

1.1 Carbon and the basic requirements of life

In its broadest sense, organic geochemistry concerns the fate of carbon, in all its variety of chemical forms, in the Earth system. Although one major form of carbon is strictly inorganic, carbon dioxide, it is readily converted by photosynthesis into the stuff of life, organic compounds (see Box 1.9), and so must be included in our consideration of organic geochemistry. From chiefly biological origins, organic compounds can be incorporated into sedimentary rocks (Box 1.1) and preserved for tens of millions of years, but they are ultimately returned to the Earth's surface, by either natural processes or human action, where they can participate again in biological systems. This cycle involves various biochemical and geochemical transformations, which form the central part of the following account of organic geochemistry. To understand these transformations and the types of organic compounds involved we must first consider the origins and evolution of life and the role played by carbon.

Growth and reproduction are among the most obvious characteristics of life, and require the basic chemicals from which to build new cellular material, some form of energy to drive the processes and a means of harnessing and distributing this energy. There is an immense range of compounds involved in these processes. For example, energy is potentially dangerous; the sudden release of the energy available from complete oxidation of a single molecule of glucose is large when considered at a cellular level. Therefore, a range of compounds is involved in bringing about this reaction safely by a sequence of partial oxidations, and in the storage and transport to other sites in the cell of the more moderate amounts of energy released at each step. We look at the geochemically important compounds involved in life processes in Chapter 2.

What makes carbon such an important element is its ability to form an immense variety of compounds—

Box 1.1 | Sediments and sedimentary rocks

Sediment is the solid material, inorganic or organic, that settles out of suspension from a fluid phase (normally water, ice or air) in which it has been transported. Over time, under the right conditions, it can undergo lithification (i.e. conversion into a solid body of rock). Various processes can be involved in lithification: compaction, cementation, crystallization and desiccation.

Inorganic sediment is supplied by erosion of material from exposed areas of high relief, and can be transported a considerable distance to the area of deposition. The composition of this **detrital** (or **clastic**) material varies, but aluminosilicate minerals are usually important. There are also biogenic sediments, resulting from the remains of organisms (e.g. calcareous and siliceous tests, peat) and **chemical sediments** formed by precipitation of minerals from solution (e.g. evaporites, some limestones and authigenic infills of pores by quartz and calcite cements).

The nature of the sediments accumulating in a particular location can change over time, allowing the recognition of different bodies of sedimentary rock. Such a body is termed a **facies**, and it displays a set of characteristic attributes that distinguish it from vertically adjacent bodies. Various distinguishing attributes include sedimentary structures, mineral content and fossil assemblages. Organofacies can also be recognized, based on compositional differences in the organic material present (Jones 1987; Tyson 1995).

primarily with the elements hydrogen, oxygen, sulphur and nitrogen, as far as natural products are concerned—with an equally wide range of properties; this is unparalleled by other elements. This variety of properties allows carbon compounds to play the major role in the creation and maintenance of life. The strength of the chemical bonds in organic compounds is sufficiently high to permit stability, which is essential in supportive tissue, for example, but low enough not to impose prohibitive energy costs to an organism in synthesizing and transforming compounds.

Another prerequisite for life is liquid water, the medium in which biochemical reactions take place and usually the main constituent of organisms. Although bacteria, and even some simple animals, like the tardigrade, can survive in a dormant state without water, the processes that we associate with life can only take place in its presence. This requirement obviously imposes temperature limits on environments that can be considered suitable for life; hence one of the criteria in the search for life on other planets is evidence for the existence of liquid water at some stage of a planet's life.

1.2 Chemical elements, simple compounds and their origins

1.2.1 Origin of elements

Carbon is the twelfth most abundant element in the Earth's crust, although it accounts for only $c.0.08\%$ of the combined lithosphere (see Box 1.2), hydrosphere and atmosphere. Carbon-rich deposits are of great importance to humans, and comprise diamond and graphite (the native forms of carbon), calcium and magnesium carbonates (calcite, limestone, dolomite, marble and chalk) and fossil fuels (gas, oil and coal). Most of these deposits are formed in sedimentary environments, although the native forms of C require high temperature and pressure, associated with deep burial and metamorphism.

Where did the carbon come from? The universe is primarily composed of hydrogen, with lesser amounts of helium, and comparatively little of the heavier elements (which are collectively termed metals by astronomers). The synthesis of elements from the primordial hydrogen, which was formed from the fundamental particles upon the initial stages of cooling after the Big Bang some 15 Gyr ago, is accomplished by nuclear fusion, which requires the high temperatures and pressures within the cores of stars. Our Sun is relatively small in stellar terms, with a mass of $c.2 \times 10^{30}$ kg, and is

Box 1.2 | Earth's structure

Temperature and pressure both increase with depth in the Earth and control the composition and properties of the material present at various depths. The Earth comprises a number of layers, the boundaries between which are marked by relatively abrupt compositional and density changes (Fig. 1.1). The inner core is an iron–nickel alloy, which is solid under the prevailing pressure and temperature ranges. In contrast, the outer core is molten and comprises an iron alloy, the convection currents within which are believed to drive the Earth's magnetic field. The core–mantle boundary lies at $c. 2900$ km depth and marks the transition to rocky material above. The **mantle** can be divided into upper and lower parts, although the boundary is quite a broad transitional zone ($c.1000$ – 400 km depth). It behaves in a plastic, ductile fashion and supports convection cells. The upper mantle layer from $c.100$ to 400 km depth is called the **asthenosphere**, and its convection system carries the drifting continental plates.

With decreasing temperature towards the surface, the top part of the mantle is sufficiently cool that it behaves as a strong, rigid solid. The cold, relatively thin, layer of solid rock above the mantle is the **crust**, which is $c.5$ – 7 km thick under the oceans but $c.30$ – 70 km thick on the continents. The topmost mantle and crust are often considered together as **lithosphere**. Under excessive strain, such as during earthquakes, the lithosphere undergoes brittle failure, in contrast to the ductile deformation that occurs within the asthenosphere.

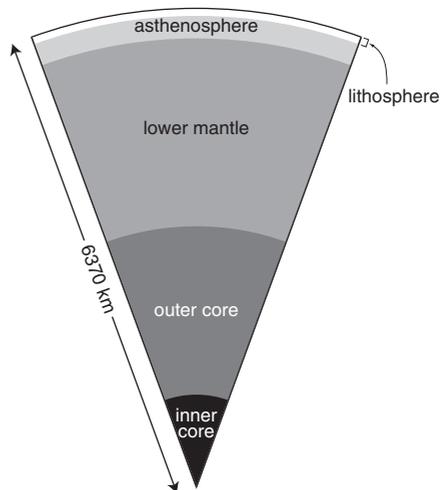
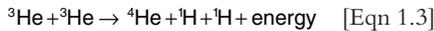
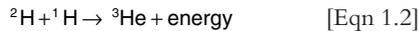
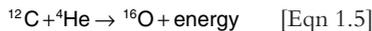
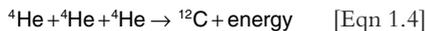


Fig. 1.1 Simplified layering within the Earth.

capable of hydrogen fusion, which involves the following reactions:



(where ${}^2\text{H}$ can also be written as D, or deuterium, and the superscript numbers represent the mass numbers as described in Box 1.3). Because of the extremely high temperatures and pressures, electrons are stripped off atoms to form a plasma and it is the remaining nuclei that undergo fusion reactions. Ultimately, when enough helium has been produced, helium fusion can then begin. This process is just possible in stars of the mass of our Sun, and results in the creation of carbon first and then oxygen:



There is still usually plenty of hydrogen left in a star when helium fusion starts in the core. If the products of helium fusion mix with the outer layers of the star it is possible for other elements to be formed. The CNO cycle is an important fusion pathway (Fig. 1.2), which primarily effects the conversion of H to He. However, the cycle can be broken, resulting in the formation of heavier elements; for example, by the fusion reaction shown in Eqn 1.5.

Only more massive stars can attain the higher temperatures needed for the synthesis of heavier elements.

For example, magnesium can be produced by fusion of carbon nuclei and sulphur by fusion of oxygen nuclei. Fusion of this type can continue up to ${}^{56}\text{Fe}$, and ideal conditions are produced in novae and supernovae explosions. Heavier elements still are synthesized primarily by neutron capture.

Our Sun is too young to have produced carbon and heavier elements. These elements in the nebula from which the Solar System was formed *c.* 4.6 Gyr ago, together with the complex organic molecules in our bodies, owe their existence to an earlier generation of stars.

1.2.2 The first organic compounds

Away from the nuclear furnaces of the stars elements can exist as the atoms we are familiar with, which in turn can form simple compounds if their concentrations are sufficiently great that atomic encounters can occur. The highest concentrations are found in interstellar clouds, and in particular in molecular clouds, where densities of 10^9 – 10^{12} particles per m^3 can exist. This is still a very low density, and the most common constituents of these clouds are H (atomic hydrogen), H_2 (molecular hydrogen) and He, which can be ionized by bombardment with high-energy particles, originating from phenomena like supernovae, and can then take part in ion–molecule reactions, such as:

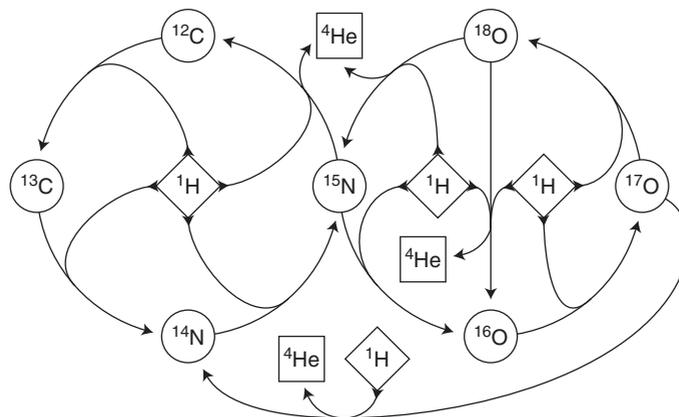
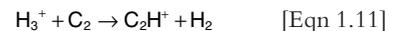
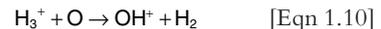
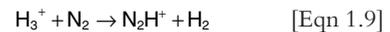
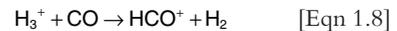


Fig. 1.2 Hydrogen fusion via the CNO cycle.

Box 1.3 | Stable isotopes

Isotopes are atoms of the same element that contain the same numbers of protons and electrons, so are chemically identical, but contain different numbers of neutrons, so their masses are different. Each element has an individual atomic number, equal to the number of electrons (or protons) in an atom (six for carbon). Electrons carry a unit negative charge but very little mass. The negative charge of the electrons in an atom is offset by an equal number of positively charged particles, protons, which have masses considerably greater than the electron. The protons exist in a nucleus, around which the electrons orbit. Also in the nucleus are uncharged particles called neutrons, with similar masses to the protons. Isotopes of an element differ in the number of neutrons in their nuclei and, therefore, in their atomic mass, which is the sum of the protons and neutrons (12 and 13 for the stable isotopes of carbon). So, in general, we can represent an isotope by ${}^m_n\text{E}$, where m is the mass number and n the atomic number of the element E , but often the atomic number is omitted for simplicity (e.g. ${}^{13}\text{C}$ instead of ${}^{13}_6\text{C}$).

Carbon is a mixture of two stable isotopes, ${}^{12}\text{C}$ and ${}^{13}\text{C}$. In the Earth as a whole the relative abundances of ${}^{12}\text{C}$ and ${}^{13}\text{C}$ are 98.894% and 1.106%, respectively. Carbon compounds of biological origin are relatively enriched in the lighter isotope, while the heavier isotope is retained in the main forms of inorganic carbon (e.g. carbonate, bicarbonate and carbon dioxide). Biogenic substances usually contain more of the lighter isotope than exists in the substrate from which the element was sequestered, a process termed **isotopic fractionation**. This is because, in the main assimilatory pathways and, to a lesser extent, the ensuing metabolic processes, the reactions involving isotopically lighter molecules of a compound, such as in the primary carbon fixation reaction of photosynthesis, occur slightly faster, a phenomenon termed the **kinetic isotope effect**. Isotopic fractionation can also take place during diffusion of a gas across a

cell membrane—e.g. the uptake of carbon dioxide by unicellular algae—because the slightly smaller molecules of lighter isotopic composition diffuse at a faster rate (see Box 3.8).

The ratio ${}^{13}\text{C}$ to ${}^{12}\text{C}$ in a geological sample is measured by mass spectrometry after converting the carbon to CO_2 . To minimize inaccuracies in measuring the absolute amounts of ${}^{12}\text{CO}_2$ and ${}^{13}\text{CO}_2$ the ratio of the two in a sample is compared with that in a standard analysed at the same time. The isotopic ratio of a sample is normally expressed by δ values (with units of permil, or ‰) relative to the standard, and its general form can be represented by:

$$\delta^m\text{E}(\text{‰}) = [\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1] \times 10^3 \quad [\text{Eqn 1.6}]$$

where m = mass number of the heavier isotope, E = the element and R = the abundance ratio of a heavier to the lightest, most abundant isotope. So for carbon we have:

$$\delta^{13}\text{C}(\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1] \times 10^3 \quad [\text{Eqn 1.7}]$$

Other biogeochemically important elements have a range of stable isotopes, as shown in Table 1.1, and the isotopic ratios are expressed using the general formula in Eqn 1.6. A different standard is used for each element, and the standard can also vary depending upon the form of the element (e.g. oxygen in Table 1.1). By definition, the $\delta^m\text{E}$ value of a standard is 0‰, so negative values for a sample indicate depletion in the heavier isotope compared with the standard and positive values indicate enrichment in the heavier isotope (for PDB ${}^{13}\text{C}/{}^{12}\text{C} = 0.011237$).

Some elements have unstable isotopes, which undergo radioactive decay, such as ${}^{14}\text{C}$ (see Box 5.5). Those of ${}^{238}\text{U}$, ${}^{235}\text{U}$, ${}^{232}\text{Th}$ and ${}^{40}\text{K}$ are responsible for the heat production in the Earth's crust.

