

## Chapter 2

# The Cosmos, the Solar System and the Primeval Earth

### 2.1 Cosmological Theories

The question of the origin of life on Earth leads directly to the question of the formation of our planet, of the solar system and of the universe. The ancient philosophers, as we have seen, attempted to answer such questions, but the models which we discuss and argue about today were proposed by scientists only in the last century.

Since cosmological theories are not a direct concern of this book, only a brief outline of this area will be given. Two developments in the last century were of particular importance and led to huge advances in knowledge:

Albert Einstein's general relativity theory and  
The discovery of the flight of the galaxies by Edwin Hubble.

The relativity theory, looked at in a very simple manner, is a theory of gravitation which brings together space and time to form one single unified phenomenon. The universe is then no longer a static system, but a dynamic one which is continually expanding. The question then arises as to whether this expansion process will continue infinitely, or whether it can be put into reverse if gravitation forces the system to collapse. This could happen if the density of the matter in the universe were to exceed a certain limiting value.

In 1922, the Russian scientist A. A. Friedman made use of Einstein's equations and concluded that the universe was expanding; the Belgian physicist G. E. Lemaître came to a similar conclusion in 1927. The latter assumed that the universe must have had its origin as an extremely small volume of matter. He invented the idea of the "primeval atom" (*l'atome primitif*). Only two years later, Erwin Hubble discovered the "flight of the galaxies": he compared the positions of the spectral lines originating from certain galaxies with those obtained in laboratory experiments and found that the lines from the galaxies were shifted slightly towards the red end of the spectrum. He interpreted this effect as being due to the galaxies moving away from the Earth and recognized the phenomenon as a Doppler effect. If this motion is calculated in reverse, the result is a very small volume of space in which some type of primeval explosion must have occurred. This process was described in 1955 by the British astronomer Fred Hoyle as the "big bang"; at that time, Hoyle was a convinced proponent of the "steady state hypothesis", which postulated a type of

equilibrium state in which material was continually being formed. Thus there was no “beginning” and no “end”: the universe as a whole remained unchanged.

**Fig. 2.1** George Gamow (1904–1968) was born in Odessa, studied in Leningrad (St. Petersburg) and emigrated in 1934 to the USA, where he taught in Washington, D.C., until 1965 and at the University of Colorado in Boulder for the last three years of his life



Today the “big bang” theory is favoured by most cosmologists. Apart from “Abbé” Lemaître, the man who did the most to popularize it and to formulate its theoretical background was George Gamow. Gamow, a Russian-born scientist living and working in the USA, had forecast the 3K background radiation of the universe.

This radiation amounts to about 400 photons per cubic centimetre and fills the whole universe. The afterglow of the big bang was discovered in 1964 by A. Penzias and W. Wilson as 3K microwave emissions, and in 1978 the two scientists were rewarded with the Nobel Prize for physics. Apart from 3K radiation and red shift, there is a third point which supports the big bang theory: calculations of the amount of helium which must have been formed since the big bang during the cooling of the expanding universe gave a value of 23–24%, which agrees very well with values determined experimentally.

The big bang theory suggests that the formation of the universe took around  $15 \times 10^9$  years. The process started with a state called the “singularity”, i.e., the beginning of time, space and matter. At the beginning of the big bang, there was an extremely hot blazing ball of matter and radiation. The closer one got to time zero, the higher the temperature of this plasma became. In this state, the four fundamental forces (strong and weak atomic forces, electromagnetic force and gravitation) are united: the normal laws of physics no longer apply. Perhaps this state cannot even be described in words. The laws which apply to the explosion itself are also unknown: the extreme values of pressure, temperature, energy and density are unimaginable for us, and no attempt at simplification should be made!

A fraction of a second after the explosion, however, the first structures emerged. Results from particle physics allow us to calculate and predict cosmic processes; we can expect that, within the first second, groups of three quarks united to form protons or neutrons. The temperature fell to around  $10^{10}$  K. The energy density was such that electrons and the corresponding antiparticles, the positrons, could not be formed from photons. Positrons and electrons annihilate each other, and the result is a small excess of electrons. One minute after the explosion, groups of two neutrons and two protons united to form the atomic nucleus  $\text{He}^{2+}$ . After three minutes, the temperature had fallen to  $10^9$  K. At that stage, the expanding universe consisted of about 24% helium and 76% hydrogen nuclei, as well as traces of light elements. Elements with an atomic number higher than helium (known to astronomers as “metals”) were formed in later stages of development of the universe. Further cooling led to the formation of hydrogen and helium atoms (by electron capture) as well as of traces of lithium. This process led to a drastic reduction in the number of free electrons, and the universe became “transparent”, i.e., photons were now able to pass through space without being scattered by free electrons.

After another few hundred million years (some astrophysicists speak of around a billion years), the temperature was around 18 K and then sank further to a value of 3 K (or to be exact,  $2.73 \pm 0.01$  K) (Unsöld and Baschek, 2001).

In a short interview, Larson and Bronn (2002) reported on the latest models, calculations and computer simulations. According to these, the first stars were formed about 100–250 million years after the big bang. They formed small protogalaxies, which were themselves the result of small density fluctuations in the still young universe. Although the universe was generally homogeneous in its early days, slight density fluctuations led to the formation of filament-like structures, similar to those of a network. At the nodes, the material (only hydrogen and helium, no metals) was denser, and the first stars were formed. To quote from the book of Genesis, “And there was light.”

How do these first stars differ from those of today? As we have already mentioned, it is mainly because of their different composition. In addition, calculations show that they must have been much heavier (100–1,000 solar masses) and thus much brighter (up to a million times brighter than our sun).

A further important difference is that the first stars did not live as long, only a few million years. As they consisted only of hydrogen and helium, the energy generation occurred in a different manner than in today’s stars, in which certain elements act as catalysts in nuclear fusion; without these catalysts, the nuclear fusion would be much less efficient. Thus the young stars needed to reach higher temperatures and to be more compact. It is assumed that temperatures around 17 times higher than that of our sun were normal. Some of the early stars exploded, forming supernovas. The heavier metals which were formed during the explosions diffused through space and influenced further developments in the universe, for example the formation of planets.

In recent years, the development of new cosmological models has caused frequent rethinking. The well-known book by Stephen Weinberg *The First 3 Minutes* (1977) gives an account of the initial processes.

James E. Peebles, professor emeritus at Princeton (2001), offers his own description. He states that “at present the house of cosmological theories resembles scaffolding which is solidly assembled but still has large gaps. The open questions are those of ‘dark matter’, ‘inflation’ and ‘quintessence’. We live in exciting times for cosmology.”

**Table 2.1** Grades for cosmological theories (from Peebles, 2001)

Hypothesis	Grade	Remarks
The universe developed from a hot, dense beginning.	<i>Very good</i>	Huge amount of supporting evidence from various areas of biology and physics.
The universe expanded according to the general theory of relativity.	<i>Good</i>	Passes all previous tests, but only a few of these were stringent.
Galaxies consist mainly of dark matter built up from exotic particles.	<i>Satisfactory</i>	Much indirect evidence, but the particles still have to be discovered and alternative theories disproved.
The mass of the universe is in general evenly distributed; it acts as Einstein’s cosmological constant and accelerates expansion.	<i>Poor</i>	Agrees well with most of the recent measurements, but the evidence is still thin, and theoretical problems are still unsolved.
The universe initially went through a phase of rapid expansion, the so-called inflation.	<i>Fail</i>	Elegant theory, but still no evidence; requires huge extension of the laws of physics.

