Dirk Schulze-Makuch
Louis N. Irwin

Life in the Universe

Expectations and Constraints

Second Edition

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*To a species of life on a water-rich planet in
an otherwise unremarkable Solar System in
an outlying part of the galaxy in an
unexceptional part of the universe, just
beginning to explore the world beyond the
home on which it began to evolve about
4 billion years ago.*

Through the curious eyes of a child we explore the Universe

Preface

Life on other worlds has been a source of speculation since ancient times. Exobiology and its derivative form, Astrobiology, now form a significant part of the scientific program for all the space exploring nations. Russia and the United States of America, the pioneers in space, have been joined by the European Space Agency, both independently and collaboratively, with a host of new missions. In Asia, the Japanese have entered the exploration of space, and the Chinese have launched a human into Earth orbit. The International Space Station and the Cassini-Huygens Mission to Saturn testify to the vigor and maturity of the international effort in space, much of which is geared toward the study of life in space and on other worlds.

With this upsurge of interest has come a host of books, mostly for a broad audience, and often for popular consumption. Nearly all have been enthusiastic about the possibility of life on other worlds. But scientific depth has often been sacrificed in favor of the laudable goal of engaging a broad audience. This book embraces the conviction that life is not restricted to our planet. But, our objective is to analyze in critical scientific detail, the fundamental, commonly held assumptions about life beyond Earth - particularly those relating to the probable cosmic preference for carbon-based life, the overwhelming focus on water as the preferred solvent for life, and the relative merits of different forms of energy for the sustenance of life.

Since the first edition of this book was published, rovers have combed the surface of Mars for ever growing evidence of oceans on the Red Planet, a lander has confirmed a hydrocarbon-soaked sandy basin fed by liquid-cut channels through hills on Titan, an orbiter has seen new geysers on several of Saturn's frozen satellites, and the ingenious observational tools of numerous talented astronomers have disclosed over 300 new planets beyond our Solar System. None of these discoveries has diminished our conviction that life is likely on other worlds somewhere, perhaps as we know it on Earth, and perhaps not. On the contrary, we have every evidence that the universe we see is physically and chemically consistent, and compatible with life in a variety of forms - some perhaps beyond our imagination.

Missions to Mars are in the pipeline every two years for the foreseeable future; another mission to the icy moons of Jupiter is on the drawing board; and sample return missions to Venus are even being discussed. These billion dollar projects will all rely on remote detection technologies. It is critically important that we search intelligently and comprehensively for the appropriate biosignatures and geoindicators that could mark or suggest the presence of life. This book is written with a particular emphasis on the scientific rationale for what we should be seeking, and how we should be looking for it.

We have also tried to write a book that treats biology with greater sophistication than most monographs in astrobiology. Certain assumptions commonly recur in the astrobiological literature: Life originates quickly once it has the opportunity to do so, but takes a long time to evolve to multicellularity. Most extraterrestrial life is probably microbial. Darwinian evolution is a requirement for life. The evolution of intelligence is an improbable event. Some of these assertions are valid; others have little foundation. We have drawn on evolutionary and ecological theory to critically evaluate these and related issues, and have documented our arguments so that the skeptical reader can pursue them to their source.

Our first edition was written with the view that a rigorous scientific approach to the possibility of life on other worlds could substantiate many of the more vague and intuitive notions held by scientists and the public alike, while placing rational constraints on many of the underlying assumptions within the growing field of astrobiology. While gratifying reviews of the first edition indicate that our effort was largely a success, we recognized from the onset some gaps and weaknesses in our treatment that a second edition would enable us to remedy. Toward that end, we have added a substantial amount of content, while updating our understanding of the universe, from our nearest neighbors in the Solar System, to the furthest reaches of our observational capabilities.

This new edition provides a more sophisticated treatment of the definition of life - an essential platform for all that follows. Our original aim, to define a living system in terms of its irreducible features and in a form that would be useful in guiding its detection wherever it might be found, has been retained. A small amount of wording has been added to the definition for clarity, but we continue to decline the temptation to define life as an abstract concept drawn merely from a collection of characteristics.

A better understanding of how life arose on Earth would provide invaluable insights into the plausibility that living systems could arise under a given set of conditions on other worlds. While sidestepping the question of the origin of life in the first edition in deference to the breadth and quality of work by others in that area, we have concluded that some consideration of this topic is essential for a treatise in astrobiology, in as much as the origin of life is part of the defining scope of the field. We by no means have endeavored to be comprehensive, but have tried to give a fair synopsis of the critical issues, including our take on what consensus may exist concerning the origin of life at the present time.

To our treatment of lessons from the history of life on Earth, we have added a significantly expanded review of the extremophilic organisms that live under the harshest conditions on our planet. Conditions that are harsh on Earth, of course, may be normative on other worlds. The desiccated surface of Mars, the acidic clouds of Venus, the volcanic convulsions of Io, and the frigid subsurface of Europa are examples of possible habitats in our neighborhood of the Solar System where organisms could persist with a semblance of the features revealed by the study of extremophiles on Earth.

The fate and future of living systems is supposed to be another of the defining subjects in the field of astrobiology. While popular treatments of the topic can be found, a serious scientific attempt to model generic scenarios for the life cycle of life itself are almost totally missing. We have now added a chapter on this topic, which has not only philosophical import, but vital relevance to our survival as a species and the persistence of life on Earth. Astrobiology, after all, is not about alien life alone.

In this edition, we also decided to examine in greater critical detail the results of the Viking Mission, which stands as an early heroic if flawed attempt to detect life on Mars, and the intense scrutiny twenty some years later of the alleged evidence for past life on Mars presented by the meteorite ALH84001. These two projects are uniquely instructive because they represent direct attempts to deduce evidence for alien life. In addition to their historical value, they point out the challenge that will likely confront us in assessing the evidence that we can realistically expect to collect for at least the near-term future.

Finally, we have added material on cosmic biogeography - revising slightly our plausibility ratings for life on several bodies in our Solar System - and updated the chapter on optimizing space exploration and the search for alien life in the light of current and foreseeable technology. Included is an emphatic restatement of our belief that robotic and human exploration of the cosmos are both scientifically necessary and inherent in our nature.

The first edition of this book had its origins in a student seminar, and the published version has been tested again by student use at both the undergraduate and graduate levels. We thank all our students, as before, for their valuable contribution. Likewise, we acknowledge with gratitude the helpful feedback and comments of many colleagues, including especially fruitful discussions and input from Penelope Boston, Alfonso Davila, James Dohm, Alberto Fairén, Wolfgang Fink, David Grinspoon, Kevin Plaxco, Antje Rusch, Phillip Rust, and Helga Stan-Lotter.

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El Paso, TX

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Louis N. Irwin

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Chapter 1
Introduction

Astrobiology studies the origin, evolution, distribution, and fate of life throughout the universe, with no direct evidence that life exists anywhere in the universe other than on Earth. But there are compelling reasons to assume that life exists pervasively throughout the cosmos. That assumption derives from empirical observations on the nature of the universe and the natural laws that govern it, from analysis of the history and properties of the one case of life that we do know, and on a logical integration of fact and theory. The science of astrobiology is thus as strong, if not as revolutionary, as Darwin's theory of evolution before fossil humans were found to prove our animal origins; as firm, if not as precise, as the astronomical predictions that Neptune must exist before it was detected; and, in our view, as certain as the conclusion that the world was a sphere before Magellan sailed around it.

This book sets forth the argument that life occurs numerous times throughout the universe. It further makes predictions about some likely characteristics of that life in most cases, explores the limits of diversity that might be found in forms of life on other worlds, and attempts to strain conventional thinking about the fundamental nature of living systems. At the same time, this book asks for no suspension of belief in or extension beyond the laws of chemistry and physics as we understand them now. It does not make predictions of a specific nature, where no basis for specificity exists. We offer our assessment about probabilities, but base those assessments on facts open to verification and a line of reasoning that invites the critical assessment of our fellow scientists. Like Darwin's arguments about the mechanism of evolution, we know that our vision of life in the universe will change through subsequent insights and observations. As the predictable discovery of Neptune gave no indication of the altogether unpredictable planetoid Pluto yet to be discovered, we realize that surprises not anticipated by us will emerge when the reality of life on other worlds is confirmed. And finally, like Magellan, we fully expect some of our calculations about life in the universe to miss their mark. But we do believe we have sketched a vision of cosmic biology that is tenable and therefore of predictive value in designing missions to search for and detect the life that is surely out there.

The argument that life exists on other worlds is straightforward and simple. It begins with the definition of life as a self-perpetuating organization of complex chemistry that uses free energy to maintain disequilibrium with its environment. It continues with the observation that wherever chemical heterogeneity and a source

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of free energy are found, the capability for life exists. It notes that our own planet, which had an abundance of both energy and complex chemistry from its earliest age, gave rise to life (or was able to sustain life introduced from another place) almost as soon as the heavy bombardment of the planet receded. It assumes that the laws of chemistry and physics act in the same way throughout the universe. It points to the vast numbers of stars in the universe, and the possibility that the total number of planets will be even larger. The argument concludes: even if the probability on any given planetary body is low that an appropriate combination of energy and chemistry is available to enable the development of sufficient complexity for life to emerge, the enormous number of planetary bodies that must exist in the visible part of the universe alone strongly suggests that life has arisen redundantly. Since the physical laws of nature pertain equally, we assume, over the entire extent of the universe, wherever those laws allow the formation of life to occur, it will. Hence, life must be widespread as well as high in numerical frequency.

We should emphasize that we do not argue that life is common. The complexities of form and function that constitute the living state are highly improbable in a statistical sense, and probably arise only under a restricted set of circumstances. The second purpose of this treatise is to critically examine what those circumstances are. To the extent that our Solar System is exemplary (we cannot yet say that it is typical), the conditions that exist on Earth, where a large range of microscopic to macroscopic forms of life have diversified, appear to be very rare. We think, therefore, that the extent of biodiversity that we see on Earth is very seldom seen anywhere else. Among the organisms that thrive on our planet, however, are many microscopic forms that potentially could occupy a number of other sites in our Solar System, as carbon polymer and water-based life essentially as we know it. In addition, however, there are circumstances substantially unlike those with which we are familiar on Earth, under which life in forms unknown to us could arise and exist, in theory. Those circumstances are found within our Solar System, and are likely to be found beyond it in abundance. The circumstances that would allow for the origin and persistence of life are not unlimited, however. Much of this work is devoted to assessing what those limits might be.

Our analysis focuses primarily on four facets that are essential to life: energy, chemistry, solvent, and habitat. To provide the reader with an overview at the outset, a brief abstract of our analysis of the possibilities and limitations of each of these facets is given below.

Energy in many forms is abundant throughout the universe. Electromagnetic energy at wavelengths visible to humans is a prominent product of the fusion reaction in all the visible stars. On Earth, a photosynthetic mechanism has evolved to capture that energy and transform it into chemical bonds with an efficiency that is difficult for any other form of energy to match. Where light is available, it thus provides an efficient, isothermal source of energy well matched to the needs of living systems. However, both inorganic and organic chemical bonds contain energy that is harvested by all non-photoautotrophs on Earth, so far as we are aware. As long as these sources of chemical energy remain available, either from cycling or a reserve not yet exhausted, they likewise provide an efficient basis for bioenergetics. Other forms of energy could in principle substitute to varying degrees light and chemical energy that support the forms of life with which we are familiar. Our theoretical calculations suggest that osmotic and ionic gradients, and the kinetic motion of convection currents, provide plausible alternatives. Thermal gradients are among the most widely available sources of energy flow, but the gradients are easily degraded and are thermodynamically inefficient. Magnetospheric energy, gravity, pressure, and other exotic forms of energy likewise could conceivably be harvested by living systems, but the amount of energy that they provide within our Solar System generally does not appear to make them competitive with light, chemistry, osmotic and ionic gradients, or convective currents as likely sources of free energy for the support of living systems.

