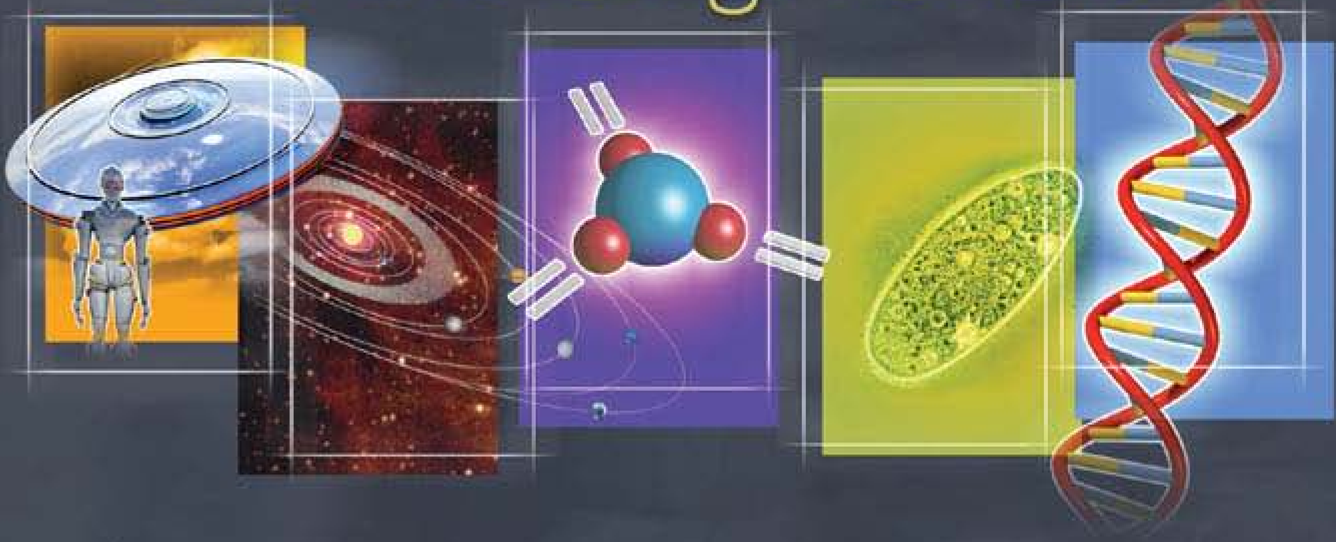
Chemical Evolution and the Origin of Life



Horst Rauchfuss

Springer

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Translated by

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Springer

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Foreword

How did life begin on the early Earth? We know that life today is driven by the universal laws of chemistry and physics. By applying these laws over the past fifty years, enormous progress has been made in understanding the molecular mechanisms that are the foundations of the living state. For instance, just a decade ago, the first human genome was published, all three billion base pairs. Using X-ray diffraction data from crystals, we can see how an enzyme molecule or a photosynthetic reaction center steps through its catalytic function. We can even visualize a ribosome, central to all life, translate genetic information into a protein. And we are just beginning to understand how molecular interactions regulate thousands of simultaneous reactions that continuously occur even in the simplest forms of life. New words have appeared that give a sense of this wealth of knowledge: The genome, the proteome, the metabolome, the interactome.

But we can't be too smug. We must avoid the mistake of the physicist who, as the twentieth century began, stated confidently that we knew all there was to know about physics, that science just needed to clean up a few dusty corners. Then came relativity, quantum theory, the Big Bang, and now dark matter, dark energy and string theory. Similarly in the life sciences, the more we learn, the better we understand how little we really know. There remains a vast landscape to explore, with great questions remaining.

One such question is the focus of this book. The problem of the origin of life can be a black hole for researchers: If you get too close, you can disappear from sight. Only a few pioneering scientists, perhaps a hundred or so in the international community, have been brave enough to explore around its edges. The question of life's origin is daunting because the breadth of knowledge required to address it spans astronomy, planetary science, geology, paleontology, chemistry, biochemistry, bioenergetics and molecular biology. Furthermore, there will never be a real answer. We can never know the exact process by which life did begin on the Earth, but at best we will only know how it could have begun. But if we do understand this much, we should be able to reproduce the process in the laboratory. This is the gold that draws the prospectors into the hills. We know the prize is there, but we must explore a vast wilderness of unknowns in order to find it.

Perhaps most exciting is that we are now living in a time when enough knowledge has accumulated so that there are initial attempts to fabricate versions of living cells in the laboratory. Entire genomes have been transferred from one bacterial species to another, and it is now possible to reconstitute a system of membranes, DNA, RNA and ribosomes that can synthesize a specific protein in an artificial cell.

Other investigators have shown that the informational molecules of Life – RNA and DNA – themselves can be synthesized within lipid vesicles.

We are getting ever closer to the goal of synthetic life, and when that is achieved we will see more clearly the kinds of molecular systems that were likely to have assembled in the prebiotic environment to produce the first forms of life.

We now think about the beginning of life not as a process restricted to the early Earth, but instead as a narrative that takes into account the origin of the biogenic elements in exploding stars, the gathering of the ashes into vast molecular clouds light years in diameter, the origin of new stars and solar systems by gravitational accretion within such clouds, and finally delivery of organic compounds to planetary surfaces like that of the Earth during late accretion. Only then can the chemical reactions and self-organization begin that leads to the origin of life.

This is the scope covered in this book, hinted at by the images on the cover that range from galaxies to planets to a DNA molecule. Horst Rauchfuss is among those rare few individuals who understand the greater evolutionary narrative, and his book is an account of the conceptual map he has drawn to help others find their own path through the wilderness.

The book begins with a brief history of biogenesis, a word that Rauchfuss prefers to use rather than phrases like "origin of life" or "emergence of life." The first chapter brings the reader from the ancient Greeks up to the present when we are seeing a near-exponential growth of our knowledge. Here he makes an effort to define life, always a difficult task, but succeeds as well as any. The book then steps through nine basic concepts that must be taken into account to understand biogenesis, with a chapter given to each. For instance, Chapters 2 and 3 describe the origin of galaxies, stars and planets, and Chapter 4 discusses chemical evolution, which is central to our ideas about life's beginnings. The material is presented at a level that can be understood by students in an introductory chemistry course. The next six chapters present facts and concepts underlying protein and nucleic acid functions in modern cells, with constant references to how these relate to biogenesis. In Chapter 10 Rauchfuss brings it all together to describe the evidence for the first forms of cellular life. This chapter is a nice example of how Rauchfuss tries to present information in a clear and interesting manner. For instance, there is considerable controversy about the evidence related to the first life on the Earth, which is based on isotopic analysis and microfossils, and the controversy is presented along with the scientists on both sides of the argument. In the last chapter and epilogue, Rauchfuss gives an overview of astrobiology, which in fact is the unifying theme of the book, and raises a series of unanswered questions that are a guide to the major gaps that still remain to be filled by experiments, observations and theory.

Chemical Evolution and the Origin of Life is well worth reading by young investigators who seek an overview of biogenesis. It is also enjoyable reading for scientists like myself who will discover that the book fills in blank spaces in their own knowledge of the field. We owe a "danke sehr!" to Horst Rauchfuss for putting it all together.

July 2008

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Preface to the English Edition

The first edition of this book was published in German, a language which is now not so widely read as it was even a generation ago. So I am very happy that Springer decided to publish an English edition. Naturally, I have tried to bring the book up to date, as the last years have seen considerable progress in some areas, which this book tries to cover.

It was unfortunately impossible to mention all the many new results in the extremely broad area of the "origin of life". Selections often depend on the particular interests of the writer, but I have tried to act as a neutral observer and to take account of the many opinions which have been expressed.

I thank my colleagues Günter von Kiedrowski (Ruhr-Universität Bochum), Wolfram Thiemann (Universität Bremen) and Uwe Meierhenrich (Université de Nice, Sophia Antipolis). Particular thanks go to my colleague Terry Mitchell from the Technische Universität Dortmund for providing the translation and for accommodating all my changes and additions.

This year has sadly seen the deaths of two of the pioneers of research on the origin of life: Stanley L. Miller and Leslie Orgel. They provided us with vital insights and advances, and they will be greatly missed. Their approach to scientific research should serve as a model for the coming generation.

Varberg, July 2008 Horst Rauchfuss

Preface

The decision to write a book on the origin (or origins) of life presupposes a fascination with this "great problem" of science; although my first involvement with the subject took place more than 30 years ago, the fascination is still there. Experimental work on protein model substances under simulated conditions, which may perhaps have been present on the primeval Earth, led to one of the first books in German on "Chemical and Molecular Evolution"; Klaus Dose (Mainz) had the idea of writing the book and was my co-author.

In recent years, the huge enlargement and differentiation of this research area has led to the formation of a new, interdisciplinary branch of science, "Exo/Astrobiology", the ambitious goal of which is the study of the phenomenon of "life" in our universe.

The following chapters provide a review of the manifold attempts of scientists to find answers to the question of "where" life comes from. Successes will be reported, but also failures, discussions and sometimes passionate controversies. It will also be made clear that very many open questions and unsolved riddles are still awaiting answers: there are more such questions than is often admitted! The vast amount of relevant scientific publications unfortunately makes it impossible to report in detail on all the components of this interdisciplinary area of natural science.

The description of scientific facts and issues is generally dealt with by two different types of author: either by scientists working on the particular problem under discussion and developing hypotheses and theories, or by "outsiders". In each case there are advantages and disadvantages: the researcher brings all his or her expertise to bear, but there is a danger that his or her own contributions and related theories may to some extent be judged one-sidedly. The "outsider", however, should be able to provide a neutral appraisal and evaluation of the scientific contributions in question. In an article in the "Frankfurter Allgemeine Zeitung" (July 9th, 2001) entitled "Warum sich Wissenschaft erklären muß", the neurophysiologist Prof. Singer refers to this problem: "on the other hand, researchers tend to overvalue their own fields, and the intermediary must be able to confront this problem with his own critical ability".

The intermediary is often forced to present complex material in a simple manner, i.e., to carry out a "didactic reduction". Such processes naturally cause problems, resembling a walk on a jagged mountain ridge. On the one side is the abyss of an inordinate simplification of the scientific conclusions (and the resulting condemnation by the experts), on the other that of the complexity of scientific thought, which is only really understood by the specialist.

Presentation of the biogenesis problem is difficult, because there is still not one single detailed theory of the emergence of life which is accepted by all the experts working in this area. There has been important progress in recent years, but the single decisive theory, which unites all the experimental results, has still not emerged. In other words, important pieces in the jigsaw puzzle are still missing, so that the complete picture is not yet visible.

This book is organised as follows: first, a historical introduction, followed by a survey of the origin of the universe, the solar system and the Earth. Planets, meteorites and comets are discussed in the third chapter, while the next deals with experiments and theories on chemical evolution. Proteins, peptides and their possible protoforms are characterized in Chaps. 5 and 6, as well as the "RNA world". Further chapters deal with important hypotheses and theories on biogenesis, for example, inorganic systems, hydrothermal vents and the models proposed by Günter Wächtershäuser, Manfred Eigen, Hans Kuhn, Christian de Duve and Freeman Dyson, as well as the problem of the origin of the genetic code. Chapter 9 provides a discussion of basic theoretical questions and the chirality problem. The search for the first traces of life and the formation of protocells are dealt with in the tenth chapter, while the last covers the question of extraterrestrial life forms, both within and outside our solar system.

Looking back, I must thank my academic teachers, Gerhard Pfleiderer and Theodor Wieland, for introducing me to biochemistry and natural product chemistry, and thus to the phenomenon of "life", the origins of which are still hidden in the darkness of the unknown.

I thank Dr. Gerda Horneck (DLR, Cologne) and my colleagues Clas Blomberg (Royal Institute of Technology, Stockholm), Johannes Feizinger (Ruhr University, Bochum), Niels G. Holm (University of Stockholm), Günter von Kiedrowski (Ruhr University, Bochum), Wolfram Thiemann (University of Bremen) and Roland Winter (University of Dortmund).

Thanks are also due to many colleagues across the world for allowing me to make use of images and information and for encouraging me to continue the work on this book.

I also thank the members of the planning office for chemistry in the Springer Verlag, Peter W. Enders, senior editor chemistry and food sciences, Pamela Frank and Birgit Kollmar-Thoni for their patience and helpfulness.

To Dr. Angelika Schulz go thanks for her exemplary editorial support in the preparation of the book, and to Heidi Zimmermann for preparing most of the illustrations.

Maj-Lis Berggren (Varberg) provided invaluable help in avoiding all the pitfalls which computers can generate. Special thanks go to my wife, who showed great patience during the time of preparing the manuscript.

Finally, a quote from Georg Christoph Lichtenberg, to whom we owe thanks for so many apposite, polished aphorisms. Lichtenberg (1742–1799) was a scientist, satirist and Anglophile. He was the first professor of experimental physics in Germany. I hope that, with respect to most of his points, Lichtenberg made gigantic mistakes in the following lines!

Eine seltsamere Ware
als Bücher gibt es wohl schwerlich
in der Welt. Von Leuten gedruckt
die sie nicht verstehen; von Leuten
verkauft, die sie nicht verstehen;
gebunden, rezensiert und gelesen,
von Leuten, die sie nicht verstehen,
und nun gar geschrieben von
Leuten, die sie nicht verstehen.

Here is one possible translation:

There could hardly be
stranger things in the world than books.
Printed by people who do not understand them;
sold by people who do not understand them;
bound, reviewed and read by people who do not understand them,
and now even written by
people who do not understand them.

Varberg, 2004 Horst Rauchfuß

Author's note: Some figures in this book are published additionally in colour in order to make them clearer.

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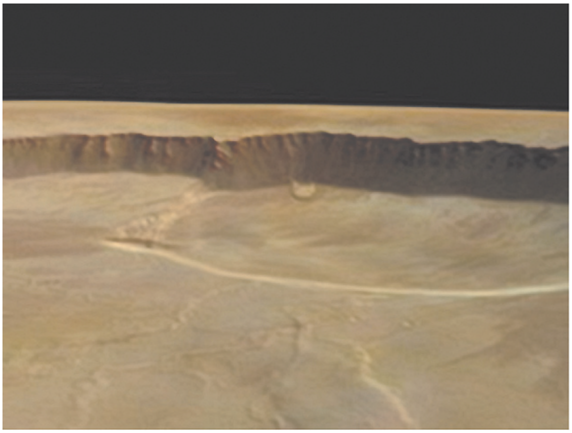


Fig. 3.1 Perspective view of part of the caldera of Olympus Mons on Mars. This view was obtained from the digital altitude model derived from the stereo channels, from the nadir channel (vertical perspective) and the colour channels on the Mars Express Orbiter. The photograph was taken on 21 January 2004 from a height of 273 km. The vertical face is about 2.5 km high, i.e., about 700 m higher than the north face of the Eiger mountain (Switzerland). With permission of the DLR

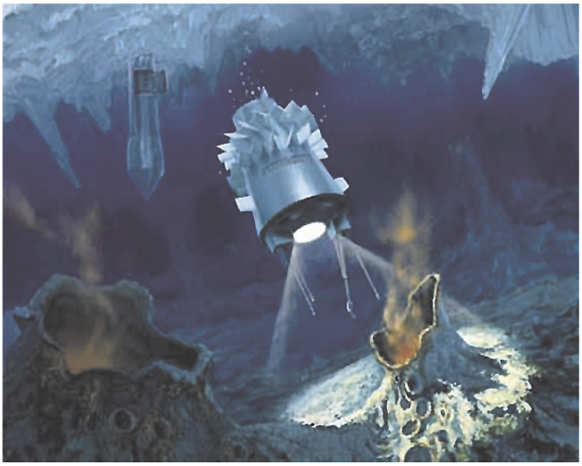
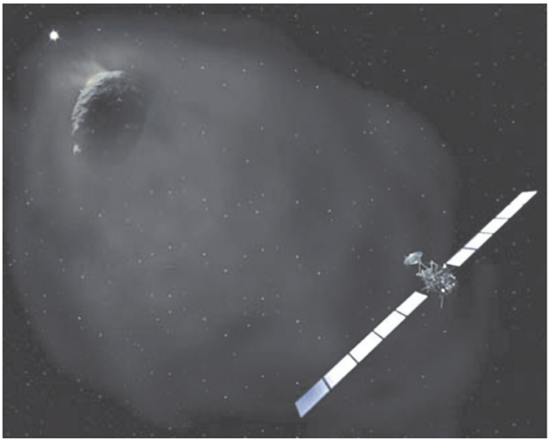


Fig. 3.3 An artist's impression of the planned "hydrobot" mission to Europa. The robot has bored through the ice layer in the moon's intermediate aqueous layer and is investigating the ocean floor. From NASA



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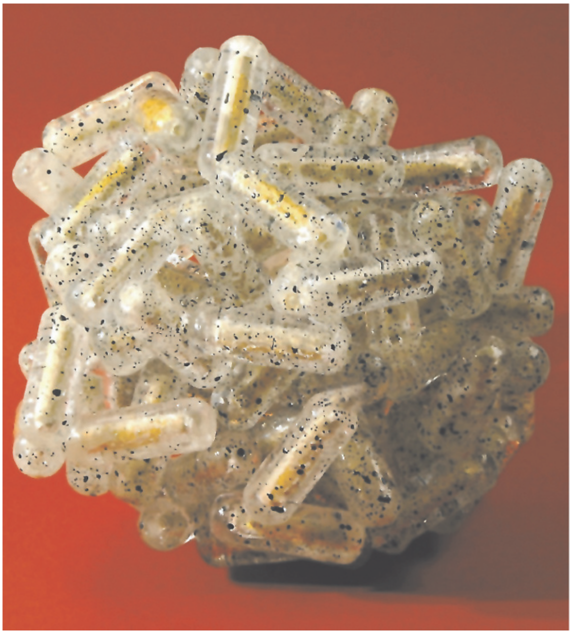