The “quintessence” hypothesis was proposed by J. P. Ostriker and Steinhardt (2001). The authors use the term quintessence (“fifth substance”) to describe a quantum force field which is gravitationally repulsive. It has a certain similarity to an electrical or magnetic field and could lead to an invisible energy field which accelerates cosmic expansion.

The most modern instruments provide ever more exact data on the structure of the cosmos and the possibility of penetrating ever deeper, almost to the boundaries of the universe. Data processing and simulation using high-performance computers increase the possibilities of devising new approaches to the solution of the many still unanswered questions. An attempt to relate the big bang theory to the string theory led American physicists to the model of the “ekpyrotic universe”. According to this hypothesis, the universe was formed in a collision of two three-dimensional worlds (branes) in a space with an extra (fourth) spatial dimension, and *not* via the big bang, the favourite model of many astrophysicists; while the big bang can explain many phenomena of cosmophysics, it cannot answer them all. Some of the basic cosmological questions are still unanswered, as is shown by the most recent research results and by models derived from them, which cast doubt on some of the previous assumptions and hypotheses.

An international research team including many French members has used the analysis of data from NASA's Wilkinson Microwave Anisotropy Probe (WMAP) to devise an amazing new model of our universe. According to this, the cosmos is not infinite and expanding because of pressure from dark energy (the cosmological standard model); instead, it is finite and has an extremely rigid topology, possibly in the form of a Poincaré dodecahedral space (Luminet et al., 2003; Ellis, 2003). There is no doubt that we can expect many new results from cosmophysics in the next few years when the results of future missions have been interpreted.

## 2.2 Formation of the Bioelements

The well-known textbook *General Chemistry* by Atkins and Beran (1992) starts by telling the reader that “the cradle of chemistry lies in the stars.” One can hardly think of a better way of emphasising the role of cosmochemistry. The synthesis of the elements, which are now logically ordered in the periodic table, can be divided into three stages, which are separated in both time and space:

The synthesis of the light elements hydrogen, helium and lithium (including their isotopes), which occurred just after the big bang;

The synthesis of the intermediate elements, which were formed in various “burning processes” and

The synthesis of the heavy elements in supernova explosions.

The temperature of the universe about three minutes after the big bang was around a billion degrees. On further cooling, tritium ( $^3\text{H}$ ) and the helium isotopes  $^3\text{He}$  and  $^4\text{He}$  remained stable. Heavier elements could not be formed because of the low concentration of deuterium: the  $^2\text{H}$  nuclei decomposed rapidly (Weinberg, 1977). Further expansion, and thus further cooling, led to a change in the behaviour of the deuterium nuclei, and in this phase, they became stable, while their concentration, however, remained low. The universe was composed of about 24% helium at that time. About 300,000 years after the big bang, the temperature was low enough to permit electrons and nuclei to unite to form atoms. Later, concentrations of matter took place at some points in the universe, and the first stars were formed. The complex processes occurring in those stars led to the synthesis of heavier chemical elements. Exactly which elements were formed depended to a large extent on the mass of the stars, which is generally referenced in publications to the mass of our own sun; thus we speak of “solar masses” as the unit. The reactions taking place in the interior of the stars are referred to pictorially as “burning”.

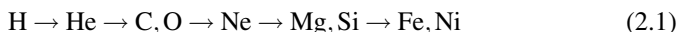
Table 2.2 lists the most important syntheses occurring in the stars. The main products include the bioelements C, O, N and S. The synthesis of the elements began in the initial phase after the big bang, with that of the proton and the helium nucleus. These continue to be formed in the further development of the stars. The stable nuclide  $^4\text{He}$  was the starting material for subsequent nuclear syntheses. Carbon-12 can be formed in a triple  $\alpha$ -process, i.e., one in which three helium

nuclei collide. However, such processes occur relatively seldom, while E. Salpeter (Cornell University) showed that a two-step reaction should be more easily realisable. A collision of two helium nuclei leads to the formation of a beryllium nucleus, which decomposes very rapidly to the starting materials unless it is hit by a further helium nucleus; the newly-formed nucleus  $^{12}\text{C}$  is stabilized by radiation emission. The lifetime of the beryllium nucleus is only about 0.05 s (Hillebrand and Ober, 1982); thus, the density of the helium nuclei must be very high in order to give a high collision probability.

**Table 2.2** The pre-supernova burning stages of a star with 25 solar masses. From: Macià et al. (1997)

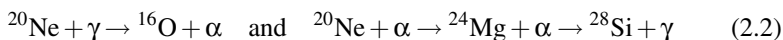
Burning process	$T$ (in $10^9$ K)	Main products	Time taken
H	0.02	$^4\text{He}$ , $^{14}\text{N}$	$7 \times 10^6$ years
He	0.2	$^{12}\text{C}$ , $^{16}\text{O}$ , $^{20}\text{Ne}$	$5 \times 10^5$ years
C	0.8	$^{20}\text{Ne}$ , $^{23}\text{Na}$ , $^{24}\text{Mg}$	$6 \times 10^2$ years
Ne	1.5	$^{16}\text{O}$ , $^{24}\text{Mg}$ , $^{28}\text{Si}$	1 year
O	2.0	$^{28}\text{Si}$ , $^{32}\text{S}$ , $^{40}\text{Ca}$	180 days
Si and $e^-$ process	3.5+	$^{54}\text{Fe}$ , $^{56}\text{Ni}$ , $^{52}\text{Cr}$	1 day

Further capture of  $\alpha$ -particles leads to the formation of oxygen and neon.  $^{16}\text{O}$  itself forms the basis for the synthesis of sulphur. The only biogenic element missing in Table 2.2 is phosphorus, which is an exception in that it is formed by a complex nuclear synthesis (Macià et al., 1997). In large stars, the reactions listed in the table take place in the following series, without stopping but over long periods of time.



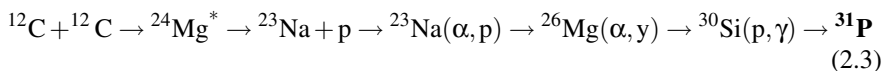
The result is a type of onion-like model of the star with an iron–nickel core in the centre. The situation is somewhat different for smaller stars: the path branches at the point where “carbon burning” ( $^{12}\text{C} + ^{12}\text{C}$ ) begins. While the heavier stars are not affected by this process, the smaller ones (4–8 solar masses) are completely torn apart by carbon burning.

In the heavier stars, a stage in which  $^{20}\text{Ne}$  is destroyed occurs subsequently to the carbon burning, but before the absorption of oxygen. The  $\alpha$ -particles formed are used up by the nuclei already present (also from neon itself) in so-called neon burning.



These reactions take place in the inner zone of stars heavier than 15 solar masses. Hydrostatic carbon burning is followed by explosive neon burning at temperatures of around  $2.5 \times 10^9$  K. Under these conditions, phosphorus ( $^{31}\text{P}$ ) can be formed, although complex side reactions also occur. In comparison with the formation of

the other five biogenic elements, the synthetic pathways which lead to phosphorus appear quite involved (Macià et al., 1997).  $^{31}\text{P}$  nuclei can be formed only in those classes of stars which, because of their mass, are able to carry out carbon and nickel burning. Some of the nuclear reaction pathways occur in only very low yields (around 2.5%), which explains the relatively low proportion of this important bioelement. The largest amount of the natural  $^{31}\text{P}$  nuclide is probably formed via the following reaction pathways:



The reaction of  $^{24}\text{Mg}^*$  to give  $^{23}\text{Na}$  takes place in around 50% yield, with the following reaction only in 5% yield. A large part of the  $^{31}\text{P}$  is destroyed by the reaction  $^{31}\text{P}(\text{p}, \alpha) \rightarrow ^{28}\text{Si}$ . More details of phosphorus synthesis and that of its compounds can be found in Macià et al. (1997) and Macià (2005).

