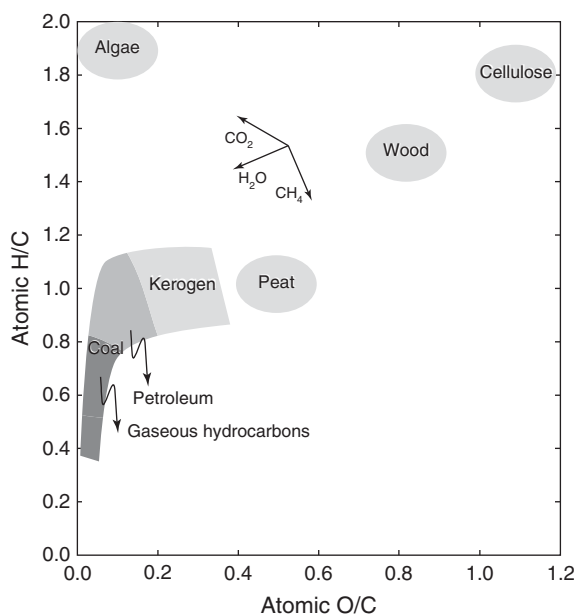


The purpose of this Chapter is a short review of how biological processes affect the geochemical pathways that would prevail in the absence of life and how they contribute to the production of specific components that can occasionally form the bulk of some biological material such as oil. Expertise in biogeochemistry requires a strong background in biology and biochemistry and also some understanding of how biomass interacts as a whole with the mineral world. Background is well beyond the scope of the present book and we will hence try to restrict ourselves to the simplest of concepts.

## 8.1 The geological record

Oxidized rocks, limestones, cherts, and phosphates contain the biological materials with the most spectacular contribution to the geological record. Modern limestones are largely formed by the accumulation of carbonate tests of foraminifera and unicellular algae such as coccolithophores. Diatom frustules contribute massive amounts of silica to sediments at the bottom of the Southern oceans. The gigantic phosphorites of Africa represent fossil hard parts (teeth and bones) or their remobilization by diagenetic fluids: they are mined to produce fertilizers for agriculture. On the sea floor, these three types of rocks are often associated with each other in areas rich in nutrients, continental platforms, wind-driven upwellings of deep seawater such as next to the coasts of Morocco and Peru and the older seawater from the Southern oceans.



**Figure 8.1** A van Krevelen (1950) plot representing the relationship between the major types of organic substances present in the geological record. The arrows indicate how loss of  $\text{CH}_4$  ( $x = 0$ ;  $y = 4$ ),  $\text{CO}_2$  ( $x = 2$ ;  $y = 0$ ), and  $\text{H}_2\text{O}$  ( $y/x = 2$ ) affects compositions in this diagram. Loss of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  from the original organic products generates kerogen. Upon further heating, loss of liquid hydrocarbons, and subsequently of gaseous hydrocarbons inclusive of methane, leaves coal as the main residue (modified from Killips and Killips, 2005).

Reduced carbon is another important remnant of biological activity. Different types of organic material are found in rocks:

- *Humic substances* are common components of soils and waters. The precursors of these very complex compounds are diverse organic compounds resistant to biodegradation such as lignin and tannins.
- *Kerogen* consists of a variety of polymers and macromolecules formed during diagenesis by microbial degradation and condensation of humic substances, which make the products progressively more insoluble in diagenetic fluids. Different types of kerogens are distinguished, which may eventually lead to the formation of liquid hydrocarbons and coal. Bitumen is the fraction of carbon compounds that can be extracted from a rock by liquid solvents.
- *Liquid hydrocarbons* (petroleum) evolve by loss of water, carbon dioxide, and methane from some types of kerogen upon heating at temperatures of 60–150 °C (the oil “window”). The nature of the end-product depends on the rate of transformation.
- *Gaseous hydrocarbons* such as methane evolve from kerogen and coal at temperatures of 150–230 °C.
- *Coal* is the residual carbon-rich material left behind after hydrocarbons have left the rock. The most abundant humic coals derive from vascular plants, whereas sapropelic coal forms from fine-grained organic particles.