All life as we know it resides in complex polymeric chemistry based on a covalently bonded carbon backbone. A systematic examination of carbon chemistry provides an impressive list of advantages that carbon has over any other compound, not only in forming the vast array of molecules required for complex systems, but by enabling the right combination of stability and flexibility for molecular transformations that underlie the dynamic complexity of life. In aqueous systems at temperatures common on Earth, carbon is so far superior to any other atom as a polymeric unit, that it has come to be the only basis for the structure of biomolecules essential for all basic metabolic processes. Silicon is the one other atom with properties similar to carbon, and its potential usefulness in living systems is shown by the fact that it too is an important constituent of many living cells. In most cases, it serves a rather passive structural role, as in the cell walls of plants, and the exoskeleton of diatoms and some other organisms. These examples could represent residual functions from a time in the history of life when silicon played a more central role, only to be replaced more effectively by carbon at a later stage. A detailed look at the chemistry of polymeric silicon reveals that it conceivably could have the combination of stability and lability exhibited by carbon, but under very different conditions, both at temperatures much higher and much lower, and in the presence of solvents other than water. Carbon bonds with oxygen and nitrogen to form parts of the polymeric chains of biomolecules, and mixed atomic backbones involving other compounds are a possibility. They already occur in some biomolecules of terrestrial life such as DNA but may be much more common elsewhere. A few other atoms have the capacity for the formation of covalent polymers, but they either occur in such low abundance, or have such inferior characteristics, that they seem a highly unlikely basis for an alternative living system.

Life as we know it requires a liquid medium. It can survive periods of dehydration, but appears to need a liquid for its dynamic transactions. We examine in some detail why life is much less likely to reside exclusively in a gaseous or solid medium. We also consider whether water is the only suitable solvent for a living system. Water does have some striking advantages, particularly with respect to carbon-based molecular interactions. At temperatures and pressures prevailing on Earth, and beneath the surfaces of numerous other planets and planetoids in our Solar System, water can exist in liquid form, and thereby provide the potential reservoir that carbon-based molecules need for their vast array of interactions. On the other hand, most of the Solar System, like most of the universe, is very unlike Earth. For smaller planetary bodies distant from a star, temperatures are much colder than on Earth. This probably represents the vast majority of planetary bodies. At those sites, water cannot be liquid (absent a source of internal heat), but methane, ammonia, ethane, methyl alcohol, and related organic compounds might be. In principle, many of them are compatible with carbon-based polymeric chemistry, and thus should be considered as possible solvents capable of supporting life. On very large planetary bodies, or on those that are tectonically active or close to a central star, very high temperatures may prevail. Under those circumstances other compounds can exist in the liquid form. In some of those cases, silicon-based polymers appear more feasible. There is no question that water is an excellent solvent for living systems, but under conditions where it cannot exist as a liquid, a few other solvents can exist in that state, and could support living processes.

Habitats can be divided grossly into those that are constant and those that are variable. The surface of a planetary body under rare circumstances as on Earth may be quite variable, providing the opportunity for fragmentation of the environment into a great variety of subhabitats with specific but periodically changing characteristics. These variations and their changes over time represent selective pressures that generate through the evolutionary process a great variety of living forms. When, as on Earth, energy and appropriate chemical environments are abundant, life can assume macrobiotic forms of great complexity. The cost of this biodiversity and complexity, however, is frequent extinction, as changing conditions in variable habitats often render biological features that were advantageous under one set of circumstances, suddenly disadvantageous under others. The cycle of speciation followed by extinction generates the biodiversity and great deviation from primordial forms of life with which we are familiar. We must remind ourselves, however, that the primordial forms are still with us as well. They are sequestered primarily below the surface, where the constancy of conditions places a premium on stabilizing selection, or the retention of successful living processes that have experienced no pressure for change for a long time. Only now are we beginning to appreciate the vastness of this subterranean, unseen biosphere; but it probably represents the most favorable and most common habitat for life throughout the universe as a whole. The consequences of subsurface life are two-fold: First, the minute size of the living spaces available restrict the size of living organisms to microscopic dimensions. Secondly, the long-term stability of the environment places a premium on stabilizing selection, which likely maintains life in an ancestral form. In those rare planetary bodies that have gaseous atmospheres, life may exist as well, but it likely is microscopic in that sphere also, though is much more likely to have deviated significantly from its ancestral form.

In the chapters that follow, we elaborate on these arguments in greater detail and discuss how life can be detected. Our vision of astrobiology is driven by our sense that life, like all of nature, is knowable in principle wherever it exists. We are strongly persuaded by scientific evidence and logic that it exists in profusion on other worlds. We believe it is likely that it exists elsewhere in our Solar System in at least a few instances, though probably in microbial form. We hope to see the day when this belief is confirmed by direct evidence. If we do not, we nonetheless are confident that a perceptive form of life somewhere, someday, will encounter life on a world other than its own. How similar or how different those forms of life will be is one of the most enticing questions of our age. This book is meant to explore the range of answers that might be offered.

Chapter 2
Definition of Life

The definition of life is a long-standing debate with no broadly accepted scientific consensus (Kolb 2007). The underlying problem in defining life is twofold. The first is that living systems use compounds that are abundant in the surrounding environment, and processes that are not intrinsically different from reactions that occur abiologically. There does not appear to exist a single characteristic property that is both intrinsic and unique to life. Rather we have to argue that life meets certain standards, or that it qualifies by the collective presence of a certain set of characteristics.

The second problem in defining life is linguistic. Life, grammatically, is a noun, which therefore calls for definition in terms of other nouns. Yet life is much more like a verb than a noun—more a process than an entity (Margulis and Sagan 1995). Defining life is analogous to defining wind. Wind is air in motion, a state of being. The molecules of wind are the same as those of air, but their dynamic state is their defining characteristic.

Life can certainly be defined through a collection of properties, but the search for life wherever it occurs depends ultimately on an ability to recognize individual entities with the properties of being alive, as distinct from their non-living surroundings. And, while life is like the wind in its pervasive distribution, it differs from wind in having finite boundaries. The challenge of defining life in the context of a cosmic biology, therefore, is to specify the defining characteristics of a dynamic process that occurs within discrete boundaries that set the process apart from its environment. While our everyday experience with life on Earth makes the distinction between the living and non-living for the most part unambiguous, a consideration of life on other worlds, where conditions may be different, and/or where life may have evolved from its inorganic precedents to a lesser degree, requires us to formulate a more formal and objective definition for life.

2.1 Problems with Common Assumptions about the Nature of Life

Historically, and still in popular usage, life has tended to be defined in terms of its dynamic features. Thus, the Random House dictionary (1987) defines life as a collection of characteristics and processes, such as metabolism, growth, reproduction

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and adaptation to the environment. This form of definition is generally followed by some biology textbooks (Campbell 1996; Raven and Johnson 1999), while others—tacitly admitting the difficulty of defining life—refer instead to its “unifying principles” (Curtis and Barnes 1986) or its “emergent properties” (Purves et al. 1998). The weakness in defining life as a collection of attributes is that any given attribute fails the exclusivity test—examples of entities that clearly are not alive can be found that exhibit one or more of these traits. The following examples will illustrate the point.

The consumption or transformation of energy is a central point in all traditional definitions of life. Energy metabolism in its most basic form consists of a collection of chemical reactions that yield energy by electron transfer. The central metabolism most often exploits the electrophilicity of carbon doubly bonded to nitrogen (C=N) or oxygen (C=O) or the electrophilicity of phosphorous doubly bonded to oxygen (P=O) (Baross et al. 2007). Living organisms obtain energy from light by photosynthesis or by other electron transfer reactions associated with chemolithotrophy (extracting energy from non-biological molecules) or chemoorganotrophy (extracting energy from molecules synthesized by other living organisms). However, inorganic analogs of these processes are well known. Electrons can be lifted into higher energy levels by various forms of energy, such as heat or ultraviolet radiation. When the electrons fall back to their lower energy levels, the energy difference between these levels is released. When ions absorb energy and release it again in the form of light, this is known as luminescence. Phosphorescence and fluorescence are special cases of luminescence and describe the phenomenon of continued emission of light after irradiation is terminated. Common minerals with the property of luminescence include gypsum and calcite. Another possibility for storing energy in the form of heat is seen in clay minerals with interlayer sites. The interlayer water and OH-groups are suitable for storing heat energy due to their high heat capacity. Thus, nonliving substances can transfer external energy into energy-yielding transitions that under some circumstances can be maintained as potential energy, just as living organisms do (Schulze-Makuch 2002b).

Another traditionally regarded property of life is growth. But just as cells grow in favorable environments with nutrients available, inorganic crystals can grow so long as ion sources and favorable surroundings are provided. Furthermore, just as the development of living organisms follows a regulated trajectory, so does the process of local surface reversibility regulate the course of silicate or metal oxide crystals that grow in aqueous solutions (Cairns-Smith 1982).

A third traditionally defined property of life is reproduction, which entails both multiplication of form and transmission of information. The visible consequence of reproduction in living organisms is the multiplication of individuals into offspring of like form and function. Mineral crystals do not reproduce in a biological sense, but when they reach a certain size they break apart along their cleavage planes. This is clearly a form of multiplication. The consequence of biological reproduction is also the transmission of information. Biological information is stored in the one-dimensional form of a linear code (DNA, RNA), that, at the functional level, is translated into the 3-dimensional structure of proteins. Prior to multiplication, the one-dimensional genetic code is copied, and complete sets of the code are transmitted to each of the two daughter cells that originate from binary fission. An analogous process occurs in minerals, where information may be stored in the two-dimensional lattice of a crystal plane. If a mineral has a strong preference for cleaving across the direction of growth and in the plane in which the information is held (Cairns-Smith 1982), the information can be reproduced. Note that in contrast to living cells, information can be stored in multiple layers in a crystal. However, copying this type of 3-dimensional information would be very challenging. Another important question is whether the stored information has actual meaning. We know that DNA has meaning because of the expressed segments of DNA (exons) that are read by the molecular machinery of the cell. However, there is no obvious way of assessing whether any ion patterns in minerals have a meaning.

Another hallmark of life is said to be adaptation to the environment. Short term adaptation can be achieved by an individual organism in a transient and reversible way, such as enzyme induction, in which cells produce enzymes specific to a particular substrate only when that substrate is present. Other examples include the adjustment of microbial size to nutrient conditions, or the movement of a cell to a nutrient source or away from toxic substances. However, clay minerals can also adapt to their surroundings. The most common adaptation for clays with interlayer sites is their response to water availability. If the outside environment is dry, water is released from the interlayer to surroundings; if the outside environment is wet, water is adsorbed into the interlayer.