## 2.3 The Formation of the Solar System

Two types of theory have been put forward to explain the formation and development of our solar system: catastrophe and evolution. The former assumes a collision or coming together of two stars. As early as 1745, the French scientist Count Buffon postulated that the Earth had been torn out of the sun by a passing comet. He estimated the age of the Earth to be 70,000 years, while theology proclaimed that the Earth was less than 6,000 years old.

It is generally accepted today that our solar system was formed in evolution processes. René Descartes (1596–1650) suggested that the solar system was formed from a gigantic whirlpool within a universal fluid and that eddies in the flow produced planets; his theory tried to explain both the formation of the sun and the motions of the planets. More than a hundred years later, the “Kant–Laplace nebular hypothesis” was put forward; this theory was much closer to modern ideas on the origin of the solar system and was due to the philosopher Immanuel Kant (1724–1804) (who was born in Königsberg/Kaliningrad) and Pierre Simon, Marquis de Laplace (1749–1827). Kant’s work “Universal Natural History and Theory of Heaven” appeared in 1755. Kant and Laplace developed their theories independently of each other, Kant describing his ideas about 40 years earlier than Laplace. Both hypotheses share the postulate that slightly denser regions of the gas-filled universe contracted more and more under the influence of gravitation (Neukum, 1987). However, the Laplace hypothesis, formulated as it is in terms of mathematical formulae, has certain weaknesses which led others to propose new catastrophe scenarios. There are indeed basic differences between the two approaches. Kant postulates a rotating primeval nebula, which forms a group of clouds. These in turn become planets as the result of further density increases, while the rest of the

nebula condenses to form the sun. Laplace, however, postulates a hot rotating gas disc, which shrinks on cooling. The disc spins very fast and casts off rings of gas, which form the planets, with the remaining matter forming the sun (Struve and Zebergs, 1962).

The process in which the solar system was formed was certainly extremely complex, so there is as yet no generally accepted theory to describe it. The different types of heavenly body (sun, planets, satellites, comets, asteroids) have very different characteristics which need to be explained using mechanisms which are valid for them all.

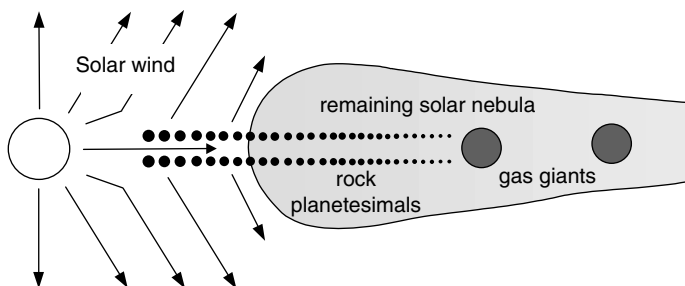
According to present-day concepts, our solar system was formed from a huge gas–dust cloud several light years across in a side arm of the Milky Way. The particle density of this interstellar material was very low, perhaps  $10^8$ – $10^{10}$  particles or molecules per cubic metre, i.e., it formed a vacuum so extreme that it can still not be achieved in the laboratory. The material consisted mainly of hydrogen and helium with traces of other elements. The temperature of the system has been estimated as 15 K.

An unknown event disturbed the equilibrium of the interstellar cloud, and it collapsed. This process may have been caused by shock waves from a supernova explosion, or by a density wave of a spiral arm of the galaxy. The gas molecules and the particles were compressed, and with increasing compression, both temperature and pressure increased. It is possible that the centrifugal forces due to the rotation of the system prevented a spherical contraction. The result was a relatively flat, rotating disc of matter, in the centre of which was the primeval sun. Analogues of the early solar system, i.e., protoplanetary discs, have been identified from the radiation emitted by T Tauri stars (Koerner, 1997).

More than 99% of the total mass of the whole system was present in the proto-sun. The formation of this disc is demonstrated by the coplanar movement of the planets and by the fact that they all rotate in the same direction around the sun. The increasingly concentrated matter in the primeval sun influenced the rotating disc of matter so that its diameter decreased and the rate of rotation of the whole system increased.

We can assume that the primeval sun rotated much faster than the present-day one and thus had a very high angular momentum. Today, however, the sun accounts for only around 0.5% of the total angular momentum of our solar system. How can we explain the discrepancy between the mass of the sun (around 99.8% of the total mass of the solar system) and its angular momentum? The “angular momentum problem” can be explained on the basis of magnetic interactions between the sun and the rotating disc of matter, which is made up of charged particles (ions and electrons). Lüst and Schlüter suggest a possible mechanism in the form of coupling between the interplanetary plasma and the sun, as in an eddy-current brake. Since (according to the law of conservation of energy) angular momentum cannot be destroyed, the sun must have given up a large part of its angular momentum to the rotating interplanetary disc, and thus to the planets which were slowly being formed.





**Fig. 2.2** The state of the incipient solar system during the T Tauri phase of the young sun. The central region around the sun was “blown free” from the primeval dust cloud. Behind the shock front is the disc with the remaining solar nebula, which contained the matter formed by the influence of the solar wind on the primeval solar nebula. From Gaffey (1997)

The young sun went through the “T Tauri phase”, in which huge streams of hot gas were blown off into space. This is an unstable phase in a star’s development and must have lasted for  $10^5$ – $10^8$  years, depending on the mass of the star. The velocity of the gas streams may have been up to 200–300 km/s. Immense amounts of material were blown out into the outer regions of the gas–dust disc, i.e., into the regions where the larger planets were later formed. In the region of the terrestrial planets, there must have been enough of the heavier elements present to withstand the solar wind, in spite of the higher temperatures and the nearness to the sun. The energy for the T Tauri phase probably came from the fusion reactions (conversion of hydrogen into helium) occurring in the sun’s interior. At this point, the sun’s atmosphere must have radiated at a temperature of between 10,000 and 100,000 degrees and emitted a vast amount of UV light. The primeval nebular disc was characterized by enormous temperature differences, depending on the distance from the sun. Its density was probably greater in the neighbourhood of the sun than in the distant regions.

Tiny microparticles came together to form microagglomerates, and these in turn formed larger clots, which then formed larger bodies, the diameter of which was initially measured in centimetres but later increased to metres: such planetary building blocks are known as “planetesimals”. Computer simulations indicate that these existed around four and a half billion years ago (Wetherhill, 1981). Planetesimals grew to form bodies which were several kilometres across, and there were often collisions in which larger bodies were swallowed up by smaller ones: a process which is not unknown in modern economics!

In the region of the terrestrial planets, there may have been several thousand planetesimals of up to several hundred kilometres in diameter. During about ten million years, these united to form the four planets—Mercury, Venus, Earth and Mars—which are close to the sun. Far outside the orbit of the planet Mars, the heavier planets were formed, in particular Jupiter and Saturn, the huge masses of which attracted all the hydrogen and helium around them. Apart from their cores, these planets have a similar composition to that of the sun. Between the planets Mars and Jupiter, there is a large zone which should really contain another planet. It

seems clear that the huge mass of Jupiter prevented the formation of a planet from the planetesimals, which already had diameters measured in kilometres. Thus, in this part of the solar system, we find only asteroids orbiting the sun. It has been estimated that the asteroid belt contains around 50,000 objects, only about 10% of which have so far been identified; asteroids can measure up to 900 km in diameter. The total mass of the asteroids is smaller than that of the Earth's moon. The three largest, Ceres, Pallas and Vesta, with diameters of 933, 523 and 501 kilometres, account for half the total mass of the asteroids.

