1 The molecular universe

Introduction

Chemistry without numbers is poetry: astrochemistry without numbers is myth. A molecule placed around a star, in a nebula, lost in the interstellar medium, on a planet or within a cell has the potential for very complex and beautiful chemistry but unless we can understand the local conditions and how the molecule interacts with them we have no idea what chemistry is really happening. To understand astrochemistry we need to understand the physical conditions that occur within many diverse molecular environments. The exploration of the molecular universe will take us on a long journey through the wonders of astronomy to the new ideas of astrobiology

The origins of life provide the motivation and excuse to investigate astrochemistry in its broadest sense, looking at molecules and their local complex chemistry using all of the tools of physical chemistry to constrain the imagination of the astrobiologist in the field and to force a re-think of the rules of biology that are prejudiced by the experience of life on Earth. The complexity of the problem places demands on the theories of science, stretching the understanding of kinetics and thermodynamics into areas where large non-ideal systems are hard to understand, although, curiously, modelling the complex chemistry of a giant molecular cloud is not dissimilar to the models of biochemistry within a cell. The size of the chemical problem quickly grows, so that the chemistry of 120 molecules in a molecular cloud must be compared with the 4500 reactions thought to be required to make a cell work. The full understanding of the chemical reactions must be modelled as a network of coupled chemical equations, which for something as comparatively simple as a candle flame can contain 350 equations.

Our mission is to explore the molecular universe with an understanding of all of the local molecular environments and constrain possible chemical reactions using the concepts of physical chemistry. With such a wide brief we need a focus and I have chosen the origins of life on Earth and on all planets – astrobiology.

1.1 The Standard Model – Big Bang theory

About 15 billion years ago the Universe and time itself began in a Big Bang. Observations of the night sky show that stars and galaxies are moving away from

Astrochemistry: from astronomy to astrobiology. Andrew M. Shaw

Table 1.1 The history of the Universe according to the Standard Model

Time since $t = 0$	Temperature	Comments
10^{-43} s	10^{32} K	Gravity is now distinct from the three other forces: strong, weak nuclear and electromagnetic
10^{-35} s	10^{27} K	Inflation of the Universe – the strong force separates
10^{-12} s	10^{15} K	Weak and electromagnetic forces separate. Neutrons and protons are formed by photon–photon collisions
10^{-2} s	10^{11} K	Electrons and positrons are formed through collisions of photons
1 s	10^{10} K	The Universe becomes transparent to neutrinos
180 s	10^{9} K	Nucleosynthesis: hydrogen, deuterium, helium and some lithium
$3–7 \times 10^{5}$ s	3000 K	Light element atoms form, and the Universe is now transparent to radiation: cosmic background is emitted
10^{9} yr	20 K	Galaxies form
Present	2.726 K	Stars and galaxies

us, telling us that the Universe is expanding. Extrapolating backwards in time leads to a point of common beginning, a singularity in space-time known as the Big Bang. Temperature is critical to the phases of evolution and subsequent cooling of the Universe, producing a number of critical times, detailed in Table 1.1. They are all predictions of the Big Bang Theory or the Standard Model of Cosmic Evolution.

Einstein's theory of relativity allows for the interconversion of energy and matter through the famously simple equation $E = mc^2$. Thus collisions between high-energy photons in the primordial fireball created particle–antiparticle pairs such as protons and antiprotons. After some 180 s and at a temperature of 10^9 K atomic nuclei such as hydrogen, deuterium, helium and some lithium were formed. The first three minutes of all time were chemically the dullest with no atoms or molecules. For a further 10^6 s the light atoms continue to be formed, marking a period where matter is created by *Big Bang nucleosynthesis*.

