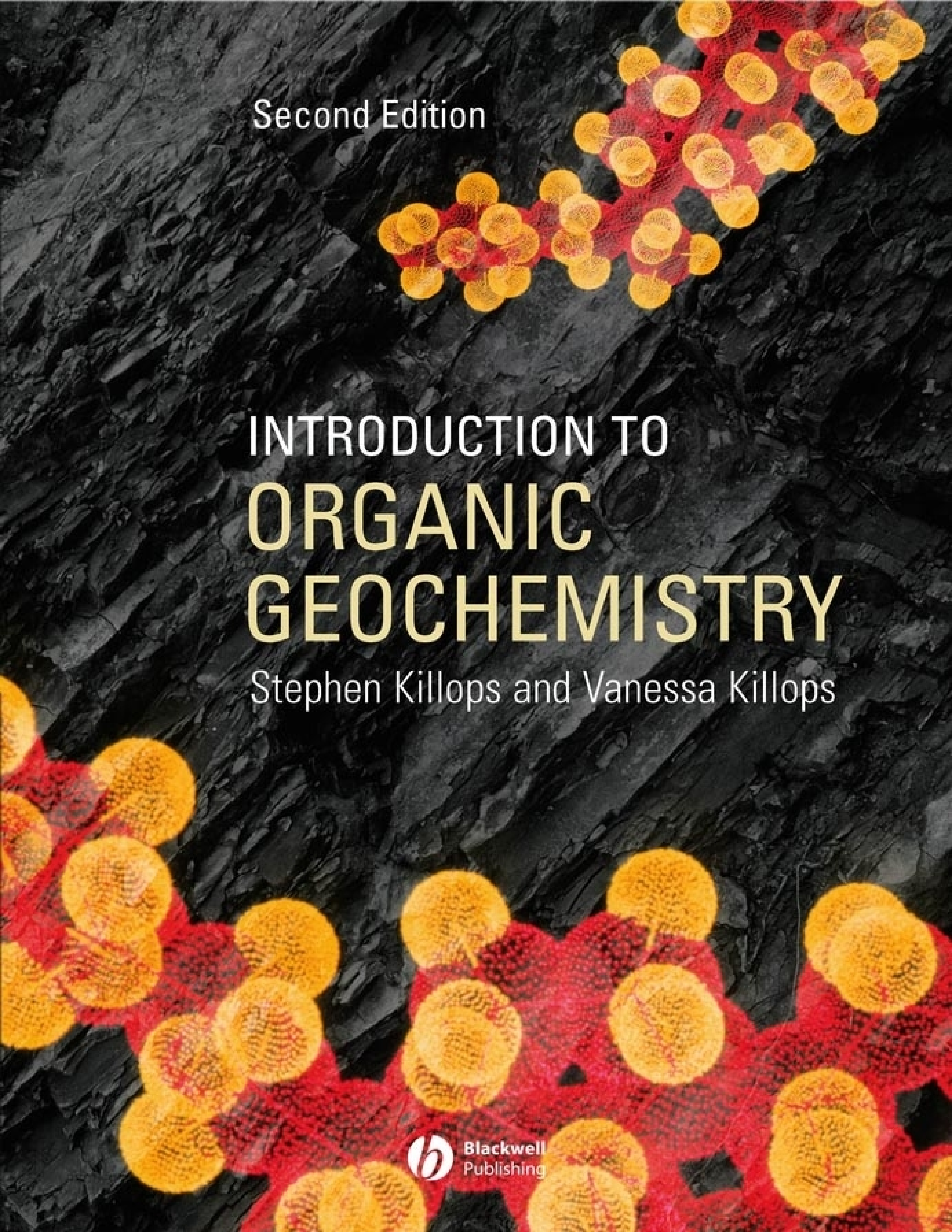

Second Edition

INTRODUCTION TO ORGANIC GEOCHEMISTRY

Stephen Killops and Vanessa Killops

Blackwell Publishing

Contents

SECOND EDITION

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Preface

To begin with, a brief statement of what constitutes organic geochemistry is probably called for. It is the study of the transformation undergone by organic matter of all types, whether of biological or manmade origin, in the Earth System. The transformations involved vary from those mediated by biological processes involved in the production of living tissue and the operation of food-chains, to those controlled by temperature and pressure at depth in the crust. Photochemical processes in the atmosphere and hydrosphere can also be important in controlling the environmental behaviour of some organic compounds.