Binzel et al. (1991) give an account of the origin and the development of the asteroids, while Gehrels (1996) discusses the possibility that they may pose a threat to the Earth. The giant planets, and in particular Jupiter, caused a great proportion of the asteroids to be catapulted out of the solar system: these can be found in a region well outside the solar system, which is named the "Oort cloud" after its discoverer, Jan Hendrik Oort (1900–1992). The diameter of the cloud has been estimated as around 100,000 AU (astronomic units: one AU equals the distance between the Earth and the sun, i.e., 150 million kilometres), and it contains up to  $10^{12}$  comets. Their total mass has been estimated to be around 50 times that of the Earth (Unsöld and Baschek, 2001).

Oort was able to show that the gravitational force of the sun in these regions is so weak that passing stars can cause great changes in the orbits of the Oort comets; they can either be steered into interstellar space, or their elongated ellipsoid orbits can bring them into the solar system (Weissman, 1998). The Oort cloud is regarded as a type of "refrigerator" for active, long-period comets. The short-period comets, however, seem to come from a region of the solar system known as the Kuiper belt, which lies beyond the orbits of Neptune and Pluto. As early as 1951, the Dutch astronomer Gerald Peter Kuiper (1905–1973) proposed that the outermost region of the solar system contained a collection of primeval material; the matter in the Kuiper belt probably derives from the period in which our solar system was formed. More than 30 smaller objects with diameters between 100 and 500 km have so far been discovered (Luu and Jewitt, 1996).

## 2.4 The Formation of the Earth

The early stages of the formation of the Earth are relatively closely linked to that of the formation of the other three terrestrial planets. Their nearness to the sun meant that light gases such as hydrogen, helium, methane and ammonia could not be held back by the protoplanets but were blown away by the solar wind and the sun's heat. Liquids such as water could not condense and went the same way as the gases. Thus, a type of fractionation occurred in the young solar system: a large proportion of the substances with high vaporisation temperatures, such as metals and silicates, remained close to the sun (Press and Siever, 1994). Elements with higher atomic numbers were not the result of processes occurring in the sun, but were derived from the interstellar cloud from which the solar system had been formed.

Because of their similar history, the four terrestrial planets have similar layer structures. However, their surfaces and atmospheres show enormous physical and chemical differences. The development of the primeval Earth via the agglomeration of planetesimals was accompanied by a vast temperature increase caused by contributions from three different phenomena:

- The energy set free by collisions with planetesimals,
- The Earth's gravitation and
- The radioactivity of the planet's interior.

The kinetic energy set free in collisions with planetesimals was proportional to the square of the velocity of the body which hit the Earth. Thus, if a planetesimal hit the Earth's surface with a velocity of 11 km/s, the amount of energy set free would correspond to the explosion of the corresponding amount of the explosive TNT (trinitrotoluene). The increased compression due to the increase in mass led to pressure increases in the interior of the planet and thus to temperature increases up to around 1,270 K (Press and Siever, 1994).

It has been estimated that the radioactive decay of the various elements provided enough heat to cause temperature increases up to 2,300 K: the long-lived radioactive isotopes  $^{235}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  still heat up the Earth's interior today. However, this energy alone was not sufficient to melt the primeval Earth. The energy set free when the denser, heavier elements (such as iron and nickel) melted and concentrated at the centre of the Earth provided an additional heat source, and gravitational energy was set free in this process. The time required for the formation of the planets depended to a large extent on their mass. It has been suggested that it took 100–200 million years for the terrestrial planets to accrete, while the giant planets probably required about a billion years.

The melting process and the differentiation of the Earth's matter according to its density caused the lighter crust minerals to migrate to the outer layers of the still young Earth, whose surface temperature at that time was such that it was covered by a sea of melted rock (Wills and Bada, 2000). This separation of materials led to the layer structure of the Earth:

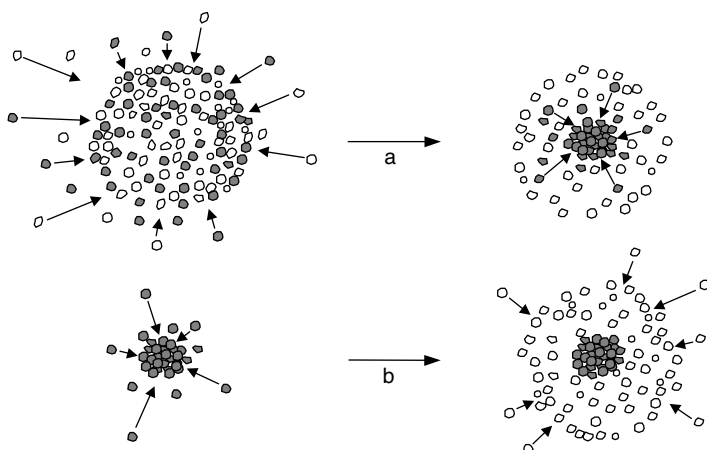
- The crust,
- The mantle (upper and lower mantle) and
- The core (outer and inner core).

The formation of the core, the mantle and the crust can be explained using two basically different accretion models:

- Homogeneous accretion and
- Heterogeneous (inhomogeneous) accretion.

According to the *homogeneous* model, the metal-containing materials (in particular iron and nickel) and the silicate-containing material of the primeval solar cloud condensed out at about the same time. The proto-Earth thus formed was composed of a mixture of these two types of matter, which differed greatly in their densities. At that time, the Earth's temperature was probably only a few hundred degrees, and

its composition corresponded roughly to that of the carbonaceous chondrites (see Sect. 3.3.2). Only later did the metals concentrate at the centre of the proto-Earth as described above.



**Fig. 2.3** According to the *homogeneous* accretion model (a), iron-containing material (black) and silicate-containing material (colorless) condensed out at the same time, i.e., the proto-Earth consisted of a mixture of the two. The concentration of iron in the Earth's core took place later. According to the *heterogeneous* model (b), the iron condensed out of the primeval solar nebula first, while the silicates later formed a crust around the heavy core. From Jeanloz (1983)

In the *heterogeneous* model, the metals condensed first and formed the core, while the silicates, which condensed later, formed an outer layer—the mantle.

Of the two models, homogeneous accretion is generally favoured. H. Wancke from the Max Planck Institute in Mainz (1986) described a variant of this model, in which the terrestrial planets were formed from two different components. Component A was highly reduced, containing elements with metallic character (such as Fe, Co, Ni, W) but poor in volatile and partially volatile elements. Component B was completely oxidized and contained elements with metallic character as their oxides, as well as a relatively high proportion of volatile elements and water. For the Earth, the ratio A:B is calculated to be 85:15, while for Mars it is 60:40. According to this model, component B (and thus water) only arrived on Earth towards the end of the accretion phase, i.e., after the formation of the core. This means that only some of the water was able to react with the metallic fraction.