The maturation of carbon-rich material can be best presented in a van Krevelen (1950) plot representing the H/C ratio as a function of the O/C ratio (Fig. 8.1), in which loss of

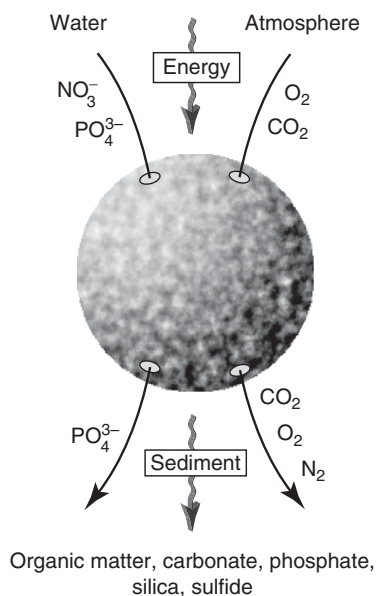
water, carbon dioxide, and methane are easily represented. The remains of vascular plants have high H/C and O/C ratios; those of algae, high H/C and low O/C ratios. Removal of H<sub>2</sub>O and CO<sub>2</sub> by heating drives organic material into the field of kerogen and then coal. Subsequent removal of liquid hydrocarbons and methane drives the residue into the field of low-H coal.

It is a classically held view that major coal deposits formed in periods following lowering of sea levels, which were the most prone to deposition in landlocked basins. In contrast, deposition of the largest oil source rocks coincided with transgressive periods and increased biological productivity. The largest fraction of mature organic matter in the crust is actually stored, not in coal, the second largest reservoir, and not in oil either, but in methane hydrates: at pressures exceeding 100 atmospheres and temperatures lower than 18 °C, methane forms liquid hydrates or clathrates which are found in very large amounts beneath the permafrost of continents at high latitudes and in the sediments of the marine continental slopes.

## 8.2 Some specifics of biological activity

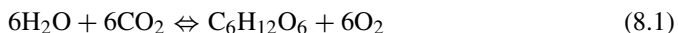
In geological cycles, biological compounds are rarely considered as a source or a sink of elements simply because biomass is only a small mass fraction of geological reservoirs, such as the ocean or even soils. The relationship of life to geochemical pathways is a bit like that of the beaver to the river: it is there to mine available energy that would otherwise have been dissipated with no profit to any living thing. There is clearly more to life than building a lodge to protect offspring against predators, but the principle is still valid: life is opportunist and gets a free ride on untapped energy flows. And just as the beaver has a strong impact on the river and associated habitats, life affects the ocean, the atmosphere, and leaves fairly strong footprints in the chemistry of sediments. A plankton-free ocean would certainly have a chemistry very different from our familiar seawater. We will see that life may even be held responsible for some remarkable geodynamic features such as no less than the stabilization of granitic continents.

Two characteristics of organic material are fairly striking. First, it rises incredibly high on the redox scale. Trading electrons between very different redox potentials is the hallmark of biological activity. Life is about pushing C and N towards the most reduced state possible and then using a multistage transfer of high-energy electrons between a reduced primary electron donor (PED) and a terminal electron acceptor (TEA) to produce mechanical work and build structural and functional molecules. The cell builds up the only energy form it can use, adenosine-triphosphate or ATP, using external inputs, so that new proteins can be synthesized for maintenance and mechanical work performed. For autotrophs (plants), the primary source of energy is solar electromagnetic radiation in the visible part of the spectrum. Pigments, most notably chlorophyll, capture this energy in a process called photosynthesis, which may be either oxygenic (cyanobacteria, algae, plants release oxygen) or anoxygenic. In most biological systems, energy is stored as



**Figure 8.2** Autotrophic life as a simple chemical plant. Nutrients are absorbed from the aqueous environment (seawater or groundwater) while  $\text{CO}_2$  needed for photosynthesis and  $\text{O}_2$  needed for respiration are ultimately derived from the atmosphere. Gaseous waste is also made of  $\text{CO}_2$  and  $\text{O}_2$ .