Table 1.1 Stable isotope abundances of biogeochemically important elements and their associated standards (after Hoefs 1997)

element	stable isotopes	(% relative abundance)	common reference standard
hydrogen	${}^1\text{H}$ (99.9844)	${}^2\text{H}$ or D (0.0156)	Vienna standard mean ocean water (V-SMOW)
carbon	${}^{12}\text{C}$ (98.89)	${}^{13}\text{C}$ (1.11)	Cretaceous Peedee formation belemnite (PDB)
nitrogen	${}^{14}\text{N}$ (99.64)	${}^{15}\text{N}$ (0.36)	atmospheric N_2 (air)
oxygen*	${}^{16}\text{O}$ (99.763)	${}^{18}\text{O}$ (0.1995)	PDB for low-temperature carbonates, otherwise standard mean ocean water (SMOW)
sulphur*	${}^{32}\text{S}$ (95.02)	${}^{34}\text{S}$ (4.21)	Canyon Diablo meteorite troilite (CDT)

*The above stable isotopes are those commonly used in geochemistry, but others exist for oxygen (${}^{17}\text{O}$ (0.0375‰)) and sulphur (${}^{33}\text{S}$ (0.75‰), ${}^{36}\text{S}$ (0.02‰)).

Among the eventual products of these reactions are methanal (HCHO, also known as formaldehyde), ammonia, water and various simple organic molecules, respectively. Just a few examples of the types of simple molecules that have been detected in interstellar space and also in comets (see Box 1.4) are given in Table 1.2. These compounds are all gases when in the interstellar medium, but are solids when accreted on to dust particles (formed *inter alia* from carbonaceous grains, and oxides of magnesium and aluminium). Interestingly, carbon dioxide has been detected in comets but not in molecular clouds, and it is likely that the more intimate associations of molecules in comets can lead to different products and perhaps more complex organic molecules. One source of energy to fuel such reactions is ultra-violet (UV) radiation from the Sun.

1.3 The origin of life

1.3.1 The young Earth

It is likely that conditions on the newly accreted Earth were not favourable for life: hence the naming of the Era from 4.6 to 3.8 Ga as the Hadean (see Appendix 3 for geological time scale). The Earth's primary atmosphere, immediately after its formation, would have probably reflected the composition of the nebula from which the Solar System formed. It would have contained mainly hydrogen and helium, which would have tended to escape the gravitational field of the Earth, but would, in any event, have been stripped away by the violent solar winds during the early T-Tauri stage of the Sun's evolution (Hunten 1993). The collision of the Earth with another body that ejected material to form the Moon before 4.5 Ga, shortly after the core and mantle had differentiated (Halliday 2000), would also have had a major influence on the atmospheric composition. The Earth's secondary atmosphere owes its existence to juvenile volatiles outgassing from the interior of the planet (although a proportion of the water may have been acquired subsequently from meteorites). In view of the composition of volcanic emissions today these volatiles probably comprised mainly water vapour, nitrogen, carbon dioxide, carbon monoxide, sulphur dioxide and hydrogen chloride, although opinions vary over the importance of reducing gases (see Box 1.5) such as methane, ammonia and hydrogen. Whether methane and ammonia could have been present depends upon whether the oxidation state of the mantle has varied, and the amount of time it took to reach its current degree of oxidation. It is believed that no free oxygen was present

Box 1.4 | Comets, asteroids and meteorites

Comets are mostly aggregates of interstellar dust, ice (H₂O, CO and CO₂) and some organic molecules. They originate from two regions in the Solar System. The most distant is the Oort cloud, which is up to 10⁵ AU from the Sun, well outside the orbit of Pluto (1 AU = Astronomical Unit, the mean orbital distance of the Earth from the Sun), and which is probably the source of the long-period comets (e.g. Hale–Bopp). The nearer is the Kuiper Belt, which lies between c.30 AU (just beyond Neptune) and 100 AU, and is the likely source of short-period comets (e.g. Swift–Tuttle). Comets are ejected from these source regions by gravitational perturbations, resulting in the usually very eccentric orbits we are familiar with. Meteor showers are associated with the Earth crossing the orbit of short-period comets (e.g. Swift–Tuttle is responsible for the Perseids). Cometary composition is believed to reflect the primordial material from which the Solar System formed.

Asteroids originate from a belt between Mars and Jupiter (c.2–4 AU), and seem to represent primordial Solar System material that failed to aggregate into a planet. As for comets, gravitational perturbations can destabilize orbits, sometimes resulting in collisions that eject fragments (meteoroids). Some asteroids have Earth-crossing orbits.

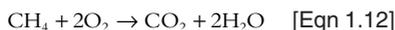
Meteorites are the grains of meteoroids or meteors that survive the journey through the Earth's atmosphere and reach the surface. Some are almost pure iron–nickel alloy, whereas others contain silicates and sulphides, and yet others (the **carbonaceous chondrites**) contain organic compounds.

Table 1.2 Some simple molecules detected in both interstellar space and comets

organic	inorganic
CH ₄	H ₂ O
H ₂ CO	CO
H ₃ COH	NH ₃
HCOOH	HCN
CH ₃ CH ₂ OH	H ₂ S
HC≡CCN	SO ₂
H ₂ CS	OCS

Box 1.5 | Oxidation and reduction

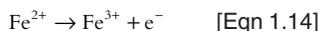
The most obvious definition of **oxidation** is the gain of oxygen by a chemical species, as in the burning of methane:



A further example is provided by the oxidation of ferrous ions (iron(II)) to ferric (iron(III)) during the sedimentary deposition of iron oxide:



Oxidation can also be defined as the loss of hydrogen, as occurs with methane above (Eqn 1.12). A further definition of oxidation is the loss of electrons. This is the net process undergone by iron in the above oxidation of iron(II) to iron(III), and can be represented by:



All three definitions of oxidation are encountered in geochemistry, and **reduction** is the opposite of oxidation. Oxidation and reduction occur in unison, because the oxidation of one chemical species results in the reduction of another, and the combination is termed a **redox** reaction.

Oxidizing conditions in sedimentary environments are termed **oxic** and are related to free oxygen being available for oxidative reactions to take place. In **anoxic** conditions there is no such available oxygen and conditions are described as reducing. In water (whether in water bodies or in sedimentary pore waters) dissolved oxygen levels of >0.5‰ (parts per thousand, or per mil) correspond to oxic conditions, while those of <0.1‰ correspond to anoxic conditions. Conditions related to intermediate values of oxygen concentration are generally described as **suboxic**.

Slightly different terms are used for zones with differing oxygen availability when biological activity is being described. Well oxygenated conditions and associated metabolic processes are described as **aerobic**, oxygen-starved conditions are **anaerobic** and intermediate conditions may be called **dysaerobic**.

near the surface for *c.*2.5 Gyr, although some may have been formed high up in the atmosphere by the photodissociation of CO₂ and H₂O (Kasting 1993). Without significant amounts of oxygen there would not have been an effective ozone layer, so life at the surface would have been exposed to damaging UV radiation (at wavelengths < *c.*300 nm, see Box 7.1).

It is thought that the formation of significant amounts of continental crust did not begin until the start of the Archaean, when heat production had fallen to levels permitting the initiation of crustal differentiation processes. Continental crust production seems to have reached a maximum in the late Archaean (3.0–2.5 Ga), although continental crust formation in the style observed at modern subduction zones did not commence until heat production had fallen still further, after *c.*2.5 Ga (Martin 1986). Not only would a lot of heat have been inherited from the accretionary processes of the Earth's formation, but the infant Earth had hardly begun to deplete its store of heat-generating radiogenic isotopes (⁴⁰K, ²³²Th, ²³⁵U, ²³⁸U; see Box 1.3 for an explanation of isotopes) and continued to experience bombardment from the remaining unaccreted debris (adding heat to the system) until the Solar System settled into its current, relatively stable, state. Cratering evidence on the Moon suggests that there was a period of particularly heavy bombardment from 4.0 to 3.8 Ga (the **Late Heavy Bombardment**; Cohen et al. 2000), which seems not to have been limited to the Earth–Moon system (Ash et al. 1996). These are hardly conditions conducive to the establishment of life, yet there appears to be microstructural and carbon isotopic evidence for the existence of life around 3.8 Ga on Earth (Mojzsis et al. 1996). If this evidence is not misleading, and the result of abiotic processes, life appeared very soon after the heavy bombardment ceased, or it appeared earlier and survived in some refuge; or it may even have originated more than once, only to be wiped out by large impacts.

Initially the surface temperature would have been too high for liquid water to exist. Until recently it was assumed that abundant liquid water was not likely to be present much before 3.8 Ga, but oxygen isotopic evidence from zircons suggests that liquid water was present at 4.4 Ga (Valley et al. 2002). The δ¹⁸O values (see Box 1.3) suggest a temperature of at most 200°C, whereas a temperature of at least 374°C would be required for a hydrosphere of the present-day size to have existed entirely in the vapour phase. So the Hadean may not have been quite so hell-like after all. Unfortunately, it is not possible to tell how hot it may have become during the Late Heavy Bombardment because of the lack of zircon evidence.

The earliest known sedimentary rocks deposited under water date from the beginning of the Archaean Era (3.8 Ga), and by 3.5 Ga oceans seem to have been widespread, based on the occurrence of sedimentary rocks and pillow lavas. The evidence for life before *c.*2.7 Ga is not conclusive. In the oldest rocks (*c.*3.8 Ga metamorphic rocks from Greenland) it relies entirely upon light carbon isotopic values, but the carbon may not always be of biogenic origin (van Zuilen et al. 2002; see Box 1.3). The earliest fossil evidence, in the form of **stromatolite**-like structures (layered domes similar to those produced today by cyanobacterial mats), is from *c.*3.5 Ga (e.g. Apex chert, northwestern Australia; Schopf 1993). However, the microstructural features in the stromatolite-like bodies, together with the bulk compositional (e.g. from Laser-Raman analysis) and isotopic characteristics of the graphitic carbon they contain, could have abiotic origins, resulting from hydrothermal activity (Schopf et al. 2002; Brasier et al. 2002). Fischer-Tropsch-type reactions (involving reduction of CO₂) in hydrothermal settings are potential sources of hydrocarbons with light carbon isotopic signatures (Lancet & Anders 1970; Horita & Berndt 1999; Holm & Charlou 2001). By 2.7 Ga there is clear evidence from chemical fossils for the presence of life, as we see in Section 1.4.1.

1.3.2 The raw material for life

The story of the evolution of life on Earth is relatively straightforward in comparison to the problem of how it first arose. The abiotic synthesis on Earth of the organic compounds necessary for the creation of life appears to require a reducing atmosphere (see Box 1.5). Early experiments with electrical discharges in mixtures of methane, ammonia and hydrogen sulphide in the presence of water created various organic compounds es-

sential for life, including many amino acids (e.g. Miller & Urey 1959), which have also been found in meteorites. However, as mentioned in the previous section, the Earth's early secondary atmosphere was probably less reducing, with a somewhat different composition. Due to the major environmental and time constraints on the abiotic synthesis of the basic compounds of life and their subsequent assembly into a viable cell (Maher & Stevenson 1988), other theories have been propounded. It has been suggested that a suitable supply of organic material could have originated from space via comets etc. (Chyba et al. 1990; Greenberg 1997). Other theories have postulated that life originated elsewhere and travelled to Earth (panspermia; Wickramasinghe et al. 1997), although the proposition that bacteria-like organisms travelled from Mars to Earth protected within cometary material (McKay et al. 1996) remains to be proven, because the evidence for biological activity is equivocal (Grady 1999).

Estimations of the amount of organic compounds produced abiotically on Earth (**endogenous**) or delivered directly by extraterrestrial bodies (**exogenous**) during the heavy bombardment 4 Gyr ago are shown in Table 1.3 (Chyba & Sagan 1992). Delivery of intact organic compounds is favoured by the gentle deceleration in the atmosphere experienced by interplanetary dust particles and intermediate-sized meteorites. In comparison, small meteorites tend to undergo complete ablation and large meteorites are often heated sufficiently to pyrolyse the organic material and render it useless for life. The estimated amount of exogenous organic material is probably effectively independent of the degree to which the atmosphere was reducing. The energy needed to produce organic compounds at the Earth's surface can be generated by impact shocks, UV light or electrical discharges, and the amounts of organic products are strongly influenced by the atmospheric

Table 1.3 Estimated endogenous and exogenous supply of organic material to Earth 4 Gyr ago (after Chyba & Sagan 1992)

source	organic production rate (kg yr ⁻¹)	
	reducing atmosphere	neutral atmosphere*
lightning	3 × 10 ⁹	3 × 10 ⁷
coronal discharge	2 × 10 ⁸	2 × 10 ⁶
UV (H ₂ S absorption <270 nm)	2 × 10 ¹¹	–
UV (CO ₂ absorption <230 nm)	–	3 × 10 ⁸
UV (H ₂ O absorption <200 nm)	3 × 10 ⁹	–
atmospheric shock (meteor)	1 × 10 ⁹	3 × 10 ¹
atmospheric shock (post-impact plume)	2 × 10 ¹⁰	4 × 10 ²
interplanetary dust particles	6 × 10 ⁷	6 × 10 ⁷

*Neutral atmosphere has H₂/CO₂ concentration ratio of 0.1.

composition. A reducing atmosphere (mostly methane and water) has an abiotic synthesis potential at least two orders of magnitude greater than a neutral atmosphere. Long-wavelength UV may have been the dominant energy source, but the influence of shock-wave energy is not easy to quantify because it is highly dependent upon atmospheric chemistry. In a neutral atmosphere, electrical discharges, UV, shock-waves and interplanetary dust particles could have made equally significant contributions to the Earth's inventory of abiotic organics.

Meteorites (see Box 1.4), and in particular carbonaceous chondrites, provide a glimpse of the chemical composition of the Solar System, because their elemental composition is very like that observed spectroscopically in the Sun and in other nearby stars. Carbonaceous chondrites contain significant amounts of organic compounds (up to 5% by weight) as well as plentiful water, but relatively few (*c.*36) have been collected soon after arrival, and there is always the danger of contamination of the indigenous organic matter in the meteorites with terrestrial material upon impact. One of the most thoroughly studied examples is the Murchison meteorite, which fell in Australia in 1969 (e.g. Engel & Macko 2001). Among the amino acids in the meteorite (Table 1.4), several that are common to biological systems (e.g. serine and threonine) were found in only trace amounts or were below detection limits, suggesting minimal contamination subsequent to impact (Engel & Nagy 1982).