Our knowledge of organic geochemistry has been expanding at such a great rate that a comprehensive text on the subject would fill many books of this size. To a newcomer, the bulk of information and the terminology adopted from a range of disciplines, such as chemistry, geology, ecology, biochemistry, botany and oceanography, can be quite daunting. However, to those not readily deterred, the fascination of the subject soon becomes apparent. If only the basics of organic geochemistry could be found readily at hand rather than scattered through textbooks and journals of a number of disciplines! These were our thoughts when we first came to the subject in the 1980s, and they subsequently provided the stimulus for this book when one of us (SDK) began teaching the subject to undergraduates and postgraduates.

This book is an attempt to present a readily accessible, up-to-date and integrated introduction to organic geochemistry, at a reasonable price. It does not assume any particular specialist knowledge, and explanatory boxes are used to provide essential information about a topic or technique. Technical terms are also highlighted and explained at their first appearance in the text.SI units are presented in Appendix 1, prefixes used to denote exponents in Appendix 2 and a geological time scale in Appendix 3. A comprehensive reference list is provided for those wishing to explore the original sources of the concepts and case studies covered, which concentrates on articles in the most readily available journals.

The text is intended to serve undergraduate and postgraduate courses in which organic geochemistry is an important component. It may also be found a useful companion by experienced scientists from other disciplines who may be moving into the subject for the first time. Whereas the first edition of this book concentrated on organic-rich deposits, of particular interest to those involved in petroleum exploration, this edition considers the fate of organic matter in general. The importance of environmental geochemistry has not been overlooked, and consideration has been given to environmental change at various times during Earth's history in order to provide a background for assessing modern changes and how the carbon cycle works. Naturally, in a book of this size it is impossible to cover everything;for example, it is not possible to do justice to the wide range of analytical techniques used in organic geochemistry, which draw on all aspects of separation science and spectrometry. However, there are many texts on these topics, some of which are listed below. We hope the topics we have selected for this edition stimulate the reader to continue studying organic geochemistry.

Further reading

Harwood L.M., Claridge T.D.W. (1997) *Introduction to Organic Spectroscopy*. Oxford: Oxford Science Publications.

Lewis C.A. (1997) Analytical techniques in organic chemistry. In *Modern Analytical Geochemistry* (ed. Gill R.), 243–72. Harlow: Longman.

Peters K.E., Moldowan J.M.(1993) *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Englewood Cliffs, NJ: Prentice Hall.

Poole C. (2002) *The Essence of Chromatography*. Amsterdam: Elsevier Health Sciences.

Settle F. (ed.) (1997) *Instrumental Techniques for Analytical Chemistry*. Englewood Cliffs, NJ: Prentice Hall.

Silverstein R.M., Bassler C.G., Morrill T.C. (1991) *Spectrometric Identification of Organic Compounds*. New York: Wiley.

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1

Carbon, the Earth and life

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—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.

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).

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 × 10^{30} kg, and is capable of hydrogen fusion, which involves the following reactions:

[Eqn 1.1] $^{1}H + ^{1}H \rightarrow ^{2}H + \text{energy}$

[Eqn 1.2] $^{2}H + ^{1}H \rightarrow ^{3}He + \text{energy}$

[Eqn 1.3] $^{3}He + ^{3}He \rightarrow ^{4}He + ^{1}H + ^{1}H + \text{energy}$

(where ^{2}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:

[Eqn 1.4] $^{4}\mathrm{He} + {}^{4}\mathrm{He} + {}^{4}\mathrm{He} \rightarrow {}^{12}\mathrm{C} + \mathrm{energy}$

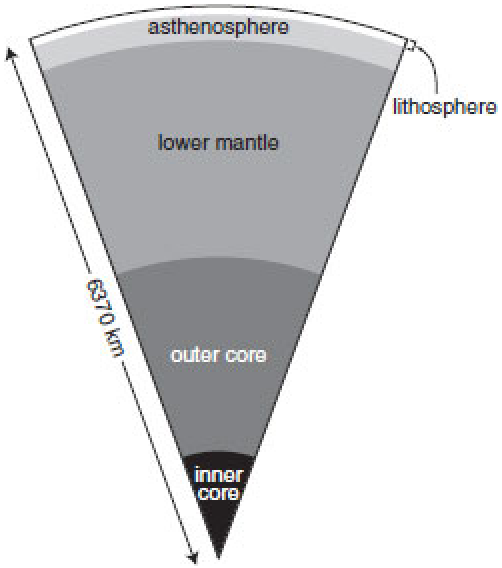
[Eqn 1.5] $^{12}\mathrm{C} + {}^{4}\mathrm{He} \rightarrow {}^{16}\mathrm{O} + \mathrm{energy}$

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.* 2900km 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*.1000–400km depth). It behaves in a plastic, ductile fashion and supports convection cells. The upper mantle layer from *c*.100 to 400km 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*.5–7km thick under the oceans but *c*.30–70km 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.