There are a number of astronomical pieces of evidence for the Big Bang Theory as we shall see, including the recent observation of the cosmic microwave background radiation, but it is far from a complete theory. However, predictions of the theory may be tested. One such prediction is the relative abundance by mass of He, which must be at least 25 per cent of the total mass. Helium is also made in stars and must contribute to the He density of the Universe and in all observations to date the observed abundance is greater than 25 per cent. There are problems associated with matter. Why is the Universe made from matter instead of antimatter? When was this decision made to stabilise matter from high-energy photons and particle–antiparticle pairs. Further, calculations of gravitational attractions of galaxies suggest the presence of large amounts of matter that cannot be seen, so-called dark matter. What is dark matter?

Table 1.2 Relative cosmic abundances of the elements

Element	Relative abundance	Element	Relative abundance
H	1	S	1.6×10^{-5}
He	0.085	P	3.2×10^{-7}
Li	1.5×10^{-9}	Mg	3.5×10^{-5}
C	3.7×10^{-3}	Na	1.7×10^{-6}
N	1.2×10^{-3}	K	1.1×10^{-7}
O	6.7×10^{-3}	Si	3.6×10^{-6}

The majority of the Universe is made from hydrogen and helium produced during the Big Bang, although some He has been made subsequently. The relative cosmic abundance of some of the elements relevant to the formation of life is given in Table 1.2, with all elements heavier than H, He and Li made as a result of fusion processes within stars, as we shall see later. The cosmic abundance is assumed to be the same as the composition of the Sun.

1.2 Galaxies, stars and planets

All matter formed within the Big Bang is attracted to itself by the force of gravity and after about 1 billion years massive proto-galaxies form. Gravitational contraction continues in more and more localised regions to form the galaxies we know today, including our galaxy, the Milky Way. The Milky Way is in a cluster of galaxies called the ‘local group’ that includes the Large Magellanic Cloud, the Small Magellanic Cloud and the Andromeda Galaxy (M31). Two of these, the Milky Way and the Andromeda Galaxy, are very luminous spiral galaxies.

The Milky Way was formed within 1 billion years of the Big Bang and has a mass of 10^9 solar masses. It formed from a large cloud of hydrogen and helium that was slowly rotating. As the cloud collapsed, conservation of angular momentum required matter near the axis to rotate very fast. As a result it spreads away from the axis and forms a flat spiralled disc some 120 000 ly in diameter and about 3300 ly thick. The Sun is approximately 30 000 ly from the centre. The nuclear bulge at the core of the galaxy contains old stars, and observations suggest that it must be hugely massive. Rapid rotation around the axis of the disc requires gravity and angular momentum, hence mass, to hold it together and this produced speculation about the existence of a black hole at the centre of the Milky Way.

The Sun formed some 4.5 Gyr ago (Gyr is a Gigayear or 10^9 years) from its own gas cloud called the solar nebula, which consisted of mainly hydrogen but also all of the heavier elements that are observed in the spectrum of the Sun. Similarly, the elemental abundance on the Earth and all of the planets was defined by the composition of the solar nebula and so was ultimately responsible for the molecular inventory necessary for life. The solar system formed from a slowly rotating nebula that contracted around the proto-sun, forming the system of planets called the solar system. Astronomers have recently discovered solar systems around other stars and, in only the briefest of looks, this has revealed a large proportion of similar planetary systems; thus the formation of planets around stars is a common process. The distribution of mass in the solar system is primarily within the Sun but distributed rather differently among the planets. The inner planets, the so-called terrestrial planets of Mercury, Earth, Venus and Mars, are essentially rocky but Jupiter, Saturn, Uranus and Neptune are huge gas giants; this needs to be explained by the formation process. Most important, however, is the formation of a planet in a habitable zone, where liquid water can exist and have the potential for life – at least if you follow the terrestrial model.