Amino acids are important because they are the building blocks of proteins, which are responsible for many cellular functions (see Section 2.3). They can exist as optical isomers (see Section 2.1.3), and life on Earth has adopted the L form rather than the D, for reasons that

are as yet unclear. The pair of optical isomers for alanine is shown in Fig. 1.3. Abiotic synthesis of amino acids in the laboratory results in equal amounts of the two optical isomers (a racemic mixture), and so it is assumed that extraterrestrial abiotic synthesis would proceed in a similar fashion. The isomeric composition of amino acids in meteorites should, therefore, provide information on their extraterrestrial origin, although few such analyses have been undertaken to date. One analysis is shown in Table 1.4, and the D/L ratio in the initial water extract shows a dominance of the L isomers. When the remaining rock was ground up and digested with acid, the amino acids that were liberated had an even greater dominance of the L isomers. Because the latter amino acids had been more protected from contamination within the rock matrix than those in the initial extract, it would seem unlikely that the L predominance is attributable to contamination by terrestrial sources after impact; instead, it probably represents the extraterrestrial source.

Further support for a non-terrestrial origin for the excess of the L isomers of amino acids in the Murchison meteorite is provided by the stable-isotope compositions, as described in Box 1.6. The origin of the L isomer

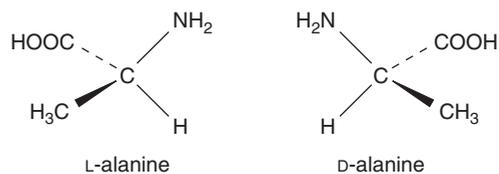


Fig. 1.3 The optical isomers of alanine.

Table 1.4 Amino acids detected in hydrolysed aqueous extracts of Murchison meteorite (after Engel & Nagy 1982)

	concentration (nmol g ⁻¹)*	D/L ratio	
		pre acid digestion*	post acid digestion†
<i>common amino acids</i>			
glutamic acid	18.2	0.30	0.18
aspartic acid	8.5	0.30	0.13
proline	13.5	0.30	0.11
glycine	45.8		
β-alanine	13.1		
leucine	1.9	0.17	0.03
sarcosine	4.7		
alanine	15.3	0.60	0.31
valine	8.6		
<i>exotic amino acids</i>			
α-aminobutyric acid	107.8		
isovaline	23.6		

*Initial hydrolysed water extract; †second hydrolysed water extract after acid digestion of rock.

excess among the meteorite amino acids remains to be explained. Could abiotic synthesis have involved unknown stereoselective pathways? Or could a racemic mixture have been subjected to alteration processes that led to preferential destruction of the D isomers, such as exposure to circularly polarized light from neutron stars (Bailey et al. 1998)? A further possibility is that the Murchison meteorite contains the residue of a once living system, with the amino acids having undergone partial racemization after death, as occurs on Earth. It is not unprecedented for racemization to be incomplete after a long period.

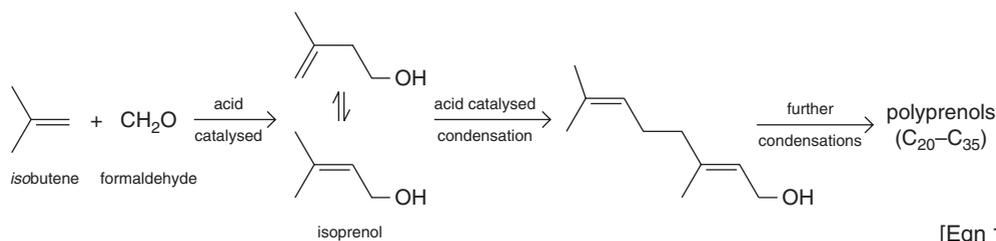
There are other chemical questions surrounding the emergence of life. For example, membranes are needed to confine the contents of cells and provide a stable, controlled environment for biochemical reactions. Some fairly simple organic molecules (**amphipathic** molecules), in which one end has an affinity for water (i.e. it is **hydrophilic**) but the other does not (i.e. it is **hydrophobic**, like oil), can naturally form membrane-like structures, which, in the presence of water, form cell-like spheres (see Box 1.7). Self-replication is another vital factor, which needs to be accomplished with minimal error. The information necessary for con-

Box 1.7 | Membrane formation

Life on Earth is based upon cells, the membranes of which keep the essential biochemical apparatus together and in a suitable environment. The formation of cell-like vesicles, effectively impermeable to water, was likely to have been a key step in the appearance and evolution of life. In modern organisms cellular membranes have inner and outer surfaces comprising hydrophilic (water-loving) groups attached to a core of aligned hydrophobic (water-repelling) hydrocarbon chains. The compounds responsible, called phospholipids (see Section 2.4.1b), have a hydrophilic head containing a phosphate group bonded to a pair of hydrophobic hydrocarbon chains via a glycerol unit. In eukaryotic membranes there are two layers of these compounds, which assemble with the hydrophobic tails pointing to the interior of the membrane and the hydrophilic heads forming the inner and outer surfaces. Compounds with hydrophilic and hydrophobic ends are often termed amphipathic (or **amphiphilic**). To help to stiffen the membrane other molecules, which must conform to precise dimensional constraints, are slotted between some of the phospholipids. In eukaryotes cholesterol is common, and lines up with its

polar alcohol end in the phosphate group layer (Fig. 1.4a).

In the organisms apparently most closely related to the common ancestor of all life, the archaeobacteria (see Section 1.3.3), rigidifying molecules are not needed because the hydrocarbon chains have regular methyl branches (every fourth carbon in the chain), which appear to confer sufficient stability to the membrane on their own. These chains are terpenoidal, formed from enzymatic condensation of C₅ isoprene units (Section 2.4.3). However, isopentenol can be produced abiotically from simple compounds likely to have been present on the young Earth; for example, by the acid-catalysed reaction of formaldehyde (methanal) and *isobutene* (Eqn 1.16). Isopentenol can undergo abiotic acid-catalysed condensation to form polyprenol chains like those in archaeobacterial membranes, which could have been readily phosphorylated by pyrophosphates or volcanically produced phosphorus pentoxide, again on catalytic mineral surfaces, with the chains eventually breaking off and assembling into a vesicle (Fig. 1.4b). This may be how the first cellular membranes formed (Ourisson & Nakatani 1994).



[Eqn 1.16]

Continued

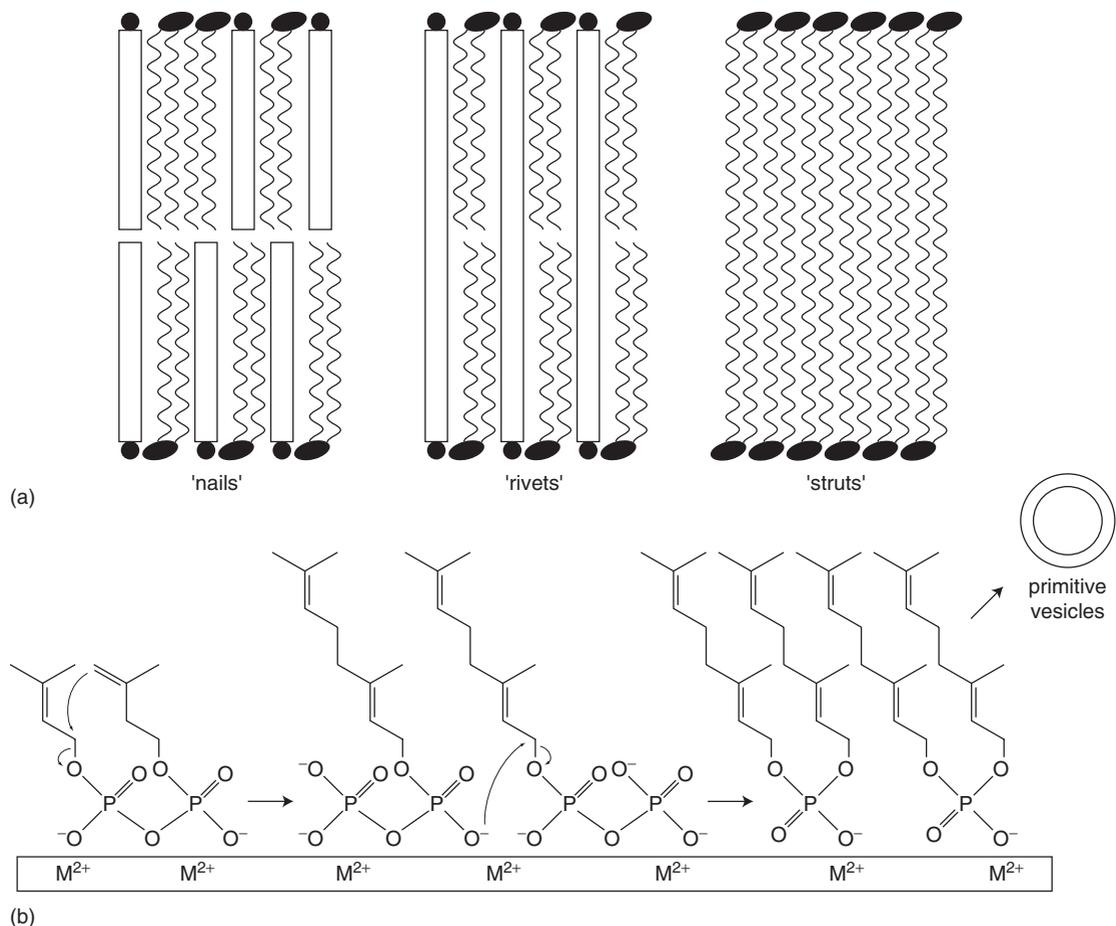


Fig. 1.4 (a) Generalized membrane structure. Hydrophobic heads of amphipathic molecules are shown in black and hydrophilic tails as wavy lines. Membrane reinforcers are shown as boxes and can be likened to 'nails' spanning half the membrane (e.g. sterols and hopanoids) or 'rivets' spanning the entire membrane (e.g. carotenoids). Where they are absent, in archaeobacterial thermophiles, the amphipathic molecules span the entire membrane and act as 'struts'. (b) Possible steps in the self-assembly of primitive membranes (M^{2+} are metal ions).

structuring an organism is carried in its genes, encoded in deoxyribonucleic acid (DNA) sequences (see Section 2.6.2). The information in DNA strands is translated into the amino acid sequences of proteins using enzymes (which are themselves proteins) and ribonucleic acids (RNAs). But which came first, the code for protein formation, DNA, or the protein catalysts (see Box 2.6) needed to make DNA work? It is believed that the early Earth was an RNA world, because RNA has been found to have some catalytic activity of the type now provided by proteins, and has the ability to carry

genetic information (Horgan 1991). Today, only RNA viruses do not use DNA as their genetic material. It is difficult to explain how pyrimidines, a basic component of nucleic acids, could have arisen abiotically, and also how all the components of molecules as complex as nucleic acids could have been assembled. As Fred Hoyle has commented, the random assemblage of such a molecule is as likely as a Boeing 747 airliner being assembled by the passage of a tornado through a junk yard. Various theories have been propounded, such as the necessary concentration of the starting materials and

Box 1.8 | Classification of organisms

Organisms (excluding viruses) can be broadly separated into **prokaryotes** and **eukaryotes** on the basis of cellular structure. Prokaryotic cells contain no nuclear membranes and their DNA is not arranged in chromosomes. Eukaryotic cells always contain a nuclear membrane and their DNA is usually in chromosomal form. There are other differences between the two cell types but these are the most useful general distinguishing features. The prokaryotes comprise all bacteria (including cyanobacteria) and are therefore unicellular (also termed the Monera). All other organisms are eukaryotes, either unicellular (the Protista) or multicellular.

The eukaryotes are often divided into two kingdoms: animals (Animalia) and plants (Plantae). This distinction is blurred in the case of flagellates, which can fall into either kingdom, and some can be classified in both. Further categorization results in the main **taxonomic ranks** shown in Table 1.6, in which the classification of humans is given as an example.

It is possible to use subcategories of the main ranks. The rank below kingdom is generally termed division for plants but phylum for animals. For the plant kingdom the following divisions are generally recognized: algae (Phycophyta), fungi (Mycophyta), lichens (Lichenes), bryophytes (Bryophyta), pteridophytes (Pteridophyta) and spermatophytes (Spermatophyta). The last two divisions comprise the vascular plants, while the Bryophyta include mosses, liverworts and hornworts. Some organisms are difficult to classify, particularly unicellular forms, and changes in classification are inevitable as our knowledge of these organisms grows.

There is flexibility in the application of classification

Table 1.6 Major taxonomic ranks, using humans as an example

taxonomic rank	classification for humans
kingdom	Animalia
division or phylum	Chordata
class	Mammalia
order	Primates
family	Hominidae
genus	<i>Homo</i>
species	<i>sapiens</i>

ranks (e.g. Holmes 1983), which can confuse the inexperienced reader. For example, some classes of algae are considered to be sufficiently distinct to warrant divisional status and so the algae as a whole become a subkingdom (even a kingdom in some classifications), and the cyanobacteria can be treated as a division of this subkingdom (the Cyanophyta). The prokaryotes can be treated as a division (Schizophyta), with the bacteria and cyanobacteria as constituent classes (Schizomycetes and Schizophyceae, respectively). The fungi are sometimes considered to be a kingdom in their own right, with two main divisions comprising the slime moulds (Myxomycota) and the true fungi (Eumycota).

In the latest taxonomic system based on rRNA sequencing, three domains have been recognized: Archaea (the archaeobacteria), Bacteria (the eubacteria) and Eukarya (the eukaryotes). When this system is used, bacteria with a lower-case 'b' is generally assumed to refer to all bacteria (archaeobacteria + eubacteria).

their catalytic reorganization on clay or iron pyrite particles, but there is no evidence of any system that could accomplish the synthesis of RNA or even other types of perhaps simpler self-replicating molecules that may have preceded RNA.

Perhaps life originated near the surface at an early stage of Earth's life and avoided complete obliteration during the heavy bombardment period by migrating to deep environments, and possibly remaining dormant for tens of millions of years (an ability demonstrated by some bacteria; Parkes 2000). It is safe to conclude that

we do not know how or where life originated, and an extraterrestrial origin may be considered as plausible as any other theory. More recently it has been suggested that the cradle of life may have been hydrothermal vents (e.g. Corliss 1990), which would have provided a ready supply of energy and raw materials for chemoautotrophs. However, on a geological time-scale an individual vent is an ephemeral feature, so would there have been enough time for life to evolve? In addition, superheated water temperatures can reach 300°C, and it is questionable whether the complex organic molecules

Box 1.9 | Autotrophes and heterotrophes

All organisms use organic material as an energy source and for growth and reproduction. How they get the necessary substrates determines their trophic status.