Long term adaptation is achieved by collective organisms through time by the essentially irreversible mechanism of natural selection. An analogous process occurs in clays, which over time can accommodate different ions at ion exchange sites that will affect the lattice structure during clay mineral formation. Also, where

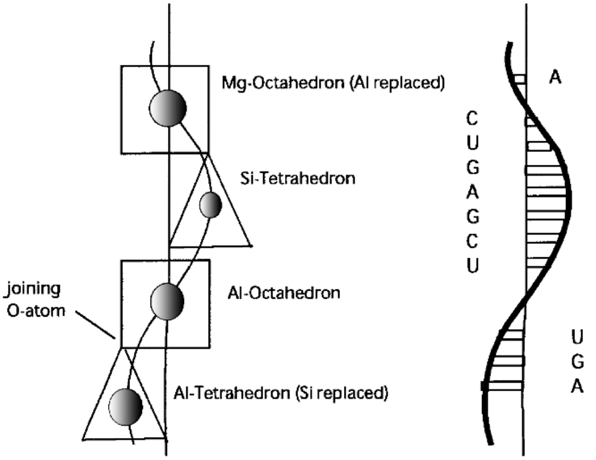


Fig. 2.1 Spiral structure of (a) amesite-$2H_2$ and (b) RNA, two-dimensional and schematic. As the nucleotide sequence in RNA codes for information, so could in principle the cation order in amesite

chemical weathering is prevalent, as in the tropics, clays can develop an outer, weather-resistant layer of aluminum oxide or silicate. Changes in mineralogy can also occur depending on the ion source and change in the environment. Dehydration reactions involving water molecules or hydroxyl ions lead in general to a structural change. In extreme cases, one clay mineral can transform into another. For example, gibbsite can transform into boehmite because of an alternation of dry and wet periods (Boulange et al. 1997).

As indicated above, good analogies can be found for each of the traditional criteria for living systems in the inorganic world, specifically for clay minerals and metal oxides (see also Fig. 2.1). A summary is provided in Table 2.1. While we are not aware of any specific minerals that display all four characteristics, there is no reason conceptually to assume that a mineral fitting the sum of all the criteria cannot exist.

At the biological edge of the interface between the living and non-living world, viruses present a similar case in reverse. By the traditional definition viruses are not considered living entities because they cannot reproduce and grow by themselves

Table 2.1 Properties of life: organic mechanism and inorganic parallel (modified from Schulze-Makuch 2002)

Property	Basic requirement	Organic mechanism	Inorganic parallel
Metabolism	Energy obtained from electron transfer	Various types of biochemical pathways including photosynthesis Energy storage as ATP or GTP	Energy uptake via heat or light, elevation of electrons to higher energy bands, where they absorb energy at specific frequencies. Energy storage by luminescence or at interlayers of clay minerals due to high heat capacity of water and OH-groups
Growth	Increase in size of single unit	Cell growth as long as nutrients are available and environmental conditions are favorable until reproduction occurs. Self-organizing as development proceeds, errors corrected by enzymes	Crystal growth as long as favorable environmental conditions prevail and a sufficient ion source is present. Local surface reversibility makes it possible to correct certain mistakes during the growth of silicate or metal oxide crystals from aqueous solution

Table 2.1 (continued)

Property	Basic requirement	Organic mechanism	Inorganic parallel
Reproduction	Multiplication of information	Various mechanisms of reproduction (most commonly by binary fission). The genetic code is duplicated and preserved through successive generations.	Crystals commonly cleave during growth. If a mineral has a strong preference for cleaving across the direction of growth and in the plane in which the information is held, new "individuals" may form and each of the new "individuals" may expose the information on the new surface (Cairns-Smith 1982)
Adaptation to Environment	Compensation for, reaction to, and development of new abilities in response to various types of environmental changes	Genetic adaptation over time through mutations, transposition of genetic material, transformation, conjugation, and transduction. Homeostatic adaptation within individuals: movement to nutrient source, cellular shrinkage or formation of spores in nutrient-poor environment, enzyme induction	Adaptation through changes in mineralogy due to changes in ion and environmental source (including transformation from one (clay) mineral to another in extreme cases). Adaptation within individuals: Adaptation to outside environment via water release or adsorption in interlayer (clay minerals), development of outer, weathering-resistant layers such as Al_2O_3 or silicate layers in tropical soils

and do not metabolize. Nevertheless, they possess a genetic code that enables them to reproduce and direct a limited amount of metabolism inside another living cell. They thus fulfill the traditional criteria only part of the time and under special circumstances. At best, by the traditional definition, they could be considered to be "reversibly alive." Since viruses presumably evolved from bacteria that clearly are alive, do they represent a case in which a living entity has been transformed to a non-living state by natural selection? Or, alternatively, if viruses were indeed the precursors of the three domains of life (Archaea, Bacteria, and Eukarya) as recently suggested (Forterre 2006), where would we draw the line between life and non-life? If we accept the proposition that viruses are not alive, how would we consider parasitic organisms or bacterial spores? Parasites cannot grow by themselves either and spores remain in dormant stages with no dynamic biological attributes until they become active under favorable environmental conditions. Thus, if we consider parasites or bacterial spores to be alive, the logical consequence would be to consider viruses alive as well.

In summary, the traditional definition of life on close examination fails to distinguish consistently between the living and the non-living world (Table 2.1). Since biology and mineralogy have both been characterized extensively on Earth, the distinction between the two is not difficult to make on our home planet. Notwithstanding the semantic ambiguities, we generally know life (or non-life) when we see it. But the definition matters more when we leave the familiar context of Earth, and encounter more exotic conditions and environments where dynamic phenomena may exist with which we are unfamiliar. In that context, semantic ambiguities become conceptual stumbling blocks and observational obstructions. For that reason, we need a definition of life that more effectively and precisely captures the fundamental essence of the phenomenon for which we are searching.

2.2 Historical Views on the Definition of Life

From the earliest days of mechanistic thinking (the Greek philosophers, in the Western tradition), but particularly with the abandonment of vitalism in the 19th century, life increasingly became recognized as a state or process, in which otherwise non-living matter and energy acquire dynamic properties that generate a state of disequilibrium distinct from its non-living surroundings.

With scientific acceptance of the theory of evolution came the derivative notion of the origin of life from non-living precursors. As formal theories about this process were advanced (Haldane 1954; Oparin 1938), and evidence consistent with a plausible mechanism were reported (Miller 1953), the need became apparent for a definition that distinguishes between living and non-living states, since that boundary (at least in concept) had to be crossed at some point in the past. As the concepts of thermodynamics became formalized in the 19th century, the low entropy state of living entities came to be appreciated as one of their most fundamental characteristics. Because of the need to distinguish between a collection of molecules that is alive and a collection of the same molecules that is not, researchers have increasingly focused on the highly ordered state of the components of living systems, and of the energy flow required to maintain that order (Brillouin 1956; Morowitz 1968; Schrödinger 1944). The thermodynamic improbability of the living state has become one of its defining features.

The ability of living systems to reproduce themselves has always been one of the clearest distinctions between living and non-living systems. Up until the 20th century, self-organization and reproduction remained as mysterious as they were distinctive. However, advances in genetics (Morgan 1915), biochemistry (Chargaff et al. 1951; Lwoff 1962), and molecular biology (Crick 1968; Watson and Crick 1953) elucidated the chemical basis of information storage and transfer in living systems, the extremely high information content of macromolecules, and the role they play in perpetuating the form and function of specific living systems. The encoding and transmission of information that enables self-assembly and reproduction have become collectively another indispensable feature of all contemporary definitions of life.

Two additional concepts have had a strong influence on modern definitions of life. The first is the contention that an essential criterion for life is the capacity for evolutionary change over extended periods of time. The second is that life is a global, as opposed to a local phenomenon.

2.3 Modern Definitions of Life

The modern attempt to redefine life in a more sophisticated way dates from Schrödinger's (1944) introduction of physical aspects such as energy states and entropy as the essence of what it means to be alive. A similar theme was developed later by Szent-Györgyi (1972). Moreno et al. (1990) focused on the autonomous nature of life by describing it as an autonomous system capable of self-reproduction and evolution. Maturana and Varela (1981) also emphasized the process of self maintenance, or "autopoiesis", as the fundamental essence of life. Lwoff (1962) and Banathy (1998) emphasized the information processing properties of life, while Dyson (1999) in a similar vein defined life as a material system that can acquire, store, process, and use information to organize its activities.

Some authors have striven for a comprehensive definition that focuses more on the continuity of life through time. Monod (1971), for instance, combined the ecological, thermodynamic, and bioinformatic properties of life, but added the ambiguous concept of teleonomy (apparent purposefulness in living organisms). Another effort at comprehensiveness is the more recent proposal of Koshland (2002) for seven pillars of life, which he designated as a program, improvisation, compartmentalization, energy, regeneration, adaptability, and seclusion. Regeneration counteracts thermokinetic degeneration, and seclusion introduces the important concept of a bounded environment.

Since all living forms operate within the constraints of environmental conditions and limitations, some authors have tried to incorporate an ecological perspective into their definitions. For instance, Feinberg and Shapiro (1980) proposed to redefine life as the fundamental activity of a biosphere—a highly ordered system of matter and energy characterized by complex cycles that maintain or gradually increase the order of the system through an exchange of energy with its environment.

These admirable attempts to include an ecological perspective illustrate one of the problems that has bedeviled historical attempts to define life: namely, the confusion between life as a process with a history, and the features of matter that constitute the state of being alive at a given moment in time. While almost all definitions of life refer in some way to reproduction as an essential feature, at a given moment an organism may be alive but not reproducing (1995). Similarly, some authors insist that the capacity for Darwinian evolution is an essential feature of life, yet any single organism during its lifetime is clearly not undergoing evolution. Thus, the condition of "being alive" needs to be distinguished from the "properties of a living system." The distinction is more than a semantic technicality, if the search for life on other worlds depends on the definition of what is being searched for. While ultimately we must know that what we discover is a "living system" capable of self-perpetuation, at the moment when we first encounter it, we need more precise and practical criteria for judging whether or not it is "alive."

The current tendency is to focus on two essential characteristics of the living state: its consumption of energy to maintain thermodynamic disequilibrium, and its ability to replicate form and function indefinitely through time. More controversial but often incorporated into modern definitions is the capacity for evolution and the interdependent nature of living systems, extrapolated in the extreme to a global extent. We will consider each in turn.

2.4 Thermodynamic Criteria

Once it is accepted that the living state maintains a high degree of order (low entropy) that persists in disequilibrium with its environment, thermodynamic considerations mandate that energy be provided to maintain that order. Nearly all modern definitions of life incorporate the assumption of a highly ordered state that degrades energy (consumes enthalpy) as a means of resisting the spontaneous tendency toward disorganization (increasing entropy) required by the 2nd Law of Thermodynamics. Life on Earth has evolved in such a way that energy is drawn from complex molecules with high free energy content, through a series of reactions that capture the release of energy as the complex molecules are broken down to simpler compounds with lower free energy contents. Photoautotrophs and chemolithoautotrophs manufacture their own chemical fuel by using the energy from sunlight or reactions with inorganic chemicals found in the environment. Heterotrophs derive their chemical fuel and carbon by consuming autotrophs, other heterotrophs, or their organic products. The energy thus harvested is used not only to maintain the highly ordered state of the system, but to power any autonomous activity (work performed) by the system. Collectively, the repertoire of chemical reactions and interactions that carry out these processes constitute metabolism, so the capacity to carry out energy-consuming metabolism in order to maintain order and perform work is either explicitly or implicitly part of most definitions of the living state.

Now that any macromolecule whose precise chemical structure is known can in principle be synthesized in the laboratory, any metabolic reaction should be inducible by placing together the right constituents in appropriate concentrations under conducive conditions in a test tube. Would a minimal set of such metabolic processes carried out exclusively in vitro constitute a living system? Most would say not, unless that system could be shown to perpetuate itself indefinitely in a stable, auto-regulated state with input only of simple constituents and energy. In the poetic words of Loren Eiseley (1946),

> … every bubble of the chemist's broth has left the secret of life as inscrutably remote as ever. The ingredients are known; they are to be had on any drug-store shelf. You can take them yourself and pour them and wait hopefully for the resulting slime to crawl. It will not. The beautiful pulse of streaming protoplasm, that unknown organization of an unstable chemistry which makes up the life process, will not begin. Carbon, nitrogen, hydrogen, and oxygen you have mixed, and the same dead chemicals they remain.