1.3 Origins of life

The age of the Earth is established by radioisotope dating at 4.55 Gyr and for most of the first billion years it suffered major impact events capable of completely sterilising the Earth and removing any life forms. The geological fossil records reveal, however, that life existed some 3.5 Gyr ago and perhaps as early as 3.9 Gyr ago. The oldest known life forms were very simple by modern standards but already had hugely complicated structures involving membranes and genetic information. The rather surprising conclusion is that life may have developed in as little as one hundred million years and at most 0.5 billion years, to evolve from the primordial soup to a viable living organism that had adapted to its local environment.

Definitions of life

There are many problems with the definitions of life, although determining what is alive and what is not is intuitively easy. At the extremes of collections of matter are the human being and the atom, with all of the possibilities in-between. Classical definitions of life taken from biology, such as ingesting nutrients, excreting by-products, growth and reproduction, all serve as good markers of life although are almost certainly prejudiced by life on Earth. What about fire? A candle flame (Figure 1.1) clearly ingests nutrients from the air in the form of oxygen and fuel from the wax. It produces waste products; it can also grow to cover large areas and certainly looks as if it might reproduce itself by creating new fires through sparks. It is localised by both a temperature and concentration gradient and might indeed be alive. However, one flame does become a copy of itself in that it will burn whatever fuel and oxidant combination available to it. In a sense it evolves and lives for as long as it can adapt to its environment. The adaptation to the environment is seen on the right-hand side of Figure 1.1 where a candle flame is burning under conditions of zero gravity in the space shuttle. The shape of the flame in air is controlled by buoyancy: the hot air inside the candle flame air is less dense than the air around it and it rises. In zero gravity the hot air does not rise because its weight is zero and so the random thermal motion results in diffusion

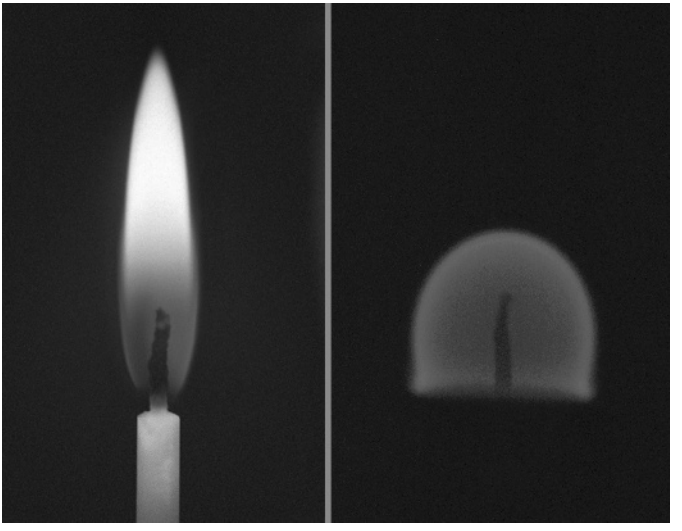

Figure 1.1 Two species of candle flame – dead or alive? The flame on the left is on Earth and the flame on the right is burning under zero gravity. (A colour reproduction of this figure can be seen in the colour section). (Reproduced from photos by courtesy of NASA)

of oxygen into the flame and combustions products away from the flame, hence the flame is now spherical. Even a complex set of chemical reactions, recognisable as a flame, has adapted to the environment. There is a consistent chemistry set within the 350 equations required to get the flame 'metabolism' chemistry to burn properly and as such it contains a recipe or a DNA. Other more impressively vague twilight life forms must include virus particles.

Viruses have no real metabolism and appear to exist in a dormant state until they find a suitable host. Then they hijack the metabolism and DNA replication apparatus of the host cell, switching the host into the production of huge numbers of copied virus particles, including some mutations for good measure. Finally, the cell bursts and the virus particles are released to infect a new host. The propagation of genetic information is important, as is the need for some form of randomisation process in the form of mutations, but it is not clear that there can be one definition for life itself. NASA has chosen the following definition:

> '*Life is a self-sustained chemical system capable of undergoing Darwinian evolution.*'

Alternatively:

> '*A system that is capable of metabolism and propagation of information.*'

Both are flaky, as even the simplest of thought will reveal.