carbohydrates (sugar). The oxygenic synthesis of glucose may be represented by the formal reaction:

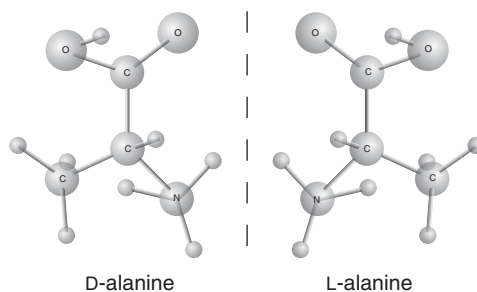


Heterotrophs burn reduced carbon prepared by other organisms: they eat food and breathe.

Breakdown of glucose to pyruvate  $\text{CH}_3\text{-CO-COO}^-$  leads to ATP production in the absence (fermentation) or in the presence (respiration) of a terminal electron acceptor, such as sulfate or nitrate. Respiration is far more efficient than fermentation to produce ATP, which explains why aerobic conditions and dissimilative reduction of nitrate, sulfate, and iron are life's 'first choice'. Alternative sources, notably the energy of chemical reactions (chemotrophs), are occasionally used.

Cell metabolism requires some major constituents and trace metals from its environment. Obtaining C from  $\text{CO}_2$  and H from  $\text{H}_2\text{O}$  is rarely an issue as long as a source of energy is present, but nitrogen must be tapped from either the atmosphere or from dissolved nitrates. For phosphate groups, the only source is the  $\text{PO}_4^{3-}$  ion released into natural waters by weathering of continents. Oxygen is the waste of photosynthesis, while  $\text{CO}_2$  is the waste of respiration. Nitrate processing eventually releases nitrogen and some phosphate also is eliminated in the ambient liquid medium (Fig. 8.2).

A second property of biomolecules is their widespread chirality (handedness): a molecule can exist under two configurations which are the mirror image of each other



**Figure 8.3** Example of chirality: alanine, which is an amino acid. The two enantiomers are mirror images of each other and cannot be superposed by any rotation. Unlabelled atoms are hydrogen. Biological alanine is L.

but cannot be superposed by rotation (Fig. 8.3). These two configurations, known as enantiomers, have a different effect on polarized light and are prefixed by D, for dextrogyre, for rotating light to the right, or L (levogyre) otherwise. Biomolecules are either non-chiral or 100 percent L or D (homochirality), most sugars being D and 19 out of the 20 amino acids being L (glycine is not chiral). The mechanism that produced homochirality in the first place is relevant to the origin of life but is not understood.

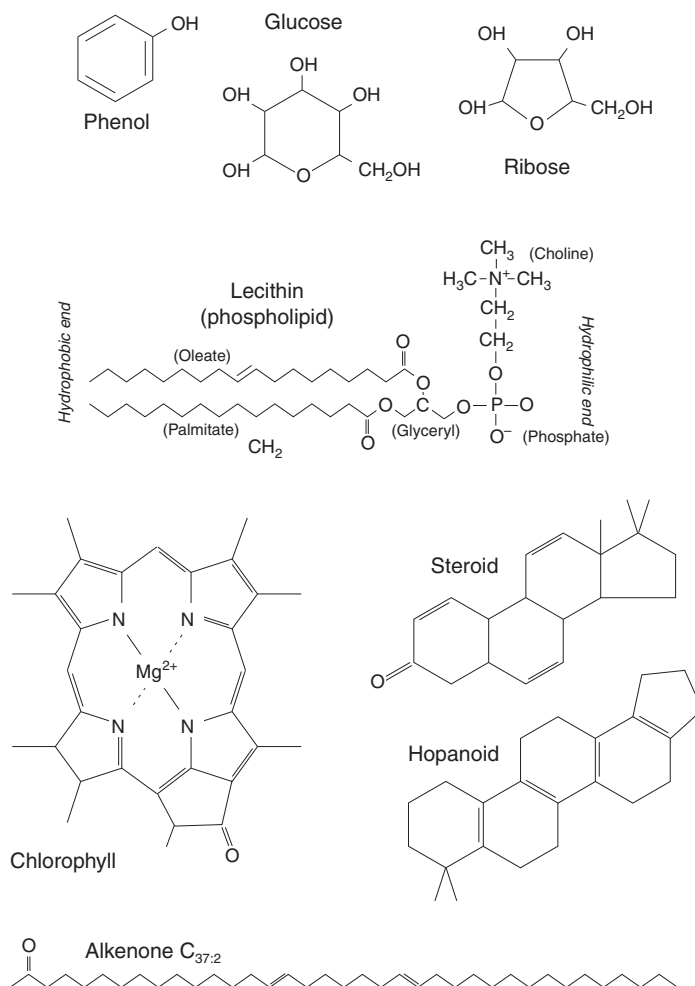
Some additional defining effects of biogeochemistry may be summarized as follows:

1. The most abundant elements in the biomass are reduced carbon, hydrogen, nitrogen, and phosphate. Fossil biomolecules are of particular economic importance since, as every living creature, humans like to turn reduced carbon into energy.
2. Biological activity affects sediment composition through the deposition of biominerals (carbonate, phosphate) or by interfering with diagenesis.
3. Over the Earth's history, biological activity has modified the composition of the atmosphere (notably by adding oxygen and removing carbon dioxide) and of the ocean. It is still today an essential parameter in climatic regulation.
4. Biological activity maintains chemical gradients such as those of nutrients in the water column.
5. Some of the original biomolecules, mostly insoluble lipids, are left untouched by diagenesis. They are true geochemical fossils and as such are called biomarkers.

We will now address some of these properties.

## 8.3 The chemistry of life

Living creatures can be divided into eukaryotes, which shelter their genes in a nucleus (e.g. plants and animals), and prokaryotes with no nuclear membrane. The second group is clearly divided by genetic analysis into archæa, which often live in unusual or extreme



**Figure 8.4** The structure of some important components of biological material and biomarkers.

environments, and (eu)bacteria. We will start this chemical tour by reviewing the main constituents of organic matter (Fig. 8.4):

1. Carbohydrates ('sugars') derive their name from their generic formula  $C_n(H_2O)_n$ . The common and simple sugar glucose  $C_6H_{12}O_6$  is a monosaccharide whose ring structural form leads to polysaccharides via condensation reactions. The commonest of these latter is cellulose, a ubiquitous component of cell walls, notably in plants but also in chitin used by arthropods and insects as shell material. Carbohydrates are the primary reserve of energy and are used to produce adenosine triphosphate (ATP).
2. Amino acids are organic (carboxylic) acids in which one carbon is attached to an amino  $NH_2$  group. They contain most of the nitrogen present in organic matter. Polymerization of amino acids via their  $NH_2$  group produces proteins. Enzymes are proteins with a catalytic function, i.e. molecules which reversibly provide the little increment of energy that helps a particular reaction go over the activation energy barrier.