Autotrophes are organisms that can manufacture their organic materials from inorganic sources, and do not rely directly upon other organisms for any of their organic chemical or energy requirements. If they obtain the energy needed for the primary C-fixation step from sunlight (i.e. photosynthesis) they are termed **phototrophes** (or photoautotrophes). If instead they obtain it from chemical energy (i.e. the energy liberated by inorganic redox reactions; Box 1.5) they are called **chemotrophes** (or chemoautotrophes) (see Box 1.10). Because the chemoautotrophes use inorganic species as terminal electron acceptors they are commonly also termed **lithotrophes**. Overall, chemosynthesis of organic matter is minor compared with photosynthesis. The amount of carbon fixed into new growth by autotrophes is often termed **primary production**.

All other organisms gain their energy supplies and organic substrates by feeding, directly or indirectly, upon autotrophes, and are termed **heterotrophes**. They comprise herbivores, saprophytes, carnivores and parasites. In geochemical terms the first two

groups are the most important. Energy is passed from the autotrophes to the various heterotrophes along food chains and ultimately reaches the top carnivores.

Herbivores represent the first link in the **grazing food chain**. Dead plant matter together with the faecal material of animals and their remains upon death are collectively termed **detritus** and pass to organisms of the **detrital food chain** in soil, water and sediments. Invertebrate animals form one group of detrital-feeding organisms, the **detritivores**, which are often termed deposit feeders if they obtain their sustenance from soil and sediments, or filter (or suspension) feeders if they scavenge it from the water column. Detritivores may, therefore, be herbivores and/or carnivores. The saprophytes obtain their organic sustenance in dissolved form by the use of extracellular enzymes, and comprise fungi and a variety of bacteria, often collectively termed **decomposers**. They may feed directly on the remains of dead plants or animals, but usually decomposition proceeds more rapidly via the comminuted products of the detritivores, due to both the greater surface area presented and the extensive disruption of protective tissues.

needed for life would be stable under such conditions. More favourable conditions may be found at the boundary between vent waters and normal seawater, where there are rapid redox and pH changes. It has been proposed that iron sulphide can form membrane-like bubbles at this interface, the surfaces of which also contain nickel sulphide and can catalyse organic synthesis and facilitate protometabolic processes (Russell & Hall 1997; Martin & Russell 2003). Subsequently, the organosulphide polymers could have taken over the membrane role, while iron, sulphur and phosphate continued to be involved in metabolic processes in the proto-organisms.

1.3.3 The common ancestor

If life originated on Earth, it has been postulated that the earliest forms may have been anaerobic prokaryotic

heterotrophes (see Boxes 1.8 and 1.9), eking out a living from the simple abiogenic organic compounds at the Earth's surface. It seems most likely that the early stages in the evolution of life were confined to aquatic environments, because water is an essential requirement for all life. A diffuse abiotic food supply would have limited the proliferation of life and, as mentioned above, the heavy bombardment by meteorites etc. (bolides) would have hampered its development at the surface.

The search for a common ancestor of life involves tracking the divergences of related groups of organisms back through time. How different groups of organisms are related to one another has traditionally been based upon physiological characteristics and the sequence of gradual changes assumed to result from random mutation. When combined with the effects of Darwinian selection, the result is the 'tree of life', with the ancestral organism of all life on Earth at its root. However, it is

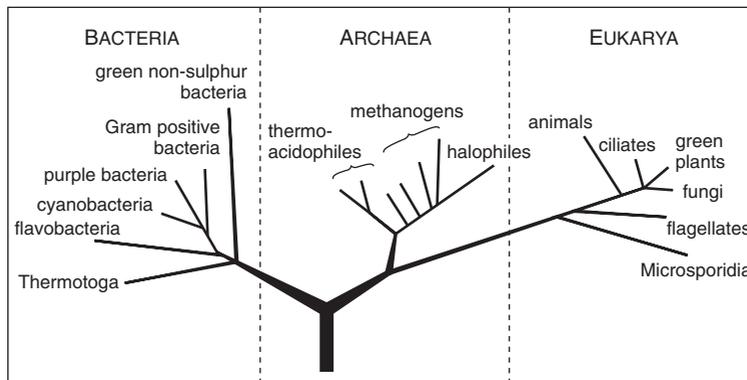


Fig. 1.5 Evolutionary relationship of organisms based on rRNA sequence comparisons, with division of the ‘tree of life’ into three fundamental domains: Bacteria (or eubacteria), Archaea (or archaeobacteria) and Eukarya (or eukaryotes) (after Woese et al. 1990).

based primarily on multicellular (eukaryotic) organisms that appeared significantly later in the fossil record than the prokaryotes. Our knowledge of the microbial world, although expanding dramatically at present, is still very limited, and it is clear that microbial morphological characteristics are too simple to enable a reliable, universal phylogenetic taxonomy to be established. A new tool, molecular phylogenetics, for examining the arrangement for the tree of life has recently become available that potentially overcomes this problem. It is based on the sequencing of nucleotides (see Section 2.6) in genes, and the assumption that random mutation occurs at a constant rate, permitting an estimation of interrelationships and the relative timing of divergences. The first studies were conducted on genes that encode ribosomal RNAs (rRNAs; Woese et al. 1990), which were chosen because they are part of a basic cell activity, protein synthesis, and so were thought unlikely to have undergone radical change and so might act as a slow, regular clock. A simplified version of the resulting tree of life is shown in Fig. 1.5, in which there are three kingdoms (or domains): the Archaea (or archaeobacteria), the Bacteria (or eubacteria) and the Eukarya (or eukaryotes). This classification demonstrates the importance of bacteria, which, by this taxonomic system, are divided into the **archaeobacteria** (methanogens, halophiles and thermoacidophiles; Woese & Wolfe 1985) and true bacteria, the **eubacteria**. The eukaryotes occupy a much less significant position than in older classifications.

Archaeobacteria are considered the most ancient form of cellular life; they are closest to the root of the tree and so are the closest extant relatives of the universal ances-

tor. They occur in extreme environments that are hostile to other forms of life — such as hydrothermal vents, fumaroles and soda lakes — and they can all tolerate high temperatures. Those that can grow at temperatures $>80^{\circ}\text{C}$ are termed **hyperthermophiles**. The highest growth temperatures so far are 113°C for *Pyrolobus fumarii* (Blöchl et al. 1997) and 121°C for an Fe(III)-reducing strain (see Box 1.13 and Section 3.3.2b) from a hydrothermal vent in the north-eastern Pacific Ocean (Kashefi & Lovley 2003). The stability of archaeobacterial enzymes at high temperatures is the key to modern DNA sequencing using the polymerase chain reaction (PCR) to amplify DNA, which relies on an enzyme from *Thermus aquaticus*, a bacterium that thrives at 70°C in hot spring communities in Yellowstone Park. The position of hyperthermophilic archaeobacteria nearest the root of the tree might be considered support for an origin of life at high temperature. In the previous section we touched upon the potential role of hydrothermal vents as sources of all the ingredients needed by chemoautotrophes. Another possibility is that the ancestral archaeobacteria could have originated at depth within the Earth, although migration to the surface becomes problematical as depth increases because growth rates, and hence migration rates, decrease, leading to entrapment and burial (Parkes et al. 1999). The subsurface bacterial biomass is extremely large, probably exceeding that of all surface-dwelling and marine organisms (Whitman et al. 1998), although activity is low at depth. The concept of a deep hot biosphere (originally proposed by Gold in 1992) is now recognized, but the depth/temperature limit has yet to be established.

The initial optimism surrounding the belief that a universal tree of life could be assembled has been tempered by the discovery that the sequences of other genomes (e.g. genes encoding for various proteins) present a different picture (Pennisi 1998). The conclusion is that genes have not all evolved at the same rate or in the same way. Some eukaryotic genomes contain what appears to be a mixture of DNA with some components associated with an archaeobacterial ancestry and others of eubacterial legacy. This could represent early organisms acquiring genes via food or even swapping DNA with neighbours. Instead of a tree branching out from a single trunk, there may have been considerable merging and splitting of lines before the offshoot of modern kingdoms. Clearly, rapid gene swapping (lateral transfer; Doolittle 1999) would have enabled early organisms to adapt to new environmental conditions, an advantage that may have ensured that the DNA code became universal, because organisms not able to read DNA-based genes would not have had such an adaptive capability. Lateral transfer complicates the task of determining phylogenetic relationships sufficiently that the universal ancestor (if there was just one) may not be traceable. At present it is not clear whether the three kingdoms in Fig. 1.5 are truly representative; it has recently been proposed that eukaryotic-like cells may have predated prokaryotes (Penny & Poole 1999).

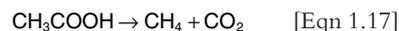
It is not only DNA that seems to have been shared by organisms; there is good reason to believe that mitochondria (the energy generators of cells) and chloroplasts (the sites of photosynthesis in plant cells) may once have been prokaryotes that were ingested by, or entered into a symbiotic relationship with, other prokaryotes (Doolittle 1998).

1.4 Evolution of life and the atmosphere

1.4.1 Atmospheric oxygen and photosynthesis

Important stages in the evolution of the Earth's surface are presented in Fig. 1.6; one of the most dramatic changes has been the development of an oxygenated atmosphere. Reducing, or at least non-oxidizing (see Box 1.5), conditions prevailed during the Archaean, and so this time belonged to the anaerobic prokaryotes. Not until the advent of oxygen-producing (oxygenic) photosynthesis could oxidizing conditions begin to develop at the surface; and only with the subsequent availability of free oxygen was it possible for multicellular, eukaryotic organisms to develop and diversify. The composition of the atmosphere has both affected and been affected by the development of life on the planet.

As mentioned in the previous section, it is possible that the first organisms were heterotrophes, obtaining their energy requirements from simple, abiotic organic compounds by fermentation. Ancestors of methanogens can be envisaged as one such group of prokaryotes, utilizing simple organic compounds like methanoic acid (HCOOH, also known as formic acid) and ethanoic acid (CH₃COOH, also known as acetic acid):



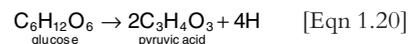
Modern methanogens can all reduce carbon dioxide with molecular hydrogen, while synthesizing carbohydrates (which can be represented by their empirical, i.e. simplest, formula CH₂O):



Carbohydrates are used in the biosynthesis of other organic compounds and to provide an energy store for the performance of normal cellular functions. In the absence of free oxygen, fermentation would have provided the energy-releasing step for anaerobic organisms, but compared to oxidation involving oxygen, it is a relatively inefficient process in terms of the amount of energy it releases. The overall fermentation of simple carbohydrates by anaerobes can be represented by:

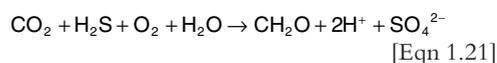


The initial step is actually the formation of pyruvic acid with the liberation of free hydrogen atoms, which can then be combined with other groups:



Fermentation is one of a number of anaerobic respiration (i.e. energy-liberating) processes that are discussed more fully in Section 3.3.2b.

Other plausible candidates for the first prokaryotes are the ancestors of chemotrophes colonizing hydrothermal vents. Today they use the oxygen dissolved in ocean water to obtain energy from the sulphides emanating from the hot springs in chemosynthetic reactions (see Box 1.10) that can be summarized by:



Clearly, anaerobic ancestors would have had to utilize a chemical energy source other than oxygen, but there is no clear evidence that anaerobic chemotrophes existed.

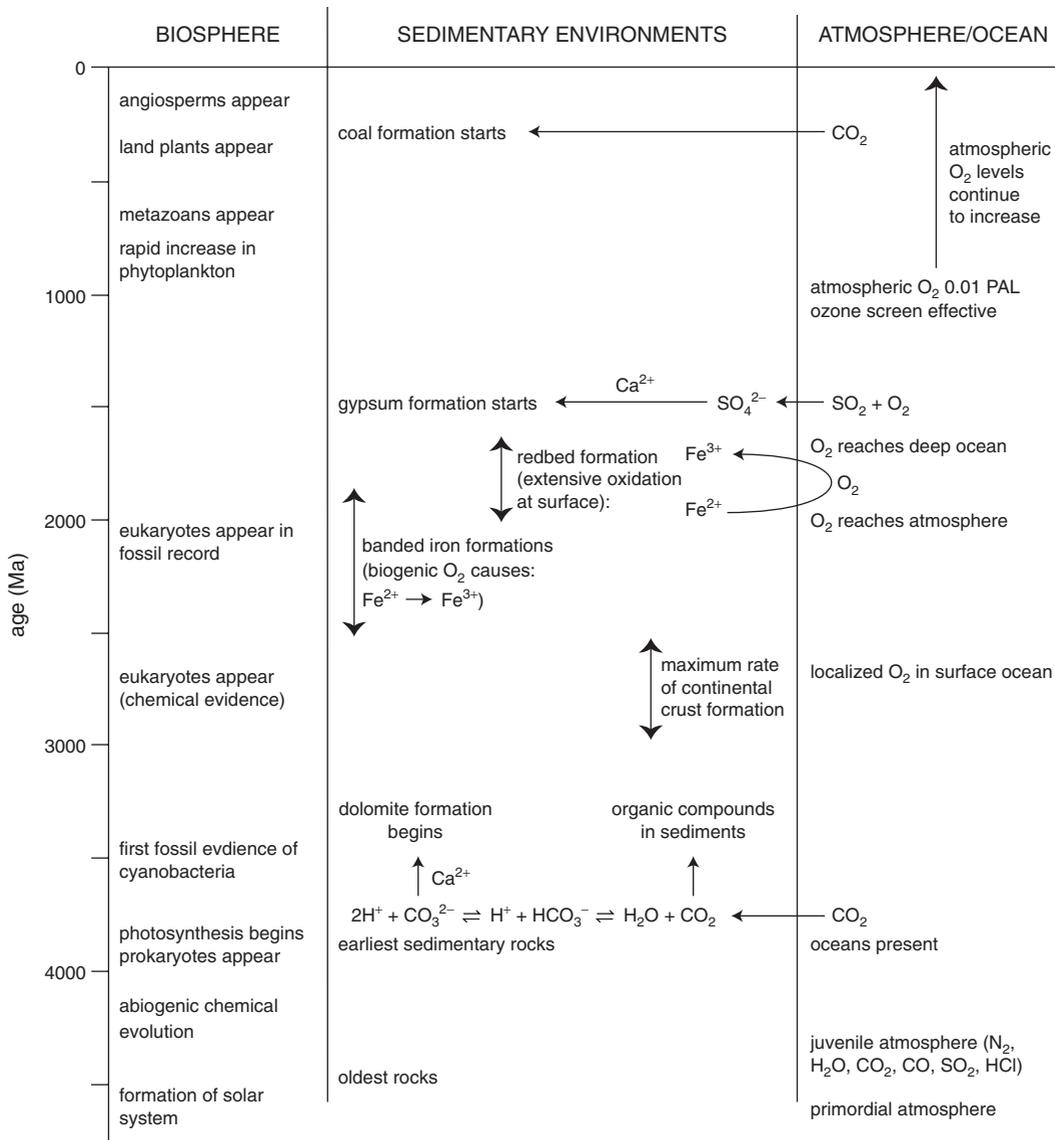
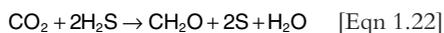


Fig. 1.6 Important events in the evolution of the Earth and life.