Specialisation and adaptation

Cellular life may have arisen spontaneously, capturing whatever prebiotic debris that was present in the primordial soup. The encapsulation process provided the first specialisation within the environment, leading to compartmentalisation firstly from the external environment and then within the cell to provide areas of the protocell with dedicated adapted function. The external barrier in biology is provided by a cell membrane constructed from a bilayer of phospholipids with added sugars to make it rigid. The phospholipid molecules are amphiphilic, containing a long fatty acid chain of 10–20 carbon atoms at one end that are hydrophobic and a phosphate head group at the other end that is hydrophilic. It is the hydrophobic–hydrophilic characteristic at different ends of the molecule that make it amphiphilic. These molecules spontaneously form vesicles and membranes called liposomes in water when the concentration is above the critical micelle concentration. The network of chemical reactions trapped within a liposome could easily form a proto-metabolism but there is still the need for an information-bearing polymer.

Looking again at biology, genetic information is stored in all organisms as either DNA or RNA. These huge polymeric molecules contain the information for the replication of the building blocks of all organisms, the proteins. The four bases, G, A, T and C, pair together as A–T and G–C, the so-called Watson–Crick base pairs, which together with the deoxyribose sugar and phosphate backbone form the α-helix of the DNA molecule, shown in Figure 1.2.

The order of the bases is important along the length of the DNA and each sequence of three bases, called a triplet, represents the words in the genetic code. Each triplet codes for an amino acid so that AAA is lysine and UGU is cystine with signals for ‘stop’, such as UGA, and ‘start’ (no simple sequence but TATA is a reasonable example) to establish the beginning of a gene. More triplets are used to code for each of the 20 or so amino acids used in living organisms and the order in which they must be put together to form a protein (Figure 1.3). The information coded within the DNA is propagated from generation to generation nearly always correctly but sometimes with mistakes or mutations. Not all mistakes are bad; mistakes that provide an advantage in the local environment are good mistakes and allow evolution. The organism with the good mistake will evolve and adapt better to its surroundings, outgrowing less-well-adapted organisms.

Proteins are constructed from long chains of amino acids linked together by a peptide bond. There are 20 common amino acids that are coded within the genome and they are all of L-optical activity. Optical activity refers to the interaction of molecules with polarised light and divides molecules into three types: those that do not rotate the plane of polarisation of the light; those that rotate the plane of polarisation to the right; and those that rotate the plane of polarisation to the left. The two types of molecules that rotate light are called chiral molecules and those that do not are called achiral. The choice of one set of chiral molecules, called homochirality, over the other set is a marker for biological activity. Although amino acids may be produced in space on the ice mantles of interstellar dust grains, they are thought to be racaemic mixtures, meaning that they have equal quantities of