Complex chemistry alone does not constitute the living state. A minimal set of chemical reactions that can maintain the form and carry out the function of the simplest cell has yet to be demonstrated experimentally, though theoretical models have been constructed and efforts to do so are underway (Luisi et al. 2006; Maturana and Varela 1981). Definitions of life therefore tend to include simply the requirement of self-sustaining metabolic autoregulation, or autopoiesis (Luisi 2003a), powered by the controlled consumption of free energy.

2.5 Bioinformatic Criteria

Metabolism is carried out in a directed, not a random, way because proteins (enzymes) catalyze specific reactions. The specificity of catalysis is due to the three dimensional structural uniqueness of the protein (Luisi 1979), and that in turn is a consequence of the one-dimensional (primary) structure conferred by the particular sequence of amino acids that make up the protein. The amino acid sequence of a given protein, with minor exceptions, is the same for that protein in every organism of the species, and to varying degrees in other species in which the protein catalyzes the same reaction. The ability to synthesize proteins of the same structure within organisms, and pass the instructions for synthesizing proteins of the same structure to succeeding generations, is based on a linear code of nucleic acid bases which can replicate themselves with high fidelity. This nucleic acid code determines not only the structure of protein catalysts, but controls many other structural and regulatory functions of the cell.

From the earliest observations of ancient people that organisms reproduce offspring as near-identical versions of their parents, the concept that information must be passed from parent to offspring has been self-evident. Thus the potential for reproduction is a vital part of any definition of life. Yet the failure of an individual organism to reproduce does not preclude it from being alive. Even if an individual organism does not duplicate itself in its entirety, it must continually replicate the macromolecular components that keep its metabolic disequilibrium operating. And for multicellular organisms, continual cellular turnover, requiring replication of all of a cell's constituents and capabilities, is the norm.

Two additional features of reproduction in living organisms need to be specified to distinguish the living state from superficially similar processes in the inanimate world. The first is that living cells and multicellular organisms reproduce near-exact replicas of themselves, with regard to size and morphology. While mineral crystals grow by replicating precise molecular configurations, the resulting overall crystal is indefinite in size. While clouds multiply, they generate offspring of variable shapes and sizes. Indeed, it is this constancy of form through successive generations that enables the assignment of a living organism to a taxonomic category that extends through time and constitutes a unique and traceable biological history. The second unique feature of biological reproduction is that it constructs its descendants from raw materials, adding the informational specificity as well as the material composition to the offspring through the mere agency of its own intrinsic metabolism.

2.6 Evolutionary Criteria

Living entities reproduce themselves through an indefinite number of cycles, ensuring survival of the information content and metabolism for which it codes, despite the demise of predecessor carriers of the information. As a result, the living state at any point in time, in any single organism, has a history. Every species has a species history, marked by changes over time that have been introduced into its genetic code, resulting in alterations of form and function. Most (but not all) of these changes are assumed to be driven by natural selection—the mechanism for biological evolution first enunciated by Alfred Russell Wallace and, in greater depth, by Charles Darwin - resulting in the designation of this type of biological change over time as 'Darwinian evolution.' Some would argue that the ability to undergo Darwinian evolution is also a defining characteristic of living systems. It clearly is not, however, a property of an individual organism; so this criterion is not useful when evaluating whether a specific entity is alive at a given point in time (Fleischaker 1990). A nuanced version of this criterion is that the living state consists of materials that have been ordered as they are, through a sequence of historical contingencies (Luisi 2003b).

2.7 Life as a Global Entity

The notion that the Earth is alive as a whole is prevalent in ancestral cultures, and was famously promulgated in the late 16th century by Bruno, but generally fell out of favor as the Renaissance progressed and inanimate chemistry and physics matured as sciences. In the 20th century, the concept was reborn in two different versions. Vernadsky (1997) argued that geology and biology are fundamentally indistinguishable – that biology is simply a particularly dynamic construction of the same material that constitutes the matter of all the Earth. Lovelock (1979, 1995) has argued that the Earth in its entirety operates as a living, self-regulating, homeostatic system whose properties derive from and define the nature of life itself (The Gaia Hypothesis). Both points of view have merit, and the Gaia Hypothesis, in particular, has some predictive value for the nature of biospheres on other worlds where living systems might be abundant (Lovelock 1965). They are not helpful, however, in assessing whether a specific entity is alive at a given point in time. Furthermore, if life exists in isolated local pockets of some other worlds, it seems unlikely that global indicators would reflect it. This is the fundamental flaw in Lovelock's (1965) a priori dismissal of the existence of life on Mars based solely on its atmospheric characteristics. At some semantic level it might always be argued that any world that harbors life at all is itself "alive," but acceptance of the argument does not have practical utility in finding and identifying local pockets of living systems.

2.8 Life as a Collection of Attributes

If a mechanistic view of life which precludes the invocation of vitalism is accepted, it follows that life arises from elements of the non-living world which are simply packaged and processed in a special way. Accordingly, it isn't surprising that many characteristics attributed to the living state can be found among entities that clearly are not alive. This leads to the somewhat unsatisfactory but necessary fallback position of defining life as a collection of attributes, no single one of which is definitive and exclusive to the living state, but all or most of which collectively must be satisfied to declare a system to be alive.

The epitome of this approach is the book by Margulis and Sagan (1995), whose title, *What is Life?*, honors the legacy of Schrödinger's (1944) earlier attempt to modernize the definition of life, but resorts to a multifaceted poetic characterization rather than a concise definition:

> Life is planetary exuberance, a solar phenomenon. It is the astronomically local transmutation of Earth's air, water, and sun into cells. It is an intricate pattern of growth and death, dispatch and retrenchment, transformation and decay. Life is the single expanding organization connected through Darwinian time to the first bacteria and through Vernadskian space to all citizens of the biosphere. Life … is a whirling nexus of growing, fusing, and dieing beings. It is matter gone wild, capable of choosing its own direction in order to indefinitely forestall the inevitable moment of thermodynamic equilibrium—death.

We see, therefore, that defining life is semantically ambiguous and operationally difficult. There is much truth and an admirable degree of esthetic appeal to the characterization of life embodied in the passage above, but a definition such as that is too florid and imprecise to guide the search for life on other worlds. A pithier and more objective definition is needed, to make the recognition of the living state as unambiguous as possible whenever and wherever it may be encountered in the universe.

2.9 A Utilitarian and Generic View

We propose, first, to sidestep the semantic difficulties of defining "life," by focusing instead on defining a "living entity" – a finite collection of matter and energy for which search parameters can be devised and criteria for recognition can be specified.

Our intent is to propose a definition that is both utilitarian and generic. The following is modified slightly from the version we first set forth in 2002 (Schulze-Makuch et al. 2002c).

We define a "living entity" as (1) a self-organizing bounded local environment in disequilibrium with its surroundings that (2) converts free energy and materials from its environment through metabolic processes that maintain a low entropy state and perform work, and that (3) reproduces its form from raw materials and its functional capabilities on the basis of an instructional code transmitted to successive reiterations of the entity.

This definition was developed to emphasize its practical use for the detection of life beyond Earth. In particular we are interested in specifying those properties of life that would suggest favorable habitats for exploration and that could be identified by remote sensing techniques now or at some time in the future. The reader is referred to Chapter 11 for practical consequences of our definition of life and to Chapter 12 on how to use it to detect extraterrestrial life. In this section we expound on the theoretical basis for our definition.

2.9.1 Self-organizing and Bounded Environments in Thermodynamic Disequilibrium

A living entity is self-organizing in that the processes necessary for its function and perpetuation arise from the particular collection of materials (molecules, for chemical systems) that constitute the entity. A flow of energy through the system activates ordered processes, some of which produce distinctive structures. Components of a living system are constrained within space distinct from their surroundings because they constitute a more highly ordered state of matter than the environment, and physical constraint prevents rapid entropic decay. This requires a boundary which is finite and discontinuous between the non-living surroundings and living contents within the bounded space. The boundary is not absolute, since materials and energy have to be exchangeable between the entity and its surroundings, but it is sufficiently impervious to maintain a clear-cut distinction between the interior and exterior of the entity. Living entities are thus thermodynamically open but far from equilibrium.

A closed natural inorganic system, isolated from its surroundings, adheres to the 2nd Law of Thermodynamics and moves spontaneously toward a state of maximum entropy. It also moves toward a minimum amount of free energy with the Gibbs free energy between reactants and products being zero at equilibrium. Life, on the other hand, maintains a high free energy state. This enables it, first, to do work on its environment. Secondly, the entropy of living systems is low because they are highly organized compared to their environments (even though the 2nd Law of Thermodynamics remains valid, as it applies to the macrocosm as a whole). Minerals fall ambiguously between these two extremes. They are highly organized and therefore have low entropy (Fig. 2.2). But in a natural system they generally move spontaneously toward a lower state of free energy. However, as previously discussed,

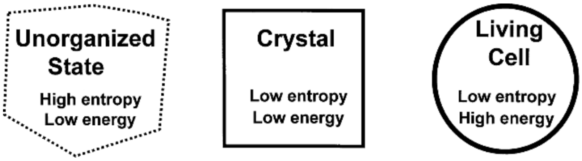


Fig. 2.2 Thermodynamic view of unorganized, crystalline and living state

some luminescent minerals can absorb energy that temporarily elevates them to a higher free energy state than their external environment. Lacking a permanent storage mechanism, however, the energy gain is generally soon dissipated.

A major distinction between living and non-living systems is the presence of biomembranes. These establish boundaries that serve to (1) preserve the high free energy state of the system from dissipation, (2) encapsulate and confine a high concentration of interacting solutes and macromolecules, and (3) carry out complex functions such as selective solute permeation, light transduction and the development of chemiosmotic potentials that generate energy gradients and provide the basis for reversible states of excitation (Deamer and Pashley 1989).

Disequilibrium on a cellular scale is made possible by the cell membrane, which enables the establishment of different solute concentrations within and outside the cell. On a supracellular scale disequilibrium conditions are created most visibly by colony-forming organisms such as stromatolites and corals, which are multicellular aggregates on a local scale (see microenvironments below). On a planetary scale, disequilibrium conditions can be established by biological processes such as photosynthesis.

As we criticized the traditional definition before by comparing it to analogs in the mineral world, it is only fair to evaluate how our definition stands up to these kinds of comparisons. Minerals do not have a membrane composed of fatty acids or similar compounds that living systems use. However, macromolecules within clay minerals can be protected. Clay particles can be linked in face to edge contact that results in an open internal framework with very high porosity (Bennett and Hulbert 1986). In such a clay fabric compartment, macromolecules (or clay minerals themselves) can be protected from disturbances in the environment. This type of framework structure can even lead to selectivity of specific ions. Some surface-active solids such as double-layer metal hydroxide minerals are capable of transporting matter against concentration gradients.

Stable disequilibrium conditions are also possible in the inorganic world but only to a limited extent (by sudden volcanic activity or for the time a hydrothermal vent is active). In a completely inorganic world plutonic rocks with their volatile components would be expected eventually to reach equilibrium with sediments, the atmosphere and ocean water. Disequilibrium conditions or concentration gradients can be maintained within clay minerals for a period of time due to geometrical constraints and large energy barriers against ion exchange. Concentration gradients are most likely to form in the geometrically tight tetrahedral sites and to a lesser extent in the more spacious octahedral sites. However, lacking a distinctive boundary comparable to a biomembrane, clay minerals cannot maintain stable disequilibrium conditions at their reactive outer edges or in their reactive interlayer sites. Thus, like any inorganic system, this system would eventually reach equilibrium with its natural surroundings. Thus, while at any given instant, disequilibrium can be achieved by inorganic processes, this condition cannot be maintained indefinitely. By contrast, living systems are able to establish order within a chaotic world and perpetuate that order as long as energy is available for resisting the inexorable tendency toward increased entropy.