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}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:

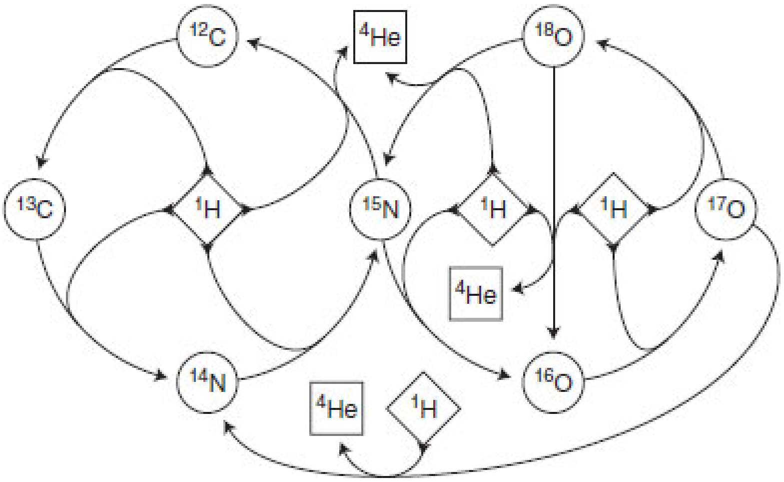
[Eqn 1.8] $H_3^+ + CO \rightarrow HCO^+ + H_2$

[Eqn 1.9] $H_3^+ + N_2 \rightarrow N_2H^+ + H_2$

[Eqn 1.10] $H_3^+ + O \rightarrow OH^+ + H_2$

[Eqn 1.11] $H_3^+ + C_2 \rightarrow C_2H^+ + H_2$

Fig. 1.2 Hydrogen fusion via the CNO cycle.



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 ultraviolet (UV) radiation from the Sun.

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 ${}^{m}_{n}E$, 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. ${}^{13}C$ instead of ${}^{13}_{6}C$).

Carbon is a mixture of two stable isotopes, ${}^{12}C$ and ${}^{13}C$. In the Earth as a whole the relative abundances of ${}^{12}C$ and ${}^{13}C$ 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 ${}^{13}C$ to ${}^{12}C$ 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 ${}^{12}CO_2$ and ${}^{13}CO_2$ 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:

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

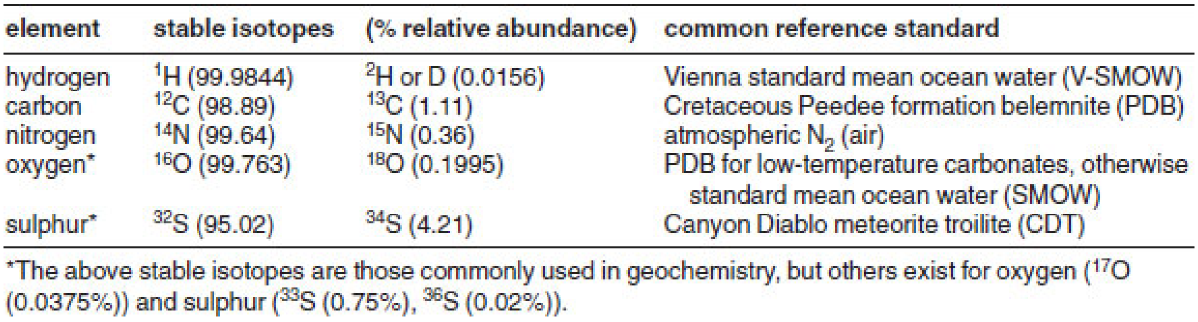
where m = mass number of the heavier isotope, E = the element and R = the abundance ratio of a heavier to the lightest, most abundant isotope. So for carbon we have:

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

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 $\delta^{m}E$ 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 $^{13}C/^{12}C = 0.011237$).