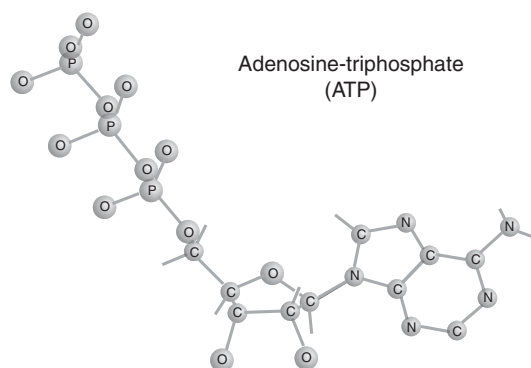


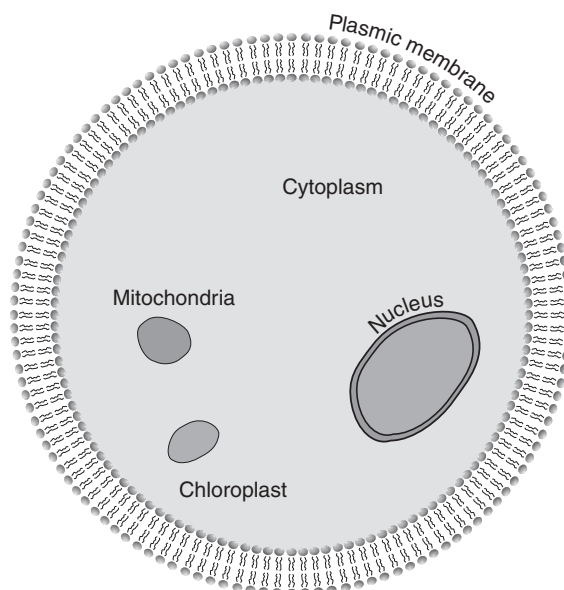
Figure 8.5

Structure and composition of adenosine-triphosphate (ATP). Hydrolysis of this compound to form adenosine-diphosphate (ADP) and phosphoric acid liberates the energy needed by the cell.

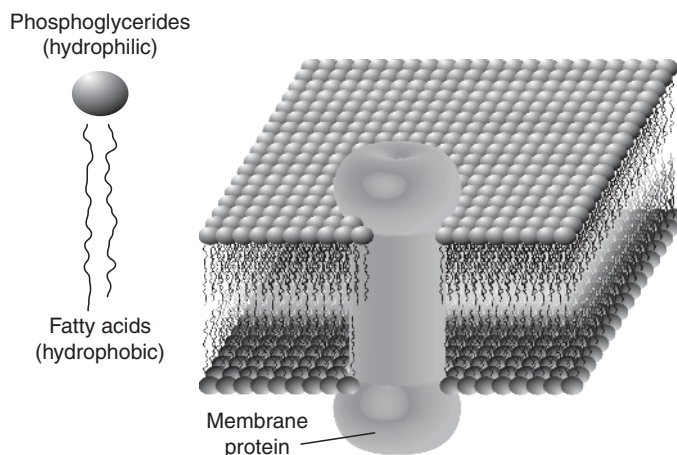
3. Lipids include the fats and the glycerides, or esters of glycerol esters with one or more fatty acids. When  $\text{PO}_4^{3-}$  groups attach themselves to one chain or more of carboxylic acids, they are known as phosphoglycerides. Tetracyclic compounds made of four pyrrole units (a five-membered ring with a nitrogen atom opposing two double carbon bonds) are biologically important as they form pigments known as porphyrines: chlorophylls (Mg) and hemoglobin (Fe) are closely related compounds. Terpenes are a broad class of lipids based on the isoprene chain ( $\text{C}_5\text{H}_8$ ), which has one unsaturated bond at each end. Many form important compounds with multiple cyclic bonds (sterols, hopanes).
4. Aromatic alcohols (phenols) condense to form lignin, the second most abundant component in plants.
5. Nucleotides contain nitrogen-bearing compounds, a pentose sugar (ribose or deoxyribose), and a phosphate. Nucleic acids are polymers of nucleotides.

The universal energy currency of cellular metabolism is ATP, a compound which combines an amino acid known as adenine, a sugar called ribose, and phosphate groups (Fig. 8.5). Hydrolysis of ATP gives adenosine-diphosphate (ADP) and phosphoric acid by releasing a very large amount of energy.

A distinction should be made between living organisms and fossil organic matter. For all practical purposes, the mass inventory of living cells is dominated by an outer plasmic membrane and an inner medium called cytoplasm, which can be either a gel or a sol depending on environmental conditions (Fig. 8.6). Vegetal cells are also wrapped in an additional film of cellulose and some plants even develop a rigid framework of lignin. Lignin and cellulose are the main initial constituents of coal. Genetic material dominated by polynucleotides (RNA = ribonucleic acid and DNA = deoxyribonucleic acid) is either loose in the cytoplasm of prokaryotic cells (e.g. bacteria) or hosted in the nucleus, in mitochondria (animals), or in chloroplasts (plants) of eukaryotic cells. In general, membranes are composed of two layers of phospholipids made at one end of hydrophilic phosphoglycerides and at the other end of hydrophobic fatty acids, which mostly consist of long chains of hydrocarbons (Fig. 8.7). The cytoplasm is a complex solution of



**Figure 8.6** The major elements of a cell are the cytoplasmic liquid and the lipidic membrane. Eukaryotes store their genetic material in the nucleus, which is also isolated from the cytoplasm by a membrane. Energy conversion is ensured by mitochondria, probably a former symbiotic bacteria. Chloroplasts are only present in plant cells and are used for photosynthesis.