Fig. 3.12 Model of an agglomerate consisting of many small interstellar dust particles. Each of the rod-shaped particles consists of a silicate nucleus surrounded by yellowish organic material. A further coating consists of ice formed from condensed gases, such as water, ammonia, methanol, carbon dioxide and carbon monoxide. Photograph: Gisela Krüger, University of Bremen

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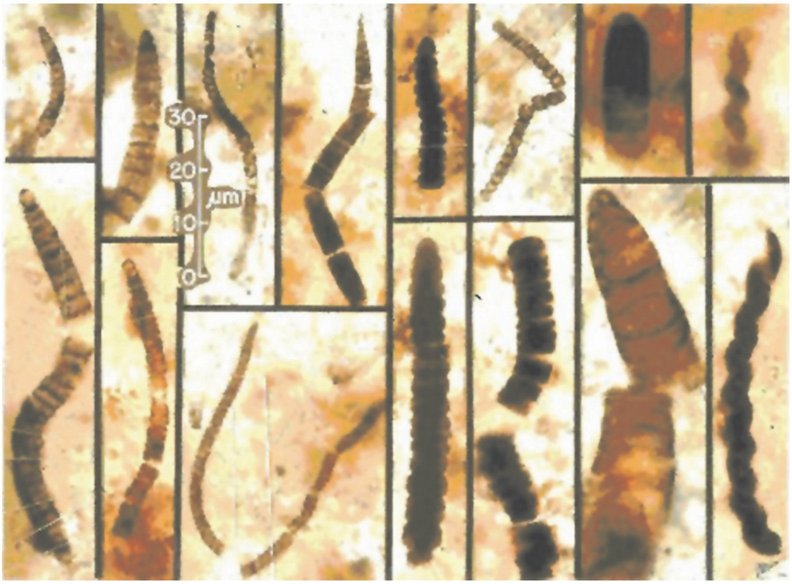


Fig. 10.1 Cellular, petrified, filamentous microfossils (cyanobacteria) from the Bitter Springs geological formation in central Australia; they are about 850 million years old. With kind permission of J. W. Schopf

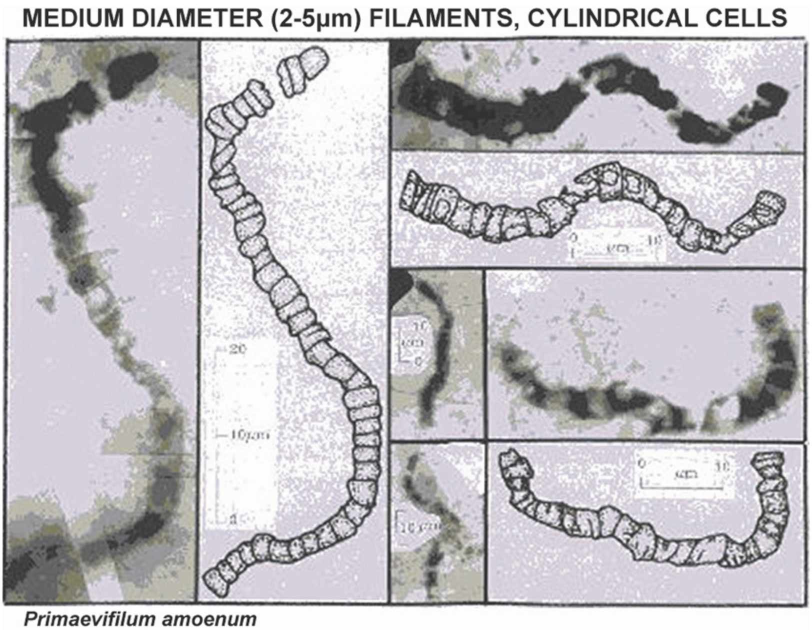


Fig. 10.2 Cyanobacteria-like, filamentous carbonaceous fossils from the 3.456-billion-year-old Apex chert in northwestern Australia; their origin and formation are still under discussion. The photographs are accompanied by the corresponding drawings. With kind permission of J. W. Schopf

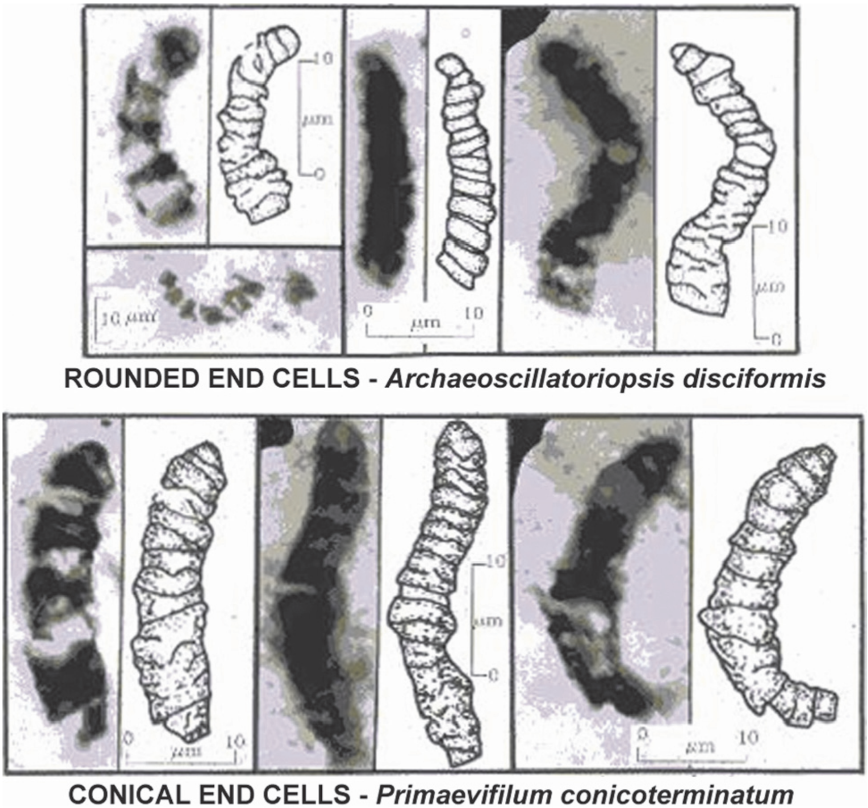


Fig. 10.3 Microfossils with differently formed end cells, from the same source as in Fig. 10.2 and thus of the same age. Again, the corresponding drawings are shown to make the structures clearer. With kind permission of J. W. Schopf

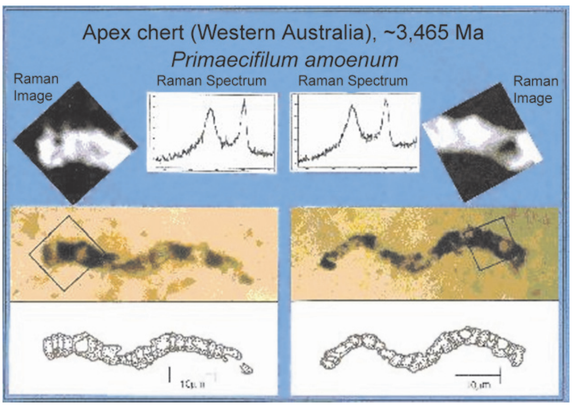


Fig. 10.4 Fossilized cellular filamentous microorganisms (two examples of *Primaevifilum amoenum*). They are 3.456 billion years old and come from the Apex chert region in northwestern Australia. As well as the original images, drawings and the Raman spectra and Raman images, which indicate that the fossils have a carbonaceous (organic) composition, are shown. With kind permission of J. W. Schopf

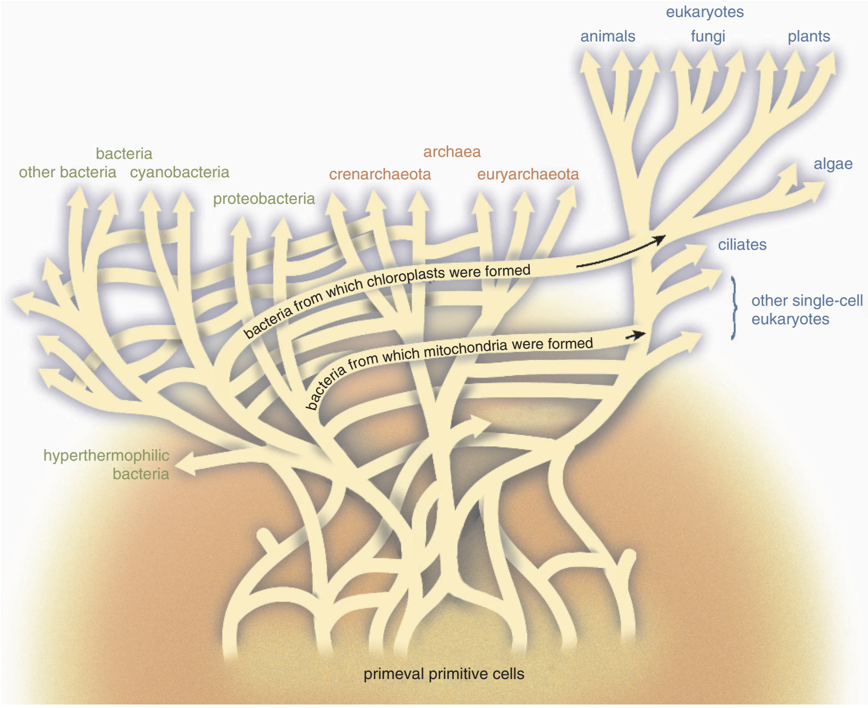
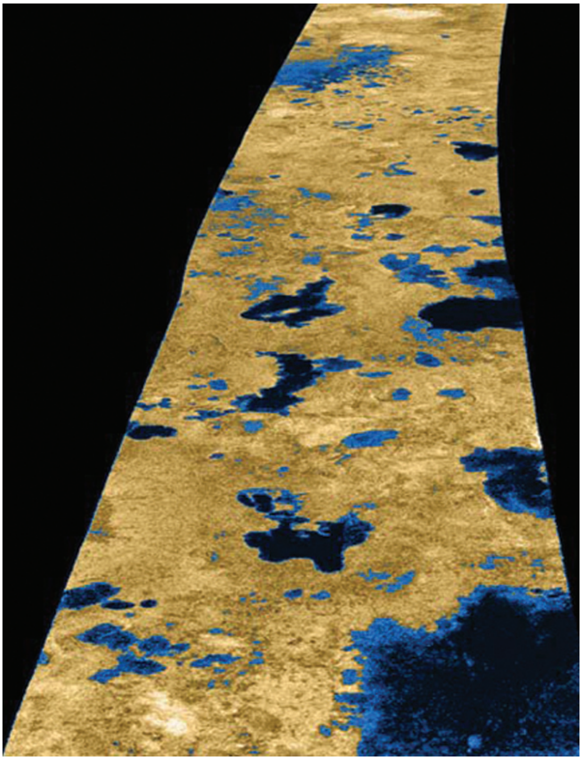


Fig. 10.11 The "modified tree of life" still has the usual tree-like structure and also confirms that the eukaryotes originally took over mitochondria and chloroplasts from bacteria. It does, however, also show a network of links between the branches. The many interconnections indicate a frequent transfer of genes between unicellular organisms. The modified tree of life is not derived, as had previously been assumed, from a single cell (the hypothetical "primeval cell"). Instead, the three main kingdoms are more likely to have developed from a community of primitive cells with different genomes (Doolittle, 2000)



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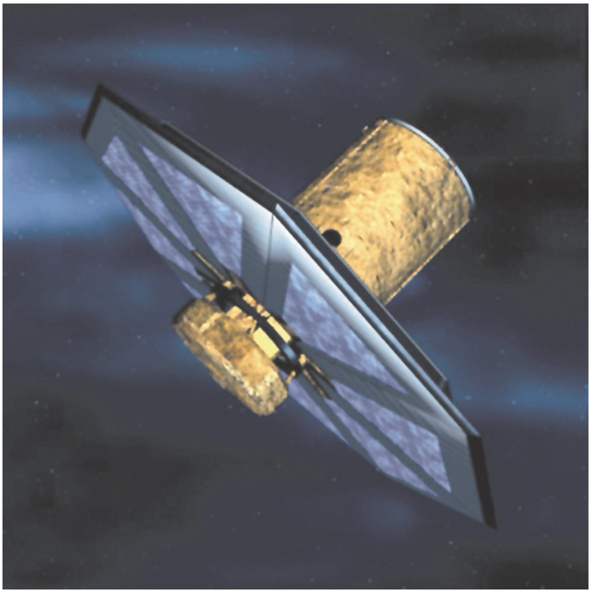

Fig. 11.5 One of the telescopes in the Darwin flotilla. With kind permission of ESA

Introduction

For more than 50 years, scientists have been working diligently towards finding a solution to the "biogenesis" problem. We have chosen to use this word rather than the expression "origin of life" or "emergence of life". Biogenesis research has involved many individual disciplines—more than normally participate in work on other scientific challenges—from astrophysics, cosmochemistry and planetology to evolutionary biology and paleobiochemistry. Biogenetic questions also have their roots in the humanities. Thus Wolfgang Stegmüller, a philosopher who taught at the University of Munich, stated in the introduction to the second volume of his "Hauptströmungen der Gegenwartsphilosophie" ("Important Trends in Modern Philosophy") that science was presently trying to "... answer questions about the construction of the universe, the basic laws of reality and the formation of life. Such questions form the basis of the oldest philosophical problems; the key difference is only that the vast arsenal of modern science was not available to the Greek thinkers when they were trying to devise their solutions." This arsenal has been greatly increased in the last years and decades.

The problem in its entirety can be characterised by means of analogies. Thus the chemist Leslie Orgel, who carried out successful experiments on chemical evolution for many years, compared the struggle to solve the biogenesis problem with a crime novel: the researchers are the detectives looking for clues to solve the "case". But there are hardly any clues left, since no relicts remain from processes which took place on Earth more than four billion years ago.

Research into the biogenesis puzzle is special and differs from that carried out in many other disciplines. The philosophy of science divides scientific disciplines into two groups:

Operational science: a group including those disciplines which explain processes which are repeatable or repetitive, such as the movements of the planets, the laws of gravity, the isolation of plant ingredients, etc.

Origin science: a group which deals with processes which are non-recurring, such as the formation of the universe, historical events, the composition of a symphony, or the emergence of life.

H. Rauchfuss, *Chemical Evolution and the Origin of Life*,

Origin science cannot be explained using normal traditional scientific theories, since the processes with which it deals cannot be checked by experiment and are thus also not capable of falsification.

So is the work done on the biogenesis problem in fact not scientific in nature at all? Surely it is! There is a way out of this dilemma: according to John Casti, if enough thoroughly thought-out experiments are carried out, the unique event will become one which can be repeated. The hundreds of simulation experiments which will be described in Chaps. 4–8 represent only tiny steps towards the final answer to the problem. However, modern computer simulations can lead to new general strategies for problem solving.

In recent years, the number of scientists working on the biogenesis problem has increased considerably, which of course means an increase in the number of publications.

Unfortunately, biogenesis research cannot command the same financial support as some other disciplines, so international cooperation is vital. The biogenesis community is still relatively small, and most of its members have known each other for many years. The International Society for the Study of the Origin of Life, ISSOL, has been in existence for around 40 years and has just added the tagline "The International Astrobiology Society" to its name; it organises international conferences every three years. The atmosphere at these conferences is very pleasant, even though there is complete unity on only a few points in biogenesis. Opponents of the evolution and biogenesis theories naturally use such uncertainties for their own arguments. The most radical of these opponents are the creationists, a group based in the USA which takes the biblical account of creation literally; they consider the beauty and complexity of life forms to be evidence for their notions.

The chapters which now follow will provide a survey of the multifarious aspects of the question of "where" life on our Earth came from.

Chapter 1
Historical Survey

1.1 The Age of Myths

When we are debating the sense of our existence, the question as to "where" all living things come from keeps coming back to plague us. Human beings have been seeking answers to this question for hundreds, or even thousands, of years. But only since the middle of the last century have attempts been made to solve the problem of biogenesis with the help of scientific methods.

In the mists of time, myths dominated the thoughts, emotions and deeds of our ancestors. The Greek thinkers used myths as a possibility of structuring the knowledge obtained from mankind's encounters with Nature; the myths mirrored people's primeval experiences. The forces of nature dominated the lives of our ancestors in a much more direct and comprehensive manner than they do today. Life was greatly influenced by numerous myths, and in particular by creation myths. These often dealt with the origin of both the Earth and the universe and with the creation of man (or of life in general). In ancient Egypt, the god Ptah, the god of the craftsmen, was originally worshipped in Memphis, the capital of the Old Kingdom. Ptah was one of the most important gods. Each of the most important religious centres had its own version of the origin of the Earth. In Memphis, the priests answered the question as to how creation had taken place by stating that Ptah had created the world "with heart and tongue". By this they meant that Ptah had created the world only through the "word"; in other words, the principle of *will* dominated creation. Jahweh, the god of the Bible, and Allah (in the Koran) created the world by the power of the word: "There shall be...."

There is no doubt that in those times, all civilisations considered that there was a connection between natural events and their myths of the Earth's creation. Thus most of the Egyptians—whichever gods they worshipped—shared the common belief that the creation of the Earth could be compared with the appearance of a mound of land from the primeval ocean, just as every year they experienced the re-emergence of the land from the receding Nile floods.