2.9.2 Transformation of Energy to Maintain a Low Entropy State and Perform Work

Maintenance of the low entropy state of living systems requires the persistent infusion of energy (Morowitz 1968), first, to enable the system to maintain its complex organization and resist dissipation toward randomness. The second requirement for an input of energy derives from the fact that living processes perform work by growing and retracting, moving through the environment, emitting energy, counteracting concentration gradients, transforming materials, erecting and breaking down structures, and other endogenous activities.

While energy transformations are characteristic of all dynamic physical and chemical systems, energy flow in non-living systems tends to result in greater disorder among all elements of the system. Energy released through different stages of the rock and water cycles, for instance, generally erodes land and distributes water to increase the entropy of the total collection of water and land toward equilibrium (lower mountains, more dispersed water and soil). The energy transformations of living systems, on the other hand, serve primarily to harvest and store the levels of free energy necessary for maintaining the highly ordered structure of the organism and performing the work that living cells carry out. The net effect for living systems, in contrast to that for non-living systems, is to maintain and often increase order at local levels and on microscopic scales.

There are two consequences to the way in which life transforms energy. One is that much of the energy is used to create and sustain a level of complexity that supports emergent functions that in their totality exceed the sum of the parts of the system. A mountain may be structurally complex but its role in the rock cycle is not dependent on the detailed organization of its individual rocks and sediments. The mountain is in essence a simple conglomerate of its component parts. The function of a living organism, on the other hand, depends critically on precisely how it is put together. Its component parts function in a coordinated manner, to generate a complex array of emergent properties, both structurally and functionally. The generation and maintenance of this complexity is one of the primary uses of the energy that living systems transform.

A second consequence of biological energy transformations is to create one or more additional microenvironments within the natural environment. The Eh (redox-potential), pH, solute composition, and structural complexity of the living cell is maintained at levels different from the extracellular environment because of the autonomous functions carried out by the cell, but not in the abiotic environment surrounding the cell. New environments can also be created on a larger scale by colony forming organisms such as stromatolites and corals, which can alter the topography of large amounts of habitat. Life-induced changes can occur even on a planetary scale, such as the change in atmospheric oxygen composition brought about by oxygen producing microbes on Earth, beginning with the emergence of photosynthesis as a uniquely biological form of energy transformation (Knoll 1999; Schopf 1994). This innovation enabled life to become autotrophic (manufacturer of its own food from the simple and abundant molecule, CO_2) on a global scale. Thus, not only is the transformation of energy a characteristic of life, but so is the ability of life to alter conditions in the natural environment.

Note the dual requirement of living systems: to resist an increase in entropy, and to perform work. Both requirements are essential for the definition of a living entity. Any fabrication or machine is, for the time being, at a lower state of entropy than, and in disequilibrium with, its environment. Indeed, such objects are known to exist on other worlds: the lifeless Huygens lander rests on Titan, and the surfaces of Mars and the Moon are littered with man-made objects. They are not alive, however, in part because they perform no work (the rovers and orbiters on Mars that still are consuming energy and performing work are not alive because they fail the criterion in the next section).

2.9.3 Information Encoding and Transmission

Order is maintained within living systems despite the turnover of its individual components because information is contained within the system that directs replacement of the lost components, regulates their relative abundance, and controls their interactions. Furthermore, when the entity reproduces itself, all the information needed for reconstitution and function is passed intact to each successive entity. That information serves to ensure a near-exact copy with near-identical functions in each reiterative, succeeding entity.

At the cellular level, this means that multiple descendent cells acquire the genetic information previously held by a single parental cell. At the level of the multicellular organism, it means that all the information for the organism's development and function is replicated, then passed through reproductive cells to the offspring (next generation). When a cell or organism can no longer maintain steady disequilibrium conditions it approaches equilibrium with its environment and therefore dies. Despite the death of the parent organism, the informational blueprint for the organism's structure and function, which for life as we know it on Earth is based on a chemical code, survives to the descendent organism, and will be transmitted from generation to generation. Despite the demise of the individual organism that harbors the code in its cells during any single generation, the transmission of the code to a subsequent generation ensures that the instructions for life specific to that particular kind of organism will persist.

Genetic codes are meaningful because of the characteristics that they impart to the systems in which they reside. However, a code of information by itself is useless if there is no meaning or consequence associated with it. The distribution of atoms in mineral lattice may be understood as a code, in that the information content of the distribution pattern is greater than zero, but there is no apparent meaning associated with it since there is no functional consequence to the pattern. Another main difference that distinguishes living systems from the mineral world is a sharp difference between substance and information. Genetic information is chemically codified in separate units (nucleic acids) of the cell that are distinct from their physical manifestation, hence the functional consequences of the code. A segment of DNA codes for a protein that carries out a particular function. If the protein is broken down, the function ceases, but the DNA that coded for the protein persists through replication and the reproduction of successive generations indefinitely. A mineral, on the other hand, may be capable of rearranging atoms and molecules in response to environmental influences such as weathering; but even if it is supposed that this rearrangement has changed the nature of information encoded in the mineral, the altered information has no effect apart from the specific rock in which it is embedded. Therefore, the information persists only so long as the mineral itself remains intact. There is no obvious consequence to the information, and no expression of it distinct from itself.

A distinctive feature of a living entity is that its construction requires only raw unorganized material from the environment, instructions provided by the informational code derived from a preceding entity, and energy. It differs from the manufacture of exact copies of inanimate objects in that the entity manufactures a copy of itself, the copy repeats the reproductive process, and this reiterative cycle of reproduction can continue indefinitely.

2.10 Implications for the Remote Detection of Life

If life conforms to the way we have defined it, our efforts will be maximized by focusing on the consequences of and requirements for the three components of our definition.

If living entities consist of bounded local environments in disequilibrium with their surroundings, we will be seeking to detect evidence of entities that stand out as collections of matter with discontinuous boundaries between themselves and their environment. Thus, any evidence of local chemical concentrations or physical properties distinct from their surroundings would be presumptive evidence for the possibility of life. In many cases, the living units may be small to microscopic, for reasons discussed in the next chapter, and therefore require high spatial resolution in the instruments sent to detect them. However, aggregates of those entities, analogous to stromatolite mats and coral reefs on Earth, may be large enough collectively for remote detection. The necessity for enclosure in a barrier, most likely and often in a liquid medium, leads us to look for particular types of molecules in particular environments – especially amphiphilic molecules.

The nature of energy transformations – a nearly universal component of all definitions of life – depends on the nature of the energy gradients available. Since the easiest and most obvious way to detect biologically driven energy transformations is probably through either localized or global effects of the transformation, our instruments need to be attuned to the forms of energy available on the planetary object of our search. Energy sources other than light or chemical energy may be used by life elsewhere, as discussed in Chapter 5. And because of the simplicity of chemical conversions as a source of energy, disequilibrium chemistry in the atmosphere or global habitat is probably relevant anywhere. Finally, because energy is transformed in order to do work by living organisms, evidence of work, such as growth, motion, repair, or maintenance of chemical, thermal, or other types of gradients is further presumptive evidence for the living state.

The third component of our definition – capacity for information encoding and transmission independent of the life span of the individual organism – will be difficult to confirm until actual samples of the candidate life forms are in hand. The constraints applied by this part of the definition for remote detection strategies are thus limited. However, this part of the definition becomes critical once candidate samples are available, for only this third component will enable confirmation that the candidate structure in question is or was alive. The validity of this point is illustrated by the fact that all the lines of evidence in support of fossil organisms in the Martian meteorite ALH84001, including the pictures of nanomicrobial-like organisms (McKay et al. 1996), are inconclusive, absent confirmation that the fossil actually derived from an organism that did in fact replicate itself from a pre-existing organism. The same applies to the very early fossil record on Earth (Brasier et al. 2002; Schopf and Packer 1987; Schopf 1993).

Our definition is geared toward the search for life on other planets and moons. The technical approaches needed for detecting life as we have defined it on other worlds is discussed in Chap. 12. However, the possibility of the existence, and hence detectability, of "alien" life on our home planet, has attracted some recent attention. Davies and Lineweaver (2005) computed probability scenarios of the origin of life and found that there is a significant likelihood that at least one more type of life has emerged on Earth and could have coexisted with known life. Cleland and Copley (2005) go even further to argue the possibility that the contemporary Earth contains a yet unrecognized alternative form of microbial life. Two counterarguments have been advanced. The first is that any "alien" life on Earth based on a different molecular architecture and biochemistry would be outcompeted very quickly. The second is that no tangible evidence of such organisms has been found in over a century and a half of microbiological study. Cleland and Copley (2005) responded by pointing to the complexity and diversity of microbial communities, and by emphasizing that microbial exploration relies heavily on detecting DNA and RNA, which may not be part of the "alien" forms of life. Wolfe-Simon et al. (2008) speculated that a type of alternative life on Earth may exist or may have existed that utilized arsenate instead of phosphate. Arsenic shares many of the same properties as phosphorous and arsenic could have been more abundant in early Earth environments such as hydrothermal vents and terrestrial desert environments.

2.11 Chapter Summary

Identifying the fundamental features of living entities is essential for identifying them on other worlds, particularly where they may exist in an unfamiliar form with novel features. There are several obstacles, however, to achieving a useful definition of life: (1) Living systems use compounds that are abundant in the surrounding environment and processes that are not intrinsically different from reactions that occur inorganically. (2) There does not appear to exist a single characteristic property that is both intrinsic and unique to life. (3) There was probably no sharp line but rather a gradual transition between a non-living and a living state of matter at the origin of life. (4) Finally, the condition of "being alive" has to be distinguished from the abstract concept of "life." We have chosen to sidestep the abstract concept in favor of defining "living entities" in a way that provides a practical guide for detecting instances of life in alien environments. We propose that living entities are (1) composed of self-organizing, local bounded environments in thermodynamic disequilibrium with their surrounding, (2) capable of transforming energy to maintain a low-entropy state and perform work, and (3) capable of information encoding and transmission through indefinite cycles of replication. Our definition contains no components that are original with us, though our emphasis on physical boundaries, implying finite structures, has seldom been accorded the priority that we give it. We are consistent with most modern efforts to define life by emphasizing the three key features of low entropy, energy transformation, and replication. This definition anticipates that detection of life on other worlds must include three determinations. The putative life form must be shown to consist of a more highly organized state than its surroundings. It must be shown to transform free energy in a form available to it, to maintain its highly ordered state and to perform work at some level. And ultimately it must be shown to reproduce itself in a manner which preserves all the information necessary to perpetuate the living state through successive, individual replications of the entities from which they were replicated. Our definition excludes notions of evolution through time or globally distributed systems, not because these concepts are irrelevant, but because they are not useful in identifying living entities at a fixed time in a local habitat.

Chapter 3
Origin of Life

The origin of life is a large and active field of research, and one chapter in this book can hardly do it justice. Yet, if we are to make reasonable inferences about the probability of life on other worlds, we must be able to gauge the possibility that living systems could have arisen (or arrived) there in the first place. And that, in turn, depends on our understanding of what the possibilities are for the origin of life anywhere. In an effort to rescue those possibilities from the realm of total speculation, we consider first what we know or infer about the origin of life on Earth, hoping that this singular example can provide some insights into and boundaries upon our thinking about the generic origins of life, wherever they have occurred. Then we use our limited understanding of what may have happened at the dawn of life on Earth, in combination with our definition of life given in Chap. 2, to focus on inferences with regard to the first cellular membranes, the first metabolisms, and the first replication mechanisms. Finally, we will discuss the implications of these insights for the predictability of life elsewhere in the universe.