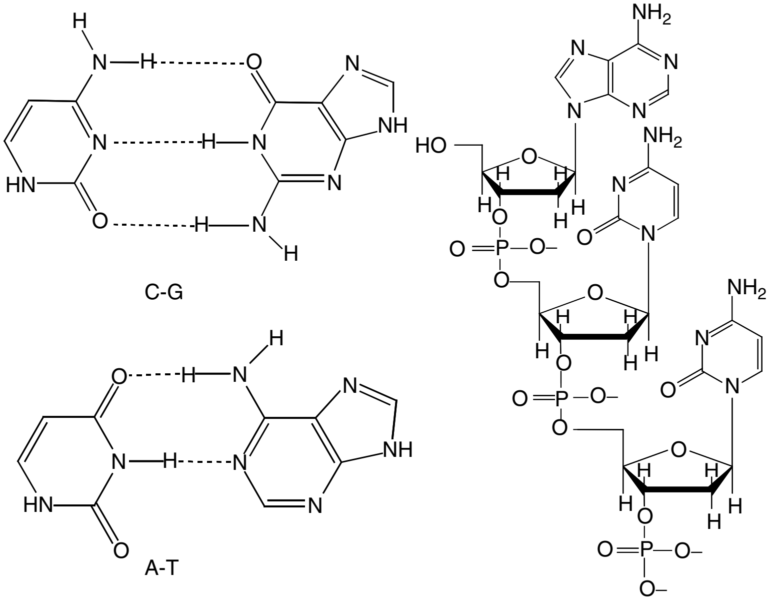

Figure 1.2 Watson–Crick DNA base pairs and the DNA backbone

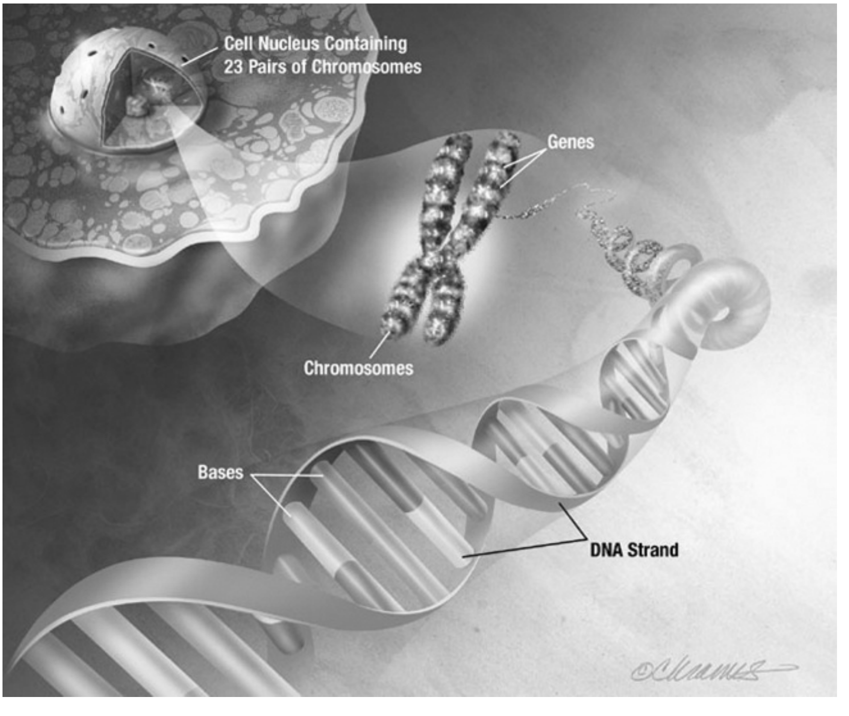

Figure 1.3 The genetic code. (Reproduced from Alzheimer's Disease Education by courtesy of the National Institute on Aging)

the L and D forms of the chiral molecules. Similar optical purity is seen in the bases of DNA and RNA and with biologically active sugars. Curiously, all sugars are D-enantiomers.

The origin of the *homochirality* is not known. There is a tiny energy difference between the optical isomers associated with a 'parity violating energy difference' of order 10^{-15}–10^{-17} J, but in general homochirality will require biological amplification favouring one enantiomer over another, i.e. 'enantiomeric amplification'. It has been suggested recently that organic synthesis in the circularly polarised light field around a star in the interstellar medium or due to chiral-specific surface reactions may also provide a mechanism for enantiomeric amplification and we shall discuss this later. Homochirality is, however, easily achieved by biological systems and may be considered as a *biomarker* – a marker for the existence of life.

It is the variety of life around the edges of the biosphere on Earth that is a testimony to its adaptation and ability to survive in harsh and extreme environments. The bacteria in the hot-water spring shown in Figure 1.4 have adapted to different temperatures and salinities.