The first autotrophes to use the Sun's energy (i.e. photosynthesizers) would also have been prokaryotic anaerobes living in aquatic environments, and they used hydrogen sulphide as a source of the hydrogen needed for carbohydrate synthesis, yielding sulphur as a by-product, not oxygen:



The nearest modern relatives of these organisms are the purple and green sulphur bacteria, which are all anaerobes.

As mentioned in Section 1.3.1, the first indirect (carbon isotopic) evidence for life appears in rocks aged some 3.8 Ga, and there are also structures dating from 3.5 Ga that have been interpreted as the counterparts of modern microbial mats, primarily formed by large

Box 1.10 | Photosynthesis and chemosynthesis

Chlorophyll-a is the primary pigment of **photosynthesis** and absorbs photons of light energy in order to convert carbon dioxide into carbohydrates. Water is essential, as it provides hydrogen, while oxygen is expelled into the environment as a by-product. Photosynthesis can be divided into a light (photochemical) stage and a dark (chemical) stage. The former requires light but is unaffected by temperature, while the latter does not require light and proceeds more rapidly with increasing temperature. These stages are presented in Fig. 1.7 and can be summarized as follows.

Light stage

- 1 Generation of energy: an electron (e^-) is liberated from chlorophyll-a upon adsorption of light energy.
- 2 Storage of energy: the high-energy electron can recombine with positively charged chlorophyll and the excess energy is used to convert ADP (adenosine diphosphate) into ATP (adenosine triphosphate) by the addition of inorganic phosphate.
- 3 Storage of reducing power: an electron from chlorophyll may be captured by a hydrogen ion (H^+), produced from the self-ionization of water, to yield a hydrogen atom, which is immediately taken up by

NADP (nicotinamide adenine dinucleotide phosphate), storing the reducing power in the form of NADPH. The chlorophyll ion can regain an electron from a hydroxyl ion (OH^-), which is also formed during the self-ionization of water, and the resulting hydroxyl radical ($OH\cdot$, which has no charge) combines with others to form oxygen and water.

Dark stage

Overall, the hydrogen stored in NADPH is used to reduce CO_2 to carbohydrate units (CH_2O). This is not a direct reaction because the CO_2 is first combined with a C_5 compound, ribulose diphosphate (RDP), which then spontaneously splits into two identical C_3 molecules, phosphoglyceric acid (PGA). Most of the PGA is used to synthesize further RDP but some is reduced by NADPH, using energy supplied by the ATP/ADP system, to give triose phosphate, which in turn is converted into the glucose phosphate from which various carbohydrates are synthesized. This assimilatory path is known as the **Calvin cycle** and is involved in all autotrophic carbon fixation, whether photosynthetic or chemosynthetic.

Plants that use the Calvin cycle alone in carbon fix-

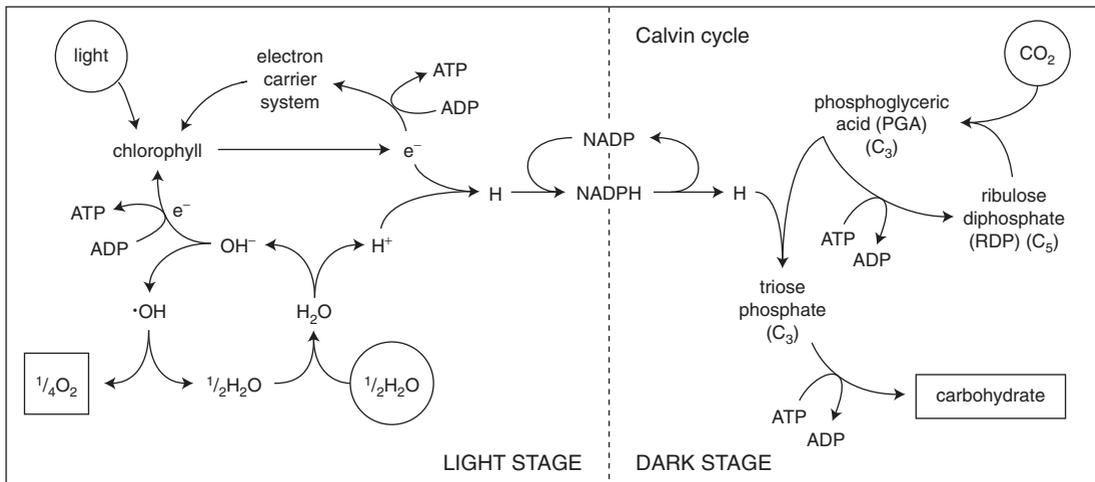


Fig. 1.7 Summary of the chemical processes involved in oxygenic photosynthesis. Net inputs are shown in circles and products in rectangles. ADP/ATP = adenosine di/triphosphate; NADP/NADPH = nicotinamide adenine dinucleotide phosphate and its reduced form, respectively.

Continued

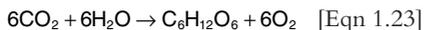
ation are termed **C₃-plants** because of the involvement of PGA, which contains three carbon atoms. Most plants and the cyanobacteria use the C₃ path. However, under conditions of high temperature and low CO₂ levels much energy can be lost by C₃-plants due to photorespiration. Two smaller groups of plants overcome this by using an additional biochemical pathway that fixes CO₂ at night. The carbon dioxide is released again within the plant tissue during the day for incorporation into the Calvin cycle. In this way stomatal pores can be closed during the day to reduce photorespiration without cutting off essential supplies of CO₂. These two groups are named after their additional mechanisms: **C₄-plants** and **CAM-plants**.

As well as the oxygenic phototrophic cyanobacteria, there are also **anoxygenic photosynthetic bacteria**, which are anaerobes (although some are O₂-tolerant), generally use simple organic compounds as a C supply, never use water as a source of hydrogen and do not produce oxygen. These anoxygenic phototrophs comprise the purple sulphur bacteria, purple non-sulphur bacteria, green sulphur bacteria, green non-sulphur bacteria and *Heliobacter*. There are also some anoxygenic aerobic photo-

heterotrophs (belonging to the proteobacteria), which are obligate aerobes, metabolizing organic substrates in the water column when available by O₂-dependent respiration, but otherwise performing anoxygenic photosynthesis. They are probably related to the purple non-sulphur bacteria (*Rhodospirillum*; Fenchel 2001).

Chemosynthesis is performed by some types of bacteria, most of which are obligate aerobes. The initial energy-generating process does not involve light or water, but utilizes the energy stored in chemicals, mainly the reduced forms of simple inorganic species. An enzyme, dehydrogenase, is used to liberate the energy (in the form of electrons) and reducing power (in the form of protons) from a chemical species such as H₂S. While the necessary compounds for chemosynthesis are generally found throughout the water column they are in highest concentrations in anoxic waters beneath areas of high productivity, resulting from the breakdown of organic constituents in detritus. Chemosynthetic bacteria are, therefore, found at the oxic-anoxic boundary (see Box 1.5).

colonies of cyanobacteria in shallow water (Schopf & Packer 1987). **Cyanobacteria** (previously classified as blue-green algae) perform oxygenic photosynthesis (i.e. oxygen is liberated), during which a complex series of processes occurs, as summarized in Box 1.10. Light energy in the visible part of the spectrum emitted by the Sun is adsorbed by a green pigment, chlorophyll. This results in the transfer of hydrogen atoms from water to carbon dioxide molecules (i.e. reduction of CO₂) to build up carbohydrate units, while oxygen is liberated from the water molecules. The overall reaction for the formation of a carbohydrate such as glucose (which contains six of the basic CH₂O units) can be simplified to:



Around 1500 extant species of cyanobacteria have been identified, some of which are colonial mat formers, while others are non-colonial and inhabit open water. Whether the anaerobic ancestral forms were oxygenic photosynthesizers is not clear; although there are many proponents of the idea that the early Archaean

stromatolites represent oxygenic photosynthesizers (e.g. Rothschild & Mancinelli 1990), others have suggested that the organisms responsible for the structures may have been non-oxygenic phototrophs or even chemotrophs (e.g. Lasaga & Ohmoto 2002). One thing is clear, however: oxygenic photosynthesis must have evolved during the Archaean. In addition to the stromatolitic evidence (Buick 1992), there is compelling molecular evidence, in the form of 2 α -methylhopanes (Brocks et al. 1999; see Sections 2.4.3e and 5.4.2e), for the presence of cyanobacteria, and by inference for oxygenic photosynthesis, dating back to 2.7 Ga, although recent phylogenetic studies suggest a somewhat later appearance of cyanobacteria, c.2.4–2.2 Ga (Blank 2004).

1.4.2 Geological record of oxygen levels

Oxygen liberated by early oxygenic photosynthesizers would have been rapidly immobilized in the generally reducing environment, primarily by the oxidation of iron from Fe(II) to Fe(III) and reducing gases emitted from volcanoes (see Box 1.5). Exactly when oxygen

reached the atmosphere and the rate at which levels subsequently rose is extremely difficult to determine, and relies on indirect evidence of minimum and maximum oxygen concentrations, as used in the construction of Fig. 1.8. The amount of oxygen in the atmosphere can be represented in various ways, such as its partial pressure (pO_2 ; Box 1.11) and the amount relative to the present atmospheric level (**PAL**).

Variations between $\delta^{33}S$ and $\delta^{34}S$ values (see Box 1.3) in Archaean sulphides and sulphates have been attributed to photodissociation of atmospheric SO_2 , a process that could only occur if oxygen was at most a trace component (due to the adsorption of the required UV radiation by O_2 and O_3), so the Archaean atmosphere seems to have been virtually devoid of oxygen (Farquhar et al. 2002; Wiechert 2002). Among other parameters that restrict oxygen concentrations are the conditions under which redbeds, banded iron formations and detrital uraninites could form, and for various aerobic organisms to survive (Kasting 1993).

For common metals with more than one oxidation state, like Fe(II) and Fe(III), the higher oxidation state is much less water soluble, so aqueous transport of iron occurs in the form of Fe^{2+} ions, whereas Fe^{3+} ions (as

in Fe_2O_3) are immobile. Banded iron formations (**BIFs**) may represent localized oxidation of Fe(II) involving the free oxygen liberated during photosynthesis. They are mostly confined to an age range of 2.7–1.9 Ga (early Proterozoic), although some are found among the oldest known sedimentary rocks dating back to 3.8 Ga in Isua (Greenland), and a few others appear to date to as recently as 1.85 Ga (Kasting 1993). The Fe(II) could have originated from hydrothermal emissions near spreading ridges in anoxic deep water and have been transported to shallow marginal basins containing slightly oxic waters, leading to the precipitation of Fe(III) (Morris & Horwitz 1983). The Fe(III)-rich bands alternate with chert, and it has been suggested that this varve-like banding could arise from the transport of Fe(II) in oxygenic phototrophes (in which the iron behaves as a micronutrient; see Box 3.7). Upwelling of nutrient-rich waters in nearshore areas, as occurs in some areas of the ocean today (see Section 3.2.5), could have resulted in seasonal blooms and the development of minor oxygen oases in surface waters. The large quantities of detritus from the phototrophes would then lead to oxidation of the iron and deposition of Fe(III)-rich bands, interspersed with iron-poor bands deposited

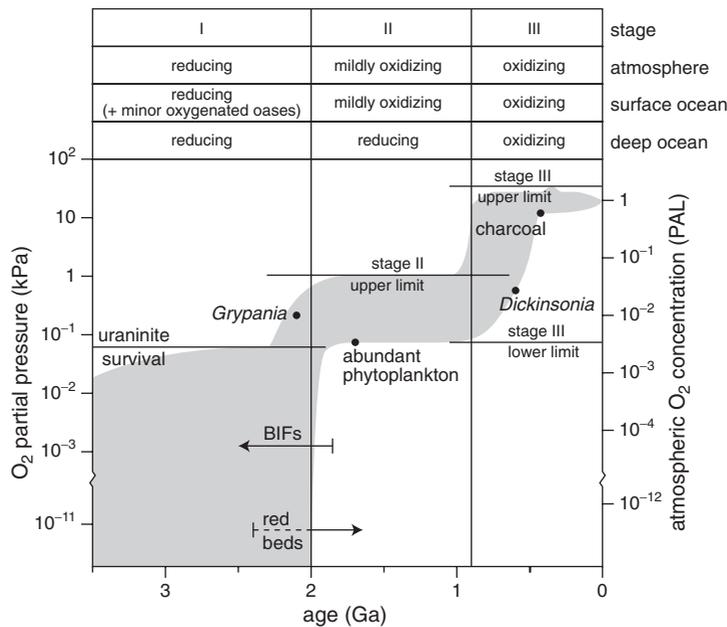


Fig. 1.8 Estimated atmospheric concentration of oxygen throughout the Earth's life (shaded area; after various sources, including Kasting 1993; Canfield 1998). Key upper and lower limits are shown; dashed line for redbeds denotes disputed data. See text for *Grypania* and *Dickinsonia*.

Box 1.11 | Partial pressure

The behaviour of gases under varying conditions of temperature, pressure and volume can be predicted to a first approximation by the ideal gas equation:

$$pV = nRT \quad [\text{Eqn 1.24}]$$

where p = pressure, V = volume, n = number of moles of gas, R = universal gas constant and T = temperature.