3.1 Scenarios for the Origin of Life

The first living systems to persist on Earth are shrouded in mystery, and the first to persist may not have been the first to exist. Erwin Schrödinger predicted that quantum mechanics would solve the riddle of how life has started, but this has not been fulfilled (Davies 2005). Despite a century of speculation and a half-century of active experimentation, there is no consensus on a coherent sequence of events that brought life forth on our planet. There is, of course, the possibility that life was brought to Earth from another world. The spread of life by panspermia, at least among the inner rocky planets which may have shared a similar wet and warm surface in their early planetary histories, cannot be discounted. But life had to originate somewhere, and how that happened is what we would like to know if we are to understand whether it could happen on any other given body in the universe, including those so isolated that panspermia would be a most unlikely explanation for the

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

genesis of life on their remote worlds. Therefore, for the purposes of this chapter, we will assume that life arose de novo on Earth, in order to see where that understanding takes us.

While we cannot say with anything close to certainty how living systems came into being, we are not totally lacking in plausible ideas. In fact, it is fair to say that consensus has crystallized around a basic outline of the major events in the origin of life, consisting approximately of the following, not necessarily in this exact order (Bada 2004): (1) Under conditions of an energy-rich neutral to reducing atmosphere, monomeric organic compounds were created from elementary molecules like H_2, N_2, CO_2, NH_3, HCN, and formaldehyde. To an unknown degree, the reservoir of monomers was probably supplemented by cometary bombardment (Chyba and Sagan 1992), which delivered organic compounds to the Earth's surface from an alien origin. (2) Monomers formed polymers and interchanged both atomic components and energy in a growing web of chemical interchange. (3) Films, micelles, or other protomembranous boundaries began to encapsulate the chemically interactive monomers and polymers, concentrating reactants and sequestering products. (4) A statistical recurrence of effective and efficient metabolites became prevalent, facilitated probably by inorganic catalysts like transition metals or heterogeneous surface minerals. (5) Reliably producible 'infopolymers' (Turian 2003) led to crude, and probably initially inexact, mechanisms of replication. (6) Refinement of replicative mechanisms enabled the emergence of ribonucleic acid (RNA) as a dominant macromolecular regulator of metabolism, with catalytic properties as well as the capacity to replicate itself. This inaugurated what has been termed the RNA world (Lazcano 1994; Orgel 1998). (7) Proteins assumed increasingly sophisticated structural and enzymatic properties, coincident with the emergence of RNA-directed protein synthesis. (8) Deoxyribonucleic acid (DNA) emerged as a stable repository for genetic information, rendering RNA an intermediate in the flow of information, as cellular life of constant form and function achieved the capacity to perpetuate itself indefinitely.

To be sure, there is a gulf of uncertainty about and between most of the steps above. How largely chaotic if not random interactions among simple organic monomers (step 2) could transition into reliably channeled metabolic pathways (step 4), for example, is an unresolved puzzle. One of the greatest "unknowns" is how the first RNA or oligonucleotide was formed. The link between the simplest early genetic codes (step 7) and the sophisticated steps of protein translation as it occurs in modern organisms (step 8) seems totally elusive. Furthermore, there is heated debate about the sequence itself (Pross 2004) – whether, for instance, sequestration and primitive metabolism (step 3) preceded or followed development of the capacity for replication (step 6). But most of the steps enumerated above have been at least convincingly modeled, and many have been demonstrated experimentally. While the steps individually, therefore, enjoy a broad degree of support, there is no consensus on the details or environments in which they unfolded during the early days of the Earth. For purposes of classification, three general scenarios can generally be recognized.

3.1.1 A Lukewarm Marine Origin of Life

The longest standing and still most influential scenario for the origin of life derives from the pioneering work of Oparin (1938) and Haldane (1954), who envisioned the synthesis of monomeric organic compounds from simple precursors prevalent in a reducing atmosphere, progressively concentrated in the early oceans to a point where critical interactions and assemblies could occur. Life emerged from this "primordial soup" (Lazcano and Miller 1994), probably at or near the surface where energy from lightning and electromagnetic radiation were readily available (Bada 2004). Dramatic support for this concept was first provided by Stanley Miller and Harold Urey, who generated amino acids by discharging electricity through a mixture of methane, ammonia, water, and hydrogen (Miller 1953). These "sparking" experiments have been reproduced countless times in many variations, with the outcome heavily dependent on the mix of starting gases and other conditions (Bada and Lazcano 2002a; Miller and Orgel 1974; Miller and Lazcano 1996). While there is considerable doubt that the early atmosphere was as reducing as assumed by Miller (Kasting and Brown 1998; Tajika and Matsui 1993; Walker 1977; Westall et al. 2001) even neutral atmospheres appropriately energized can give rise to larger organic molecules. When supplemented by cometary delivery of interstellar compounds such as HCN, formaldehyde, aldehydes, nitriles, and acetylenes (Oro et al. 1992; Chyba and McDonald 1995; Miller and Orgel 1974), there is little question that monomeric precursors for biotic molecules could have accumulated in Earth's early oceans (Keosian 1968).

Nor is there serious doubt that energy would have been readily available on the surface of the early Earth. The amount of energy from lightning and coronal discharges has been estimated to be substantial (Chyba and Sagan 1991). Lithoautotrophy would have been a potential energy source in the deep subsurface (McCollom 1999; Stevens and McKinley 1995). Impact shocks and ultraviolet light at the surface were probably substantial (Chyba and Sagan 1992). Fast tidal cycling (Lathe 2004), and even sound have also been advanced as energy sources for prebiotic evolution. Finally, thermal energy has been modeled as a primordial force for biogenesis, before it was rendered non-competitive by the evolution of photosynthesis (Muller 1985, 1993, 1995).

A major problem with the prebiotic soup scenario is that polymerization by condensation in water is difficult, and even optimistic estimates of the concentration of organic precursors leaves the prebiotic oceans relatively dilute in organic molecules. Hence, a concentration mechanism is generally assumed to have been necessary. Cyclic dessication, as produced by freeze-thaw cycles (Miller and Orgel 1974) or the periodic filling and dehydration of tidal pools (Irwin and Schulze-Makuch 2005), for example, could facilitate condensation reactions. While this scenario is generally presumed to proceed at moderate (Bada and Lazcano 2002b) if not cool (Miller and Orgel 1974) temperatures, Fox (1977) argued the importance of heat-driven desiccation as the mechanism for prebiotic organic condensation. For those reactions that are favored at low temperatures, sequestration in ice would also provide a means of concentration.

3.1.2 A Benthic Thermophilic Origin of Life

Interest in the possibility that life on Earth may have originated at ocean depths near hydrothermal vents has been spurred by the fact that the deepest rooted organisms in the tree of life include a number of thermophylic Archaea (Stetter 1998; Woese 1979). Wächtershäuser (1988, 2007) has developed a theory of a chemo-autotrophic origin of life in a volcanic iron-sulfur world, in which underwater volcanic exhalations gave rise to pioneering organisms comprised of an organic superstructure built on a metallic core. Support is provided by the demonstration that peptide bonds can form by activation of amino acids with CO on (NiFe)S surfaces at high temperatures (Huber and Wächtershäuser 1998). Attractive features of the theory include the incorporation of inorganic chemistry, which facilitates the transition from prebiotic to living processes, the plausibility of forming peptide bonds which are otherwise difficult to assemble in weak aqueous solutions, and a ready explanation for the prevalence of thermophiles among the deepest-rooted organisms in evolutionary history. However, counterarguments contend that the variety of biomolecules that can be produced by this process is much less than that which the sparking experiments can yield (Lazcano 2004). And the fact that the most ancient forms of life are thermophilic could simply represent the survivors of a hot-ocean bottleneck at the dawn of evolution (Nisbet and Sleep 2001). An intriguing argument based on amino acid associated codon frequencies in barophilic (pressure-loving) organisms has been made by Di Giulio (2005) in support of the origin of the genetic code at ocean depths.

3.1.3 An Ice Water Origin of Life

Sea ice provides some attractive features as a possible habitat for the origin of life. Its dynamic freeze-thaw cycles at the water-ice interface, and the formation of liquid inclusions within solid surroundings, alternately concentrates and dilutes sea water solutions, and provides substrates for catalytic actions. Trinks et al. (2005) proposed that sea ice may have provided the optimal conditions for early replication of nucleic acids, and supported the concept by using cyclic temperature fluctuations to produce polyadenylic acid from a polyuridylic acid template in artificial sea ice. They linked the sea ice environment to a reactor where UV light from the sky, partly circular polarized by the influence of the ice structure, provides a very active energy source at the surface (Trinks et al. 2005). A cubic meter of sea ice contains about 10^{14} to 10^{15} compartments or a network of channels with a combined surface of 10^5 to 10^6 m^2. In these brine channels macromolecules are concentrated and have a chance to react. Peptides are relatively easy to synthesize under these conditions as they assemble under temperatures down to $-20°C$ (Liu and Orgel 1997). Stribling and Miller (1991) cooled down artificial sea water mixed with monomers to $-18°C$ and obtained complementary RNA oligomers with chain lengths of up to 12-15. Monnard et al (2003) performed template-free poly(A) synthesis experiments at

−18°C and obtained oligo(A) with chain lengths of up to 17. Vlassov (2004) observed complex RNA evolving at temperatures below the freezing point. They also found that RNA degradation slows down markedly at low temperatures preserving RNA molecules of significant complexity. While the notion of biogenesis at ice-cold temperatures may be counter-intuitive, the possibility that it could be so has great astrobiological relevance, in view of the large number of icy bodies that are likely pervasive throughout the universe (Lipps and Schulze-Makuch 2008).

3.1.4 A Comprehensive Scenario for the Origin of Life

Regardless of the habitat, energy source, and chemical details of the earliest events in biogenesis, we think a scenario can now be constructed that contains the essential elements common to most theories and consistent with most experimental evidence about the origin of life. We begin with the broadly held view that monomeric organic compounds, such as simple carbohydrates, amino acids, and nitrogen bases, are formed by prebiotic chemical reactions driven by robust energy gradients during the terminal phase of the Great Bombardment (Bada 2004; Miller and Lazcano 1996), supplemented by delivery of organic constituents to Earth by meteorites (Chyba et al. 1990). Lacking consumer organisms or biocatabolic reactions, the early Earth accumulated these organic monomers to sizeable concentrations in primordial seas. In formative habitats recurrent cycles of polymerization and depolymerization occur. This is easiest to envision at a water-air interface in shallow reservoirs such as ephemeral tide pools driven by tidal cycles of desiccation and rehydration (Irwin and Schulze-Makuch 2005; Lathe 2004), with polymerization (by dehydration condensation) alternating with depolymerization (by hydrolysis) reactions (Fig. 3.1); but analogous processes could take place in ice inclusions or at deep ocean vents (Burton et al. 1974; Chan et al. 1987; Lahav and Nir 1997; Orenberg et al. 1985). Since all monomers would be capable of forming bonds through condensation reactions, the combinatorial possibilities initially are vast and virtually random, forming many permutations of bases + amino acids, bases + sugars, sugars + amino acids, or all three. Collectively, these compounds constitute a vast and ever-changing population of protopolymers.