Some bacteria require extreme temperatures, e.g. hyperthermophile organisms require hot water to live and will not survive below 90°C. The extremophile bacteria are from a general class of organisms that have adapted and thrive in extreme living conditions found in deep-sea marine environments and deep subsurface colonies. These bacteria may make up most of the collection of biological organisms on Earth that form the biota. The molecular classification of organisms based on the length of the genome suggests that the last common ancestor was a hyperthermophile

Figure 1.4 Hyperthermophile bacteria at Prismatic Lake in Yellowstone National Park. (A colour reproduction of this figure can be seen in the colour section). (Reproduced from a photo of Prismatic Lake by courtesy of National Park Service, Yellow Stone National Park)

bacterium. Far from being descended from the apes, we are actually descended from bugs. Measurements of the survival of bacteria in space suggest that, in the form of spores or dried cells, the survival in space is possible at least for the 6 years that the experiments have been taking place. The transfer of life from planet to planet is then a real possibility. The recent extensive analysis of meteorite ALH84001 suggests that there may be structures within the rock that look like fossil organisms. The meteorite was ejected from the surface of Mars probably by a collision and then made a rapid transit to Earth perhaps as quickly as 60 000 years. This meteorite express-delivery service suggests that not only are we descended from bugs but perhaps even from Martian bugs.

1.4 Other intelligent life

The prospect of intelligent life anywhere in the Universe has been puzzling astronomers and recently astrobiologists, and there have been some attempts to estimate probabilities. This led Drake to construct a now famous equation that collects the ideas together: the Drake equation. It is a mathematical representation of factors relating the probability of finding life and, in particular, an intelligent civilisation elsewhere in the Universe. This is an extreme example of 'hypothesis multiplication' and should be treated with caution. The equation is written:

$$N_c = R_s f_p n f_l f_I f_c L \tag{1.1}$$

where N_c is the number of intelligent civilisations in the Universe with whom we might communicate, R_s is the rate of formation of stars in the galaxy, f_p is the fraction of stars that have planetary systems, n is the average number of habitable planets within a star's planetary system, f_l is the fraction of habitable planets upon which life arises, f_I is the fraction of habitable planets upon which there is intelligent life, f_c is the fraction of civilisations interested in communicating and L is the average lifetime of a civilisation.

The problem comes with assessing the values of the factors to place within the equation and this leads to some very optimistic or pessimistic estimates.

- R_s: There are approximately 10^{11} stars in our galaxy and given that the age of the galaxy is some 10 Gyr the rate of star formation is then approximately 10 stars per year.

- f_p: This could be as large as 0.5 but may be complicated by binary stars and other local factors: pessimistically it is 0.01 and optimistically 0.3–0.5.

- n: Our solar system may have had as many as three habitable planets (Earth, Mars and maybe Venus, at least for a while), however giant planet formation may have removed inner terrestrial-type planets by collision during the formation process: optimistically it is 3, pessimistically 0.01.

- f_l: Is life the product of a collection of simple chemical processes, in which case it should be everywhere, or is it more of a fluke: optimistically it is 1, pessimistically 10^{-6}.

- f_I: Intelligence on Earth took 4.5 Gyr to evolve and many stars do not live this long (dependent on their mass) so they choose some extremes: optimistically it is 0.5 and pessimistically 10^{-6}.

- f_c: If they are like human beings then everybody wants to talk so, lets say, 1.0.

- L: This has been a few tens of years in the case of our civilisation and we may yet destroy ourselves within 10 000 years: optimistically it is 1 billion years and pessimistically 100 years.

Performing the optimistic sum gives $N_c = 5 \times 10^9$ and the pessimistic sum gives $N_c = 10^{-13}$.

The Drake equation is a just a mathematical way of saying 'who knows' but it does allow the factors that might control the origins of life to be identified; that said, it is probably the worst calculation in the book.