An ideal gas is one whose molecules are infinitely small compared to the size of the container housing the gas, behave perfectly elastically in all collisions (i.e. there is no loss of kinetic energy) and do not react with or attract each other. One further property is assumed, that the duration of collisions is negligible (so that the effective number of molecules in motion remains constant).

From the ideal gas equation it can be seen that, at constant temperature and volume, the pressure exerted by any gas is proportional to the number of molecules (or atoms, if the gas is monatomic, such as helium and argon). This is because pressure is a consequence of molecules colliding with the container walls, so the more molecules, the more collisions. For a mixture of gases, the total pressure is related to the total number of molecules present. To put this another way, the total pressure of the mixture is equal to the sum of the pressures that each gas would exert if it alone occupied the container. This is Dalton's Law of **partial pressures**. So atmospheric pressure is approximately given by:

$$P_{\text{atmospheric}} \approx pN_2 + pO_2 + pAr + pCO_2 \quad [\text{Eqn 1.25}]$$

at other times (Cloud 1973). More recently it has been suggested that iron-oxidizing bacteria could account for the deposition of BIFs (Konhauser et al. 2002).

An upper limit of atmospheric O_2 based on BIF deposition is ≈ 0.08 PAL. The earliest postulated eukaryotes in the fossil record, *Grypania spiralis* (believed to be an alga), have an age of 2.1 Gyr (Han & Runnegar 1992), and so overlap with BIFs. It is assumed they required at least 0.01 PAL of dissolved O_2 (Runnegar 1991), while most eukaryotic microbes require at least 0.05 PAL (Jahnke & Klein 1979). Although the fossil

record of eukaryotes dates back to 2.1 Ga, there is molecular evidence, in the form of steranes (derived from sterols; see Sections 2.4.3f and 5.3.3d), for the emergence of eukaryotes at least 2.7 Gyr ago (Brocks et al. 1999), in the form of unicellular algae, which are phototrophes and members of the phytoplankton (Box 1.12).

In contrast to BIFs, **redbeds** are formed under oxidizing, subaerial conditions, and are characterized by quartz grains coated with haematite (Fe_2O_3). They are generally absent from the geological record before ≈ 2 Ga, although there are some disputed redbeds that date back to ≈ 2.4 Ga, which presents the possibility of some overlap with BIFs (Kasting 1993).

Unlike iron and other common metals, the higher oxidation state of uranium, U(VI), is water soluble, and its lower oxidation state, U(IV), is insoluble. So during the deposition of detrital uraninites, which are mostly older than 2 Gyr, the level of atmospheric oxygen must have been low, < 0.01 PAL (Kasting 1993; Rasmussen & Buick 1999). Large-scale deposition of detrital pyrite (FeS_2) similarly mostly occurred before 2 Ga.

The iron content of **palaeosols** (fossil soils) can also provide some information on atmospheric oxygen levels, although the interpretation is not straightforward and unanimous agreement upon the evidence has yet to be reached. The identification of palaeosols is not always easy, and assessment of the losses of iron (as Fe(II)) by leaching depends on a knowledge of the parent rock from which the soil formed and various environmental factors, such as the $O_2:CO_2$ ratio in the groundwater responsible for the leaching. The palaeosol record appears to indicate that atmospheric O_2 levels were ≤ 0.004 PAL prior to 2.25 Ga, and rose to ≥ 0.15 PAL after 1.92 Ga (Rye & Holland 1998).

Another major increase in atmospheric O_2 may have occurred towards the end of the Proterozoic (Knoll et al. 1986; Derry et al. 1992; Des Marais et al. 1992), providing the opportunity for more complex, multicellular eukaryotes to evolve. Further evidence for such an increase is provided by the isotopic record of sedimentary marine sulphides (Canfield 1998; see Box 1.13). From ≈ 2.3 to between 1.05 and 0.64 Ga the sulphur isotopic fractionation was $\leq 4\%$ with respect to marine sulphate, suggesting low sulphate levels, consistent with limited oxygenation of the atmosphere and surface waters, sufficient to allow enough oxidation of sulphide to sulphate for the use of sulphate-reducing bacteria in deeper anoxic environments. Enough sulphide may have been produced by these bacteria to remove dissolved iron(II) as pyrite. So for a large part of the Proterozoic bottom waters remained anoxic and sulphidic

Box 1.12 | Plankton classification

Plankton are organisms living primarily in the upper part of the water column and although often capable of some motion, particularly vertical migration in zooplankton, are unable to maintain their overall lateral position and drift with the oceanic currents. Buoyancy aids such as oil bodies are sometimes present. The plankton can be divided into phytoplankton and zooplankton.

Phytoplankton are photosynthesizing microorganisms, usually dominated by unicellular algae. However, free-floating cyanobacteria (unicellular forms rather than the colonial mat formers) and photosynthetic bacteria should also be strictly included by this definition. **Zooplankton** are animals ranging from unicellular microorganisms (**protozoa**) to multicellular organisms (**metazoa**). Many of the smaller zooplankton are herbivores, feeding on phytoplankton, and are, in turn, food for larger carnivorous zooplankton.

Classification of the plankton as a whole is often made on the basis of size (Fig. 1.9). The **ultrananoplankton** (or picoplankton) is composed almost entirely of bacteria, the **nanoplankton** of algae (phytoplankton), and the macro- and megaplankton of animals (zooplankton), mainly invertebrates.

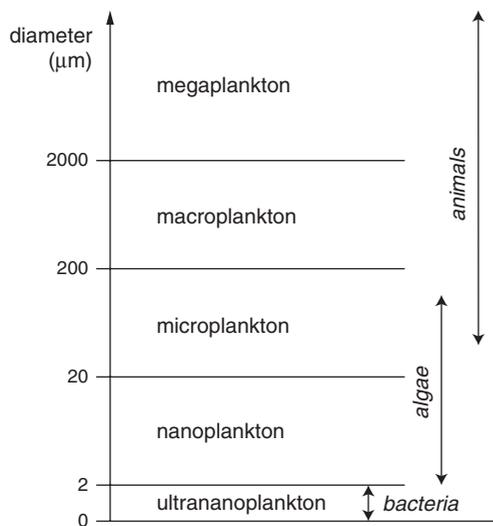


Fig. 1.9 Size classification of plankton (the 0.2 to 2 μm size range is often termed the picoplankton).

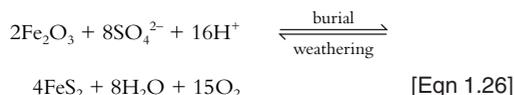
(**euxinic**), while surface waters were oxygenated but contained only modest amounts of sulphate (Canfield 1998; Shen et al. 2003). Subsequently, the S isotopic fractionation recorded by pyrite was much greater ($51 \pm 10\%$), suggesting that higher sulphate concentrations were available to the sulphate reducers and that some bacterial sulphide oxidation must have contributed to the fractionation (Box 1.13). At this point oxygen concentration must have increased above 0.05–0.18 PAL (Canfield & Teske 1996; Canfield 1998).

Piecing together all the above indicators leaves us with the envelope of possible atmospheric O_2 content represented by the shaded area in Fig. 1.8. There seems to be reasonable agreement among the indicators of redox conditions that a major increase in atmospheric oxygen occurred around 2 Ga. It is possible that the mantle had effectively been oxidized by then (its iron is in the form of silicates and oxides) as a result of the mixing and exposure to surface conditions caused by tectonic activity. In addition, tectonic activity decreased in the early Proterozoic (from 2.5 Ga), leading to smaller inputs of hydrothermal Fe(II) and reducing gases, which would have aided the increase in levels of atmospheric oxygen. A second major increase in atmospheric oxygen appears to have occurred at $c.0.9$ Ga, triggering the evolution of aerobic organisms, and particularly the metazoa. Three stages are shown in Fig. 1.8, the first corresponding to a predominantly reducing environment, with minor oxygen oases in the surface waters of the oceans and an upper atmospheric O_2 limit of $c.0.08$ PAL. The third stage corresponds to oxygenated conditions, for which O_2 levels could not have fallen below 0.002 PAL or the deep ocean would have remained anoxic (on the basis of mass balance considerations; Kasting 1993). During the intermediate stage (II), the deep waters of the ocean appear to have been anoxic, but the surface environment was partially oxidizing.

It has been estimated that atmospheric O_2 would have to have reached 0.01–0.1 PAL in order for an effective ozone layer to develop (Kasting 1987). The increase in abundance of phytoplankton, the dominant phototrophes of surface waters, noted during the early Proterozoic in Fig. 1.8 may reflect the improved growth conditions afforded by an ozone screen, protecting the delicate photosynthesizing organisms from the harmful effects of UV radiation (see Box 7.1). The earliest phototrophes may have had some protection from UV by the photolysis products of methane, given the likely activity of methanogens (Kasting 1991). The development of oxidizing conditions in the atmosphere and ocean would have put severe ecological pressure on the prokaryotes that had originated and evolved in reducing

Box 1.13 | Isotopic fractionation in sulphides and its relationship to oxygen levels

The burial/weathering relationship between oxygen and pyrite can be simplified to the following overall reaction (Holland 1984):



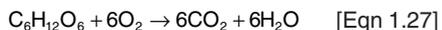
The conversion of sulphate into sulphide in the burial reaction results from the activity of sulphate-reducing bacteria, which strip the oxygen from sulphate to use in the oxidation of organic matter, thereby obtaining energy (see Box 3.10). The major source of sulphate for sulphate-reducing bacteria, which appear to have emerged *c.*2.4 Gyr ago (Blank 2004), is oceanic water, but the levels would have been very low prior to the development of an oxidizing atmosphere and the large-scale oxidation of sulphide to sulphate. As for all biochemical reactions, the assimilation of S involves isotopic fractionation favouring the lighter isotope (³²S; Box 1.3). However,

at low sulphate concentrations of <100 mg l⁻¹, bacterial sulphate reduction (BSR) results in negligible isotopic fractionation, so that the sulphide produced is ≤4‰ lighter than the precursor oceanic sulphate (Canfield & Teske 1996). At higher concentrations, BSR is observed to result in fractionations of 4–46‰.

Isotopic fractionations >46‰ appear to require additional fractionation processes to be involved, such as bacterial sulphide oxidation, which would afford a supply of sulphate with a lighter isotopic signature than that of average oceanic water (Canfield & Thamdrup 1994; Canfield & Teske 1996). Sulphur-oxidizing bacteria are confined to the zone of steep oxygen and sulphide gradients between oxic and anoxic environments, so their presence requires atmospheric oxygen to be *c.*5–18% of its present concentration. These bacteria appeared some 0.76 ± 0.32 Gyr ago (Canfield & Teske 1996). Since the late Proterozoic, bacterial processes have been important in the interconversion of sulphate and sulphide (and also of iron(II) and iron(III)), as represented in Fig. 1.10.

conditions. Modern descendants of these organisms, the archaeobacteria, have been forced into extreme environments, and it is likely that competition for ecological niches from newly evolving organisms would have played an important part. Aerobic heterotrophic prokaryotes, in contrast, became widespread and important in the recycling of organic material.

With free oxygen in the atmosphere, the advantages of aerobic respiration could be exploited, a process that can be represented by the reverse of Eqn 1.23 (i.e. the converse of oxygenic photosynthesis):



Aerobic respiration is a much more efficient process than fermentation, releasing about 18 times more energy, and so it is no coincidence that the proliferation of the eukaryotes began *c.*2 Gyr ago. The soft-bodied Ediacaran fauna (e.g. the worm-like *Dickinsonia*) that dates from *c.*580 Myr ago, towards the end of the Proterozoic, probably required O₂ levels of at least 0.03 PAL (Runnegar 1991), and the subsequent diversification of eukaryotes in the Cambrian is arguably testament to the importance of oxygen.

During the Phanerozoic, atmospheric O₂ concentrations have probably remained fairly constant, within *c.*0.7–1.7 PAL (i.e. 15–35% by vol., cf. present-day 21%; Berner & Canfield 1989). The charcoal lower limit in Fig. 1.8 corresponds to 0.6 PAL (12% by vol.), the level at which vegetation fires can occur forming charcoal, which is found in the fossil record since the rise of woody plants *c.* 425 Ma (Chaloner 1989). The dramatic increase in photosynthesis and coal formation during the Carboniferous is responsible for the modelled increase in O₂ at *c.*300 Ma to possibly as much as 1.7 PAL (35% by vol.), although at such elevated levels runaway vegetation fires become a likelihood, which would limit the O₂ levels (hence the upper limit for stage III in Fig. 1.8). Although it has been questioned whether O₂ levels could have risen much above 1.2 PAL (25% by vol.; Lenton & Watson 2000), a variety of adaptations has been noted that could be associated with elevated oxygen levels around the Carboniferous–Permian boundary, such as gigantism in insects and invasion of the land by vertebrates (Graham et al. 1995; Dudley 1998). The 1.2 PAL limit was based on studies of the spontaneous combustion of paper (Watson et al. 1978), but the lignified tissues of trees contain more

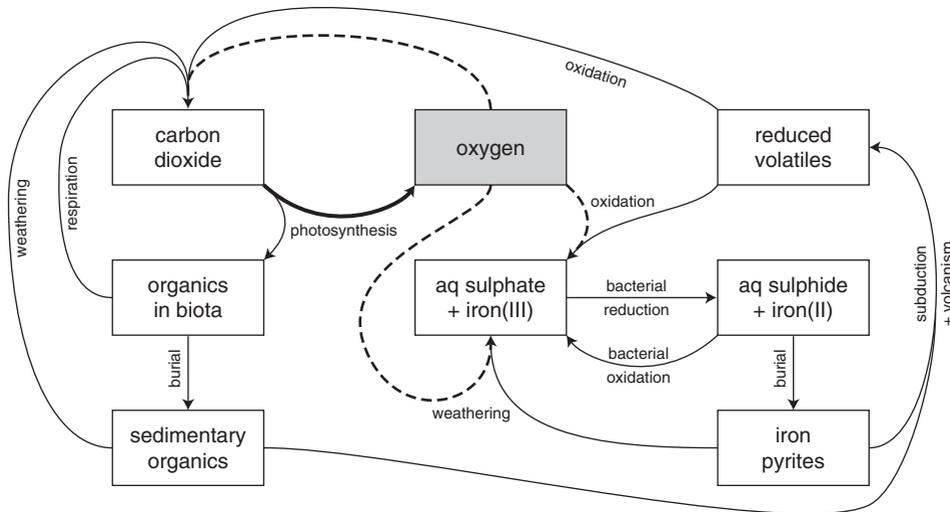


Fig. 1.10 A summary of the main processes involved in the regulation of atmospheric oxygen levels (aq = aqueous; reduced volatiles include CO and SO₂). Oxygen removal processes are shown by broken lines, and generation by the bold line.

water and the charring of the outer layers resists complete combustion, so atmospheric oxygen levels could have approached 2PAL before runaway wild fires were induced (Wildman et al. 2004). In fact, extensive fires produce abundant charcoal, which resists degradation, leading to greater C burial and hence potentially favouring higher atmospheric oxygen concentrations.