Each concentration (or desiccation) cycle would destroy many protopolymers, but some would be more stable than others and survive to the next influx of monomers during the succeeding dilution cycle. Residual molecules from each concentration cycle provide a more concentrated and somewhat biased set of constituents for the next dilution-concentration (rehydration-dehydration) cycle. A succession of reconstitution and destruction cycles brings about continual change in the composition of local reservoirs, but integrated over a vast number of parallel reservoirs across the planet and extending through long periods of time, a progressive increase in complexity of constituents fills each pool. The contents are not the same across pools, but certain molecular motifs gradually emerge with higher frequency because of greater stability and/or favorable thermodynamic characteristics (Fig. 3.2). While the average complexity of the protobiomolecular pool would

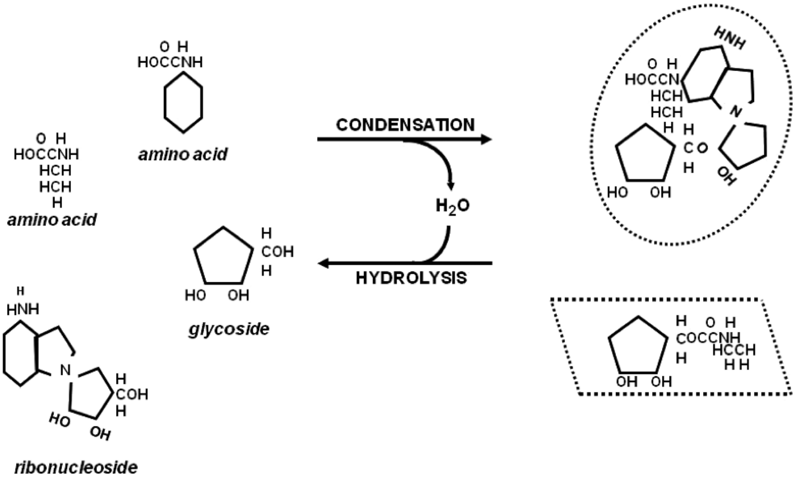


Fig. 3.1 Schematic effect of cyclic concentration and dilution in the formation of glyconucleopeptides. Organic monomers combine in various combinations when concentrated, often splitting upon dilution, and recombining perhaps differently in the next concentration cycle

progressively increase under the scenario above, it would initially remain well below that of a living cell, primarily because directed replication would be absent. By definition, therefore, the system would not be alive (Lazcano 2004; Schulze-Makuch et al. 2002c). However, it would approximate replication of the overall capabilities of the system because of residual constituents carried over through each concentration-dilution cycle, and the bias that the residual contents would exert toward the reconstituted contents of the succeeding reservoir, achieving the "statistical chemistry" envisioned by Calvin (1969) and Dyson (1982) as important steps toward life.

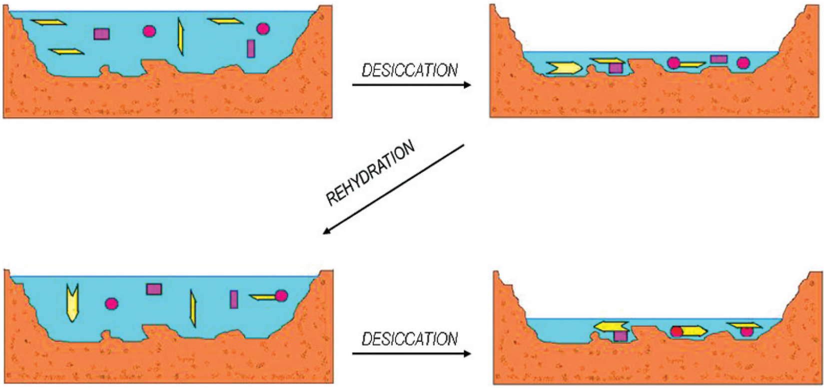


Fig. 3.2 Schematic representation of condensation, hydrolysis, and recondensation of proto-biomolecules. Though basically undirected, interactions with a substrate could favor certain product combinations over many reiterations of dehydration-rehydration cycles

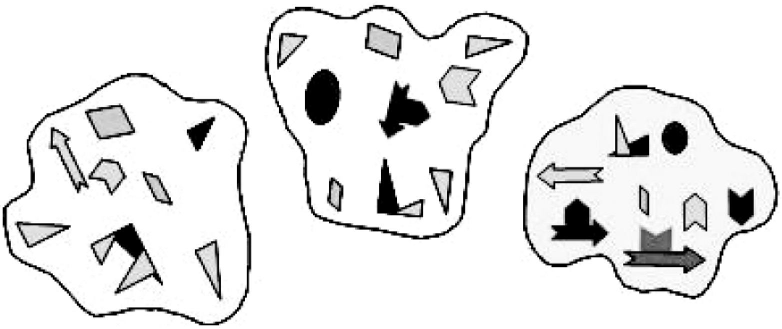


Fig. 3.3 Schematic representation of primordial pools of prebiotic reactants. Contents vary across pools, but certain molecular motifs gradually emerge with higher frequency because of greater stability and/or favorable thermodynamic characteristics

Increased heterogeneity of reservoir contents enables a more complicated web of interactions. As protopolymers elongate, they acquire limited catalytic and autocatalytic functions, by virtue of assuming secondary and tertiary conformations. This in turn sustains an increasingly complex set of intermediary metabolic reactions. Consolidation of thermodynamically favorable interactions leads to reiterative sequences that represent the early stages of a primitive replication process, which is initially inexact but not random (Fig. 3.3).

Over a long succession of dissolution and reconstitution cycles, certain interactions will recur with greater frequency than others due to thermodynamically favorable biases, and the biased composition of the reactant pools. Systematic energy transfer reactions likewise become more standardized, as certain reactions – predisposed by survival of selective precursors and substrates from previous concentration cycles – form protometabolic pathways (Fig. 3.4).

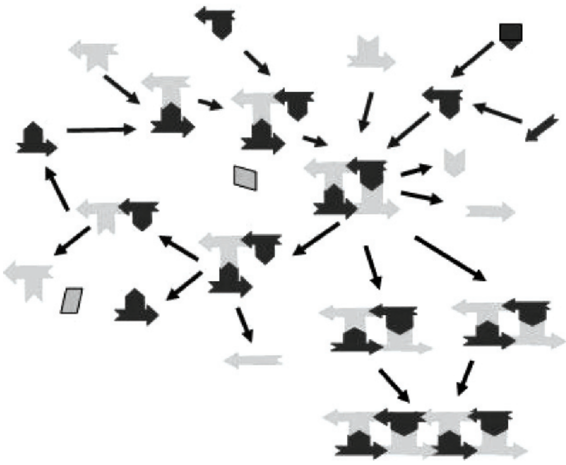


Fig. 3.4 Schematic view of a simple form of replication. Only four constituents with appropriate complimentarity could generate non-random polymeric sequences

Once high-energy bonds become readily produced by energy-harvesting reactions within the increasingly complex network of chemical interactions, endergonic as well as exergonic reactions occur. Encapsulation of these protometabolic events within lipid-bounded vesicles establishes a selective barrier between the internal and external environment, resulting in protocells. Now with the emergence of enclosed entities distinct from the environment, natural selection kicks in, promoting the survival of those with favored protometabolic pathways and progressively refining molecular processes and machinery leading to the RNA World. This, in turn, frees primeval and inexact replicative mechanisms from dependence on mineral or other structural substrates, all traces of which thereafter disappear (Cairns-Smith 1982). With the advent of both the coding and catalyzing capabilities of RNA, and the structural and catalytic properties of other macromolecules whose synthesis is directed by RNA, cellular life becomes totally distinct from the non-living environment, and evolves into the full-blown DNA-RNA-protein world that has persisted to the present day.

3.2 Inferences for the First Cellular Membranes

The cells of all living organisms on Earth use a selectively permeable membrane to preserve the high free energy state of the system from dissipation, encapsulate and confine a high concentration of interacting solutes and macromolecules, and carry out complex functions such as selective solute permeation, substrate interaction, and energy transduction. The core of these membranes is made from amphiphilic lipids such as fatty acids and phospholipids, in which the hydrophilic ends of the molecules are oriented toward the outer aqueous environment, while the hydrophobic ends are pointed toward the inside of the membrane core.

The formation of vesicles from amphiphilic molecules appears to be relatively easy. Deamer and Pashley (1989) extracted organic material from meteorites that formed cell-like membranes. The spontaneous formation of vesicles appears to be characteristic of phospholipid compounds and similar materials. There are a variety of suggestions of how the first vesicles could have formed to become the precursor of the cell. Chang (1993) proposed bubble formation and breaking in the ocean-atmosphere interface as likely mechanisms for closing vesicles. Russell and Hall (1997) suggested the formation of iron sulfide membranes, precipitated as bubbles at submarine hydrothermal vents, as primordial cell membranes in a step leading to life. Deamer et al. (2002) pointed out that amphiphilic molecules having carbon chains lengths greater than six carbons form micelles as concentrations increase above a critical value. At chain lengths of eight carbons and higher, bilayers begin to appear in the form of membranous vesicles, which become the dominant structure as concentrations increase further (Fig. 3.5).

Phospholipids appear to be ideally suited as cell membrane constituents for life on Earth. That does not limit the possibilities though. In principal, many amphiphilic molecules could serve as a cellular boundary. Conditions different in temperature, pH and redox-potential of the liquid medium could favor amphiphilic compounds

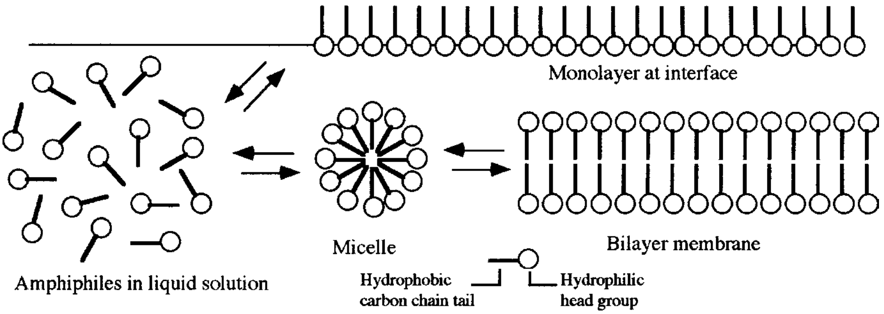


Fig. 3.5 Self-assembled structures of amphiphiles (from Deamer et al. 2002)

other than phospholipids. Amphiphilic compounds with outwardly oriented polar groups are well adapted for separating internal and external compartments submerged in a polar solvent. If the liquid environment were hydrophobic rather than hydrophilic, as likely on Titan, polar head groups at the surface of the membrane would be repelled by the hydrophobic solvent. How would a membrane be constructed in such an environment? Would molecules consisting of polar groups flanked by hydrophobic chains provide effective compartmental barriers in an organic milieu? Empirical studies are needed to answer this question. Since Titan may well represent a prototype of certain exotic environments found on other worlds, the search for membranes of a different composition from those known for terrestrial organisms should be a priority for laboratory research in astrobiology.

3.3 Inferences with Regard to the First Metabolism

The chemical reaction that supported the first life on Earth must have been simple but very efficient. A reaction that appears to fit this description is the oxygenation of hydrogen to water. The oxidation can occur with oxygen or some other oxygenated compound:

$$H_2 + {}^1\!/\!{}_2 O_2 \rightarrow H_2O \tag{3.1}$$

Reaction 3.1 yields an energy of 237.14 kJ/mol (or 2.6 eV) per reaction. There are various lines of evidence for why this reaction has such a central meaning: (1) hydrogen is the most common element in the universe, and gaseous hydrogen molecules are supplied by volcanic outgassing and by the abiotic reaction of water with basaltic rocks (Stevens and McKinley 1995), so are readily available, (2) oxygen or oxygenated compounds are common in the universe and also readily available for reaction, and (3) close relatives of the most ancient microbes on Earth use this reaction for metabolism. On Earth, where volcanic activity, and with it carbon dioxide, are common, this reaction is often coupled to the reduction of CO_2 and called methanogenesis (Eq. 3.2).