1.5 Theories of the origin of life

There is no one correct theory for the origin of life on Earth or any habitable planet, although many have been presented. The current set of ideas is summarised in Figure 1.5. Aside from the theory of creation, which seems particularly hard to test, the testable theories of the origins of life divide into two: *extraterrestrial* or panspermia, the theory that life was seeded everywhere somewhat randomly; and *terrestrial*, that life originated *de novo* on Earth or other habitable planets around other stars. The theories of terrestrial origin are more favoured but the recent discovery of habitable planets and life within any solar system suddenly makes panspermia more likely.

Terrestrial theories divide into an organic or inorganic origin for life. If life started with organic molecules, how were these molecules formed from prebiotic conditions, perhaps in what Darwin called a 'little warm pool' or a primordial soup theory? The endogenous production of organic material provides a continuous link from a prebiotic planet to a complete organism. However, conditions may have been habitable for organic material from outside the planet, exogenous origin, to land on Earth, perhaps delivered by meteorites or comets. The energy source for life could also be organic such as in photosynthesis or inorganic chemistry around hydrothermal vents. Indeed, perhaps inorganic material surfaces catalysed the formation of the first set of self-replicating molecules or a primitive organism called a 'surface metabolite'?

Extraterrestrial theories suggest that life is formed wherever the chemistry will allow the formation of life, either randomly or perhaps directed by some guiding

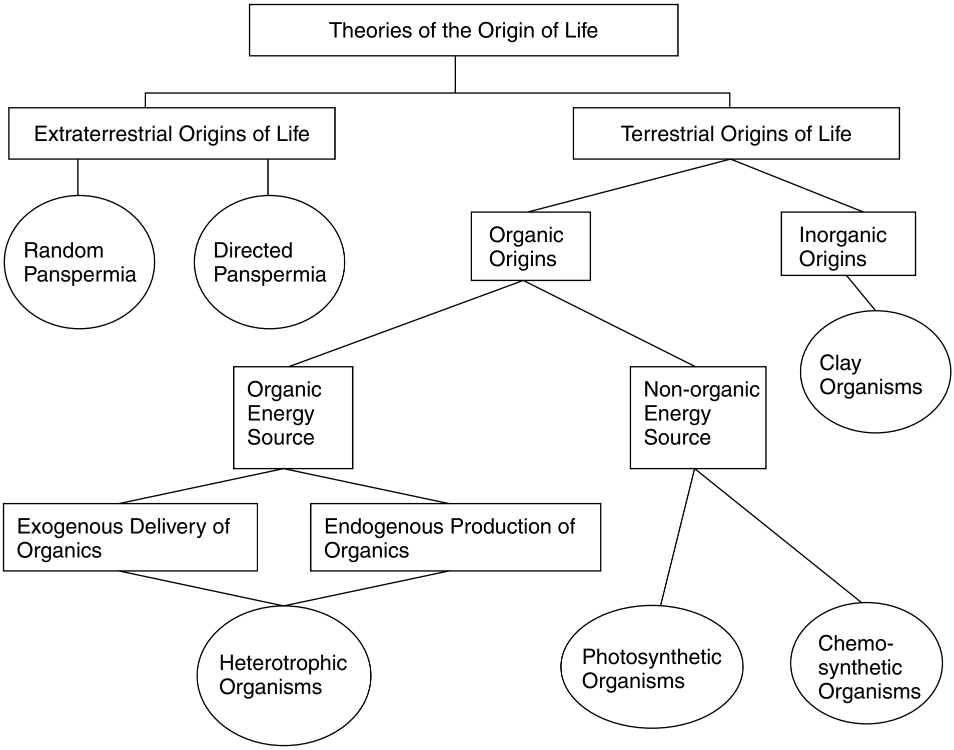

Figure 1.5 Theories of the origins of life. (Reproduced from Davis and McKay 1966 by courtesy of Kluwer Academic Publishers)