A similar connection between the world around us and cosmology can be found in the land between the Tigris and Euphrates. The Earth was regarded as a flat disc, surrounded by a vast hollow space which was in turn surrounded by the firmament of heaven. In the Sumerian creation myth, heaven and Earth formed

An-Ki, the universe ("heaven–Earth"). An infinite sea surrounded heaven and Earth. In Mesopotamia, water was regarded as the origin of all things, and from it had sprung both the Earth's disc and the firmament, i.e., the whole universe. The Babylonian Enuma-Elish legend describes the birth of the first generation of gods, which included Anu (the god of the heavens) and Ea (the god of the Earth) from the primordial elements: Apsu (fresh water), Tiamat (the sea) and Mummu (the clouds).

In the Nordic creation myth, which can be found at the beginning of the Edda, we encounter Ginnungagap, a timeless, yawning void. It contains a type of supreme god, Fimbultyr, who willed the formation of Niflheim in the north, a cold, inhospitable land of fog, ice and darkness, and in the south Muspelheim (with light and fire). Sparks from Muspelheim flew onto the ice of Niflheim. This caused life to emerge, and the ice giant Ymir and the huge cow Audhumbla were formed.

> From "The Seeress's Prophecy" (3, 57):
> Young were the years when Ymir made his settlement,
> There was no sand nor sea nor cool waves;
> Earth was nowhere nor the sky above,
> Chaos yawned, grass was there nowhere.
> (Larrington, 1999)

Under Ymir's left arm were formed a giant and a giantess. Since the cow Audhumbla found no grass on which to feed, she licked salty ice blocks, and from under her tongue emerged Buri the Strong, who had a son, Bör. He in turn had three children with Bestla: Odin (Wotan), the most important of the gods, Vili and Vé. The Earth itself was formed only at this stage. The frost giant Ymir was vanquished, and from his corpse came Midgard, the land of men, from his blood the oceans, from his bones and teeth the mountains and cliffs, from his hair the trees and from his

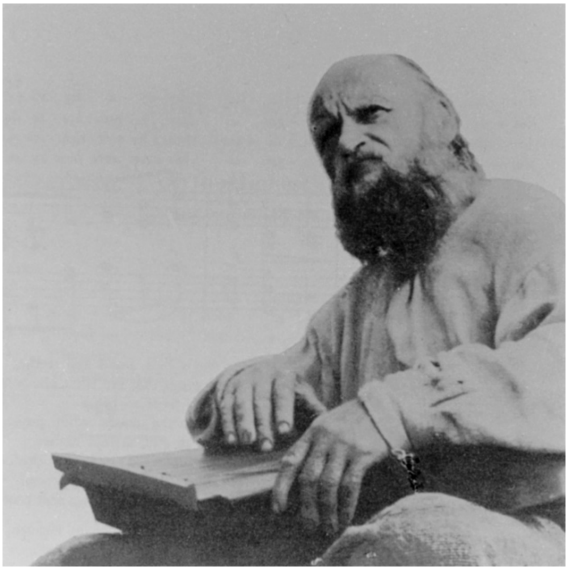

Fig. 1.1 Rune singer with his instrument, the kantele

skull the heavens. His brain was thrown into the air by the gods, and from it were formed the clouds. Flowers and animals just appeared. One day, the three sons of Bör were walking on the beach and came upon Ask, the ash, and Embla, the elm. Man and woman were formed from the two trees, and Odin breathed life and spirit into their bodies. Vili gave them intelligence and emotions, and from Vé they got their faces and their language. We know neither when these myths first appeared, nor the history of their emergence.

Several hundred kilometres further east, in Finnish Karelia, the nineteenth century saw the birth of legends which were passed down by word of mouth from generation to generation. Elias Lönnrot, a doctor, collected these fables and used them to create the Finnish national epic, the "Kalevala", which starts with a creation myth. In the first rune, the daughter of the air lets herself fall into the sea. She is made pregnant by the wind and the waves. The duck, as water mother, comes to her, builds a nest on her knee, and lays her eggs. These roll into the sea and break, giving rise to the Earth, the heavens, the sun, the moon and the stars:

From one half the egg, the lower,
Grows the nether vault of Terra:
From the upper half remaining,
Grows the upper vault of Heaven;
From the white part come the moonbeams,
From the yellow part the sunshine,
From the motley part the starlight,
From the dark part grows the cloudage.
(Kalevala, Rune I, translated by John Martin Crawford, 1888)

At the beginning of the orchestral prelude to his opera "Rheingold", Richard Wagner brilliantly shaped the myth of creation in music, which describes nature in its primordial state, at the absolute beginning of all things. For many bars there is no modulation, no chordal variation. Then a chord in E flat minor appears; first the tonic can be heard in unfathomable depths, followed by the addition of a fifth, which finally becomes a triad. The "nature motive" develops as the leitmotif of all creation (Donington, 1976).

The nature leitmotif

But now let us go back again, many centuries: the Greek philosophers tried to explain the formation of living systems by compounding matter (which is by nature lifeless) with the active principle of "gestalt". The "gestalt" principle is so powerful that it can breathe life into inert matter.

For Aristotle (384–322 BC) there was only one type of matter; this could, however, exist in four basic forms: earth, air, fire and water, all of which could be converted one into the other. Observations of natural phenomena only came second in ancient Greece, though. Biological processes were considered to be very important, and attempts were made to explain the behaviour of, for example, water, air, rain, snow and heat. The Greeks did this by relating their observations to cause and effect. For Aristotle, experiments (in the sense of questions posed to nature) were not suitable ways of getting information, as they involved menial operations which were only carried out by slaves. Aristotle's teachings actually represent a cognition theory, in which general observations are used to make decisions on individual cases.

The atomists, for example, Leucippus, Democritus and Epicurus, thought that a phenomenon could be explained when its individual elements were known; in contrast, Aristotle was of the opinion that that was not enough, since such information refers only to the material basis. In order to be able to understand things and processes, three further "origins", "principles" and "reasons" must be known.

The "four reasons why", which Aristotle attributed to all things which were subject to change, are: causa materialis, the material cause; causa efficiens, the efficient cause; causa formalis, the formal cause, and causa finalis, the final cause. The first three causes exist for the last one, as it is the whole reason that the other three causes are implemented; they are to the final cause what the means are to the end, and form the process of which the final cause is the goal.

The final cause was the most important for Aristotle, just because it was what was actually reached at the end of the process. Aristotle's teaching dominated the way people thought well into the Middle Ages. Thus, the "four reasons why" were of great importance for western philosophy.

Interestingly, the teachings of Democritus (460–371BC) did not become so important, although in the sense of natural science (as we now know it), they were much more relevant. Leucippus was Democritus's teacher, and thus the scholar took over the basic ideas of atomic theory from his teacher: atoms as tiny particles, too tiny to be visible, which were everlasting and could not be destroyed. They were supposedly made from the same material, but were of different sizes and weights. According to Democritus, life arises from a process in which the small particles of the moist earth combine with the atoms of fire.

Empedocles, born around 490 BC in Agrigent (Sicily), was a member of the group known as the eclectisists (the selectors), because they selected ideas from systems which already existed and put them together to form new theories. According to Empedocles, the lower forms of life were formed first, and then the higher organisms; first plants and animals, then human beings. Initially both sexes were united in one organism; the separation into male and female took place later. These ideas appear to contain elements of modern scientific theory.

1.2 The Middle Ages

Many centuries passed between the hypotheses of the Greek philosophers and the development of new ideas, and of vague models of how life on Earth might have developed. However, a completely new methodology was now used: while the Greeks had merely reflected on how things might have happened, their successors used experiments.

The often luckless alchemists were looking for the "transmutatio metallorum", the transmutation of non-noble metals into gold. Here, of course, they remained unsuccessful. Attempts to create a "homunculus", a human being in a test tube, also failed completely. The work "De generatione rerum naturalium" (On the generation of natural things) by Paracelsus did the most to spread the idea of tiny creatures in a test tube. Three hundred years later, the "homunculus" found its way into world literature in Goethe's "Faust".

The idea of "spontaneous generation", the emergence of life from dead matter, dominated medieval ideas of biogenesis. It was supported and confirmed by experiments. Thus, mice, frogs, worms and other animals could apparently appear from decaying, but formerly living, material. The famous Doctor van Helmont demonstrated an experiment for the "original procreation" of mice: a jug (with no lid) was filled with wheat and dirty underclothes, and after 21 days, changes occurred—particularly in the smell! A certain "ferment" from the underclothes permeated the wheat and turned it into mice! There were, however, critical observers: while at the court of Ferdinand II of Tuscany, the Italian doctor and poet Francesco Redi (1626–1698) showed that the white maggots found in decaying meat came from eggs laid by flies: no maggots are formed if the decaying meat is stored in a vessel covered with gauze. In spite of such proofs, the theory of spontaneous emergence of life remained attractive.

L. Joblot also showed that it is not possible for life to occur spontaneously: he prepared an extract of hay, which he poured into two vessels, one of which was immediately sealed with parchment. As expected, microorganisms grew only in the open vessel. Regrettably, Joblot's results were not taken seriously by his contemporaries.

In the middle of the eighteenth century, there was a violent scientific argument about the spontaneous generation of life between the Englishman J. T. Needham (1713–1781) and the Frenchman G. de Buffon on the one side, and the Italian L. Spallanzani (1729–1799), who taught natural history at the University of Pavia, on the other. Both parties carried out experiments similar to those of Joblot, but came to opposite results. Needham filled vessels with mutton broth or other organic materials and sealed them. Because he did not work in a sterile manner, microorganisms grew in the vessels. He and Buffon interpreted this result as a proof of spontaneous generation. Spallanzani, however, carried out his experiments very carefully and under sterile conditions—and obtained completely different results. Both sides then carried out many other experiments; however, they could not convince each other, and so the question of the spontaneous emergence of life remained open.

The learning process with respect to the problem of the origin of life took place in a manner similar to the three stages described by the French philosopher Auguste Comte (1798–1857) for the linear history of progress in human culture. These three stages are:

Stage 1: The theological and mythological period. Reality is described as the result of supernatural forces (polytheism, monotheism, animism).

Stage 2: The age of metaphysics. The supernatural beings (gods) are replaced by abstract terms, powers or entities.

Stage 3: The scientific or positive age. The unification of theory and practice, which is the result of a combination of rational thinking and observation, allows us to recognize relationships and similarities. Ideally it is possible to describe many single phenomena on the basis of one unified postulate, i.e., to formulate a scientific law.

Comte's three-stage principle can be applied not only to the intellectual development of all mankind, but also to the individual development of a single human being. It can also be applied to the development of an individual science: at first there is a dominance of theological and mythical concepts, followed by the phase of metaphysical speculation, and finally the advanced stage of positive knowledge.

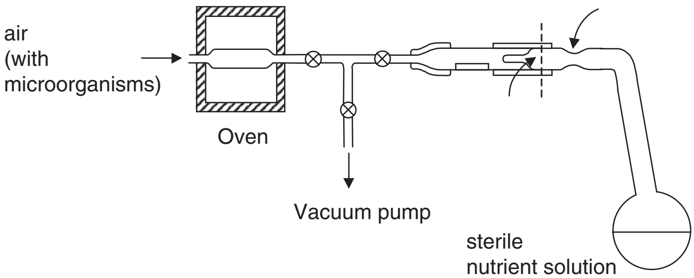

Fig. 1.2 Pasteur's apparatus: if the oven is not switched on, the microorganisms in the air enter the sterile culture solution and multiply. If the oven is switched on, they are killed by the heat. After Conaut (1953)

Around 1860, the French Academy of Science decided to award a prize to the scientist who could unambiguously settle the question of the spontaneous emergence of life. Louis Pasteur (1822–1895) used some elegant experiments to show that a *de novo* synthesis of microorganisms from various materials of organic origin was not possible. He demonstrated that all microbes are descended from existing microorganisms. Pasteur showed that air itself contained various types of microorganism; if air is filtered through guncotton, the latter retains the microorganisms. If the guncotton is then dissolved in a mixture of ethanol and ether, the cells can readily be identified under the microscope in the solution, and they multiply if the latter is transferred to a sterile culture medium. If, however, the air is heated before being passed into boiled culture broth, the cells are killed by the heat. Pasteur's opponents argued that by heating the stream of air, he had destroyed the vital force.

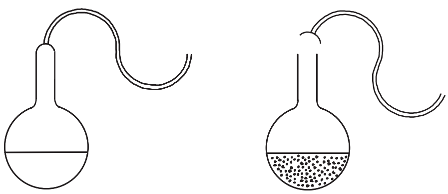

Fig. 1.3 Pasteur's swan-necked flasks: in the first flask, the unbroken neck hinders contamination; if the neck is broken off as in the second flask, the sterile culture medium is invaded by microorganisms. After Pasteur (1862)

In order to disprove this theory, Pasteur used swan-necked flasks; unheated air could now enter the sterile culture solution. But in this case, the microorganisms in the air were deposited in the long S-shaped neck and did not enter the culture medium. If, however, the neck of a flask was broken off, they could enter the solution and multiply.

In 1864, Louis Pasteur received the well-deserved prize of the Academy in recognition of his achievements. However, Pasteur's experiments provided no information on *how* life was formed.

At around this time, there was much scientific debate about the theory of the origin of species proposed by Charles Darwin (1809–1882), a theory which was to change the world. Darwin himself was very cautious about making statements on biogenesis. It was still too early to answer such questions, because neither results from the science of cell biology nor an extensive knowledge of our planet, the solar system and the cosmos were available.

1.3 Recent Times

The huge disquiet which had been caused by Darwin's principles also led to new ideas on the origin of life. According to H. Kamminga from the University of Cambridge (1991), there are two approaches (from about 1860 and 1870), which differ greatly in their profound metaphysical assumptions on the nature of life and of living organisms. The first assumed that life is an aspiring property of nature. Living things are a product of lifeless matter and evolved in the course of the history of the universe. The other approach postulated that life is a fundamental property of the cosmos and that living things have always existed somewhere in the universe. This second approach, considered scientifically, cannot provide an answer to the question as to the origin of life; it reappeared in the form of the panspermia hypothesis.

The ideas of the well-known physiologist from Bonn, Eduard Pflüger (1829–1910), seem to predate modern theories: he assumed that, under the specific conditions of the primordial Earth, fundamental constituents of protoplasma could have developed from cyanide-type compounds or polymers derived from them (Pflüger, 1875).

The idea that microbes could migrate across the universe was supported by scientists with a worldwide reputation, such as H. von Helmholtz, W. Thomson (later Lord Kelvin) and Svante Arrhenius. This hypothesis was still accepted by Arrhenius in the year 1927, when he reported in the "Zeitschrift für Physikalische Chemie" on his assumption that thermophilic bacteria could be transported within a few days from Venus (with a calculated surface temperature of 320 K) to the Earth by the radiation pressure of the sun (Arrhenius, 1927). The panspermia hypothesis, which seemed to have disappeared in the intervening decades, was reintroduced in the ideas of Francis Crick (Crick and Orgel, 1973). It still exists in a modified form (see Sect. 11.1.2.4).

Fig. 1.4 The Swedish physical chemist Svante Arrhenius (1859–1927), who received the Nobel Prize for chemistry in 1903 for his work on electrolytic dissociation

The deciding impulse which introduced biogenesis into scientific discussion came from Russia. After the upheavals of the civil war, that country was the subject of worried observation by the rest of the world. It was assumed that no great scientific achievements would be possible there. Then, in 1924, a book on the material basis of the origin of life on Earth appeared in "Red Russia". Its author was Alexandr Ivanovich Oparin (1894–1980) from the Bakh Institute of Biochemistry in Moscow (Oparin, 1924). Basically, the Oparin hypothesis makes the following assumptions:

The prebiotic atmosphere had reducing properties, so that the bioelements C, O, N and S were present in reduced form as CH_4, H_2O, NH_3 and traces of H_2S.

This primeval atmosphere was subjected to various energy sources, such as electrical discharge, solar radiation and heat from volcanoes; these led to the formation of small organic molecules.

These chemical substances accumulated in the hydrosphere, which thus became a "dilute soup" from which the first forms of life evolved spontaneously.

Not all points of this hypothesis are now accepted. Some of the assumptions on the physicochemical state of the primeval Earth have undergone considerable revision in the light of more recent results. Oparin answered the question as to how he came to think that organic molecules could be formed from methane, ammonia, water and hydrogen by referring to ideas he obtained from Mendeleev's hypothesis on the inorganic origin of oil (Oparin, 1965). The concept of a reducing primeval atmosphere was supported by the idea that free oxygen would have immediately destroyed organic molecules by oxidation. In addition, it was already known in 1924 that the sun consisted mainly of hydrogen.

Only four years after Oparin's book was published in Russia, the English scientist J. B. S. Haldane (1928) published an article whose ideas strongly resembled those of Oparin. We now know that Haldane had no knowledge of Oparin's publication, and when the two first met, many years later, they immediately agreed that Oparin had priority. Haldane's assumption of a reducing primeval atmosphere was based on completely different observations: he concluded from anaerobic glycolysis, which is used by many contemporary living organisms as their primary source of energy, that life must have originated in a reducing environment. The ideas described above have gone down in scientific history as the "Oparin–Haldane Hypothesis". Unlike Haldane, Oparin continued to study the biogenesis problem until his death and, in particular, published articles on the formation of protocells. A recent short but detailed survey and assessment of Oparin's life's work was provided by Miller et al. (1997) in their article "Oparin's 'Origin of Life': 60 Years After".