For oxygen to build up in the atmosphere the rate of oxygenic photosynthesis must exceed that of O₂ consumption by sinks. A summary of interactions between the main sinks and sources of oxygen is shown in Fig. 1.10. Major processes consuming oxygen are the oxidative weathering of sedimentary organic matter and reduced minerals (primarily iron(II) and sulphide from pyrite), the atmospheric oxidation of reduced volatiles in volcanic emissions and the conversion of biomass back into CO₂ during respiration (Petsch & Berner 1998; Berner et al. 2003).

The amount of oxygen presently in the surface environment gives us an estimation of the amount of phototrophic biomass that has ever been produced and has been locked away from aerobic respiration by burial in sedimentary rocks. It is a minimum value because of the removal of oxygen into other sinks. Molecular oxygen (O₂) is not particularly soluble in water, so most of it resides in the atmosphere (1.2×10^{18} kg) rather than in the oceans (7.8×10^{15} kg). From Eqn 1.23 we can estimate the corresponding amount of phototrophic material that must have been produced as $\approx 1.1 \times 10^{18}$

kg, or $\approx 4.5 \times 10^5$ Gt of C (see Appendices 1 and 2 for units of mass). However, there is only ≈ 600 Gt of C in living biomass today, which would only have generated an atmospheric oxygen concentration of ≈ 0.001 PAL. Clearly, a large amount of organic material must be locked away from oxidation. The long-term burial of organic matter in sedimentary rocks is the key to the build-up and maintenance of high levels of oxygen in the atmosphere (Van Valen 1971).

If oxygen is produced by the reduction of carbon dioxide, then atmospheric CO₂ levels must have declined over the life of the Earth, and there is evidence that this has indeed occurred. The climatic implications of changes in atmospheric CO₂ levels and how the global carbon cycle operates are addressed in Chapter 6, after the various elements of the carbon cycle have been introduced in the intervening chapters. For the moment, we continue with a more detailed look at the evolution of life in terms of the organisms that are most important by way of their contributions to the organic matter that is eventually buried in sedimentary rocks.

1.5 Major contributors to sedimentary organic matter

1.5.1 Major present-day contributors

Autotrophes, and particularly phototrophes, provide the energy needed by all other organisms, the

heterotrophes. The energy stored in the form of reduced carbon—the organic material in the tissues of organisms—is transferred along a food chain by the feeding of heterotrophes. There can be several links, or **trophic levels**, in a food chain, but energy transfer between adjacent trophic levels is not very efficient. Of the organic matter consumed at a particular trophic level some is lost in excreted material, and of the energy that is assimilated only part is available for growth and reproduction (the elements that constitute net production). Heterotrophes at higher trophic levels (i.e. carnivores) often expend a considerable proportion of assimilated energy on movement in obtaining food and the resulting high respiration levels generally lead to low net production. The effect can be seen in the low numbers of top carnivores, like the large cats in Africa, compared to the herbivores upon which they prey.

The efficiency of energy transfer between adjacent trophic levels can be measured from the ratio of the net production at the higher level to that at the lower level. Values of this ratio, known as the **transfer efficiency**, in terrestrial and marine ecosystems are typically only *c.* 10%. Net production is, therefore, significantly higher for the main primary producers than for organisms at higher trophic levels. This explains why phytoplankton (see Box 1.12) are the major contributors to marine and lacustrine sedimentary organic matter, and higher plant remains dominate in peat mires (although a considerable amount of higher plant material is also transported to sedimentary environments in coastal areas and lakes). Today, marine and terrestrial primary production are of similar size and have been so since about the Cretaceous, but earlier in the Earth's history marine production was dominant, and was, indeed, the only form of photoautotrophy before plants began to colonize the land, possibly in the Ordovician, but certainly by the Silurian.

The transfer efficiency from phytoplankton to zooplankton, the first step in the marine grazing chain, appears to be a little higher than average at *c.* 20%. This is partly due to the greater digestibility of phytoplankton compared with terrestrial plants, particularly the more woody species. Zooplankton can, therefore, be a significant source of organic matter for sediments, whereas other animals at similar trophic levels do not appear to be important in this respect. As a result of the predator–prey link, concentrations of zooplankton tend to be greatest where phytoplanktonic production is high. However, the transfer efficiency to herbivorous zooplankton is often lower in areas of highest productivity and there is a consequential increase in the proportion of phytoplanktonic remains reaching the

sediment and passing to the detrital food chain (see Box 1.9) or undergoing preservation.

There is one further major contributor to sedimentary organic matter, bacteria. A large proportion of the energy flow in ecosystems can pass through the detrital food chain, in which heterotrophic bacteria are prominent participants. Heterotrophic bacteria are important in all sedimentary environments, and although they consume organic detritus they supplement the organic matter with their own remains. In some environments autotrophic bacteria may also be important (e.g. the Black Sea; see Section 3.4.3c).

Although bacterial biomass may be relatively small, bacterial productivity can be very high in aquatic environments. For example, in the Caspian Sea the biomass and productivity of heterotrophic bacteria have been estimated to be about half the corresponding values of the phytoplankton (Bordovskiy 1965), while in the Black Sea bacterial production (autotrophic and heterotrophic) may be an order of magnitude greater than that of the phytoplanktonic algae. Consequently, the organic-rich remains of bacteria may make significant contributions to most, if not all, sedimentary organic matter.

There are, therefore, four major sources of sedimentary organic matter, in general order of importance: phytoplankton, higher plants, bacteria and zooplankton. Fungi, perhaps surprisingly, do not appear to make significant contributions to sedimentary organic matter. Although they are important organisms in terrestrial environments they are much less so in marine environments, where decomposition is primarily carried out by bacteria.

A much simplified summary of the flow of energy through an ecosystem is shown in Fig. 1.11 (n.b. the chemical energy supply utilized by chemoautotrophes is omitted). Eventually the solar energy originally captured by photoautotrophes is released to the environment by respiration, either via the grazing (herbivore–carnivore) food chain or via the detrital food chain. In the latter, the action of detritivores (see Box 1.9) in comminuting the larger particles of organic matter facilitates bacterial decomposition.

1.5.2 The fossil record of major contributors

The fossil record can be used to gain information on the relative importance of organisms throughout geological time but it has limitations, such as the inherent tendency to give undue weight to those organisms that have recognizable preservable parts, while organisms comprised of only soft tissue are grossly underrepresented

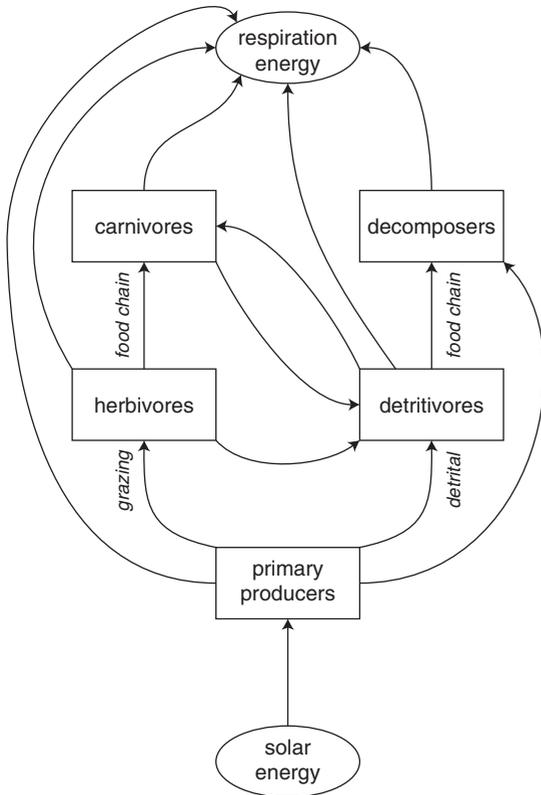


Fig. 1.11 Simplified representation of energy flow through an ecosystem (a proportion of herbivore and detritivore remains is recycled directly by decomposers).

(e.g. Briggs & Crowther 2001). This means that organism numbers and productivity may not be accurately reflected. For example, the predominant phytoplankton of the Palaeozoic (acritarchs, green algae and cyanobacteria) had cell walls composed of organic material and so were less likely to leave evidence of their existence than the phytoplankton secreting calcareous or siliceous **tests** (skeletal parts) that became dominant in more recent times.

Formation of dark, organic-rich, marine shales appeared to be widespread in the early Palaeozoic but was generally less common after the Silurian. This change coincides with an increase in abundance of herbivorous zooplanktonic remains in the fossil record and so could be interpreted as reflecting increasing importance of the grazing food chain at that time, resulting in less detritus reaching marine sediments in general. However, as is seen in Chapter 3, other factors are important in determining whether organic matter undergoes long-term

preservation, and it is possible that herbivores were no less abundant during the early Palaeozoic than later but may have lacked identifiable preservable parts.

Because of the problems associated with selective preservation in interpreting the fossil record, the representation of the evolutionary trends in the groups of organisms shown in Fig. 1.12 should be treated with caution; the width of bars is only intended as a guide to trends in the relative abundance within each group of organisms, and even this limited assessment is extremely difficult for bacteria and fungi. In the absence of preserved hard parts, chemical evidence in the form of specific compounds may provide information on contributing organisms, but again this approach is limited with respect to fungi. Preservation potential, whether applied to hard parts or specific molecules, is often referred to as **taphonomy**.

1.5.3 Evolution of marine life

Throughout the Archaean, prokaryotes, in the form of photosynthetic bacteria and cyanobacteria, were the main producers of organic carbon. The resting stages (cysts) of early unicellular eukaryotic organisms, probably representing planktonic algae and referred to as **acritarchs**, first appeared in the fossil record at *c.*1.85 Ga and became abundant from *c.*1.0 Ga.

Stromatolite abundance is seen to decline from *c.*1.0 Ga, and at an increasing rate from 850 Ma. This could reflect competition from the emerging groups of benthonic algae for the favourable shallow-water environments (the term **benthonic** is generally applied to organisms that live on top of or within sediments). It might also reflect the effects of grazing by herbivores, although the earliest fossil evidence of what appear to be animals, the soft-bodied multicellular Ediacaran faunas, dates from the end of the Proterozoic (the Vendian Period, *c.*610–540 Ma). It is unknown whether the Ediacaran organisms are the ancestors of the succeeding Cambrian faunas, despite their pronounced physiological differences, or whether they represent an evolutionary dead end (Fortey 1997). A large range of invertebrate phyla appeared explosively in the fossil record at the beginning of the Cambrian, and we have a good indication of their feeding habits from the remarkable preservation of their soft tissues in the Burgess Shale (Gould 1991; Fortey 1997). The grazing and detrital food chains were clearly well developed by that time. It seems an inescapable conclusion that the organisms associated with the Cambrian ‘explosion’ did not appear out of thin air but must have had Precambrian ancestors, which were perhaps too small to leave a visi-

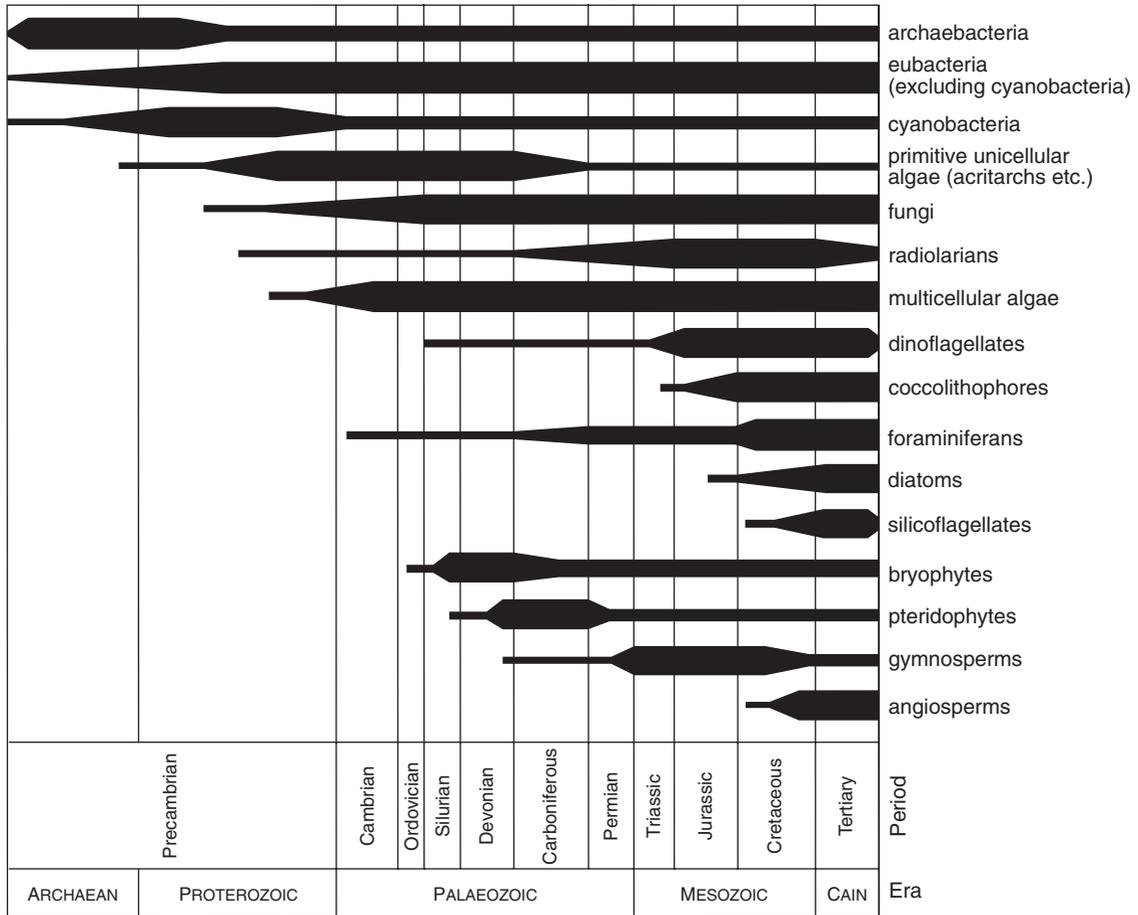


Fig. 1.12 Evolution of some important contributors to sedimentary organic matter. Bar widths reflect relative abundance trends within each group of organisms. Early origins of cyanobacteria are equivocal (see text).

ble fossil record (as is true for many members of the modern zooplankton; Fortey 1997).