force. The discovery of extrasolar planets with a habitable zone that allows liquid water to exist suggests that conditions with the right energy balance and molecular inventory could produce life spontaneously. The idea of a prebiotic planet capable of supporting life must be ubiquitous. The temptation, however, is to assume that what we see today has a direct lineage with the prebiotic Earth or any planet and this cannot be the case. Mass extinction events abound in the fossil record on Earth, not least of which is the famous meteorite impact that killed the dinosaurs, as seen in Figure 1.6. Impacts in the early stages of the formation of the Earth were very common, as is witnessed by the cratering scars on the surface of the Moon. A similar stream of meteorite impacts must also have collided with the Earth and a large meteorite, several kilometres in diameter, certainly impacted on the surface of the Earth near the Yucatan peninsula in Mexico some 65 million years ago. The Chicxulub crater shows an impact large enough to cause global heating of the Earth's atmosphere and vaporisation of some if not all of the oceans, wiping out the dinosaurs and many more apparently evolutionally fragile species on the planet at the time.

Evidence for early collisions is also present in the fossil record, suggesting that the diversity of species present on Earth has been reduced considerably on several occasions, perhaps removing some 90 per cent of species. Some organisms

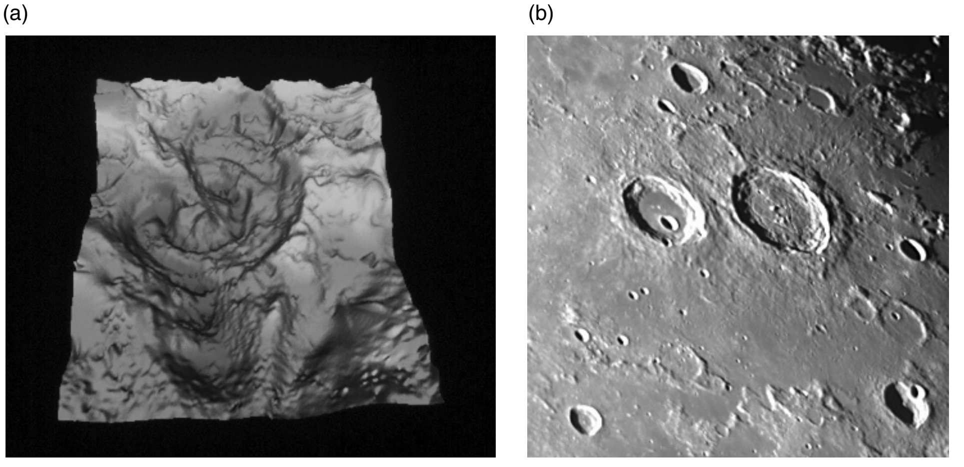

Figure 1.6 Impact frustration: (a) the Chicxulub crater, seen as a three-dimensional gravity map, thought to be responsible for the extinction of the dinosaurs; (b) the cratered surface of the Moon. (Reproduced from photos by courtesy of NASA)

may have survived by collecting biologically active molecules from the debris of other species. Replication and amplification result in the formation of the complex processes of translation and transcription of the genome, synthesis of proteins and the design of cellular metabolism. How modern life evolved may be a very different question to how life occurs spontaneously as a product of prebiotic chemistry and may look very different to the astrobiologist in the field. Astrobiology cannot be limited to the ideas of biology on Earth.

Concepts and calculations

Concepts	
Standard Model	The theory of the origins of the Universe
DNA base pairs	The general structure of the information-bearing molecule used in biology on Earth
Homochirality	The general idea of biomarkers for the existence of life, in this case a preference for one optical isomer over another
Extraterrestrial origins of life	Life was delivered to the Earth (or any planet) by meteorites of cometary material, leading to the idea of panspermia
Terrestrial origins of life	The molecules of life were built on Earth, perhaps in the primordial soup or little warm pool
Impact frustration	A process typified by the extinction of the dinosaurs where the Earth's surface may have been sterilised of all life forms by the impact of a large meteorite or comet
Calculations	
Drake equation	Use of this equation, including estimates of the optimistic and pessimistic calculations, for the existence of other life forms