Other scientists took up Oparin's ideas, used them for their own concepts, and tried to form organic molecules from inorganic starting materials. The Mexican scientist A. L. Herrera reported in 1942 in an article entitled "A New Theory of the Origin and Nature of Life" on his investigations with "sulphobes" (Herrera, 1942). These are morphological units ("lifelike forms") which he obtained from reactions between thiocyanates and formalin. Sulphobes are spherical in form, with a diameter between 1 and 100 µm, and can interact with their surroundings; thus they can adsorb dyestuffs. In some ways, they resemble the coacervates studied by Oparin and his school (Sect. 10.2.2).

Another type of experiment on chemical evolution was due first to Groth and Suess and later to Garrison. They studied the type of energy which must be applied to a simulated primeval atmosphere in order to form organic building blocks for biomolecules, starting from inorganic materials. Groth and Suess (1938) studied the influence of UV light on simple molecules, while Garrison (1951) carried out similar experiments using ionising radiation.

Then came the year 1953, and with it important events, both political and scientific in nature: the death of Stalin and the determination of the structure of DNA; in addition, a scientific article was published in "Science" by a previously unknown author, Stanley L. Miller. Its title was "A Production of Amino Acids under Possible Primitive Earth Conditions" (Miller, 1953).

In a footnote, Miller thanked the Nobel Prize winner Harold C. Urey for supervising his Ph.D. thesis work. Thus, this experiment became known as the "Miller–Urey experiment" (Sect. 4.1). Not only was the broader public impressed by these results, but also the small group of scientists who were more or less closely involved with the question of the evolution of life. The successful synthesis of protein building blocks from a simulated primeval Earth atmosphere generated activity in several laboratories, leading in the next few years to important new results. The great importance of the Miller–Urey experiment is due particularly to the fact that it showed for the first time that the problem of the origin of life can be approached by means of scientific method, i.e., *experimentally*.

1.4 The Problem of Defining "Life"

Scientific theory states that one of the most important tasks of science, and scientists, is the task of definition. Thus it becomes absolutely necessary to define the phenomenon known as "life". Very few terms which are used so frequently have been defined in such an unsatisfactory manner. The paradox is that the more we know about life, the more difficult it becomes to define it satisfactorily. There is still *no* clear definition of the term "life" which is accepted by all the scientists studying this phenomenon (Cleland and Chyba, 2002).

Various definitions have been proposed, and, depending on one's scientific standpoint, a suitable one may be available. Several of these definitions will be presented below. A completely satisfactory answer will, however, probably only be found when more detailed results on the origin of life become available.

Sixty years ago, Erwin Schrödinger asked the question, What is life? His English-language book with that title, which appeared in 1944 (Schrödinger, 1944), is based on a series of lectures which he had given at the University of Dublin. He was seeking an answer to the question, How can the processes in time and space, which take place within the limits of a living organism, be explained by physics and chemistry? There is no doubt that his book had an important influence on the development of modern biology, and it already hinted at certain lines of development in molecular biology.

As stated above, biologists and scientists from other related areas have so far not been able to agree on a single definition of the term "life" (Barrow, 1991). This is in no way surprising, since more than 100 attributes and properties have been found to characterize life (Clark, 2002). There is a certain amount of agreement on the distinguishing features of a living system. In his lecture given at a conference held in Trinity College Dublin in September 1993 to celebrate the 50th anniversary of the Schrödinger lectures on the subject "What is Life?", Manfred Eigen defined three basic characteristics which have so far been found in all living systems:

Self-reproduction: without this process, information would be lost after every generation.

Mutation: without it, information would be invariant—and thus no development of the species would be possible.

Metabolism: without this, a living system would reach an equilibrium state, from which, again, no development would be possible.

The physical chemist Luigi Luisi, ETH Zürich (1998), made clear the vital importance of an agreed definition for future progress in biogenesis research. He proposed five definitions for the term "life" and suggested that a definition agreed on by as many scientists as possible would make it possible to define the goals for future research projects, on the basis of that general definition.

When life is to be defined, it is necessary for the purposes of biogenesis research to limit the discussion to the simplest life forms. This type of reduction is necessary in order to be able to make a clear division between inanimate and animate objects. Even for "reduced systems", the boundaries between the two become unclear, as shown by the example of viruses. A definition of minimal life makes it possible to ignore the complex properties of higher living organisms, such as consciousness, intelligence or ethics.

According to Luisi, a definition of life must satisfy the following criteria:

It should be possible to make the distinction between animate and inanimate as clearly and as simply as possible, by means of experiments.
The criteria for making the distinction should be verifiable across a wide range.
The definition should include both forms of life which are already known and hypothetical pre-life forms. It should be logically self-consistent.

The definitions of "life" which have been formulated in the NASA Exobiology Program as general working definitions are as follows:

1. "Life is a self-sustained chemical system capable of undergoing Darwinian evolution."

This definition was previously used by Horowitz and Miller (1962). An undefined external energy source was included in this definition. The growing influence of the "RNA world" can be seen in the second NASA definition:

2. "Life is a population of RNA molecules (a quasispecies) which is able to self-replicate and to evolve in the process."

The following definitions proposed by L. Luisi go further than the NASA definitions:

3. "Life is a system which is self-sustaining by utilizing external energy/nutrients owing to its internal process of component production."

Instead of "reproduction" or "replication", the more general term "production" was used. The third definition includes the first definition. However, because it contains neither Darwinian nor genetic specification, this definition takes both coded and uncoded life into account. Since the term "population" is not included, the definition can be applied to single objects such as robots.

In the next definition, there is a limitation of the smallest life forms:

4. "Life is a system which is spatially defined by a semipermeable compartment of its own making and which is self-sustaining by transforming external energy/nutrients by its own process of components production."

This definition excludes all systems which do not have a spatial boundary to their synthetic machinery, for example pure RNA replication. The walls of a test tube or the banks of a "warm, little pond"[1] cannot be included as boundaries in the sense of definition four.

Taking these limitations into account, Luisi suggests a fifth and last definition:

5. "Life is a system which is self-sustaining by utilising external energy/nutrients owing to its internal process of component production and coupled to the medium via adaptive changes which persist during the time history of the system."

Here there is no limitation, as some scientists consider one to be unnecessary. The order of the definitions is not arranged with respect to their quality.

These attempted definitions are extremely useful, since they force biogenesis researchers to define their own standpoints. They make it possible to develop new working hypotheses for future research projects. According to Luisi, "Once you have the intellectual clarification in front of you, you have the challenge to realize it in the laboratory." However, the definitions presented above are not good enough for all the scientists working in this area.

Other characteristics of life have been formulated by Daniel E. Koshland Jr. (University of California at Berkeley) as the "Seven Pillars of Life". They are as follows:

1. A program
2. Improvisation
3. Compartmentalisation
4. Energy
5. Regeneration
6. Adaptability
7. Seclusion

This list contains life characteristics which are contained in most of the definitions we have seen. However, two or three of the "pillars" are unusual:

Point 2 describes the possibility that a system can change its program in order to adapt to new environmental conditions.

Point 5 takes into account that thermodynamic losses must be compensated for.

The last pillar can perhaps be compared with "privacy" in the social world. This property of life makes it possible for many biochemical processes to take place independently in a cell without disturbing one another (Koshland, 2002).

The search for life in the cosmos requires a generalised, universal definition of life. This must take into account the properties of systems ranging from viruses, prions, denucleated cells or endospores to life in a test tube, computer viruses or even to robots which are capable of self-replication.

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[1] This phrase is taken from a letter written by Charles Darwin (1871) that contains vague references to chemical evolution: "…if we could conceive in some warm, little pond with all sorts of ammonia and phosphoric salts, light, heat, electricity etc. present that a proteine compound was chemically formed…".

Results from philosophical considerations on language show that attempts to define life lead to a dilemma, similar to that which occurred when trying to define water before molecular theory existed. Since no analogous theory of the nature of living systems exists, an infinite controversy as to the definition of life is unavoidable (Cleland and Chyba, 2002).

"The definitions of life are extremely controversial". So begins a publication on the problem of the definition of life which appeared as late as 2004. This publication is written by three Spanish scientists from the Centre for Astrobiology (INTA/CSIC) in Madrid, the University of València and the University of the Basque Country in San Sebastian (Ruiz-Mirazo et al., 2004). Their "general definition" of life introduces two new terms into the discussion: "autonomy" and "open-ended evolution capacities".

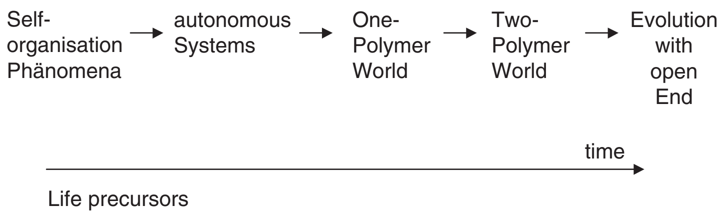

Fig. 1.5 Schematic representation of the evolution of life from its precursors, on the basis of the definition of life given by the authors. If bioenergetic mechanisms have developed via autonomous systems, the thermodynamic basis for the beginning of the archiving of information, and thus for a "one-polymer world" such as the "RNA world", has been set up. Several models for this transition have been discussed. This phase of development is possibly the starting point for the process of Darwinian evolution (with reproduction, variation and heredity), but still without any separation between genotype and phenotype. According to the authors' definition, life begins in exactly that moment when the genetic code comes into play, i.e., in the transition from a "one-polymer world" to a "two-polymer world". The last phase, open-ended evolution, then follows. After Ruiz-Mirazo et al. (2004)

In addition, the authors suggest that all such systems must have a semi-permeable active boundary (membrane), an energy transduction apparatus and (at least) two types of functionally interdependent macromolecular components (catalysts and records). Thus, the phenomenon of life requires not only individual self-replication and self-sustaining systems, but it also requires of such individual systems the ability to develop a characteristic, evolutionary dynamic and a historical collectivist organisation.

A hypothesis put forward by the British physicist James Lovelock, the Gaia hypothesis, is related to the problems just discussed. This hypothesis is supported by several well-known scientists, such as the American biologist Lynn Margulis and the theoretical physicist Freeman Dyson (Dyson, 1992). According to the Gaia hypothesis, the Earth itself can be regarded as a type of living organism. In ancient Greece, Gaia was the Earth goddess, who balanced out inequilibria which developed from interactions between heaven and Earth. There are various arguments in support of

Gaia; on the other hand, it also appears possible that the Earth is a highly resistant system which can deal with changes such as those induced by catastrophes.

In an alternative theory, the results of population dynamics rather than Darwinian natural selection are responsible for the regulation of environmental conditions (Staley, 2002).

It is not yet possible to make a final decision on Gaia, a hypothesis which also requires further studies and experiments to give a clear answer and thus a deeper understanding of our existence.

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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

H. Rauchfuss, *Chemical Evolution and the Origin of Life*,

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

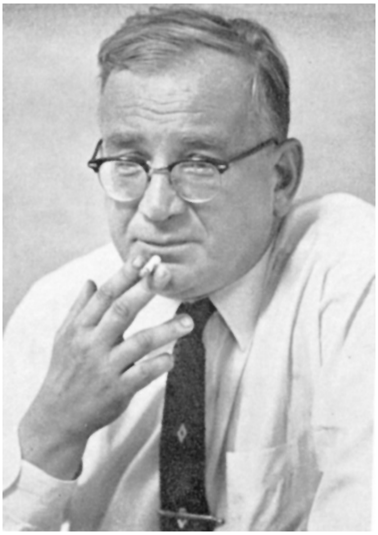

Fig. 2.1 George Gamow (1904–1968) was born in Odessa, studied in Leningrad (St. Petersburg) and emigrated in 1934 to the USA, where he taught in Washington, D.C., until 1965 and at the University of Colorado in Boulder for the last three years of his life

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 15×10^9 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 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 ± 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.	*Very good*	Huge amount of supporting evidence from various areas of biology and physics.
The universe expanded according to the general theory of relativity.	*Good*	Passes all previous tests, but only a few of these were stringent.
Galaxies consist mainly of dark matter built up from exotic particles.	*Satisfactory*	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.	*Poor*	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.	*Fail*	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}H) and the helium isotopes ^{3}He and ^{4}He remained stable. Heavier elements could not be formed because of the low concentration of deuterium: the ^{2}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}He was the starting material for subsequent nuclear syntheses. Carbon-12 can be formed in a triple α-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}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: Maciá et al. (1997)

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

Further capture of α-particles leads to the formation of oxygen and neon. ^{16}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.

$$\mathrm{H} \rightarrow \mathrm{He} \rightarrow \mathrm{C,O} \rightarrow \mathrm{Ne} \rightarrow \mathrm{Mg,Si} \rightarrow \mathrm{Fe,Ni} \tag{2.1}$$

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" ($^{12}C + ^{12}C$) 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}Ne is destroyed occurs subsequently to the carbon burning, but before the absorption of oxygen. The α-particles formed are used up by the nuclei already present (also from neon itself) in so-called neon burning.

$$^{20}\mathrm{Ne} + \gamma \rightarrow {}^{16}\mathrm{O} + \alpha \quad \text{and} \quad {}^{20}\mathrm{Ne} + \alpha \rightarrow {}^{24}\mathrm{Mg} + \alpha \rightarrow {}^{28}\mathrm{Si} + \gamma \tag{2.2}$$

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 2.5×10^9 K. Under these conditions, phosphorus (^{31}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}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}P nuclide is probably formed via the following reaction pathways:

$$^{12}\mathrm{C} + ^{12}\mathrm{C} \rightarrow ^{24}\mathrm{Mg}^{*} \rightarrow ^{23}\mathrm{Na} + \mathrm{p} \rightarrow ^{23}\mathrm{Na}(\alpha,\mathrm{p}) \rightarrow ^{26}\mathrm{Mg}(\alpha,\mathrm{y}) \rightarrow ^{30}\mathrm{Si}(\mathrm{p},\gamma) \rightarrow \mathbf{^{31}P} \quad (2.3)$$

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

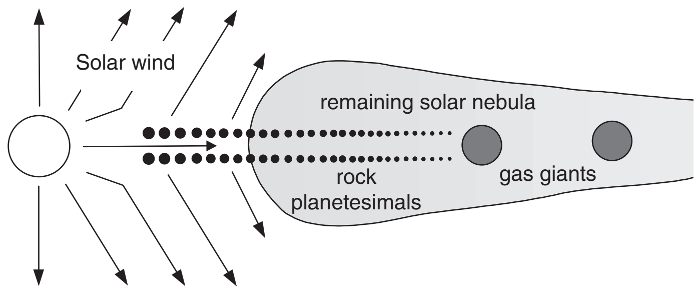

Fig. 2.2 The state of the incipient solar system during the T Tauri phase of the young sun. The central region around the sun was “blown free” from the primeval dust cloud. Behind the shock front is the disc with the remaining solar nebula, which contained the matter formed by the influence of the solar 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}U, ^{232}Th and ^{40}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.

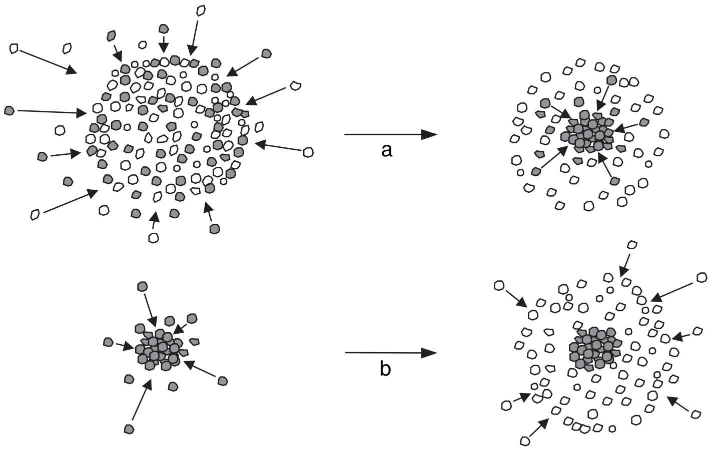

Fig. 2.3 According to the *homogeneous* accretion model (**a**), iron-containing material (black) and silicate-containing material (colorless) condensed out at the same time, i.e., the proto-Earth consisted of a mixture of the two. The concentration of iron in the Earth's core took place later. According 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 CO_2 and H_2O, since the gas from the interior could only have come into contact with FeO and Fe_2O_3 silicates in the mantle. If, however, metallic iron had been distributed throughout the mantle, the iron and the FeO silicates would have had a reductive influence on the gases: the gas exhaled into the atmosphere would then have consisted of CH_4, H_2 and 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).

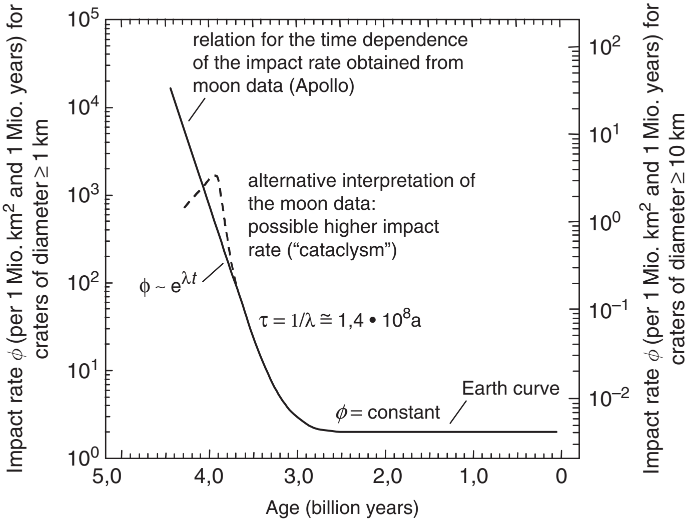

Fig. 2.4 Time dependence of the rate of impact of comets and asteroids on the surface of the Earth and primeval Earth (derived from Apollo moon data). With kind permission of Prof. Neukum (1987)

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_2 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 ^{143}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).

