported relative to the PDB standard) of benthic foraminifera. An uncertainty of several degrees results from our ignorance of the volume of polar ice in the Tertiary (3% of the total hydrosphere today): the temperature scales on the right assume a world without ice. The broad fluctuation range over the last million years or so is due to the glacial-interglacial oscillations (figure redrawn from Zachos *et al.*, 2008).

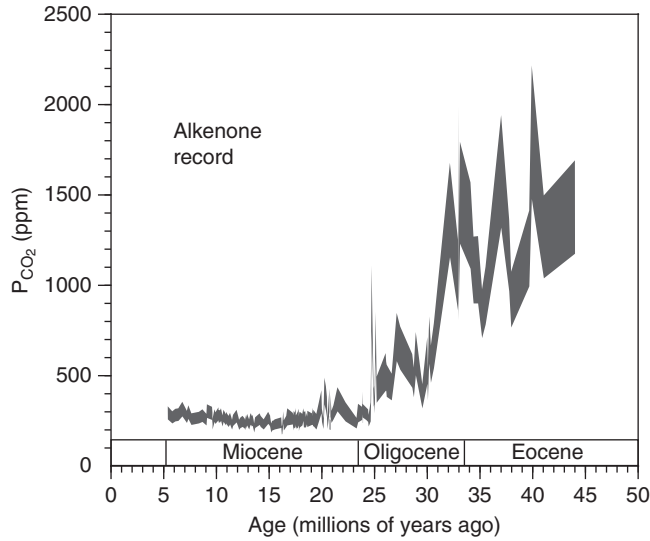


Figure 9.5

Atmospheric pressure of carbon dioxide deduced from the  $\delta^{13}\text{C}$  of alkenones. The global trend of oceanic cooling since the end of the Cretaceous is particularly visible for the deep ocean (see previous figure). It reflects a drop in atmospheric  $\text{CO}_2$  and therefore a decline of the greenhouse effect (Pagani *et al.*, 2005).

Inasmuch as  $\delta^{13}\text{C}$  of alkenones is a reliable indicator of atmospheric pressure of carbon dioxide, this cooling is probably associated with a drop in  $P_{\text{CO}_2}$  by a factor of four (Fig. 9.5). The strong decline of the greenhouse effect over the last  $\approx 55$  Ma therefore explains the global cooling of the planet and the advent of the “icehouse” thermal regime.

Carbon dioxide is injected into the atmosphere by volcanoes. Erosion then transfers it to the hydrosphere by reactions similar to those described by (7.30) above. It is then removed from the ocean by precipitation of carbonate and by sedimentation in the form of reduced carbon (kerogen, petroleum, or coal). Some of the reduced organic carbon in the sediment is re-oxidized as  $\text{CO}_2$  by oxygen in the air when rocks are exposed by erosion; the naturally occurring oil seeps of hydrocarbon-rich areas of California and the Persian–Arabian Gulf are evidence of this. Human activity is accelerating this process through the burning of fossil fuels in power plants and transport. Some of the sedimentary carbonates are removed from the surface system via subduction zones, but we do not know exactly how much of this  $\text{CO}_2$  is returned to us by decarbonation at depth and orogenic volcanism in those parts of the world. It appears, however, that the quantity of carbonates at the Earth’s surface has increased significantly over geological time.

How atmospheric  $P_{\text{CO}_2}$  can have changed so much over 70 Ma is still somewhat under discussion. One hypothesis is that fluctuations in volcanic emissions of  $\text{CO}_2$  forced the system. The Cretaceous was indeed a period of intense volcanic activity. The rapidly widening rifts of the dislocating Pangea supercontinent were preceded by strong bursts of volcanic activity such as the Ontong–Java oceanic plateau in the Western Pacific, the Caribbean–Columbia plateau, the Rajmahal and Deccan traps in India, and the Paraña–Etendeka traps of South America and South Africa. The greenhouse effect was very

intense and we all picture the luxuriant forests where dinosaurs roamed. Provided enough nutrients were available, a high pressure of atmospheric  $\text{CO}_2$  increased primary productivity in the ocean. It also enhanced intense weathering, and thus induced strong fluxes of alkalinity to the ocean and massive limestone sedimentation. The Cretaceous is indeed a period characterized by remarkable carbonate sedimentation, in particular on continental shelves.