The chemical composition of the Earth's interior determined the character (the oxidation state) of the primeval atmosphere. If metallic iron had collected in the Earth's core in the early phase of the accretion, the exhalations from the interior of the Earth would have consisted mainly of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , since the gas from the interior could only have come into contact with  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  silicates in the mantle. If, however, metallic iron had been distributed throughout the mantle, the iron and the  $\text{FeO}$  silicates would have had a reductive influence on the gases: the gas exhaled into the atmosphere would then have consisted of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{NH}_3$  (Whittet, 1997).

The thin, newly formed Earth's crust, consisting of light silicates, swam on the surface of the sea of magma. It was often broken apart by collision with planetesimals of various sizes. The formation of the crust was a complex process, many details of which are as yet not understood. This admission points to the fact that we do not have much geological evidence from this early phase of the Earth's formation.

A vital event in the further development of the Earth was its collision with a smaller planet, possibly as big as Mars. It is assumed that this gigantic collision took place between four and four and a half billion years ago (Sleep et al., 2001), and that it also resulted in the birth of our moon (Luna), which was formed from partially vaporized matter from the Earth. It is likely that not all of the proto-Earth was melted by the energy set free in the collision, but that sections of it remained in their original form. However, more exact information is not yet available.

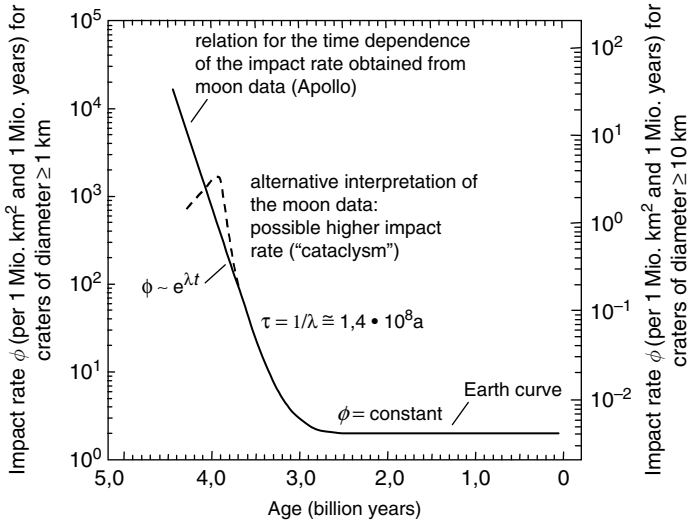
A corroboration of the theory that the moon was formed mostly from material coming from the Earth is due to researchers from the Max Planck Institute for chemistry in Mainz (Münker et al., 2003). The chemical analysis of material from the surface of the moon shows great similarity with material from the Earth's crust; however, there are certain differences. For example, the concentration of iron on the moon is much lower than that on Earth.

The two rare earth elements niobium (Nb) and tantalum (Ta) were the main subject of study in the investigation referred to. Both elements have very similar properties and almost always occur together in our solar system. However, the silicate crust of the Earth contains around 30% less niobium (compared to its "sister" tantalum). Where are the missing 30% of niobium? They must be in the Earth's FeNi core. It is known that the metallic core can only take up niobium under huge pressures, and the conditions necessary for this may have been present on Earth. Analyses of meteorites from the asteroid belt and from Mars show that these do not have a niobium deficit.

A similar niobium deficit to that on Earth was found on the moon, although the latter's lower mass would preclude the existence of pressures high enough to lead to an absorption of niobium by the FeNi core. It is thus very likely that the moon was formed from material derived from the heavenly body which collided with the Earth and from the proto-Earth's silicate-rich crust around 4.4 billion years ago.

The earlier assumption that Luna was a body which had been captured by the Earth can now be regarded as relatively unlikely. The same is true for the "double planet hypothesis", according to which Luna and the Earth were formed at the same time from condensing primordial matter (Taylor, 1994). There are, however, still disagreements on the point in time at which the collision occurred and on the masses and the physical states of the heavenly bodies involved (Halliday and Drake, 1999).

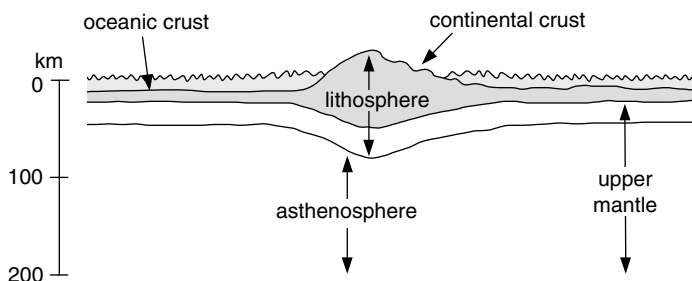
An evaluation of the number of moon craters per unit area (differentiated according to the diameter of the craters) as a function of the time at which the collisions leading to their formation occurred indicates that the processes involved were similar to those which could have occurred on Earth. It is likely that the bombardment reached a maximum around four billion years ago and dropped after about another billion years to the present rate of collision (Neukum, 1987).



**Fig. 2.4** Time dependence of the rate of impact of comets and asteroids on the surface of the Earth and primeval Earth (derived from Apollo moon data). With kind permission of Prof. Neukum (1987)

There are still great uncertainties as to the time frame in which the Earth's cooling occurred, and thus as to the formation of the Earth's crust and the continents. N. H. Sleep et al. from the Department of Geophysics at Stanford University and from NASA's Ames Research Center listed those factors involved in the cooling process, which should be taken into account. They concluded that temperatures at the primeval Earth's surface in the range 333–383K were present for only a relatively short time; in geological terms, "short" means several million years (perhaps as little as one million years). This temperature range is exactly that in which thermophilic microorganisms can exist. Since the composition of the primeval atmosphere, and thus the magnitude of the CO<sub>2</sub> greenhouse effect, is not known, the time available for the formation of the first continents is also unclear. Initial answers to the question of the size and nature of the early continents can be obtained by measurements on isotopes with long half-lives, such as the neodymium isotope <sup>143</sup>Nd. This is a product of decomposition of the radioactive isotope samarium-147 (Hofmann, 1997).

Many properties and characteristics of the Earth are determined by plate tectonics, according to the theory of which the lithosphere is not a closed shell; instead it consists of about a dozen large, rigid plates. These are constantly in motion—on a geological timescale. Each of the plates moves as an independent unit and "swims" on the softer, but more dense, asthenosphere (Press and Siever, 1995).



**Fig. 2.5** The outer shell of the Earth, the lithosphere, is a solid, rigid layer. It consists of the crust and the outer parts of the mantle. The lithosphere swims on the flexible, partially melted part of the mantle (the asthenosphere). Figure simplified after Press and Siever (1994). With permission of W. H. Freeman and Company, New York

The thickness of the Earth's continental crust is only about five thousandths of its radius. The crust and the oceans together make up only about 0.4% of the total mass of the Earth. The two magmatic minerals, basalt and granite, are present mainly as the material of the ocean floor (basalt) or the continental plates (granite). The latter (with an average density of  $2,700 \text{ kg/m}^3$ ) is the much older material. Thus, some types of granite are up to 3.8 billion years old and have in that time never undergone fusion; the basalts, however, have probably been through several fusion cycles due to subduction.

## 2.5 The Primeval Earth Atmosphere

All the models of the chemical composition of the atmosphere of primeval Earth are hypothetical. Samples from this period of development of the Earth are not available! And the oldest rocks give us only a limited amount of information.

"The chemical composition of the primeval atmosphere is a central point of argument in the debate on the formation of life." This short remark made by M. Gaffey (1997) from Rensselaer Polytechnic Institute, Troy, New York, hit the nail on the head, and nothing has changed since!