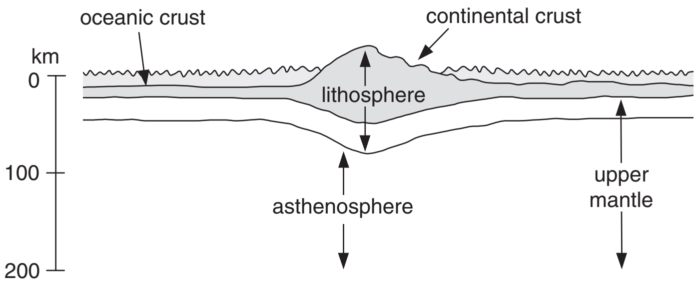

Fig. 2.5 The outer shell of the Earth, the lithosphere, is a solid, rigid layer. It consists of the crust and the outer parts of the mantle. The lithosphere swims on the flexible, partially melted part of the mantle (the asthenosphere). Figure simplified after Press and Siever (1994). With permission 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 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 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 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 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 H_2, H_2O, CH_4 and 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 Fe^{2+} to Fe^{3+}.

The result would then be a weakly reducing atmosphere containing H_2O, CO_2, H_2 and CO, but *almost no* CH_4! In addition, strongly reducing molecules such as CH_4 and 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 CH_4 and NH_3 dissolved in erupting magma had been several orders of magnitude lower. It has also been suggested that CH_4 and NH_3 could have been transported to the primeval Earth by comets and meteorites. The photochemical reduction of CO_2 in the presence of Fe^{2+} has also been discussed. A tragic natural catastrophe which occurred some years ago shows that 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: $H_2/H_2O = 0.01$ and $CO/CO_2 = 0.03$. Nitrogen is very difficult to detect, and only traces of ammonia are found. In addition, highly variable amounts of the following are present: SO_2, H_2S, elementary sulphur, HCl and B_2O_3. Small amounts of H_2, CH_4, CO and 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 CO_2 content of the planetary atmosphere plays a vital role. A relatively high 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 Müllen (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}O in zirconia crystals which are between 3.9 and 4.28 billion years old. This leads to the assumption that the zirconia ($ZrSO_4$) 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 $10^{-5\pm1}$ 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 CO_2 concentration in the primeval atmosphere was 100–1,000 times higher than today. Since 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 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.

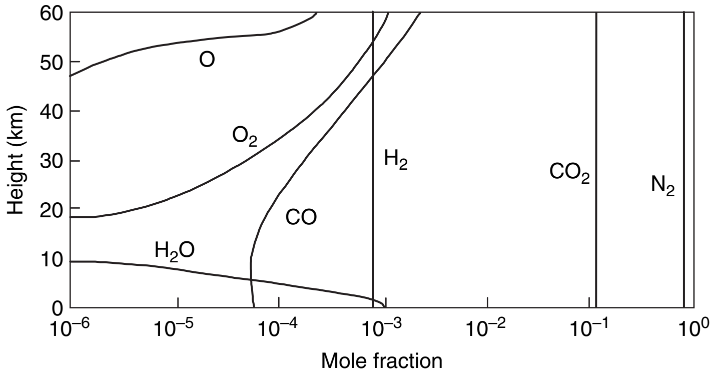

Fig. 2.6 The main components of a typical weakly reducing primeval atmosphere as a function of the altitude above the Earth's surface. The "mole fraction" refers to the mixing ratio of the atmospheric mixture at an assumed surface pressure of one atmosphere. After Kasting (1993)

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 Eggler, 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 H_2S, CO_2 and 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 H_2O 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 µm. The synthesis of water in the warm regions of the galaxy probably occurs according to the following reaction mechanism:

$$O + H_2 \rightarrow OH + H \quad (2.4)$$

$$OH + H_2 \rightarrow H_2O + H \quad (2.5)$$

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 $0.6–4.8 \times 10^{-4}$, and thus of a similar magnitude to the value of 1.6×10^{-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).

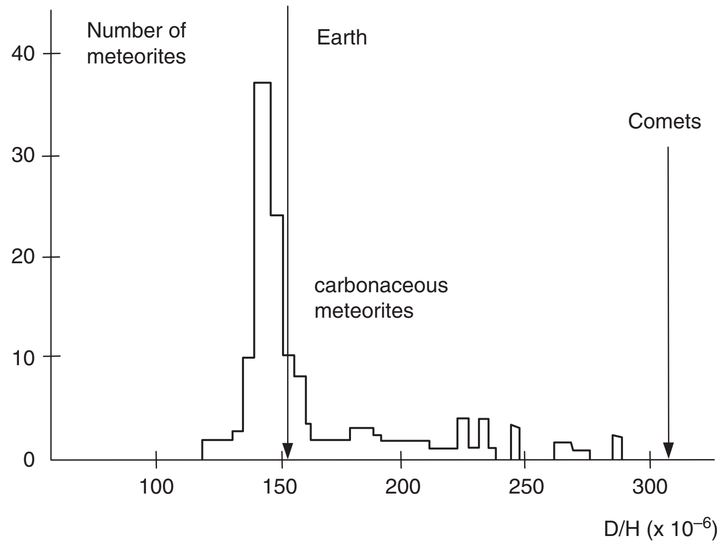

Fig. 2.7 The distribution of the ratio of the two hydrogen isotopes (D/H) in carbonaceous meteorites compared with that on Earth and in the comets. According to this distribution, most of the water on Earth must have had its origin in meteorites. From Robert (2001)

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_2 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 Fe^{2+} to Fe^{3+} provided a possibility for the reduction of nitrites and nitrates to ammonia. This reaction would have been of great importance, as 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 NH_3 with the help of Fe^{2+}, thus raising the pH of the oceans to 7.3. Temperatures above 298 K favoured this reaction, which can be written as:

$$6\,Fe^{2+} + 7\,H^+ + NO_2^- \rightarrow 6\,Fe^{3+} + 2\,H_2O + NH_3 \qquad (2.6)$$

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 NH_3 is formed from N_2 with the help of H_2S. The presence of freshly precipitated FeS (prepared from $FeSO_4$ by precipitation with Na_2S at room temperature under an argon atmosphere) was found to be vital: aged FeS is inactive. In this reaction, FeS is converted to 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, NO_2, N_2O and 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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Chapter 3
From the Planets to Interstellar Matter

3.1 Planets and Satellites

The best classification of the development of planetary research is due to Kuiper, the father of modern planetology, who distinguishes three phases:

First, the three centuries of basic, classical discoveries (Galilei, Kepler, Laplace et al.).

The second phase, beginning at the end of the nineteenth century, was linked to the development of astrophysics and astrophotography; this phase was, however, marked by a *decrease* in scientific interest in planetary research.

Phase three, the renaissance of planetology, starting around 1960, caused in particular by the rapid development and successes of space travel.

In this chapter, we will deal particularly with those planets and moons which are relevant to the question of the origin of life.

The planets of the solar system are normally divided into two groups, according to their chemical composition:

The inner, or terrestrial, planets, from Mercury to Mars, including the planetoids. These have masses between 0.06 and 1 Earth masses, densities between 3,000 and 5,500 kg/m^3, and similar structures:

A relatively thin upper layer, the crust
A mantle
A core

The gas giant planets: Jupiter, Saturn, Uranus and Neptune. The planet Pluto has a status of its own, and has recently been renamed a dwarf planet.

3.1.1 Mercury

This planet, the nearest to the sun, has almost no atmosphere; its surface is covered with craters. During the formation of Mercury, planetesimals were able to impact the planet's surface without any resistance. Thus, the lack of erosion processes (due to wind and/or water), which could flatten the surface, left the craters as they originally were. There are great temperature differences between the day and the night side of Mercury's surface, from 600 down to 100 K. Radar mapping (using wavelengths of 3.5 cm) indicates the presence of water ice at the poles, in craters which have probably never been reached by the sun's rays (Slade et al., 1992). According to one hypothesis, Mercury was once a moon of Venus and was shifted to a new orbit around the sun by an unknown event.

Until now, Mercury has only been studied more closely by one spacecraft (Mariner 10, 1974), since its nearness to the sun means that spacecraft approaching it are subject to particularly extreme conditions. NASA's MESSENGER (Mercury Surface, Space, Environment, Geochemistry and Ranging) was launched in 2004 and is planned to reach Mercury in March 2011, and then to orbit the planet. The main tasks of the MESSENGER mission are to map the planet, to make measurements of its magnetic field and to collect data relevant to its geological and tectonic history (Solomon, 2007).

3.1.2 Venus

Apart from the sun and the moon, Venus is the brightest heavenly body. It is the only satellite of the sun which is greeted during an emotional aria in a well-known opera: Wolfram von Eschenbach serenades the brightly shining Venus in Wagner's *Tannhäuser* with the words "O Du mein holder Abendstern wohl grüss' ich Dich so gern" ("O my fair evening star, I always gladly greeted thee").

The surface of Venus is hidden under an unbroken layer of clouds 45–60 km above it. Recently, the planet has been subjected to a complete cartography by radar satellites. Its atmosphere contains 96% CO_2 by volume, the remainder consisting of N_2, SO_2, sulphur particles, H_2SO_4 droplets, various reaction products and a trace of water vapour. The water is probably subject to photolytic decomposition. Noble gases are more abundant than on Earth: ^{36}Ar by a factor of 500, neon by a factor of 2,700, and D (deuterium) by a factor of 400.

Because of the CO_2 greenhouse effect, the annual average temperature at the surface of Venus is around 733 K, and there is intense atmospheric activity. Results from the Cassini spacecraft did not confirm the earlier assumption that lightning is very frequent. According to Gurnett et al. (2001), flashes of lightning either occur very seldom, or are completely different from terrestrial electrical discharges. The turbulences at the surface of Venus are extremely vehement: wind speeds of up to 360 km/h have been measured, which means that the cloud layer moves 60 times faster than the planetary surface. The surface pressure is 90 times greater than that at sea level on Earth. New model calculations show that the climate of Venus has changed in a significant manner across only a few hundred million years (Prinn, 2001). According to the Bullock-Greenspoon model, Venus was colder between 600 and 1,100 million years ago. Two main processes now control the climate of Venus:

Global warming, mainly determined by the CO_2 greenhouse effect
Cooling, caused by reflection of solar irradiation due to the presence of thick clouds of sulphuric acid

There are now doubts as to whether Venus is in fact extremely hostile to life. An audacious theory suggests that the cloud cover in the Venusian atmosphere could have provided a refuge for microbial life forms. As the hot planet lost its oceans, these primitive life forms could have adapted to the dry, acid atmosphere. However, the intensity of the UV radiation is very puzzling. The authors suggest that sulphur allotropes such as S_8 act on the one hand as a UV umbrella and on the other as an energy-converting pigment (Schulze-Makuch et al., 2004).

The Venus Express spacecraft launched by the European Space Agency (ESA) in November 2005 reached its goal in April 2006. Its main purpose was to find out more about the (still not understood) super-rotation of the Venusian atmosphere, which causes clouds to circulate the planet in about four earth days. Venus takes 243 earth days to rotate about its own axis.

The VIRTIS apparatus (Visible Infrared Thermal Imaging Spectrometer) on board can observe the atmosphere and the cloud layers at various depths (on both the day and the night side of the planet). VIRTIS has also provided data for the first temperature map of the hot Venusian surface. These data have led to the identification of "hot spots" and thus provided evidence for possible volcanic activity (www.esa.int/specials/venusexpress).

3.1.3 Mars

Western man has had a special relationship with the planet Mars for many centuries. The Romans venerated the red planet as the god of war, and in Italy it later became the god of fruitfulness and the god of the peasants. The astronomer Tycho Brahe (1546–1601), born in the then Danish and now Swedish province of Skåne, determined the exact position of Mars by means of precise observations of the heavens. The discovery of the telescope by the Dutch physicist and mathematician Christiaan Huygens (1629–1695) made it possible to determine the rate of rotation of the planet. Huygens determined the period of rotation as 24.5 hours; the value accepted today is 24.623 hours, making clear how great an achievement his measurements, carried out 250 years ago, in fact were! The Italian astronomer Giovanni Schiaparelli (1835–1910) discovered *canale* on the surface of Mars; in Italian, "canale" means not only canals, but other water-bearing systems. The "canal hypothesis" was the subject of great interest, not only among scientists but also among authors of fiction.

The planet Mars is smaller than the Earth: its diameter is 6,762 km, compared with the Earth's 12,760 km. Our neighbour planet has only a very thin atmosphere (surface pressure 0.005–0.010 atm), so its surface can easily be observed. The atmosphere consists of the following (volume percentages given):

∼ 95% CO_2
∼ 2.5% N_2
∼ 1.5% Ar
∼ 1% other noble gases
∼ 0.1% O_2 and CO, formed from CO_2 by photodissociation

Recently, sulphur has also been found on the surface of Mars; it was probably deposited from the atmosphere and originated in volcanic activity. Sulphur was also found in meteorites which probably originated on Mars (Farquhar et al., 2000). The mean surface temperature is ∼210 K (at night 150 K and during the day 270 K).

Ice has been found at the poles: new measurements of Mars' southern polar region indicate the presence of extensive frozen water. The polar region contains enough frozen water to cover the whole planet with a layer of liquid approximately 36 ft deep. A joint NASA–Italian Space Agency instrument on the European Space Agency's Mars Express spacecraft provided these data (NASA press release, 15 March 2007). It must be assumed that volcanic exhalations contained large amounts of water.

The planet Mars provides another sensation: it has the highest and largest volcano in the solar system, Mons Olympus (25 km high). Volcanologists disagree about the formation of this huge volcano, but there are several models which attempt to explain its formation. Not only the extreme size and height of the volcano, but also the almost circular high escarpment which surrounds it make the volcano unique (Helgason, 1999).

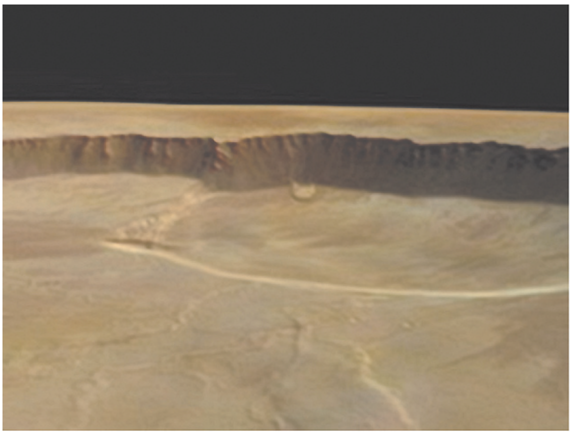

Fig. 3.1 Perspective view of part of the caldera of Olympus Mons on Mars. This view was obtained from the digital altitude model derived from the stereo channels, from the nadir channel (vertical perspective) and the colour channels on the Mars Express Orbiter. The photograph was taken on 21 January 2004 from a height of 273 km. The vertical face is about 2.5 km high, i.e., about 700 m higher than the north face of the Eiger mountain (Switzerland). With permission of the DLR

The surface of Mars is covered by meteorite craters, some up to 200 km in diameter. The question as to whether water exists on Mars has been the subject of scientific controversy for many years (see Chap. 11). Costly Mars missions with the goal of mapping the surface have afforded important results on now dry river valleys. The weather on Mars is characterized by ground-level fog, thin ice clouds and (often very violent) dust storms, which vary not only seasonally but also daily. The question as to whether our neighbour planet harbours life (of any kind), or if it ever did so, gave rise to a media sensation at a NASA press conference on August 7, 1996. The researchers, who had been studying the 1.9 kg Mars meteorite ALH 84001, came to the conclusion that it bore clear evidence of previous life forms:

A certain carbonate species with magnetite and iron deposits: microorganisms could have been involved in its formation.
Organic compounds: polycyclic aromatic hydrocarbons, in particular phenanthrene ($C_{14}H_{10}$), pyrene ($C_{16}H_{10}$) and chrysene ($C_{18}H_{12}$), which were detected using high resolution mass spectrometry.
Structures which showed similarities with microorganisms (McKay, 1996).

There was, however, much criticism of these optimistic results, in particular from the palaeontologist William Schopf from UCLA.

Not only would proof of the existence of life on Mars be a great sensation, but even the discovery of precursors of life, such as biomolecules or building blocks for their formation, would change our perspective greatly (see also Chap. 11).

3.1.4 Jupiter

The planet Jupiter occupies a special position in the solar system. It is the largest and heaviest planet, with a mass of 1/1,047 that of the sun. Jupiter consists almost solely of hydrogen and helium with a ratio similar to that found in the sun itself: He:H $\approx$ 1:10. Small amounts of some heavier elements are present, such as B, N, P, S, C and Ge. The density of Jupiter has been calculated as 1,300 kg/m^3. Its atmosphere can be divided into three zones (starting from the outermost):

- The zone of the ammonia clouds (temperature $\sim$140 K),
- The zone of the NH_4SH clouds, also containing NH_3, H_2 and He ($\sim$200 K) and
- The zone of the ice clouds, consisting of water ice crystals and H_2/He gas ($\sim$270 K).

The planet does not have a real surface; instead, there is a gradual transition from the H_2/He mixture to the central body, which consists of molecular hydrogen. Since there is no actual surface, temperatures can only be expressed in terms of their corresponding pressures.

Around 85% of the total amount of hydrogen is present as a metallic phase. It is assumed that there is a silicate rock core with a temperature estimated to be

24,000 K. This mass of rocky material probably formed the nucleus for condensation and attracted large amounts of the H_2/He-rich solar material around 4.5 billion years ago, acting as a galactic vacuum cleaner.