**Figure 8.7** A simple membrane is made from a double layer of phospholipids, long molecules made from a hydrophilic head of phosphoglyceride and a long tail of hydrophobic fatty acid. Large proteins are used to ferry various components, such as  $H^+$  or  $K^+$ , through the membrane.

proteins, glucides, and about one percent of inorganic ions, notably  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Fe^{2+}$ ,  $Cl^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$ . Again, the polynucleotides are a repository of  $PO_4$  and amino  $NH_2$  groups, and nitrogen-containing cycles. We have already met the Redfield ratio which states that the C:N:P proportions in plankton are in the proportions of 115:15:1. [Table 8.1](#) shows the inorganic composition of a sample of dry plankton material.



**Table 8.1** Elemental composition of the marine plankton (Martin, 1973). Concentrations in  $\mu\text{g g}^{-1}$  except for Na, K, Mg, Ca which are in  $\text{mg g}^{-1}$

	Na	K	Mg	Ca	Sr	Ba
Phytoplankton	14	1.3	1.6	0.7	147	33
Zooplankton	11	1	1	0.2	132	16
	Al	Fe	Mn	Cu	Zn	
Phytoplankton	110	224	6			
Zooplankton	94	199	11	6	100	

## 8.4 Biominerals

What comes around goes around. In a world with no biological activity, sediments would probably be deposited on the ocean floor on average at pretty much the same rate as they are in our biological world. Alkalinity, phosphate, and dissolved silica liberated from the continents by erosion would be transported from the continents to the oceans and create huge carbonate, phosphate, and silica deposits. Iron and manganese would come out of black smokers at the bottom of the ocean and precipitate as metalliferous sediments near mid-ocean ridges. Even the most soluble compound, NaCl, has a residence time in the ocean of 300 My: elements can only accumulate in the ocean for as long as solubility is not exceeded or as long as they are not scavenged by detrital particles. In the end, what precipitates on the ocean floor is what came through estuaries and other inputs. Beyond the accumulation of organic matter discussed in the previous section, the role of biology with respect to inorganic elements is somewhere else: it changes the site and sometimes the mineral form under which minerals leave the ocean.

How life separates elements and recombine them into insoluble compounds to fit its own needs may vary. One of the main functions of membranes is to use energy to temporarily defeat the second principle of thermodynamics and the destructive power of diffusion and mixing: building a hydrophobic wall between the inside and the outside of a cell, or between different compartments of the same cell brings diffusion to a halt simply because it locally removes the aqueous diffusing medium. Membrane proteins nailed through the membrane take over and act as guarded gates to transfer elements individually (Fig. 8.7). They are fueled by ATP, the standard energy source, and therefore do not have to comply with the normal rules of diffusion. How proteins can be so selective with respect to particular elements is not a trivial question. Coordination is of course an important parameter, but the simple ligands, such as citrate, lactate, and oxalate, have the same order of preference, known as the Irving–Williams stability order, which for divalent ions is  $(\text{Mg}^{2+}, \text{Ca}^{2+}) < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ . This means for instance that, under similar conditions, the  $\text{Cu}^{2+}$  lactate and citrate will be more stable than the  $\text{Fe}^{2+}$  lactate and citrate, respectively. Other parameters are used by specific proteins to capture a particular

ion, such as the charge, the ionic radius, the pH, the concentration of the ligand, the redox potential, multiple complexation, and even the spin of the element. The cell utilizes this complex arsenal to manipulate the crystallization pathway of some particular minerals.