However, we need information on the atmospheric composition in order to plan and carry out simulation experiments. Although the four terrestrial planets originated from the same solar matter, their atmospheres are completely different. This is due to:

- The strengths of their gravitational fields,
- Their distances from the sun,
- Their ability to reflect solar radiation (albedo) and
- In a later phase of development, the existence or non-existence of life.

Among the terrestrial planets, the situation of the Earth is special. Its atmosphere (around 21% oxygen and 78% nitrogen by volume) is completely different from

those of its neighbours. Venus and Mars have atmospheres consisting almost solely of  $\text{CO}_2$  (around 95% by volume) but with very different partial pressures. In the case of nitrogen content, the Earth has only one primordial “relative” in the whole solar system: Saturn’s moon Titan, with its thick nitrogen envelope (see Sect. 3.1.6). Since its formation, the atmosphere of the Earth has changed its composition drastically several times. Only traces of the components of the primordial solar nebula have been found. It is likely that cosmic material had already undergone segregation before its aggregation to form the planets (Schidlowski, 1980). The present low concentration of the noble gases on Earth indicates that only between  $10^{-7}$  and  $10^{-11}$  of the primordial noble gases remain. The elements helium, neon and argon are among the most common in the universe. Their rarity on the Earth, and their low chemical reactivity, were the reasons for their late discovery, only about 110 years ago. The noble gases have two very different origins:

Radioactive decomposition of labile elements (such as uranium, thorium or potassium) and

Synthesis during nuclear processes occurring in the interior of the sun.

Only the lightest gases, such as hydrogen and helium, could easily escape the gravitational field of the Earth. In contrast to earlier assumptions, it is now believed that the young Earth probably had either no atmosphere at all or only a very thin one, since the proportion of the primeval solar nebula from which the terrestrial planets were formed consisted mainly of non-volatile substances.

About 50 years ago, it was thought that the primordial Earth must have been surrounded by an envelope with the composition of the primeval solar nebula. The gas masses around the giant planets Jupiter and Saturn with their strongly reducing atmospheres of hydrogen, (helium), methane, ammonia and water were considered to be the models. This idea, of which Oparin and Urey were the main proponents, is still around today, although in a much modified form. It appears certain that the primeval atmosphere contained no oxygen. The thesis of a strongly reducing primeval atmosphere was strongly supported by the sensational experiments carried out by Miller and Urey (1953) (see Sect. 4.1). However, two years earlier, the American geochemist William Rubrey (1951) had suggested that volcanic exhalations, with their high concentration of  $\text{CO}_2$ , were the main source of the gases of the primeval atmosphere. The Miller/Urey experiments were followed by other successful syntheses under strongly reducing atmospheric conditions, so that Rubrey’s postulate was initially ignored. However, doubts soon arose, due to two points:

Because of its low mass, the Earth was (and is) unable to retain large amounts of hydrogen and

The volcanic exhalations of today consist mainly of water and  $\text{CO}_2$ . There are good geological, geochemical and geophysical grounds for the assumption that today’s exhalations are not much different than those produced around four billion years ago. However, we must assume that at that time there was very much more volcanic activity than today.



If the primeval Earth's atmosphere was indeed formed only from volatile components emitted by the primitive, newly formed Earth's crust, its composition must have depended on the time at which it was formed, i.e., whether this was before or after the formation of the iron-rich Earth's core (Joyce, 1989):

Gas emission *before* core formation: contact with metallic iron leads to a strongly reducing atmosphere containing only  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}$ .

Gas emission *after* core formation: the redox state in the iron-containing minerals of the Earth's crust is determined by the ratio of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

The result would then be a weakly reducing atmosphere containing  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CO}$ , but *almost no*  $\text{CH}_4$ ! In addition, strongly reducing molecules such as  $\text{CH}_4$  and  $\text{NH}_3$  would have been relatively quickly decimated by photodecomposition (Owen, 1979).

According to James F. Kastings (1993) from the Institute of Geosciences at Pennsylvania State University, an expert on this problem, reducing gases could only have been set free if the tendency for oxygen release from the  $\text{CH}_4$  and  $\text{NH}_3$  dissolved in erupting magma had been several orders of magnitude lower. It has also been suggested that  $\text{CH}_4$  and  $\text{NH}_3$  could have been transported to the primeval Earth by comets and meteorites. The photochemical reduction of  $\text{CO}_2$  in the presence of  $\text{Fe}^{2+}$  has also been discussed. A tragic natural catastrophe which occurred some years ago shows that  $\text{CO}_2$  escapes from the Earth's crust in large amounts even today. Lake Nyos, a lake in Cameroon, occupies the crater of an extinct volcano. A gas cloud which suddenly erupted from the lake (its volume has been estimated as around one cubic kilometre) flowed over the edge of the crater and down the mountain, killing 1,700 people and 3,000 animals (Decker, 1997).

H. D. Holland (1984) estimated the average ratios of the content of volcanic exhalations as follows:  $\text{H}_2/\text{H}_2\text{O} = 0.01$  and  $\text{CO}/\text{CO}_2 = 0.03$ . Nitrogen is very difficult to detect, and only traces of ammonia are found. In addition, highly variable amounts of the following are present:  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , elementary sulphur,  $\text{HCl}$  and  $\text{B}_2\text{O}_3$ . Small amounts of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{HF}$  have been detected. As early as 1962, Holland suggested that the primeval atmosphere must have gone through two stages:

A highly reduced state, which was characterized by gases which were in equilibrium with metallic iron and

A more oxidized state, in which the gases found today in volcanic exhalations were present.

This initial hypothesis was later revised, since some researchers (such as Walker et al., 1983) were able to show that, according to the model of inhomogeneous accretion, metallic iron was removed from the Earth's crust in a very early phase and accumulated in the core. These results led to the now generally accepted theory that the young Earth was surrounded by a weakly reducing atmosphere.

The  $\text{CO}_2$  content of the planetary atmosphere plays a vital role. A relatively high  $\text{CO}_2$  partial pressure was certainly an important precondition for solving the problem of the "faint, young sun". It is assumed that the sun was much cooler four billion

years ago than it is today, as first suggested by Sagan and Mullen (1972). Theories on the structures and development of the stars show that the radiation intensity of the sun has increased by 25–30% in the course of the history of the solar system. According to Gough (1984), the sun was colder because of the lower He/H ratio in the sun's nucleus. In general, the surface temperature of a planet depends on three factors:

The radiation energy emitted by the sun.

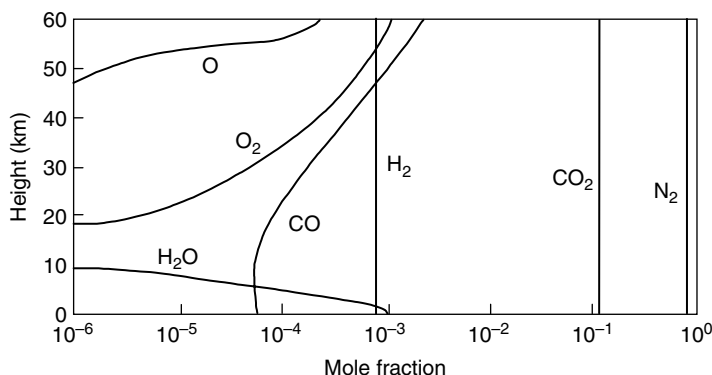
The fraction of the sun's energy which is reflected back into space (albedo); the non-reflected energy maintains the temperature of the atmosphere and the surface.