Research on Jupiter has progressed greatly in the last decades. The Galileo mission, which started in 1989, provided important data on Jupiter and its moons. The Galileo spacecraft had a special probe on board, which left the mother craft and entered Jupiter's atmosphere on December 7, 1995. A great deal of heat was generated in the process: temperatures of around 16,000 K were measured at around the 5 mbar level (Seiff et al., 1997). The probe flew for about an hour before disintegrating in the depths of the Jovian atmosphere. The data which it transmitted to the Galileo spacecraft provided information on temperature, pressure, chemical composition (and also isotope ratios) of the atmosphere, its water content, and on electrical discharges (Young, 1996). Surprisingly, the water concentration measured by the probe was only about 10% of that expected; it is unclear whether this was merely a local phenomenon, or whether it is characteristic for the whole atmosphere of Jupiter. The giant planet rotates around its axis in about ten hours, and thus compensates for its lack of mass by its enormous rotary motion. The latter causes the outer visible atmosphere to be very dynamic: it exhibits conspicuous, complex zones parallel to the degrees of latitude. Rapidly rotating planets are characterized by many regular dynamic phenomena, which are due to the Coriolis force.

In 1994, a unique incident occurred: the impact of the Shoemaker-Levy comet on the Jovian atmosphere. The strong gravitational field of Jupiter caused the comet to break up before it could enter the atmosphere, and the parts of the comet crashed separately into the atmosphere one after the other. This unique spectacle was observed by many observatories and also by the Galileo spacecraft and the Hubble telescope. It led to the discovery of yet another phenomenon: the most intensive aurora effects in the solar system, observed at Jupiter's poles. Astronomers assume that the energy for these comes from the planet's rotation, possibly with a contribution from the solar wind. This process differs from that of the origin of the aurora on Earth, where the phenomenon is caused by interactions between the solar wind and the Earth's magnetic field.

One more important property of Jupiter must be mentioned: the Earth owes its relatively "quiet periods" (in geological terms) to the huge gravitational force of the giant planet. Jupiter attracts most of the comets and asteroids orbiting in its vicinity, thus protecting the Earth from impact catastrophes!

3.1.5 Jupiter's Moons

The four brightest and largest Jovian moons are also called the "Galilean moons", as Galileo Galilei discovered them in 1610 and gave them their names: Io, Europa, Ganymede and Callisto, in the order of their orbits around Jupiter. The system of Jupiter and its four moons has many similarities to the solar system as a whole, in particular the extreme regularity and the planar orbits (Stevenson, 2001).

3.1.5.1 Io

As already mentioned, the moon Io is the innermost of Jupiter's satellites. Its density is 3,550 kg/m^3, similar to that of the terrestrial planets, and the colour of its surface ranges from yellow gray to orange red. The latter colour may be due to the presence of S_2O, as sulphur and sulphur compounds play a vital role in the chemistry of Io, the surface rocks of which contain large amounts of potassium and sodium compounds. The greatest sensation was the discovery of an active volcano by one of the Voyager missions in 1979. The eruption of the volcano, known as "Prometheus", spews out matter to a height of 100 km above the moon's surface. Nine other volcanoes have since been discovered on Io, which during their active phases emit sulphur- and oxygen-containing gases as well as molten sulphur and sulphur dioxide; these exhalations reach heights of up to 250 km. Because of its volcanic activity, the surface of Io is relatively flat; impact crater structures are hardly visible. An answer to the question of the energy source for the volcanic activity of Io was soon found: like the other Galileic moons, but in particular because it is so near to Jupiter, the orbit of Io is elliptic. This leads to tidal forces which generate frictional heat in its interior. It seems likely that the moon has remained in its present state for about the last two billion years. The atmospheric pressure of Io is around 10^{-10} bar of SO_2 at temperatures between 60 and 120 K.

The SSI (solid-state imaging) camera on board the Galileo spacecraft transmitted impressive high-resolution pictures of Io's volcanic activity. Active lava lakes, lava "curtains", calderas, mountains and plateaus can be seen (McEwen et al., 2000). The Hubble telescope detected both S_2 gas and SO_2 in a SO_2 to S_2 ratio of 1:4 in the smoke trail of the volcano Pele. This value suggests an equilibrium between silicate magmas in the neighbourhood of the quartz–fayalite–magnetite buffer (see Sect. 7.2.2).

Io is one of the most interesting objects in planetary research. However, it is completely irrelevant to the biogenesis problem, in complete contrast to the Jovian moon Europa.

3.1.5.2 Europa

Jupiter's moon Europa has only been the subject of intense scientific investigation in recent years; it is considered to be a member of that small group of heavenly bodies which could perhaps accommodate life (or a precursor of life). About 20 years ago, the Voyager passes afforded sensational pictures of Europa. These showed a network of linear bands, of differing breadths, on a very bright surface. The mean density was calculated as 3,018 $\pm$ 35 kg/m^3, and the surface temperature measured was 90–95 K. Circumstantial evidence points to either a surface consisting of water ice, or the presence of liquid water or "warm ice" under the surface. Three models were proposed (Oró et al., 1992):

– *The thin ice model*: the silicates are mainly hydrated, so there is a thin layer (a few kilometres) of water ice above the silicates.

– *The ice-ocean model*: Europa's core consists of dehydrated silicates, since heat production made dehydration possible. Around the core, there is a thick layer of liquid water (about 100 km), and above that a thin layer (about 10 km) of water ice.
– *The thick ice model*: enough heat was generated in the interior of the moon to dehydrate the silicates. The water set free froze to give an ice layer about 100 km thick.

The first model appears unlikely, since it would entail the presence of more ancient collision craters on the moon's surface. The decision as to whether the second or third model is favoured depends on the question as to whether the amount of heat generated by tidal friction was low enough to allow the water mass to freeze completely. Theoretical considerations and calculations suggest that the second model is probably most likely to be correct. More recent results, in particular from the Galileo mission in October 1996, provided pictures of the moon's surface with much higher resolution than before. They showed episodic separation of the surface plates, with the crevasses being filled up by material from lower layers (either ice or water) (Sullivan et al., 1998). Convection of the solid ice layer may be involved, i.e., the formation of ice domes and ridges caused by the motion engendered by the upthrusting, warm ice masses (Pappalardo et al., 1998).

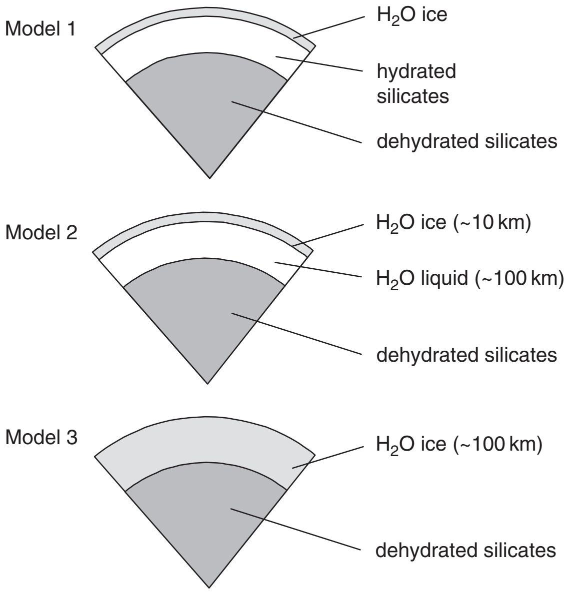

Fig. 3.2 The three possible models for the inner structure of the Jovian moon Europa: model 1 has a thin layer of ice at the surface, model 2 is the ice-water model and model 3 involves a thick ice layer

A further piece of evidence for the presence of an ocean below the ice surface was found by Carr et al. (1998) during their analysis of pictures with resolutions of 1.2 km, 180 m and 54 m per pixel: local icebergs are visible. A more exact morphology indicates that liquid water is present under the ice surface. Using data from the Galileo NIMS (Near-Infrared Mapping Spectrometer), McCord et al. (1998) from the University of Hawaii found evidence for the presence of salts on the moon's surface. The water absorption bands recorded at 1–2.5 μm showed the presence of hydrated minerals (magnesium sulphates, sodium carbonates and mixtures of the two). These can be detected in the surface lines (ridges) and the optically denser regions of the surface. New IR and UV spectral data from the Galileo probe (Carlson et al., 1999a) and model measurements under simulated "Europa conditions" in the laboratory can only be interpreted in terms of the presence of hydrogen peroxide (H_2O_2). This is probably formed by radiolysis at the water surface, since the Jovian moon is subjected to violent bombardment, originating from Jupiter's magnetosphere, by energy-rich electrons, protons and S and O ions.

Carlson et al. (1999b) compared laboratory spectra and Galileo data and suggested that hydrated sulphuric acid is the main component in the dark surface material, which probably also contains sulphur polymers modified by radiation chemistry. A sulphur cycle involving three sulphur species is suggested: sulphuric acid (H_2SO_4), sulphur dioxide (SO_2) and sulphur polymers (S_x).

Before data from the Galileo mission became available, the interior structure of the moon was still basically unknown. The data obtained during two encounters of the probe with Europa (E4 and E6) on December 19, 1996, and February 20, 1997 (Anderson et al., 1997), indicated the presence of an inner core with a density of 4,000 kg/m^3. This could be a metal core with a radius of about 40% of that of the moon, surrounded by a rock mantle with a density of 3,000–3,500 kg/m^3. Two further approaches of the probe to Europa made refinement of the model possible (Anderson et al., 1998), and they concluded that the moon's interior may consist of a mixture of silicates and metals. If the moon does in fact have a metallic core, estimation of its diameter is not possible because of its unknown composition.

Moore (1998) suggested that the data available could be interpreted in terms of an ice crust 10–15 km thick. Christopher Chyba from the SETI Institute (Mountain View, California) has published articles in *Nature* (2000), the *Proceedings of the National Academy of Sciences* (2001a) and in *Science* (2001b) in which he suggests that a detailed study of this Jovian moon is necessary: he discusses the possibility of a complex ecosystem, nourished by the radiation coming from outer space, on or in the ice layers of the moon. The planned Europa orbiter mission may provide certainty on this, but at least another five years of uncertainty lie ahead. The use of a submersible robot to study the (possible) ocean layer and its floor has been discussed.

Such a mission would require successful drilling through the moon's surface ice layer (Rummel, 2000; de Morais, 2000): testing of a new apparatus required for the study of Europa's ice could be done in the subglacial Antarctic Lake Vostok, under the Antarctic ice. It does not, however, seem appropriate to test such technologies in this extremely sensitive environmental situation. However, Russian scientists are carrying out drilling studies on Lake Vostok (Inman, 2006).

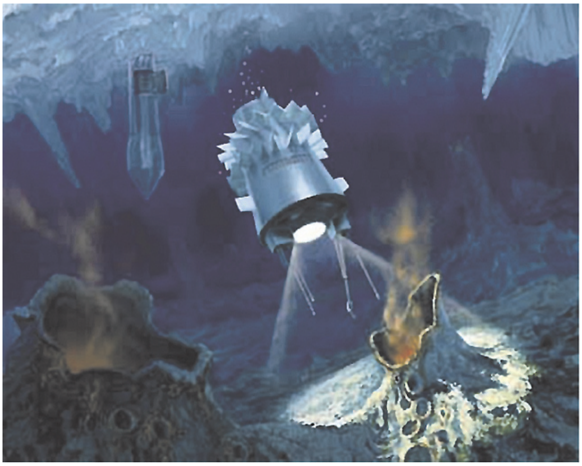

Fig. 3.3 An artist's impression of the originally planned "hydrobot" mission to Europa. The robot has bored through the ice layer in the moon's intermediate aqueous layer and is investigating the ocean floor. From NASA

Recent work suggests that there may have been a period in Europa's history when an extreme greenhouse effect led to temperatures which would have sufficed for reactions necessary for chemical evolution. According to this (unproven) hypothesis, building blocks for biomolecules or even primitive life forms could have existed. The authors assume that there is a high probability that bioelements could have been "delivered" by comets (Chyba and Phillips, 2002).

3.1.5.3 Ganymede and Callisto

These two Jovian moons are in some respects quite similar. They probably consist of rocky material and frozen water (in a ratio close to 1:1) and, in contrast to Europa, are covered by a large number of craters caused by collisions with other heavenly bodies.

Ganymede has a diameter of 5,268 km and is thus the largest moon in the solar system; it is in fact larger than the planet Mercury. Reflection spectra provided by the NIMS apparatus on the Galileo spacecraft suggest that the surface of Ganymede contains aqueous material (McCord et al., 2001). As on Europa, it is likely that this material is in fact frozen $MgSO_4$ sols formed in liquid layers under the surface. A careful evaluation of the pictures of the moon's surface led to a great deal of speculation; thus, some authors discuss a secondary encrustation of the moon's surface due to tectonic or volcanic processes (Schenk et al., 2001). Volcanic eruptions could have brought liquid water or solid water ice to the surface. The tectonic activity on Ganymede may have been much greater than has previously been assumed (Kerr, 2001).

Callisto orbits Jupiter at a distance of 1.9 million kilometres; its surface probably consists of silicate materials and water ice. There are only a few small craters (diameter less than a kilometre), but large so-called multi-ring basins are also present. In contrast to previous models, new determinations of the moon's magnetic field suggest the presence of an ocean under the moon's surface. It is unclear where the necessary energy comes from: neither the sun's radiation nor tidal friction could explain this phenomenon. Ruiz (2001) suggests that the ice layers are much more closely packed and resistant to heat release than has previously been assumed. He considers it possible that the ice viscosities present can minimize heat radiation to outer space. This example shows the complex physical properties of water: up to now, twelve different crystallographic structures and two non-crystalline amorphous forms are known! Under the extreme conditions present in outer space, frozen water may well exist in modifications with as yet completely unknown properties.

3.1.6 Saturn and Its Moon Titan

The giant planet Saturn is in many ways similar in its chemical and physical properties to Jupiter. However, it has the lowest density of all the bodies in the solar system. The cloud structure and the chemistry of Saturn's atmosphere resemble those of Jupiter, but the structures on the ring planet appear more diffuse and less clear, because of the presence of a layer of haze. The best-known feature of Saturn is the ring discovered by Christiaan Huygens in 1659, which is 278,000 kilometres in diameter and whose fine structure was determined only in 1978, 1980 and 1981 by the Pioneer 11, Voyager 1 and Voyager 2 missions. The material in the ring probably has its origin in a former Saturnian moon which came too close to the planet and was torn apart. It appears that the ring system is only about three kilometres thick and that its total mass is only about one millionth of that of Saturn itself.

Titan is certainly the most interesting and most important moon in terms of the subject of this book. It was discovered by Christiaan Huygens in 1655 and is a highly unusual planetary satellite: it is the only moon in the solar system which has a real atmosphere. The only two bodies which are surrounded by a thick layer of nitrogen are Titan and the Earth. Titan is the second largest moon in the solar system, and with a diameter of 5,150 km, it is larger than the planet Mercury. Its mass is sufficient to bind the nitrogen atmosphere, but not to retain hydrogen. The Voyager mission had provided data on Titan's atmosphere, and these were complemented on July 3, 1989, when Titan eclipsed the giant star 28 Sagitarii (Sicardy et al., 1990; Hubbard, 1990). The pressure at the surface of Titan is around 1.5 atm, and the atmosphere contains, by volume, 90% nitrogen; in 1944 Kuiper found that methane was also present. Titan's atmosphere has regions of haze which are between 200 and 300 kilometres thick. The IR spectrometer aboard the Voyager spacecraft detected the following carbon compounds: HCN, C_3H_8, methylacetylene, diacetylene (C_4H_2), cyanoacetylene (HC_3N), cyanogen (C_2N_2), CO and CO_2.

Why does only Titan have such a massive atmosphere, in contrast to the other similarly sized Jovian moons (which are closer to the sun, but have an escape velocity of the same magnitude)? One explanation is that the orbit of the Jovian moons lies within the sphere of influence of Jupiter's strong magnetosphere, whereas Titan is only slightly affected by the magnetosphere of Saturn. Its greater distance from the sun could also be important, since lower temperatures favour the incorporation of volatile gases into clathrates (cage compounds) and thus bind them to the moon. Titan's temperature is between 70 and 180 K, the minimum occurring at a height of about 70 km; the surface temperature is about 94 K. The planet's density suggests the presence of approximately equal amounts of water ice and rocky material. The information presently available indicates that Titan consists of a core made of rocky material, which is surrounded by layers of water/ammonia and water/methane clathrates. Its distance from the sun is 9.5 AU, i.e., it is subject to only about 1% of the amount of solar radiation which reaches the Earth.

Studies carried out on Earth, for example, by the NASA infrared telescope on Mauna Kea (Hawaii), showed albedo variations which indicated the presence of "holes" in the Titanian cloud formations (Griffith, 1993). It is, however, still unclear as to whether these inhomogeneities result from differences in the surface composition. Lorenz et al. (1997) reported large variations in Titan's atmosphere due to photochemical processes. The methane contained in the dense nitrogen atmosphere is decomposed by solar and thermal radiation, and its content may be replenished from methane lakes or from clathrates.

The common properties of Titan and our Earth have led to great scientific interest in this Saturnian satellite, which can be considered as a type of "extraterrestrial laboratory" in which a series of chemical and physical processes occur which are similar to those involved in chemical evolution on the primeval Earth.