So how can we be invoking a reduced carbonate precipitation during the high  $P_{\text{CO}_2}$  bouts of the Quaternary and apparently the opposite for the Cretaceous? This is actually a matter of kinetics. The residence time of alkalinity in the ocean is  $\approx 100\,000$  years. We also remember that the mean time of oceanic overturn is 1600 years by today's standards, i.e. geologically instantaneous. For temperature and  $P_{\text{CO}_2}$  fluctuations on this time scale or faster, such as those imposed by astronomical forcing, the incoming and outgoing fluxes of alkalinity are not balanced and carbonate precipitation reflects short-term external changes. For time scales  $> 100$  ka, like the steady high  $P_{\text{CO}_2}$  conditions of the Cretaceous, steady state is achieved and what comes around goes around: the abundant carbonate series precipitated on the seafloor represent the alkalinity lost by the ocean and therefore must have been compensated for by a corresponding alkalinity flux to the ocean. The conclusion remains that the Cretaceous was a time of high chemical erosion rate and therefore of high  $P_{\text{CO}_2}$ . Observations on different time scales therefore provide opposite conclusions on  $P_{\text{CO}_2}$  changes.

An alternative explanation of climate control, suggested by the isotope geochemistry of strontium in seawater, is that of tectonic forcing. In marine carbonates, the  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio is so low that it has barely varied with time since deposition (see (4.15)). Consequently,  $^{87}\text{Sr}/^{86}\text{Sr}$  remains frozen near its original value and therefore at the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of seawater (from which the limestone is derived) at the time of sedimentation. The reason for this is that the concentration in the alkali element Rb (whose behavior is very similar to that of K) is very low compared with that of the alkaline-earth element Sr (whose behavior is very similar to that of Ca). It has been observed that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater as recorded in marine carbonates has increased since the Cretaceous (Fig. 9.6). This increase is evidence of the increased input of continental strontium with its far higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.711 on average) than that of strontium derived from the weathering of basalts (0.702). We will see later that this difference reflects the high Rb/Sr ratio of the continental crust. This value points to increased erosion, while the evidence of carbon isotopes and the general cooling of climates and of the ocean since the Cretaceous argue against increased emissions of volcanic  $\text{CO}_2$ . This suggests, then, more efficient erosional processes, and it has been proposed that the collision between India and Asia, and the resulting uplift of the Himalayas in the Tertiary, were responsible for the decline in atmospheric  $\text{CO}_2$ . The high elevation of the Himalayas and the monsoon regime that dominates this area favor particularly intense mechanical erosion. South and southeast Asia therefore account for a large fraction of the sediment produced in the world. In contrast to the dissolved loads of rivers flowing into the Atlantic, suspended solids and sediments are carried to the Indian Ocean (e.g. along the Ganges and Indus) or to the Pacific (e.g. along the Mekong and Yangtze). This second scenario emphasizes the consumption of  $\text{CO}_2$  and explains climatic cooling by the more intense erosion resulting from the uplift of the Himalayas.