The "greenhouse effect" of the atmosphere: a fraction of the infrared radiation is emitted from the surface, absorbed by the atmosphere and reflected back to the surface.

If we assume a radiation loss of the sun of 25–30% in comparison with today's values, the primeval Earth would have had a surface temperature below the freezing point of water (provided that all other factors which influence the surface temperature remained basically unchanged).

Geological proof that liquid water was prevalent on the primeval Earth's surface is provided by sedimentary rocks, whose age has been shown to be greater than 3.8 billion years, as well as by stromatolite-forming bacteria which have been dated to 3.5 million years ago. It appears hardly possible that these could have existed on an ice-covered Earth's surface. Another indication of the presence of liquid water has apparently been found by Stephan Mojzsis and co-workers (University of California at Los Angeles), who found an enrichment of the oxygen isotope  $^{18}\text{O}$  in zirconia crystals which are between 3.9 and 4.28 billion years old. This leads to the assumption that the zirconia ( $\text{ZrSO}_4$ ) crystallized from molten rock which was in contact with water (Mojzsis et al., 2001). If the cool young sun did not go through an albedo catastrophe, the presence of a larger greenhouse effect than that present on Earth today must be assumed.

Sagan and Mullen (1972) showed that water vapour alone cannot be responsible for the required greenhouse effect. Ammonia, a photochemically unstable compound, cannot have served as an additional component; it is also not found in abiotic sources. Carl Sagan and Christian Chyba (1997) suggested the following: an atmospheric distribution ratio of around  $10^{-5\pm 1}$  for ammonia could have been enough to compensate for the heat deficit of the weak, young sun. Perhaps organic molecules in aerosols in the higher layers of the atmosphere absorbed the UV irradiation from the sun. According to Owen and Cess (1979), carbon dioxide and water sufficed to solve the problem of the weak, young sun, if it is assumed that the  $\text{CO}_2$  concentration in the primeval atmosphere was 100–1,000 times higher than today. Since  $\text{CO}_2$  and water are still the major exhalation products of active volcanoes, this assumption appears justified. If the Earth had been tectonically more active, a higher  $\text{CO}_2$  output would have been expected. The bioelement nitrogen probably remained in the atmosphere, as an inert element, during the whole history of the Earth.



**Fig. 2.6** The main components of a typical weakly reducing primeval atmosphere as a function of the altitude above the Earth's surface. The "mole fraction" refers to the mixing ratio of the atmospheric mixture at an assumed surface pressure of one atmosphere. After Kasting (1993)

Our knowledge of the processes which led to the formation of the primeval Earth's atmosphere has increased considerably. However, estimates of its percentage composition are still extremely tentative. The uncertainty is underscored by recent work, according to which the young Earth's atmosphere may have been (weakly?) reducing after all. Since a redox-neutral composition of the primeval atmosphere does not favour prebiotic chemistry, a reducing atmosphere would have had a much more positive influence on the synthesis of biomolecules and their predecessors (Kasting and Egger, 2002; Schwartz, 2002).

A model of the primeval Earth atmosphere presented by Tian and co-workers supports these ideas. It has caused lively discussion, as the hydrogen content is suggested to be two orders of magnitude higher than that previously assumed. According to this model, the atmosphere was rich in carbon dioxide and thus not a methane-rich Miller–Urey atmosphere, but it contained around 30% hydrogen. The model, which is a hydrodynamic escape model, is based on the hydrogen volcanic outgassing levels observed today, taking into account the (relatively low) additional amount due to the higher geological activity of the young Earth. For a hydrogen-rich atmosphere, hydrogen escape into space is limited by the availability of external UV irradiation (EUV) from the sun; a lower hydrogen escape naturally leads to a higher atmospheric hydrogen content (Tian et al., 2005; Chyba, 2005).

Such a thought-provoking model was naturally subject to criticism; Catling (Department of Earth Science, University of Bristol) considered the calculations to be unrealistic, since (for example) the authors had underestimated the temperatures of the upper layers of the atmosphere. The prompt answer of the authors to these criticisms was quite clear: "Hence, the ancient atmosphere was hydrogen rich" (Catling, 2006; Tian et al., 2006). J. F. Kasting and M. Tazewell (2006) have given a detailed account of the climate of the primeval Earth and the composition of its atmosphere.

## 2.6 The Primeval Ocean (the Hydrosphere)

It is clear that liquid water is the main prerequisite for all phases of biogenesis. Water is characterized by a series of unusual properties. Its molecular weight alone suggests that, like  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and  $\text{SO}_2$ , it will exist as a gas under normal conditions at the Earth's surface. That it is a liquid is due to the formation of hydrogen bonds between individual  $\text{H}_2\text{O}$  molecules, and its excellent solvent properties are due to their polar nature (Brack, 1993). The interactions between biochemically important species and water are extremely complex in nature. However, water also seems to play an important role in the formation of stars. According to H. Nisini (2000), water in the warm, star-forming regions of the galaxy acts as a coolant in the interstellar gas and removes the excess energy set free in processes involving protostellar collapse. The water may exist as a gas or as ice on interstellar dust particles. The discovery of this phenomenon was made by the Infrared Space Observatory (ISO), which recorded IR spectra at 100–200  $\mu\text{m}$ . The synthesis of water in the warm regions of the galaxy probably occurs according to the following reaction mechanism:



The special position of the Earth among the terrestrial planets is also shown by the availability of free water. On Venus and Mars, it has not until now been possible to detect any free water; there is, however, geological and atmospheric evidence that both planets were either partially or completely covered with water during their formation phase. This can be deduced from certain characteristics of their surfaces and from the composition of their atmospheres. The ratio of deuterium to hydrogen (D/H) is particularly important here; both Mars and Venus have a higher D/H ratio than that of the Earth. For Mars, the enrichment factor is around 5, and in the case of Venus, 100 (de Bergh, 1993).

Water can be found, in all three aggregate states, almost everywhere in the universe: as ice; in the liquid phase on the satellites of the outer solar system, including Saturn's rings and in the gaseous state in the atmospheres of Venus, Mars and Jupiter and in comets (as can be shown, for example, from the IR spectra of Halley's comet). The OH radical has been known for many years as the photodissociation product of water.

But how did water get to the surface of the emerging primeval Earth? There are no clear answers to this important question. Two sources are considered likely:

An internal one: by gas emission after accretion of the Earth, and

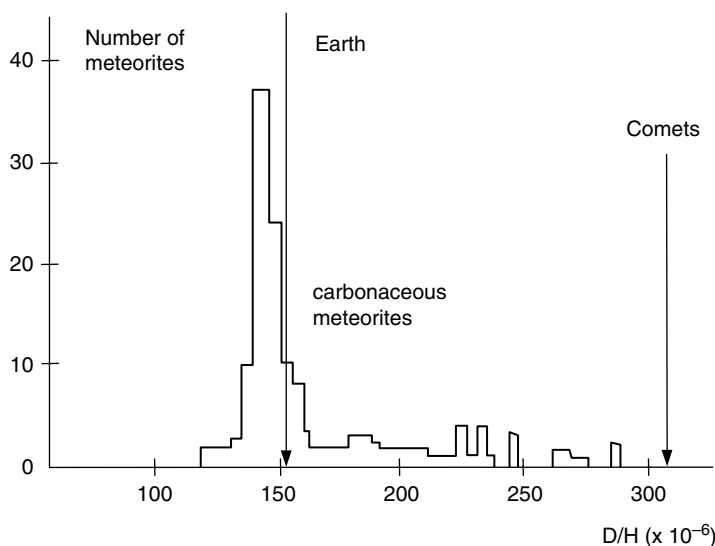
An external one, via collisions with comets and asteroids which contained water.