Some elements have unstable isotopes, which undergo radioactive decay, such as ^{14}C (see Box 5.5). Those of ^{238}U, ^{235}U, ^{232}Th and ^{40}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}H (99.9844)	^{2}H or D (0.0156)	Vienna standard mean ocean water (V-SMOW)
carbon	^{12}C (98.89)	^{13}C (1.11)	Cretaceous Peedee formation belemnite (PDB)
nitrogen	^{14}N (99.64)	^{15}N (0.36)	atmospheric N_2 (air)
oxygen*	^{16}O (99.763)	^{18}O (0.1995)	PDB for low-temperature carbonates, otherwise standard mean ocean water (SMOW)
sulphur*	^{32}S (95.02)	^{34}S (4.21)	Canyon Diablo meteorite troilite (CDT)

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

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 near the surface for *c*.2.5 Gyr, although some may have been formed high up in the atmosphere by the photodissociation of CO_2 and H_2O (Kasting 1993). With-out 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*.300nm, see Box 7.1).

Box 1.4 Comets, asteroids and meteorites

Comets are mostly aggregates of interstellar dust, ice (H_2O, CO and CO_2) and some organic molecules. They originate from two regions in the Solar System. The most distant is the Oort cloud, which is up to 10^5 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_2O
H_2CO	CO
H_3COH	NH3
H^3COOH	HCN
CH_3CH_2OH	H_2S
HC≡CCN	SO_2
H_2CS	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:

[Eqn 1.12] $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

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

[Eqn 1.13] $4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$

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:

[Eqn 1.14] $Fe^{2+} \rightarrow Fe^{3+} + e^-$

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**.

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 (^{40}K, ^{232}Th, ^{235}U, ^{238}U; 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 δ^{18}O 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 CO_2) 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 essential 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 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.

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_2S absorption <270 nm)	2×10^{11}	–
UV (CO_2 absorption <230 nm)	–	3×10^8
UV (H_2O 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 H_2/CO_2 concentration ratio of 0.1.

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 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.

Fig. 1.3 The optical isomers of alanine.

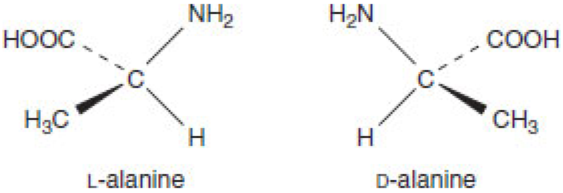
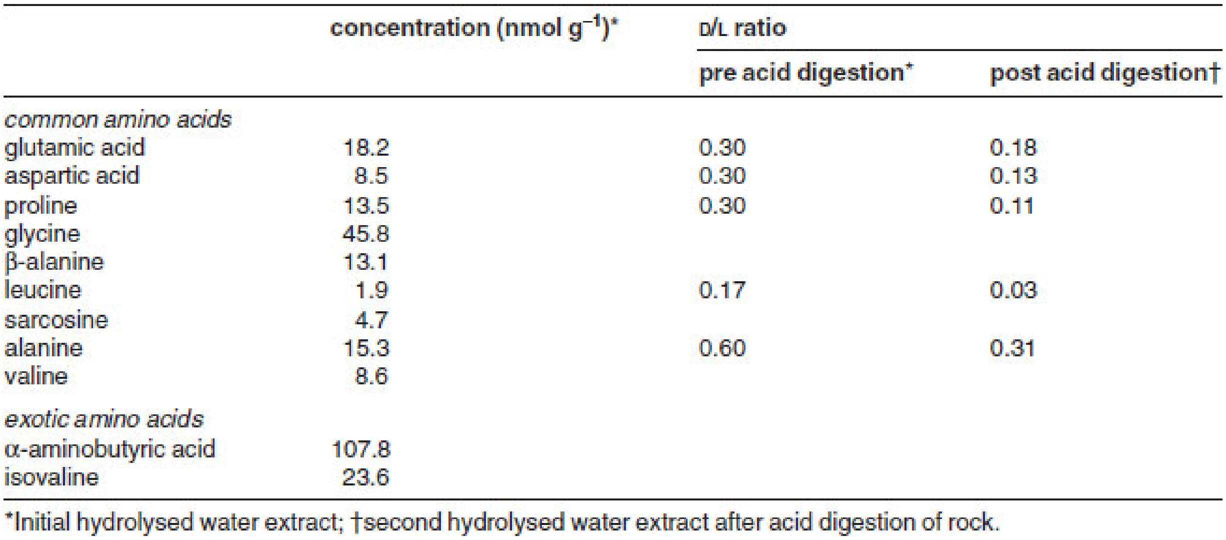


Table 1.4 Amino acids detected in hydrolysed aqueous extracts of Murchison meteorite (after Engel & Nagy 1982)



	concentration (nmol g^{-1})*	D/L ratio	
		pre acid digestion*	post acid digestion†
common amino acids			
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		
exotic amino acids			
α-aminobutyric acid	107.8		
isovaline	23.6		

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