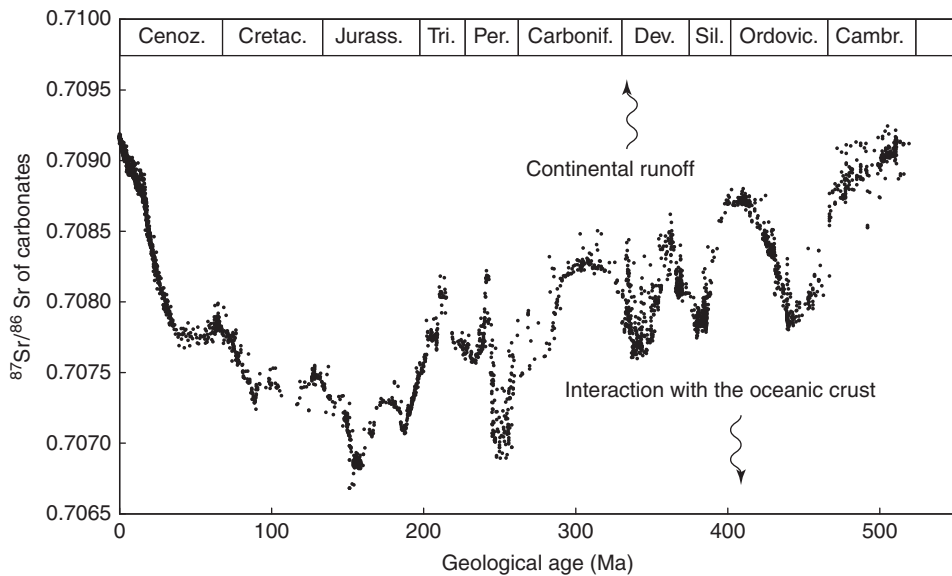


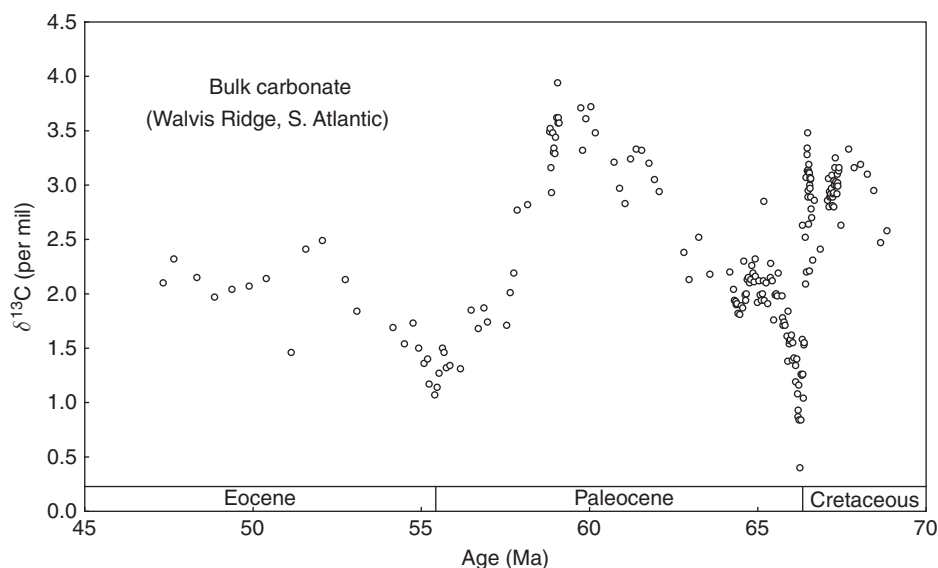
Figure 9.6

Evolution of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in marine carbonates over geological time. The very low Rb content of these rocks ensures that the record of the ratio has not been significantly altered by radioactive ingrowth since deposition. The rapid increase in this ratio since the end of the Cretaceous is attributed to uplift of the high- $^{87}\text{Sr}/^{86}\text{Sr}$  Himalayas, which accelerated the input to the ocean of radiogenic strontium from the ancient basement of the mountain range. This indicates tectonic forcing of the rate of erosion with enormous climatic consequences.

### 9.1.3 Biogeochemical catastrophes in the Phanerozoic

The biogeochemical evolution of our planet is perturbed by occasional events perturbing the long-term trends described in the previous section. At about 65 Ma, i.e. at the boundary between the Cretaceous and the Paleocene, the Earth was impacted by a large asteroid (recently identified as the impactor of the Chixculub crater in the Yucatan) which triggered such huge atmospheric and oceanic effects that most living groups, and in particular dinosaurs and ammonites, disappeared in the aftermath of the collision. The correlation between the so-called K/T boundary mass extinction and a large meteoritic impact was first identified by the presence all over the world of a thin layer of sediments rich in iridium, a metal from the platinum family, that is orders of magnitude more abundant in meteorites than crustal rocks. Other mass extinctions, such as that taking place at the boundary between the Permian and the Triassic, have been ascribed to similar planetary-wide catastrophes.

The geochemical consequences of the K/T boundary event are quite spectacular: the  $\delta^{13}\text{C}$  of the bulk carbonate deposited either at the bottom of the ocean, as depicted in Fig. 9.7 for the South Atlantic (Shackleton and Hall, 1984), or on land, decreases instantaneously by some 2–3 per mil. It has also been found that the  $\delta^{13}\text{C}$  difference between benthic and pelagic organisms which reflects the  $\delta^{13}\text{C}$  gradient in the water column (Fig. 7.13) disappears, which indicates a nearly instantaneous collapse of global biological productivity.