If the starting materials for the primitive nebula from which the planets were formed were not completely homogeneous, it is possible that thermodynamically more stable, hydrated silicates could have been localized closer to the Earth during its formation than to the orbit of Venus. This would have meant that our sister planet would

have had much less water available, even during its formation. In the case of water set free by gas emission, the exhalation rate determined the amount of water made available.

The second important source for the hydrosphere and the oceans are asteroids and comets. Estimating the amount of water which was brought to Earth from outer space is not easy. Until 20 years ago, it was believed that the *only* source of water for the hydrosphere was gas emission from volcanoes. The amount of water involved was, however, unknown (Rubey, 1964). First estimates of the enormous magnitude of the bombardment to which the Earth and the other planets were subjected caused researchers to look more closely at the comets and asteroids. New hypotheses on the possible sources of water in the hydrosphere now exist: the astronomer A. H. Delsemme from the University of Toledo, Ohio, considers it likely that the primeval Earth was formed from material in a dust cloud containing anhydrous silicate. If this is correct, *all* the water in today's oceans must be of exogenic origin (Delsemme, 1992).

Comets probably consist of at least 40% water. The hypothesis that the waters of the ocean have their origin in cometary mass is supported by the following result: the D/H ratio in Halley's Comet is  $0.6\text{--}4.8 \times 10^{-4}$ , and thus of a similar magnitude to the value of  $1.6 \times 10^{-4}$  found in terrestrial ocean water. Both values agree with those found for meteorites (Chyba and Sagan, 1997). François Robert from the Museum de Minéralogie in Paris has also come to a similar conclusion; he reported a good agreement between the D/H ratios of the ocean and carbonaceous chondrites (Robert, 2001).



**Fig. 2.7** The distribution of the ratio of the two hydrogen isotopes (D/H) in carbonaceous meteorites compared with that on Earth and in the comets. According to this distribution, most of the water on Earth must have had its origin in meteorites. From Robert (2001)

New computer simulations of the accretion process of the protoearth indicate that only a few large bodies with a high water concentration collided with the Earth during the later bombardment. They apparently came from the same region of the asteroid belt as the carbonaceous chondrites.

One of the greatest difficulties in estimating the amount of material which came from asteroids and comets lies in determining the amount of material which would have remained on the Earth's surface after the collisions, in comparison with that which escaped from its gravitational field and disappeared into space. The amount of energy set free in such collisions in turn depends on various parameters, the values of which can only be estimated. Some of these correlate with results on the number and size of the moon's craters (the Lunar Cratering Record), which are themselves subject to a number of uncertainties (Chyba, 1990). Differing rates of impact by extraterrestrial objects have been estimated for the other three terrestrial planets. In the case of Mars, the factor compared to Earth is 0.7 for long-period comets and 2.0–3.6 for short-period comets; the lower mass of Mars has led to greater atmospheric erosion.

Estimates of the mass of the primeval oceans diverge greatly: they lie between 0.2 and 0.7 of the mass of the present oceans. The range of variation of the figures given by the different models show that there are many uncertainties involved in the calculations. One of these lies in water loss due to solar UV irradiation, which would have led to a decomposition of the water in the upper levels of the atmosphere; the hydrogen thus set free would have escaped into space. This process probably occurred mainly during the accretion phase. Its involvement in the fractionation of the elements and the noble gases is indisputable. According to estimates made by some authors, the amounts of water involved might have been as high as several ocean masses, as the intensity of the "extreme solar UV" (EUV) flux in the early periods of the Earth's history would have been 1.3 times greater.

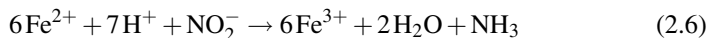
What chemical composition can we assume for the ocean? Unfortunately we have no clear results. Apart from the chemical components, it would be desirable to have information on temperature and pH values. We also do not know whether there was one single primeval ocean, or whether there were several. It is also possible that there were lakes and ponds with differing compositions. We must not forget that huge changes must have taken place on the primeval Earth's surface during the space of a few hundred million years.

If the primeval atmosphere did not contain enough CO<sub>2</sub> to maintain a greenhouse climate, the much lower solar irradiation at that time would have led to frozen oceans. But that would make almost all the assumed synthetic mechanisms for the formation of biomolecules impossible! Bada et al. (1994) consider "external help" as a way out of this dilemma. They assume that the energy from meteor impacts (diameters up to around 100 km), converted into heat, would have sufficed to melt the oceanic ice. If such a process were to have occurred periodically, chemical evolution reactions (see Chap. 4) could have taken place in the ice-free periods and have led finally to biogenesis.

We know nothing of the pH value of the primeval ocean. However, the acidic character of volcanic exhalations must have meant that the young ocean was also

acidic. In later phases of the early history of the Earth, however, washing out due to intense rain could have led to neutral pH values. The possibility that the primeval ocean was basic in character has also been discussed (Abelson, 1966). In this case, the water from the erosion of basic regions of the Earth's crust must have changed the pH value. In today's oceans, the pH value is close to 8, and it is possible that this value varied only a little across the many million years of the Earth's history. The salt content of the young ocean was probably higher than today, but again we have no exact information (Wills and Bada, 2000). It is likely that the primeval ocean contained not only dissolved salts, but also substances which were in some cases highly toxic. The cooling process of the Earth's surface, i.e., of the still thin, cooling crust, proceeded very slowly, since the generation of heat by radioactive decomposition was about four times as intense as today (Mason, 1992). The atmospheric pressure was also probably higher than today, so that the boiling point of the ocean would also have been higher, i.e., above 373 K.

According to Summers and Chang from NASA's Ames Research Center, Moffett Field (1993), the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  provided a possibility for the reduction of nitrites and nitrates to ammonia. This reaction would have been of great importance, as  $\text{NH}_3$  is required in many syntheses of biogenesis precursors. The authors assume that nitrogen was converted to NO in a non-reducing atmosphere, and thence to nitrous and nitric acids. These substances entered the primeval oceans in the form of "acid rain", and here underwent reduction to  $\text{NH}_3$  with the help of  $\text{Fe}^{2+}$ , thus raising the pH of the oceans to 7.3. Temperatures above 298 K favoured this reaction, which can be written as:



The question of the prebiotic origin or formation of ammonia has recently been discussed by a group in Jena; they devised a method in which  $\text{NH}_3$  is formed from  $\text{N}_2$  with the help of  $\text{H}_2\text{S}$ . The presence of freshly precipitated FeS (prepared from  $\text{FeSO}_4$  by precipitation with  $\text{Na}_2\text{S}$  at room temperature under an argon atmosphere) was found to be vital: aged FeS is inactive. In this reaction, FeS is converted to  $\text{FeS}_2$  (iron pyrites). The reaction occurred under mild conditions, i.e., at atmospheric nitrogen pressure and at temperatures between 343 and 353 K. The yield of ammonia (with respect to 3 moles of iron sulphide) was 0.1% (3 mM). The experiments were carried out extremely carefully, so that contamination (e.g., by NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$ ) could be excluded (Dörr et al., 2003). These experimental results support the hypothesis of a chemoautotrophic origin of life (see Sect. 7.3).

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