Table 3.1 Chemical composition of the Titan stratosphere at a height of 80–140 km (Raulin, 1998)

Compound or element	Percentage composition in the stratosphere
Nitrogen (N_2)	0.90–0.99
Methane (CH_4)	0.017–0.045
Hydrogen (H_2)	0.0006–0.00014
Ethane (C_2H_6)	1.3×10^{-5} (equator)
Ethyne (C_2H_2)	2.2×10^{-6} (equator)
Propane (C_3H_8)	7.0×10^{-7} (equator)
Hydrocyanic acid (HCN)	6.0×10^{-7} (north pole)
Carbon monoxide (CO)	2.0×10^{-5}

Several laboratories, including that of F. Raulin in Paris (Coll et al., 1998) and of J. Ferris in the USA (Clarke and Ferris, 1997) have carried out experiments on simulated Titan atmospheres; these indicate that methane and nitrogen can exist side by side (Table 3.1).

While the presence of methane indicates a reducing atmosphere, that of nitrogen fits better into a (weakly) oxidising environment. It is believed that the present composition of Titan's atmosphere is the result of chemical or radiation-induced reactions.

Laboratory simulation experiments involve several problems. The mixing ratios of the reacting gases depend strongly on the height of the assumed reaction space above Titan's surface and thus on the gas pressures and the corresponding temperatures. An additional problem is provided by "reactor wall effects" and the incomplete exclusion of impurities such as oxygen. Both factors are absent in outer space but can lead to huge errors in laboratory simulations.

As can be seen from Table 3.1, the Titanian atmosphere contains a relatively large amount of ethane. Laboratory results show that methyl radicals ($H_3C\cdot$), which are primary products of methane photolysis, may be present in the upper reaches of the atmosphere:

$$2CH_4 \xrightarrow{h\nu} 2CH_3 + 2H\cdot \tag{3.1}$$

$$2CH_3 \rightarrow C_2H_6 \tag{3.2}$$

The short-wavelength radiation necessary for this decomposition is absent in the lower layers of the atmosphere; it is likely that the photolysis of ethyne occurs via C–H cleavage to give radicals, which react with methane to give methyl radicals, the recombination of which affords ethane:

$$C_2H_2 \xrightarrow{h\nu} H\cdot + \cdot C_2H \tag{3.3}$$

$$\cdot C_2H + CH_4 \rightarrow C_2H_2 + \cdot CH_3 \tag{3.4}$$

$$2\cdot CH_3 + M \rightarrow C_2H_6 + M \tag{3.5}$$

$$(M = \text{catalyst})$$

Calculations showed that this indirect photolysis occurs between 2.5 and 4 times faster than the processes occurring in the upper atmosphere. Analogous reactions were described by Clarke and Ferris (1997):

$$\text{For } C_4H_2 : C_4H_2 \xrightarrow{h\nu} H\cdot + \cdot C_4H \tag{3.6}$$

$$\cdot C_4H + CH_4 \rightarrow C_4H_2 + \cdot CH_3 \tag{3.7}$$

$$\text{For } HCN : HCN \xrightarrow{h\nu} H\cdot + \cdot CN \tag{3.8}$$

$$\cdot CN + CH_4 \rightarrow HCN + \cdot CH_3 \tag{3.9}$$

$$\text{For } HC_3N : HC_3N \xrightarrow{h\nu} H\cdot + \cdot C_3N \tag{3.10}$$

$$\cdot C_3N + CH_4 \rightarrow HC_3N + \cdot CH_3 \tag{3.11}$$

$$\text{For } C_2N_2 : C_2N_2 \xrightarrow{h\nu} 2\cdot CN \tag{3.12}$$

$$\cdot CN + CH_4 \rightarrow HCN + \cdot CH_3 \tag{3.13}$$

The hydrogen set free can add to unsaturated compounds; these reactions occur in the lower reaches of the Titanian atmosphere. Hydrogen cannot escape from the upper atmosphere before it reacts. The authors suggest a catalytic scheme in which reactive hydrogen atoms are converted into molecular hydrogen (H_2) without a net loss of unsaturated compound (here C_4H_2):

$$C_4H_2 + H\cdot + M \rightarrow \cdot C_4H_3 + M \tag{3.14}$$

$$\cdot C_4H_3 + H\cdot \rightarrow C_4H_2 + H_2 \tag{3.15}$$

The photochemistry of Titan's atmosphere can be summarized as follows: the unsaturated compounds are formed from HCN and C_2H_2, which is derived from CH_4. Methane decomposition leads to further ethane formation.

Two important substances have so far *not* been found on Titan: the noble gas argon and water. The analysis of the results of the successful Cassini mission may soon shed light on this mystery.

Joseph et al. (2000), from the laboratory of J. Ferris, used a new type of flow reactor for simulation experiments designed to investigate the reason for the haze formation in the Titanian atmosphere; this apparatus made it possible to use very small amounts of gases, so that concentration ratios close to those actually present on Titan could be reached. Thus, extrapolation was no longer necessary, and the undesirable reactor wall effects were negligible. Mixtures containing N_2, CH_4, H_2, C_2H_2, C_2H_4 and HC_3N were used. The analysis of the volatile reaction products formed on irradiation were carried out using IR and nuclear magnetic resonance spectroscopy, and IR was also used to study the solid products (haze and dust particles). Size distribution and morphology were determined using scanning electron microscopy.

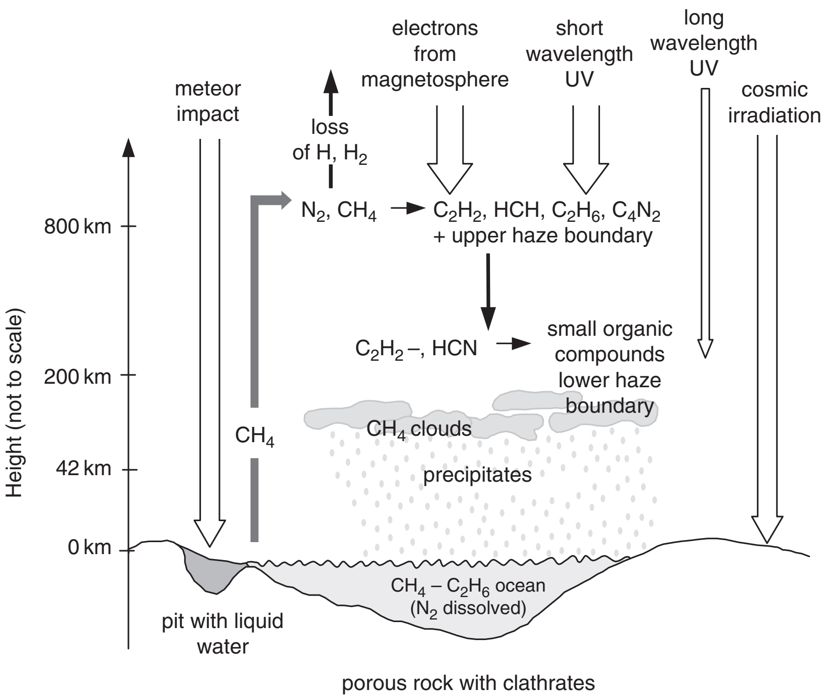

Fig. 3.4 Summary of the processes which may occur on Saturn's moon Titan (Clarke and Ferris, 1997)

Some of the data thus obtained are necessary for the interpretation and analysis of information which will be provided by the Huygens spacecraft. The Cassini–Huygens project, which is carried out jointly by NASA and ESA, started in 1997 with the launch of a Titan IV/Centaur rocket. After passing close to Venus, Earth and Jupiter, the spacecraft was brought into orbit around Saturn on July 1, 2004. Apart from an extensive research program, which includes studies of Saturn's magnetic field as well as a close look at its rings, the Titan project was one of the most spectacular. After orbiting several times around Titan, the Huygens probe landed on its surface at 12:34 GMT on January 14, 2005.

The problem of the seasonal changes in Titan's atmosphere was studied by T. Tokano from the Institute of Geophysics and Meteorology at the University of Cologne using a general circulation model (Tokano et al., 1999; Tokano, 2000). As expected, methane plays an important role, although its origin is unknown, since this hydrocarbon is rapidly decomposed by photochemical processes, as discussed above. Loveday et al. (2001) reported on the thermodynamic behaviour of methane hydrates, which may well be present in large amounts on the surface of this Saturnian moon, perhaps as a methane clathrate layer 100 kilometres thick. Such methane/ice clathrates also exist on Earth, particularly in the ocean depths and in permafrost regions. One cubic metre of such a clathrate can theoretically set free 164 cubic metres of methane and 0.8 cubic metres of water. However, if methane hydrates are present on Titan, they will be subject to much more complex conditions than they are on Earth.

The structures of the thick layers of haze which surround Titan, and which are in some ways comparable to the smog we know so well on Earth, are a mystery to scientists. It is possible that a numeric simulation model has solved the problem (Rannou et al., 2002): their results suggest that winds are responsible for the seasonal variations of the haze structures. The tiny particles which form the haze move from one pole to the other during a Titanian year (which corresponds to 4 years on Earth). This new model also explains the formation of a second separate haze layer above the main layer: this is formed from small particles which are blown to the poles and separate from the main haze layer before later returning to it.

The most recent results from the successful Cassini–Huygens mission will be discussed in Sect. 11.1.1.3.

3.1.7 Uranus and Neptune

Although Uranus and Neptune also belong to the group of gas giant planets, they are constructed differently from Jupiter and Saturn:

They are smaller than the two giant planets and

They contain, by weight, only about 15–20% hydrogen and helium. The greater part of the planetary mass consists of rocky material and water ice (a mixture of H_2O, NH_3 and CH_4).

Uranus The temperature in the Uranus atmosphere, which consists of molecular hydrogen containing around 12% helium, is close to 60 K. A methane cloud layer has been detected in the lower layers of this atmosphere. The planet is surrounded by a magnetosphere which extends into space for about ten times the diameter of Uranus. The planet has 27 moons of various sizes and is surrounded by a ring system which consists of thin dark rings. The planet is unusual in two respects: its tilted axis and retrograde rotation.

Neptune Small amounts of methane colour the H_2/He mixture of the Neptunian atmosphere blue. Energy sources in its interior are probably responsible for the fact that Neptune radiates 2.6 times as much energy as it receives from the distant sun. Triton is the largest of the eight moons and has a clearly structured surface, a world which compares to no other (Kinoshita, 1989). Voyager 2 has given us remarkable pictures of Triton's surface from a distance of only 38,000 kilometres. An icecap consisting of frozen methane and nitrogen was found in the southern polar region: its temperature is 37 K, which makes it the coldest object ever detected in the solar system. Trails of "smoke", which seem to come from geyser-like eruptions, were also detected. The material ejected from the surface may consist of a mixture of water and liquid methane; nitrogen in liquid or vapour form has also been suggested (Söderblom et al., 1990). In these exhalations, dark-coloured material is flung to a height of 8 kilometres. The moon is surrounded by a layer of nitrogen, which is 700–800 kilometres thick and contains about 0.01% methane. The density of the Triton atmosphere is, however, very low: the atmospheric pressure at the moon's surface is only about 1/70,000 of that at sea level on Earth.

3.1.8 The Dwarf Planet Pluto and Its Moon, Charon

In August 2006, the International Astronomical Union redefined the term "planet" and decided that the former ninth planet in the solar system should be referred to as a "dwarf planet" with the number 134340. The dwarf planet Pluto and its moon, Charon, are the brightest heavenly bodies in the Kuiper belt (Young, 2000). The ratio of the mass of the planet to that of its moon is 11:1, so the two can almost be considered as a double planet system. They are, however, quite disparate in their composition: while Pluto consists of about 75% rocky material and 25% ice, Charon probably contains only water ice with a small amount of rocky material. The ice on Pluto is probably made up mainly of N_2 ice with some CH_4 ice and traces of NH_3 ice. The fact that Pluto and Charon are quite similar in some respects may indicate that they have a common origin. Brown and Calvin (2000), as well as others, were able to obtain separate spectra of the dwarf planet and its moon, although the distance between the two is only about 19,000 kilometres. Crystalline water and ammonia ice were identified on Charon; it seems likely that ammonia hydrates are present.

3.2 Comets

The appearance of a comet in the sky is something which fascinates many people; the comet's long tail of luminescent material moving rapidly in the dark night sky has been the subject of much speculation across the centuries. Aristotle mentions comets, which he considers to consist of substances which evaporate from the Earth's surface and ignite when they reach great heights. In the Middle Ages, comets induced fear and trepidation: their appearance was considered to herald catastrophic events to come. Tycho Brahe is seen as the father of modern cometary research. He realized that the comet which appeared in 1557 had an orbit which took it beyond that of the moon; thus, Aristotle's theory, which was still adhered to at that time, must have been wrong. Brahe assumed that the comet orbited around the sun, so that the old, geocentric model of the universe could not possibly be correct. However, he did not abandon this model, but instead merely modified it.

We have learned a great deal about comets in the intervening centuries, but there still remain some unanswered questions.

3.2.1 The Origin of the Comets

Comets, like planetoids and meteorites, belong to the group of small heavenly bodies. According to the nature of their orbits, we distinguish two groups:

Long-period comets: their extended ellipsoidal orbits reach far outside our solar system (up to half the distance to the next fixed star). This group includes the comet Kohoutek, discovered in the 1970s, which requires about 75,000 years for a single orbit.

Short-period comets: these display a strong tendency for their farthest point from the sun (aphelia) to coincide with a giant planet's orbital radius, so that we can distinguish so-called "comet families". The Jupiter family of comets is the largest and numbers around 70 comets. The shortest orbital period known is that of the short-period comet Encke—about 3.3 years.

According to Delsemme (1998), the two groups of comets originated as follows:

Short-period comets are thought to have originated in the Kuiper belt (Luu and Jewitt, 1996).

The source of long-period comets is thought to be the Oort cloud (Weissmann, 1998).

The latter group was probably responsible for the early bombardment of the protoplanets. Delsemme believes that the cometary nuclei of the members of the Jupiter family never experienced temperatures greater than 225 K. The values suggested for the others are: Saturn family, 150 K; Uranus family, 75 K; Neptune family, 50 K. During many million years, these comets got mixed together in the Oort cloud (which has a diameter of around 50,000 AU).

It has recently been suggested that the comets also went through a number of subtle, but important, evolutionary processes in the Oort cloud and the Kuiper belt. Thus, their present nature is probably not the "original" one, as was previously thought (Stern, 2003). The assumption that the material which comets contain is in the same state as it was when the solar system was formed must be revised or modified. The evolutionary mechanisms to which they were subjected are likely to have changed their chemical composition.

The following mechanisms have been suggested:

The evaporation of volatile components by heat from supernovae or passing stars
Collisions with other heavenly bodies
Radiation chemical processes involving cosmic and UV irradiation
The extremely low density of material in interstellar space (ISM gas and ISM nuclei), which could affect the cometary material in the course of millions of years

According to these research results, comets can no longer be considered as genuine relicts (unchanged material witnesses) of the period 4–4.5 billion years ago (Stern, 2003).

3.2.2 The Structure of the Comets

Comets consist of three elements: the nucleus, the coma and the tail.

The cometary nucleus This is not normally visible. Nuclear diameters lie in the range of 1–15 km, with masses of 10^{12}–10^{15} kg. The American astronomer F. L. Wipple (1950) developed the now generally accepted model of the "dirty snowball", according to which the nucleus consists of various types of ice: in particular, water ice, methane ice and carbon dioxide ice. The ice contains dust particles with differing compositions, about a third being organic material. These particles are of great importance for the issue of biogenesis.

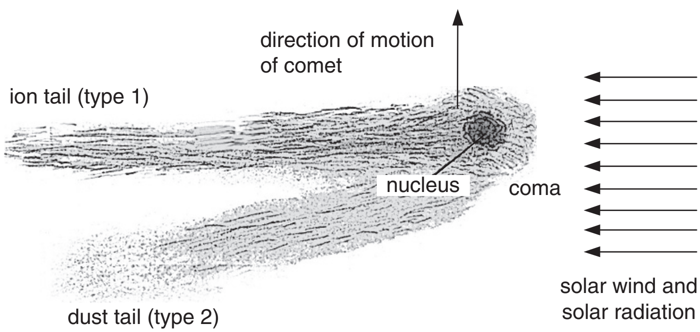

Fig. 3.5 Structure of a comet

The cometary coma The coma and the nucleus form the head of the comet; the streams of dust and gas released by the comet form a very large, extremely tenuous atmosphere called the coma, which can have a spread up to around 10^4–10^5 km. The coma is not developed when the comet is a long way from the sun, but when it comes closer (at around 5 AU), the ice mixture begins to sublime and is ejected as a gas stream. Dust particles are entrained at a velocity of around one kilometre per second.

The comet's tail The tail only develops when the comet is inside the orbit of Mars and can reach a length of between 10^7 km and one AU. It is not always straight but is often curved. This happens when the comet is subject to strong solar winds, i.e., during periods of greater solar activity. Two types of tail can be distinguished:

Type 1: long, thin tails of gas, mainly containing molecular and radical ions such as N_2^+, CO^+, OH^+, CH^+, CN^+, CO_2^+ and H_2O^+.

Type 2: these consist of dust particles around 1 µm in diameter. They are influenced strongly by the radiation pressure of the sun, which is, however, weaker than the pressure of the solar wind.