A distinction can be made between minerals formed as a by-product of cell metabolism or activity (biologically induced mineralization) and minerals that are an integral part of the organism physiology (biologically controlled mineralization):

1. *Biologically induced mineralizations.* Cyanobacteria and their stromatolite constructs are one of the earliest examples of an organism precipitating calcite. Precipitation of iron and manganese oxyhydroxides is frequent as a consequence of bacteria creating a reducing environment which converts  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  into low-solubility  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ . It is also known that bacteria play a strong role in the precipitation of silica from hydrothermal springs. Apatite forms upon decay of biological matter. A form of pyrite, called framboidal for its raspberry-like appearance, is an example of biologically mediated sulfide precipitation.
2. *Biologically controlled mineralizations.* The most important biominerals of this type are carbonates (foraminifera) and silica (diatoms and radiolarians), which cover broad expanses on the sea floor. These minerals are mostly used to confer protection and mobility to the organisms. A spectacular case is intracellular precipitation of nicely aligned magnetite crystals in so-called magnetotactic bacteria.

## 8.5 Biological controls on the ocean–atmosphere system

Consequences of this biological activity on the chemistry of the ocean–atmosphere system are very significant. Today, the alkalinity flux through the ocean is regulated by the precipitation of organic calcite. Phytoplankton acts on the atmosphere by the photosynthetic production of oxygen, which is balanced by the respiration of both the phyto- and the zooplankton. What limits the process is not very well understood: it is believed, as suggested by John Martin, that the availability of micronutrients, notably Fe and Zn, may keep productivity in check. The story goes that during a seminar at Woods Hole, John Martin rose and said “Give me a half tanker of iron, and I will give you an ice age.” The project IRONEX, designed to test this assumption, supports this view: south of the Galapagos Islands, in the Eastern Pacific, in waters naturally rich in major nutrients because of the very low latitude, addition of 445 kg of iron triggered a strong algal bloom with a clearly visible change in chlorophyll levels and measurable effects on dissolved  $\text{CO}_2$ .

Export of organic matter towards the sediment acts as a  $\text{CO}_2$  pump and a source of  $\text{O}_2$  for the ocean–atmosphere system. The fate of buried carbon controls the long-term evolution of atmospheric oxygen. If sedimentary C is oxidized, either because it is oxidized during diagenesis or because the sediment is shoved up against continental margins, reaction with atmospheric oxygen converts it back to carbon dioxide. This phenomenon can be seen at work today in the natural oil seeps of the Persian Gulf. If sediments are subducted with oceanic lithospheric plates, carbon is injected into the mantle and the atmosphere inherits the leftover oxygen irreversibly.