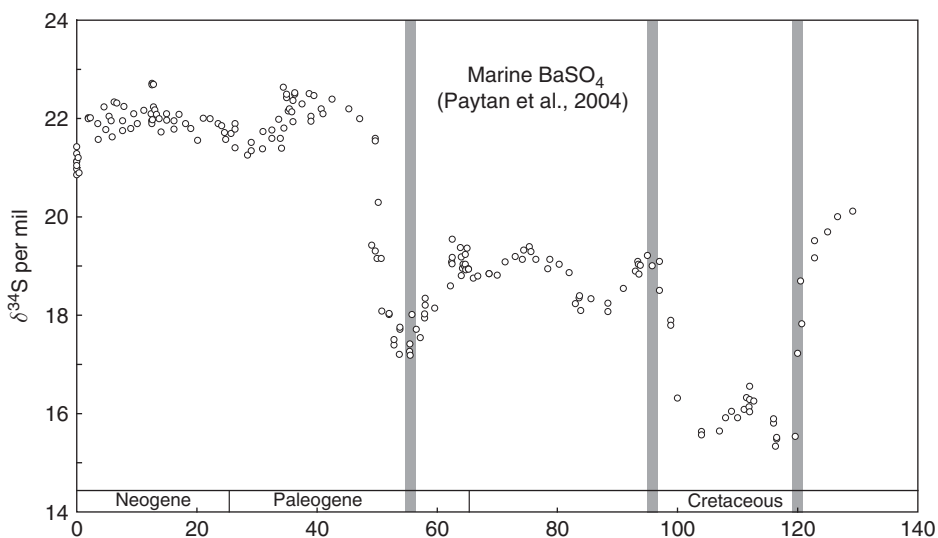
**Figure 9.7**

Carbon isotope compositions of the bulk carbonate in sediments from the Deep Sea Drilling Project hole 237 cored on the Walvis Ridge, South Atlantic (Shackleton and Hall, 1984). The sharp drop of the  $\delta^{13}\text{C}$  values at the Cretaceous-Paleocene boundary and the lack of a C isotope difference between benthic and pelagic species (not shown) indicate that burial of organic material with negative  $\delta^{13}\text{C}$  suddenly came to an end, thus signaling the failure of organic productivity. In contrast, the sharp decline of the  $\delta^{13}\text{C}$  values at the end of the Paleocene is visible in both benthic and pelagic species: it is believed that this event represents the sudden release of methane from isotopically light methane hydrate trapped in sediments into the atmosphere.

Other events have a different geochemical signature and the associated mass extinction hence presumably must be due to different effects. The Paleocene–Eocene boundary at 55 Ma (Fig. 9.7) is also characterized by a sharp  $\delta^{13}\text{C}$  decline, but this time both the benthic and pelagic organisms are shifted by approximately the same amount. It is believed that large amounts of isotopically light carbon were suddenly released into the ocean and the atmosphere. A common interpretation is the destabilization, for reasons that still remain to be established, of very large masses of methane hydrates present in sediments and permafrost and the liberation of large amounts of lethal methane gas into the atmosphere.

A third type of biogeochemical catastrophes which, however, have rarely led to extinctions of the same amplitude as meteoritic impacts, are the oceanic anoxic events (OAEs). These are episodes of deposition of sulfide-rich anoxic sediments rich in heavy metals known as black shales and resembling the organic-matter-rich, oxygen-starved laminites deposited at the bottom of the Black Sea today. The best known of these short events took place during the Toarcian (183 Ma), the early Aptian (120 Ma), and at the Cenomanian–Turonian boundary (93 Ma). It is not well understood whether they represent oxygen deficiency in the water column such as at the bottom of the Black Sea, or rather increased burial of organic material.

The unstable character or the redox conditions of the oceanic system is best demonstrated by the secular evolution of sulfur isotopes since the Cretaceous (Fig. 9.8).



**Figure 9.8** Sulfur isotope compositions of marine barites,  $\text{BaSO}_4$ , throughout the Cretaceous and the Tertiary (Paytan *et al.*, 2004). The shaded bars represent OAEs (Oceanic Anoxic Events). The sharp changes in  $\delta^{34}\text{S}$  reflect strong variations in the burial rates of sedimentary pyrite and global changes in the redox system of the ocean.

Paytan *et al.* (2004) analyzed the sulfur isotope compositions of marine barite ( $\text{BaSO}_4$ ), a mineral oversaturated in the surface ocean but undersaturated at depth. As for most sulfates, sulfur isotope fractionation upon barite precipitation is very small. The obvious advantages of this mineral over more common evaporites are its clearly marine origin and its shown immunity to diagenetic reworking. By about 125 Ma, the  $\delta^{34}\text{S}$  decreased by 4 per mil, oscillated up and down for most of the Cretaceous and the Paleocene, and sharply increased to modern marine-sulfate values at about 55 Ma (22‰); it has stayed nearly constant ever since. There is probably no correlation with OAEs. Although such large variations must reflect variable burial rates of sedimentary pyrite, the fast rate of change, in particular at 55 Ma, suggests either very large sulfur fluxes or fairly low sulfate concentrations in the ocean.

## 9.2 The rise of atmospheric oxygen

### 9.2.1 The 2.1 Ga crisis

Charles Lyell's uniformitarianism states that "the present is key to the past," which asserts that fundamentally the same geological processes operate today as in the distant past. In modern language, we could simply state that the Earth has long since reached some form of steady state. Although this view proved helpful to elucidate some geological observations, the memory of the first geological times did not just disappear overnight. If there is a