3.2.3 Halley's Comet

A great deal of information on the structures of comets was obtained during the investigations of Halley's Comet carried out in 1986. A total of six spacecraft were involved: Giotto (Europe), Vega 1 and 2 (USSR), Suisi and Sakigake (Japan) and ICE (USA). The Giotto spacecraft came as close as 600 km to the comet, while Vega 1 and 2 passed it at distances of 9,000 and 18,000 km, respectively. The first three spacecraft contained mass spectrometers for the analysis of the gas and dust, as well as other sensors. The Giotto spacecraft built by ESA had the following instruments on board: camera, gas and ion mass spectrometer, particle impact mass spectrometer, particle impact detector, optical photometer, ion sensor, electron analyser, ion cluster analyser, analyser for high-energy particles and magnetometer. The spacecraft was able to determine the dimensions of the cometary nucleus, which were $16 \times 8 \times 8$ km; it thus has the form of a rotation ellipsoid, similar to that of a peanut. Its brightness varied in 2.2 and 7.4 days respectively, so that rotation around both the long and the short axis must be assumed. The dark nucleus probably contains carbonaceous material, with a very low reflectivity and a surface temperature of around 330 K.

The mass of Halley's Comet is about 10^{14} kg, and thus its mean density is only 200 kg/m^3. The rate of loss of material has been estimated as 5,000 kg/s. The nucleus is loosely packed and exhibits point craters and chasms from which gas and dust escape. These emissions consist mainly of water vapour ($\sim$80% by volume) as well as 6% CO, $<$ 3% CO_2, $\sim$2.5% CH_4, $\sim$1.2% NH_3 and $<$ 6% N_2 (Flechtig and Keller, 1987). At the point where Giotto came nearest to the comet, the estimated amount of water being ejected was close to 15,000 kg/s, while that of dust particles was between 6,000 and 10,000 kg/s. Ions derived from water were detected in the vicinity of the comet's head, e.g., $[H(H_2O)_n]+$ (n = 0, 1, 2, 3) as well as H^+, $H_2{}^+$, C^+ and CH^+ (Mason, 1992). The cometary dust consisted of particles between 10^{-4} and 2 mm in diameter, but mostly below 10^{-2} mm. The analysis carried out by the dust particle mass spectrometer showed the presence of much more of the light elements H, C and N than found in the primitive meteorite class C1 (see Sect. 3.3.1), and indeed the dust spectra of the comet indicated that the light elements are present in amounts almost as great as in the sun, i.e., the cometary material has a similar composition to that of the primeval solar nebula.

The analytical data obtained, particularly by the PUMA mass spectrometer on board Vega 1 during the flyby, indicate the presence of a large number of linear and cyclic carbon compounds, such as olefins, alkynes, imines, nitriles, aldehydes and carboxylic acids, but also heterocyclic compounds (pyridines, pyrroles, purines and pyrimidines) and some benzene derivatives; no amino acids, alcohols or saturated hydrocarbons are, however, present (Kissel and Krueger, 1987; Krueger and Kissel, 1987).

3.2.4 Comets and Biogenesis

More than 45 years ago, the chemist John Oró from the University of Houston, Texas, suggested that biomolecules or their precursors could have been formed in space and brought to our Earth by comets (Oró, 1961). Delsemme made similar suggestions at the ISSOL Conference in Mainz in 1983 (Delsemme, 1984).

Which results led to the idea that comets are important in the evolution of life? For more than ten years, some scientists have believed that life has (possibly) existed on Earth for more than 3.5 billion years; recently, however, doubts have arisen as to whether this is really the case. It does seem clear that the heavy bombardment of the primeval Earth slowly started to decrease about 3.8 billion years ago. Many biogenesis researchers believe that a period of about 300 million years after the bombardment ceased would not have been long enough for life to evolve from inanimate systems. Thus the idea that comets (or perhaps even meteorites) played a role in the biogenesis process on Earth is quite appealing. Three possibilities are under discussion:

Life itself was brought to Earth from somewhere in the universe.
The heavenly bodies which landed on Earth already had *biomolecules* "on board".
These bodies brought *building blocks* to Earth for the synthesis of biomolecules.

Until a few years ago, it was considered impossible that biomolecules or their precursors could have survived the huge temperatures which would have been generated when comets hit the Earth. Today it seems possible that about 0.1% of such substances could have remained unchanged. A comet with a diameter of around 3 km may contain around 10^{27} dust particles. If 0.1% were to reach Earth unchanged, there would still be 10^{24} intact particles around 1 mm in size.

Similar arguments led Bernstein (1999a) to conclude that organic molecules formed in outer space could have been brought to Earth by comets. Laboratory experiments under simulated outer space conditions showed that polycyclic aromatic hydrocarbons (PAH) stabilized by an ice matrix led, under oxidising conditions and with UV irradiation, to the synthesis of aromatic alcohols, ketones and ethers. As expected, reducing atmospheres caused the formation of hydrogenated aromatic hydrocarbons. The product analysis was carried out by IR spectroscopy and mass spectrometry (Bernstein, 1999b). Such experiments under simulated deep space conditions indicate the fundamental importance of water ice, and thus of its various modifications. As we have already noted, at least 13 different forms of water ice are known. Several ice modifications may be present under deep space conditions, i.e., extremely low pressures, low temperatures (particularly in the range of 10–65 K), and the influence of strong radiation (Blake and Jenniskens, 2001). Cosmic UV irradiation leads to the formation of high-density, amorphous ice, which can flow like water. It is assumed that organic molecules can be formed within this ice modification.

The March 2002 issue of *Nature* contains two articles which report the synthesis of amino acids during UV irradiation of ice under cosmic conditions, one from Europe and one from the USA. Bernstein et al. (2002) report the synthesis of the three amino acids glycine, serine and alanine when a mixture of water, methanol, ammonia and hydrocyanic acid (in a ratio of 20:2:1:1) is irradiated at temperatures below 15 K. The European group (Muñoz Caro et al., 2002) was able to synthesize 16 amino acids as well as some other substances. They used a 2:1:1:1:1 mixture of water, methanol, ammonia, carbon monoxide and carbon dioxide. The reaction conditions used were similar to those of Bernstein's group. It is surprising that the composition of the starting materials has such a great influence on the product mixture. The Muñoz Caro approach uses less water and gives more amino acids, including bis(amino acids). The relative amounts of the mono(amino acids) synthesized are similar to those detected in the analysis of the Murchison meteorite, though the latter did not contain any bis(amino acids).

While accepting the high quality of these results, Everett L. Shock from the Department of Earth and Planetary Research of Washington University, St. Louis, poses the critical question as to whether the many simulation experiments really help us in answering the question of the origin of life on Earth (Shock, 2002).

Missions to investigate comets have taken place or are planned.

Rosetta The Rosetta mission was planned to reach the comet Wirtanen in 2013, to orbit it for eleven months and then to land and study the comet's surface. The start, planned for 2003, had to be postponed until 2004. This ESA mission involves the use of a lander ("Philae") developed by the German DLR, which is to take and analyse samples from the surface of the cometary nucleus. In May 2003, the scientific committee of ESA decided that the mission's goal should be changed to the comet 67P/Churyumov-Gerasimenko. The start, using an Ariane 5G+ rocket, took place at the Kourou space centre (French Guiana) in February 2004. Rosetta is expected to reach its new goal after a flight lasting ten years and ten months. The lander had to be modified to take into account the different gravitational force of the larger comet (www.esa.de).

Although Rosetta left Earth in 2004, it had still not covered even a half of its journey by 2007; the swingby of Mars in February 2007 was successful, and two more swingby manoeuvres will follow.

Stardust February 7, 1999, saw the start of NASA's Stardust mission: the cometary probe, the first mission to collect cosmic dust and return the sample to Earth, has a time-of-flight mass spectrometer (CIDA, Cometary and Interstellar Dust Analyser) on board. This analyses the ions which are formed when cosmic dust particles hit the instrument's surface. In June 2004, the probe reached its goal, the comet 81P/Wild 2, getting as close as 236 km! The CIDA instrument, which was developed at the Max Planck Institute for Extraterrestrial Physics in Garching (near Munich), studied both cometary dust and interstellar star dust.

The spacecraft landed in Utah on January 15, 2006, carrying valuable freight. It had collected several tens of thousands of particles, between 1 and 300 μm in size, from the vicinity of 81P/Wild 2. Initial studies indicated that the material was of both presolar and solar origin. A high proportion of the silicate particles (olivine, anorthite, and diopside) were larger than expected; they consist of high-temperature minerals which were formed in the inner regions of the solar nebula. The cometary dust was collected in two ways: with aluminium foil and with aerogel, an extremely low-density material.

More detailed investigations will take some time; polycyclic aromatic compounds have already been detected, some of which contain nitrogen and oxygen. Methylamine and ethylamine were also found. Contamination from the spacecraft seems unlikely. This first mission to return from the depths of the cosmos was a complete success (Brownlee et al., 2006; Hoerz et al., 2006).

The interstellar dust was shown to contain quinone derivatives as well as oxygen-rich condensed aromatic compounds; the quinones were present in both hydrated and carboxylated form. Very little nitrogen was present in the compounds detected. The cometary material, however, contained condensed nitrogen heterocycles. Hardly any oxygen was detected in the solid phase of the cometary dust: it possibly evaporates from the tail of the comet in the form of water or oxidized carbon compounds. The authors assume that these analytical results could lead to a reconsideration of the current biogenesis models (Kissel et al., 2004; Brownlee, 2004).

Mission Deep Impact In July 2005, NASA steered a projectile, about 370 kg in weight, at the comet 9F/Tempel (dimensions $4 \times 4 \times 14$ km), in order to obtain more exact information on its structure and composition. The impact was visible from Earth; the Rosetta spacecraft discussed above also sent pictures to Earth. The dust/ice ratio determined after the impact is very probably greater than unity, so that comets are probably "icy dustballs" rather than (as had previously been surmised) "dirty snowballs". The density of the cometary nucleus, which seems to consist of porous material, is roughly equal to that of ice. The impact set free around 19 GJ of energy, corresponding to the explosion of 4.5 tons of TNT; between ten and twenty thousand tons of cometary material were split off, of which between three and six thousand were dust. The large amount of dust prevented observation of the impact crater, which was estimated to be about 30 m deep and may have had a diameter of 100 m (Kueppers et al., 2005; Feldman, 2005; A'Hearn, 2006 and Burnett, 2006).

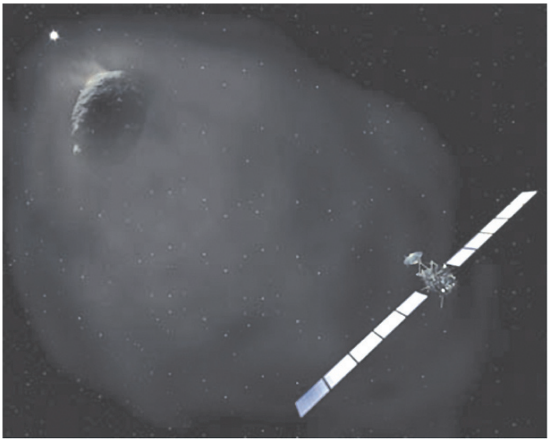

Fig. 3.6 Artist's impression of the planned approach of "Rosetta" to the comet 67P/Churyumov/Gerasimenko in the year 2014. ESA picture

3.3 Meteorites

Although this was contrary to popular, and also scientific, belief at the time, the German physicist Ernst Florens Friedrich Chladni (1756–1827) postulated that rocks could in fact fall from the heavens. His statement was supported by eyewitnesses who had observed the descent of meteorites. In France, Jean Baptiste Biot (1774–1862) was able to convince the Academy of Sciences in Paris that they should revise the memorandum which they had published ten years previously and agree that the meteorite fragments which had been found could in fact have their origin in outer space.

Alexander von Humboldt (1769–1859) recognised meteorites as being a source of extraterrestrial material. Several well-known chemists carried out analyses of material from meteorites, starting at the beginning of the nineteenth century. Thus Louis-Jacques Thenard (1777–1857) found carbon in Alais meteorites; these results were confirmed in 1834 by Jöns Jacob Berzelius, who by dint of very careful work was also able to detect water of crystallisation in meteoritic material.

Today, there is consensus that meteorites are the most important source of material from outer space. Their study is interesting from two points of view:

They contain the oldest material from precursors of the Earth and the solar system.
Their impact on Earth may possibly have delivered important biomolecules (or their precursors).

Fig. 3.7 Jöns Jacob Berzelius (1779–1848), professor of chemistry in Stockholm and discoverer of the elements selenium, silicon, thorium and zirconium. He introduced the modern chemical symbols and also the term "organic chemistry". From the book *Berzelius, Europaresenären* by C. G. Bernhard; with kind permission of the Royal Swedish Academy of Sciences

3.3.1 The Classification of Meteorites

There are two types of meteorites:

Undifferentiated meteorites: these are derived from asteroids which never underwent the heating which leads to fusion. They consist of millimetre-sized spherules (chondrules) embedded in a matrix.
Differentiated meteorites: they come from asteroids which have been through a fusion process which led to a more or less clear separation into nucleus, mantle and crust.

According to the *Catalogue of Meteorites* (1985), there are four main groups of meteorites:

Chondrites
Achondrites
Stony iron meteorites
Iron meteorites

Only the chondrites are undifferentiated.

The chondrules contained in the chondrites contain olivine, pyroxene, plagioklase, troilite and nickel-iron; they can make up 40–90% of the chondrites. Chondrules are silicate spheroids, fused drops from the primeval solar nebula. Because of their differing constitution, chondrites are further subdivided: one group in particular is important for the question of the origin of life, and has thus been intensively studied—that of the carbonaceous chondrites.

3.3.2 Carbonaceous Chondrites

Carbonaceous chondrites (C-chondrites) account for only 2–3% of the meteorites so far found, but the amount of research carried out on them is considerable. C-chondrites contain carbon both in elemental form and as compounds. They are without doubt the oldest relicts of primeval solar matter, which has been changed only slightly or not at all by metamorphosis. C-chondrites contain all the components of the primeval solar nebula, apart from those which are volatile; they are often referred to as "primitive meteorites".

The C-chondrites are subdivided further into eight subgroups. The Orgeuil meteorite, which fell in the nineteenth century in France, belongs to the group CI 1, while the Allende meteorite, which fell near the Mexican village Pueblita de Allende, is of type CV 3. Both meteorites were carefully collected only a few weeks after their impact on Earth (avoiding contamination as far as possible) and passed on to scientific institutions. The element carbon occurs not only as carbonates; "exotic" forms such as diamond, graphite and silicon carbide have also been detected (Hoppe, 1996). These latter three species are considered to provide indications of the connections between stellar materials in the presolar nebula (Lugmair, 1999).

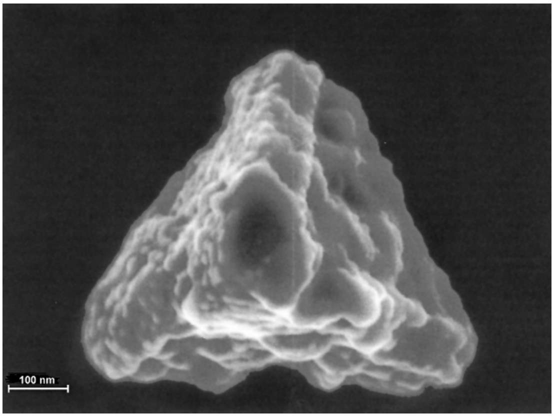

Fig. 3.8 A grain of silicon carbide (smaller than a micrometre) more than 4.57 billion years old, as seen under a scanning electron microscope. The grain was found in the Murchison meteorite and was formed in the presolar nebula (Lugmair, 1999)

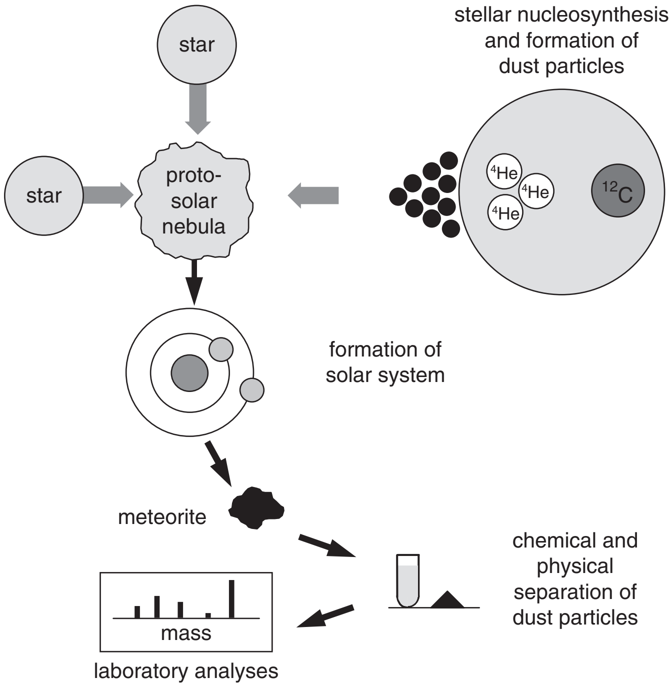

Fig. 3.9 Greatly simplified representation of the path taken by the material under study, beginning with nucleosynthesis and ending with laboratory analysis. Circumstellar dust (a component of the primeval presolar nebula) which was contained in asteroids or comets came to Earth in meteorites and was then available for exact study (Lugmair, 1999)

Table 3.2 The commonness of elements (log *n*) in the solar system, in the sun and in carbonaceous chondrites of type C1, with respect to hydrogen log $n(\mathrm{H}) = 12$, i.e., $n(\mathrm{H}) = 10^{12}$ (Unsöld and Baschek, 2001)

Atomic number		Sun	C1-chondrite
1	H	12.0	–
2	He	11.0	–
9	F	4.6	4.5
11	Na	6.3	6.4
12	Mg	7.5	7.6
14	Si	7.6	7.6
16	S	7.2	7.3
19	K	5.1	5.2
26	Fe	7.5	7.5

3.3.2.1 The C-Chondrites

The pulverized meteorite material is extracted using a series of solvents of differing polarity. The extracts contain mixtures of discrete compounds, such as amino