## 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

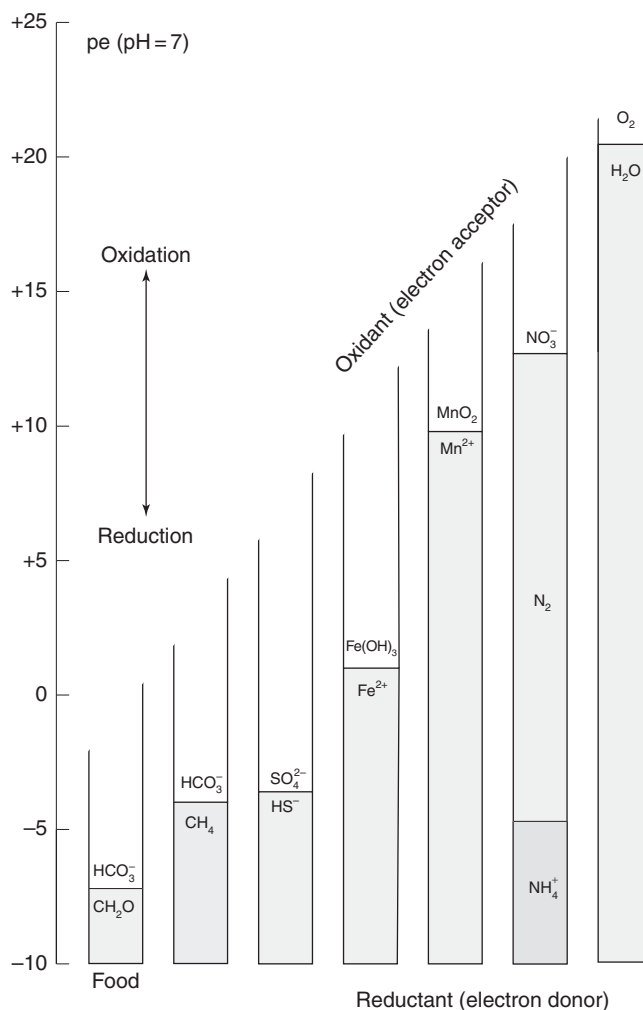


Figure 8.8

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 CH<sub>2</sub>O (food) is supposed to be present in excess. The energy driving its oxidation (upward) into HCO<sub>3</sub><sup>-</sup>, 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 FeS<sub>2</sub>, 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.

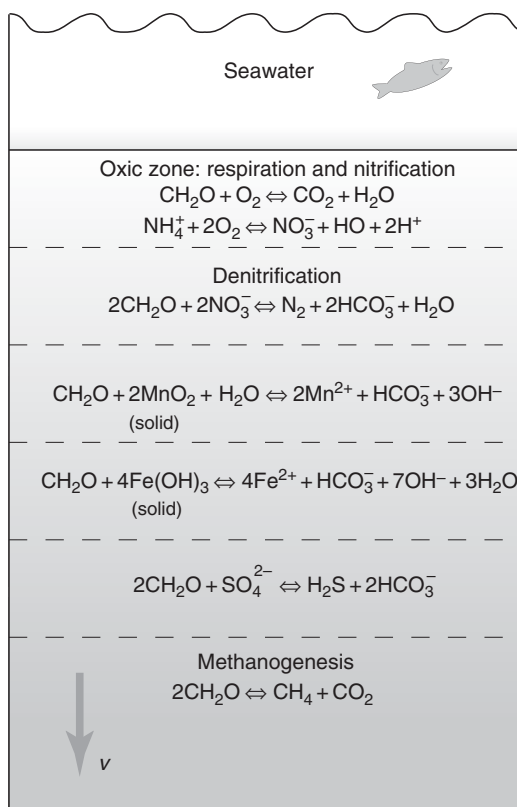


Figure 8.9

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  $\text{pH} < 2$ .

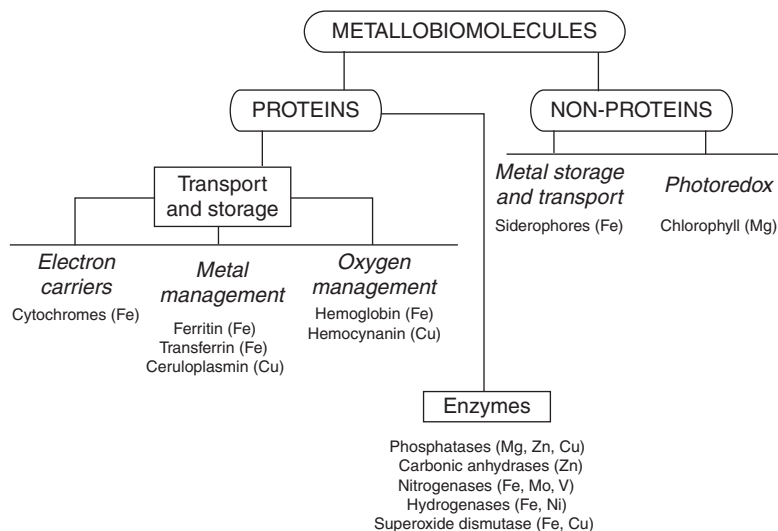
During diagenesis, humic compounds evolve into kerogen which, upon heating between 50 and 120 °C evolves into the hydrocarbons of crude oil. Oil is normally preserved when it seeps out from its primary site of formation towards a porous reservoir. Further heating induces the cracking of hydrocarbon chains 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](#).