As noted above, the early phytoplanktonic communities had organic cell walls (e.g. **dinoflagellates**), but during the Mesozoic, planktonic organisms appeared that secreted calcium carbonate (i.e. calcareous) tests. Hard coatings would have offered a degree of protection from predation, until predators developed effective means to breach the shells (like rasps). Among these calcareous organisms nanoplankton, particularly **coccolithophores**, dominated primary production (see Box 1.9), and zooplanktonic **foraminiferans** also made a significant contribution to biogenic sediments. Siliceous phytoplankton (i.e. secreting silica tests), especially **diatoms** and **silicoflagellates**, became impor-

tant in the Late Cretaceous and Cainozoic. The main primary producers within the phytoplankton today—in terms of net production—are the diatoms, but also important are the dinoflagellates, coccolithophores, silicoflagellates, cyanobacteria and prochlorophytes. In terms of numbers of cells, the **prochlorophytes** (the smallest of the picoplankton and related to the cyanobacteria; Partensky et al. 1999) are the most abundant, followed by the cyanobacteria.

The abundance of the fossilized remains of herbivorous zooplankton (see Boxes 1.9 and 1.12) is relatively low for the early Palaeozoic but increases subsequently for orders such as the **radiolarians** and foraminiferans (both protozoa of the class Rhizopoda). Grazing of phytoplankton by zooplankton greatly reduces the

direct contribution of the former to sedimentary organic matter. However, there is still an indirect input via detrital material from zooplankton, comprising both their faecal pellets and their remains upon death, and in this respect the most important zooplankton today are **copepods** (small crustaceans) and foraminiferans.

Multicellular (macroscopic or macrophytic) algae appeared during the late Proterozoic and increased in numbers during the early Palaeozoic. These organisms were generally non-planktonic, being attached to the substrate, and so can be considered as benthonic organisms. They can be classified according to colour: green (Chlorophyta), red (Rhodophyta) and brown (Phaeophyta). The Devonian saw significant changes in the evolution of the algae, with many forms dying out and others replacing them. Some forms were different from earlier and later types, and among them may be representatives of the first plants to attempt colonization of the land.

Fungi appear to have evolved alongside the algae, and there are unicellular (yeasts) as well as colonial forms. Their evolutionary record is, however, difficult to piece together due to the lack of preservable parts. Fossil remains have been found in Archaean marine sediments and today fungi are highly successful in terrestrial environments. Fungi probably invaded the land at the same time as plants.

1.5.4 Evolution of terrestrial life

The last important group of photosynthesizing organisms to appear were the terrestrial **vascular plants**, probably evolving from ancestral green algae. They are commonly termed the **higher plants** in order to differentiate them from the lower plants such as algae. The bryophytes (mosses, hornworts and liverworts) probably also originated from ancestral algae; they can be important contributors to peat (e.g. *Sphagnum*), although their overall contribution to sedimentary organic material is relatively minor.

The colonization of the land by plants began in the Ordovician, based on an age of *c.* 475 Ma for the earliest known fossil spores, which appear to have derived from liverwort-like plants (Wellman et al. 2003). By this time there was a well developed ozone (O₃) layer providing protection against harmful UV radiation. Aquatic plants are supported by the density of water, do not require protection from desiccation and have their nutrient requirements delivered to all parts by the water they inhabit. Like aquatic plants, bryophytes do not have a vascular system, and so are restricted to areas of plentiful water supply. In order to spread across the continents in

the relatively dry and low density medium of air, land plants had to develop structural tissues to provide support, cuticles to protect against dehydration and a vascular system to deliver water and nutrients to all parts. The early vascular plants were prostrate forms, like the bryophytes, minimizing the need for support. They reproduced by spore formation, again like the bryophytes, and areas with standing water or subject to flooding (e.g. tidal mud-flats) were ideal primary habitats, transporting spores and gametes, as well as supplying all the water needed by the plants. *Cooksonia* is generally accepted as the earliest erect pteridophyte-like plant (Briggs & Crowther 2001). Diversity, distribution and size of land plants increased greatly during the Devonian, the major vascular plant types belonging to the psilophytes, a class of the pteridophytes (see Box 1.8). As plants increased in size their photosynthetic requirements increased, so a larger surface area was required for the capture of light as well as CO₂ (levels of which in the atmosphere were declining, although still high). The solution to this problem was the development of leaves from modified branches (Stewart & Rothwell 1993).

Dense vegetation stands grew during the Late Devonian and Carboniferous, when the clubmosses (lycopsids) and horsetails (sphenopsids) reached their peak of development, forming the great coal forests of the period. These plants grew to considerable size, with heights of 45 m or so for the largest clubmoss, *Lepidodendron*. When the climate changed and the swamps dried out at the end of the Carboniferous some of the larger of the pteridophytes died out, but survivors remain today among the ferns and clubmosses, and one horsetail, *Equisetum*. The first large woody trees, which were important members of early Late Devonian forests, were the progymnosperms (e.g. *Archaeopteris*), which reproduced by spores and had a fern-like foliage.

Seed-bearing plants (spermatophytes), in the form of the **gymnosperms**, emerged during the Late Devonian from pteridophyte ancestors. Important orders of the gymnosperms were cycads, conifers and ginkgoes, and they dominated the terrestrial flora until another group of seed-bearing plants, the **angiosperms**, rose to prominence by the mid-Cretaceous. Although of diminished importance, members of the gymnosperms exist today, most notably the conifers of the temperate regions. The angiosperms, or flowering plants, emerged in the Early Cretaceous, and are generally characterized by broad and veined leaves, in contrast to the needles of gymnosperms. They are highly versatile and successful, and their productivity is reflected in the large coal deposits of the Cretaceous and Tertiary. Grasslands are a relatively recent feature and, although

not important contributors to sedimentary organic matter, they serve as a useful example of the evolution of the photosynthetic pathway (Box 1.10). Grasses (*Poaceae*) first appeared during the Oligocene, utilizing the C_3 pathway of earlier organisms. C_4 grasses seem to have emerged later in the Miocene (Cerling et al. 1993), and today dominate at latitudes less than 40° , where the ability to keep stomata closed during the hottest times of the day provides a competitive advantage. In contrast, C_3 grasses dominate in regions with cool growing seasons.

1.5.5 Ecosystem variations

The broad picture painted in the preceding sections of the temporal variations in the Earth's biota is the result of the interplay of many factors, including gradual evolutionary changes as well as relatively rapid (in geological terms) and catastrophic events. The overall trend is one of increasing diversity, as organisms adapted to the plethora of habitats available. So the explosive radiation at the beginning of the Cambrian is not unexpected, but can diversity continue to increase indefinitely, as suggested in the overall trends in Fig. 1.13? A basic tenet of ecology is that if two species occupy precisely the same ecological niche (i.e. the same habitat, environmental conditions, food source etc.), one will be out-competed by the other and become excluded from the niche (a potential mechanism for extinction); this is the principle of competitive exclusion (e.g. Begon & Mortimer 1986). The great diversity of life on modern coral reefs shows how large the range of ecological niches can be, and it would seem that the diversity ceiling has yet to be reached for the Earth as a whole.

Estimating diversity is far from easy, and depends upon how taxonomic distinctions are made on the basis of the preserved physiology, which contributes to the different appearance of the trends (a) and (b) in Fig. 1.13 (Benton 1995). Nevertheless, the fossil record is not one of uninterrupted diversity increase; the trend is punctuated by sharp declines, marking mass extinctions, near several period boundaries (Hallam & Wignall 1997). The five largest mass extinctions occurred in the Late Ordovician, Late Devonian, Late Permian, Late Triassic and end-Cretaceous (Fig. 1.13a). Three major, distinct, faunal groups have been recognized among Phanerozoic marine organisms with skeletal parts that are generally well preserved: the Cambrian, Palaeozoic and Modern faunas. Each of these groups has a characteristic assemblage of taxa that remains relatively stable over a significant time period, as shown in Fig. 1.13a (Sepkoski 1984). Although the Cambrian faunal diversity was decreasing throughout the Ordovician, while

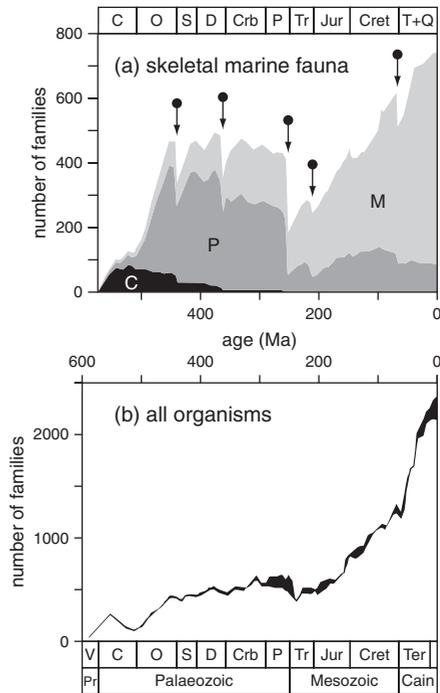


Fig. 1.13 Diversity trends in (a) marine fauna with preserved skeletal hard parts (C = Cambrian fauna, P = Palaeozoic fauna, M = Modern fauna, • = major extinctions; after Sepkoski 1984); (b) all organisms (variation in line thickness reflects uncertainty in taxonomic differentiation; after Benton 1995).

the Palaeozoic faunal diversity was increasing, the first three of the major extinction events clearly had a major impact on the Cambrian fauna, and similarly the Late Permian extinction brought about a dramatic decline in the Palaeozoic faunal diversity. As life recovered from the extinction events, new families and species appeared relatively rapidly, filling the vacated niches.

Perhaps the best known of the mass extinctions is that associated with the demise of the dinosaurs at the Cretaceous–Tertiary boundary, which has been attributed to a meteorite impact (Alvarez et al. 1980; Kruge et al. 1994; Skelton et al. 2003), although natural climate change may also have been a factor. Planktonic organisms (particularly foraminiferans, calcareous phytoplankton and radiolarians) were also severely affected. On land, trees seem to have been devastated, with the recovery period marked by the proliferation of ferns. The pollen record is dominated by fern spores, and hence known as the fern spike, which is observed

throughout the world (Nichols et al. 1986; Vajda et al. 2001).

However, the mass extinction with the greatest impact occurred in the Late Permian, with >60% of marine and terrestrial families disappearing (Erwin 1993, 1994; Benton 1995). Over a period of <1 Myr, 85% of the main species were wiped out (Bowring et al. 1998). The extinction event also brought an end to the *Glossopteris* flora, which dominated the forests at high southern latitudes, and their northern equivalents, the *Cordaites* flora of Siberia (Retallack 1995). There was a corresponding proliferation of fungal spores (Eshet et al. 1995; Visscher et al. 1996). Lycopsids dominated for c.5 Myr in the tropics (e.g. Europe), and conifers did not proliferate until the mid-Triassic (Looy et al. 1999). The cause(s) of the extinction event are a matter for speculation due to the lack of sufficiently precise dating of events. Some of the factors that may have been instrumental in affecting ecosystems on a global scale are listed in Table 1.7.

Global changes in ecosystems clearly have the potential to affect the type and amount of organic material deposited in sediments and, as we have seen, can be driven by extinction events as well as more gradual evolution resulting from random mutation. Less dramatic but equally important influences on ecosystem composition and evolution are major climatic changes. The Earth has experienced ice ages at various times—during the late Proterozoic, the Late Carboniferous–Early Permian and the Quaternary—which we examine in Chapter 6. The arrangement of continents can play a key role in modifying climate as well as having a direct

influence on the variety of habitats. The continents have been assembled in one large mass at least three times in the Earth's history, at c.250 Ma (Pangaea), c.600 Ma (Vendian), c.1.0 Ga (Rodinia) and possibly also c.1.9 Ga (Rogers & Santosh 2002). During such periods climate and ecosystems are uniform over large areas, potentially restricting diversity (Valentine & Moores 1970). For example, during the Devonian and Carboniferous, as Pangaea was assembling, large areas of the northern hemisphere land mass (Laurasia) were subjected to an almost uniformly warm and moist climate, as in the present-day tropics. Under these conditions a uniform *Lepidodendron* flora of the Laurasian coal swamps flourished, while a large area of southern hemisphere land mass (Gondwana) was covered by ice sheets. During the Permian, the *Glossopteris* flora (named after the dominant sporophyte) produced significant coal deposits at high southern latitudes across what is now Antarctica, Australia, South America and India, and there was an equivalent flora at high northern latitudes, but arid conditions prevailed over a wide expanse of Pangaea at lower latitudes. As Pangaea split up and dispersed during the Mesozoic, the distinctions between habitats and their associated plant communities became more pronounced.

While the spread of marine organisms throughout the oceans is largely unhindered by topographical obstacles, a uniform distribution does not always result even after sufficient time has elapsed for extensive colonization to occur by a newly evolved species. Coastal and shelf environments are more extensive during periods of continent dispersion, and there is more opportunity for local populations of marine organisms to become isolated and undergo divergent evolution. The arrangement of continents can also have a marked effect on oceanic currents and climate. Today, there are latitudinal variations in distributions of both abundance and species of phytoplankton related to climate, oceanic circulation and nutrient distribution patterns, and there is no reason to believe that such controls did not operate in the past. Such variations and the factors that control microorganism distributions in saline and freshwater environments are discussed in Chapter 3. But first, in the next chapter, we review the organic composition of organisms in order to understand why the composition of sedimentary organic matter varies.

Table 1.7 Some factors that may have influenced ecosystems on a global scale

bolide impacts
bursts of cosmic radiation, e.g. nearby supernovae
magnetic reversals—loss of protection from charged particle fluxes
dispersal of continents
sea-level changes—particularly their effect on area of shelf seas
climatic change—particularly rapid periods of change (e.g. volcanic CO ₂ emissions)