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{3.2}$$

The reduction of CO_2 is energetically unfavorable but proceeds because of the net energy gain by the oxidation of 2 hydrogen molecules to water. The net energy gain of this reaction is 130.63 kJ/mol or 1.4 eV (474.28 kJ/mol of energy gained by the oxidation of two hydrogen molecules to water minus the 343.65 kJ/mol lost by the reduction of carbon dioxide to methane).

This kind of reaction can set the stage for a simple feedback process or pre-ecosystem. If the methane produced is exposed to oxygen-rich conditions, for example in some oceanic layer, it would be favorable to oxidize the methane back to carbon dioxide with an energy gain of 6.1 eV to close the loop for a nutrient cycle. However, the H_2 would not return to its molecular state, but most likely would be incorporated into some other chemical compound. Thus, the limiting compound in this feedback cycle is the supply of molecular hydrogen.

As an alternative, hydrogen may be oxidized in a simple but efficient reaction with the help of sulfur or iron as shown in Eqs. 3.3 and 3.4, respectively.

$$H_2 + S \rightarrow H_2S \tag{3.3}$$

$$H_2 + 2Fe(III) \rightarrow 2H^+ + 2Fe(II) \tag{3.4}$$

The energy yield from reaction 3.3 is 33.4 kJ/mol (0.36 eV per reaction) and 148.6 kJ/mol (1.6 eV per reaction) for Equation 3.4. Both of these reactions provide sufficient energy to form energy-storing compounds (the terminal phosphate bond in ATP, a later development of high-energy storage efficiency, needs only about 0.3 eV per molecule to form). Iron and especially sulfur are readily available in volcanically active regions, thus the arguments made above for Eq. 3.1 can be made equally strong for reactions 3.3 and 3.4. The major advantage of oxidation of hydrogen via oxygen is its superior energy yield. However, on early Earth molecular oxygen was very rare. Also, in an early development state this reaction may have been too energy-rich, and the more benign oxidation of hydrogen to hydrogen sulfide may have been more controllable and suitable. A similar feedback mechanism as elaborated above for the oxidation of hydrogen via oxygen can be established for sulfur, iron and other compounds as well (Schulze-Makuch 2002). This indicates that the use of chemical energy, by itself or as a feedback cycle allowing microbial differentiation, should be fairly easy to establish. Photosynthesis on the other hand, is a much more complex mechanism with many intermediate steps, and because of its complexity probably evolved after chemoautotrophy. Also, photosynthesis requires the conversion from light energy back to chemical energy (to build energy storage compounds such as ATP, cellular components etc); which adds another layer of complexity. Hose et al. (2000) found that green sulfur bacteria that used photosynthesis outside of a cave oxidized hydrogen sulfide to elemental sulfur inside the lightless cave environment. This finding could support a hypothesis that Photosystem I (simplified in Eq. 3.5) may have developed from the chemotrophic oxidation of hydrogen sulfide, and that the observed green sulfur bacteria are capable of switching back to the older chemotrophic metabolic pathway when needed. Other opinions exist, however. Hartman (1998), for example, proposed photosynthesis as the key to the origin of life.

$$2H_2S + CO_2 + \text{light} \rightarrow CH_2O + H_2O + S_2 \tag{3.5}$$

Based on the previous discussion, it appears that the oxidation of hydrogen coupled to the reduction of some other compound is the most fundamental metabolic pathway for chemotrophic life. However, it does not mean that the first organisms were necessarily based on this type of metabolism. The oxidation of hydrogen does not occur under temperature and pressure conditions on Earth's surface without very good catalysis. Chemoautotrophic organisms have more complex internal requirements than for example heterotrophs feeding on organic macromolecules (McClendon 1999). Thus, heterotrophic organisms that gobbled up high-energy organic molecules present on the primordial Earth are a feasible scenario for the first cells on Earth. However, given the abundance of hydrogen and carbon in the universe, and the pervasiveness of volcanic activity, at least in our Solar System, it seems reasonable to infer that life elsewhere, would also be based on chemoautotrophy; if not initially, then shortly after organic molecules become scarce (not being replenished at a high enough rate), and that chemoautotrophic life would probably oxidize hydrogen, possibly combined with the reduction of carbon dioxide.

3.4 Inferences for the First Replication Mechanism

Replication is the ultimate challenge for origin of life researchers. The pre-evolutionary emergence of mechanisms for replication of genetic information are difficult to imagine, primarily because of the involvement of proteins whose structure presupposes a coding mechanism. Benner (2002) pointed out that a suitable biopolymer would have to be able to replicate, catalyze, and evolve without a loss of properties essential for replication, which is achieved in DNA and RNA by repeating charges. Since RNA has been shown to be capable of some catalytic activity (Cech 1985; Ferris 1993; Schwartz 1993), in principle it could have served as the first template and catalyst for its own replication (Lazcano 1994). However, the RNA found in contemporary cells is quite labile to environmental degradation. If that was the case at the advent of life, before ribonuclease enzymes were common, RNA would not have been plausible as either the first replication template or agent. Furthermore, in order to be a suitable replicator under early terrestrial conditions, RNA molecules would have to have been very simple and capable of reproducing at a very low error rate. It is not clear whether RNA could have fulfilled this requirement. What was needed was a biopolymer that could be reproduced autocatalytically and undergo chemical evolution. Lipids, peptide nucleic acids (PNA), threose nucleic acids (TNA), peptides, and proteins have also been considered as the basis for the origin of life on Earth (Bada and Lazcano 2002b; Chaput and Szostak 2003; Nielsen 1993; Orgel 1998; Schöning et al. 2000). In the view of many theorists, a prior stage in the evolution of life – an intermediate link long since lost in the evolutionary progression toward the current complicated mechanism – is needed to explain how replication was first achieved. In an alternative view, Dyson (1999) suggested that random populations of molecules evolved metabolic activities and that natural selection drove the evolution of cells toward greater complexity for a long time before the superior replication system based on nucleotides existed. In this view the first RNA would have been "parasitic" to these early cells and later evolved to the benefit of both entities, very similar to the process of the incorporation of mitochondria into eukaryotic cells.

The difficulty of identifying the first replicator led Bernal (1967) to propose the idea that clays or minerals were actively involved in the origin of life. This appears reasonable on the grounds that many properties of life can also be exhibited by minerals, especially clay minerals and metal hydroxides, as discussed before (Table 2.1). Cairns-Smith (1982, 1985, 1986) suggested catalytic clay surfaces as the first genetic mechanisms. A variety of biogenic compounds have been observed to interact with clays such as fatty acids, sugars, amino acids and proteins. Ferris (1993) even observed the formation of RNA oligomers on montmorillonite. The role of mineral templates in the ordering of proto-polynucleotides has been emphasized by Lahav and his colleagues (Chan et al. 1987; Lahav 1991; Lahav and Nir 1997; Lazard et al. 1987, 1988; Orenberg et al. 1985). Huber and Wächtershäuser (1998) have shown the synthesis of peptides on a (NiFe)S surface. Wächtershäuser (1994) and Huber and Wächtershäuser (1998) have proposed a sequence of mineral catalysts, which spontaneously form positive feedback synthesis involving both organic and inorganic compounds. It is interesting to note that adsorption and binding of DNA on clay and sand particles protects the DNA against degradation by nucleases without inhibiting its transforming ability (Khanna and Stotzky 1992; Lorenz and Wackernagel 1987; Paget et al. 1992). RNA can establish an even stronger interaction with clay than DNA. Single stranded RNA, in fact, can interact with the clay substrate, not only by the formation of hydrogen bonds between the phosphate groups of the RNA and the silanol or octahedral Al(III) groups of the clay, but also through its nitrogen bases. The same would be much more difficult for a double stranded molecule such as DNA with its nitrogen bases inside the double helix (Franchi et al. 1999). This adds further circumstantial evidence that RNA came before DNA and that mineral surfaces are in some way involved in the first replication mechanism. DNA and RNA both use complimentary rather than identical components for replication. A replicator copying identical components seems to be more simplistic and the precursor of RNA and DNA may have functioned that way. It should be pointed out that chemical coding of information is not the only possibility. In principle, any type of stored information that can be replicated and transmitted from one generation to the next would be workable (for a proposed alternative mechanism on replication with magnetic orientations, see Fig. 9.1).

3.5 Other Inferences

3.5.1 Size

Although life can certainly be macroscopic (we are evidence of it), life's origin must have occurred microscopically. Bounded microenvironments must have a surface to volume ratio that allows diffusion throughout the cell in a brief period of time. Anything larger would slow the rate of essential metabolic reactions to a presumably non-viable level and require large amounts of energy to maintain the structural integrity of the cell. At the same time, a cell has to be large enough to host the molecular machinery required for carrying out its metabolic and reproductive functions. While eukaryotes developed internal specializations such as membrane bounded organelles to enable growth to larger sizes, the first organisms were surely simpler, undifferentiated, and correspondingly minute. While the revolutionary fusion of two or more prokaryotic cells apparently led to the subcellular specialization that enabled eukaryotes to assume an increase in cellular size by an order of magnitude (Margulis and Sagan 1995), the further revolutionary innovation of multicellularity was required to bring about the emergence of macroscopic organisms (Cowen 1995).

It has also been argued that there is a lower as well as upper limit to size. Schrödinger (1944) discussed why we observe organisms the size they are. The disordered activity of thermal motion is too prone to generate random deviation from the statistical determinism upon which a complex set of interactions depends, if the number of interacting components is not very large. A cell too small to contain a sufficient number of reactants would thus be subject to the risk of failure due to "sampling errors" in the normal course of its chemical and physical activities. However, convincing empirical confirmation of a definite lower limit for the size of a viable cell is not available, and evidence is accumulating on nano-sized bacteria about 100-fold smaller than common bacteria. For example, 100-200 nanometer (nm) large bacteria were identified in mammalian cells (Ciftçioglu and Kajander 1998; Kajander et al. 1997; Kajander et al. 2001) and 400 nm large hyperthermophilic archaea from a submarine hot vent (Huber et al. 2002). However, Schieber and Arnott (2003) interpreted nanobacteria as a by-product of enzyme-driven tissue decay. Support of the nanobacteria hypothesis was more recently provided by Baker et al. (2006), who recovered an acidophilic Archaea with DNA and RNA, which had a cell volume of less than 0.006 cubic micrometers. This observation is particularly significant, in the light of claims that particles in the Martian meteorite ALH48001, which are much smaller than conventional terrestrial bacteria, could represent the remnants of life on Mars (see Chap. 12.2).

3.5.2 Environmental Conditions

Predictions of how life could have originated and on what planetary bodies life could be expected to exist would be greatly enhanced if the environmental conditions under which life can form were known. However, even on Earth we are uncertain of the conditions under which life originated. Many researchers (e.g., Kompanichenko 1996; Stetter 1998) favor a hyperthermophilic origin of life based on the abundance of organisms discovered at hydrothermal vents on the ocean floors and the results from molecular biology, which appear to indicate that the universal tree of life is rooted in hyperthermophiles. However, high temperatures are generally detrimental to organic synthesis reactions, and the hyperthermophilic last common ancestor could have been simply a deep sea survivor from a near-sterilizing meteor impact. Others have proposed an origin for life on Earth by panspermia, the transport of living forms to Earth from an extraterrestrial source (Arrhenius 1903; Crick and Orgel 1973; Hoyle 1983) . The exchange of viable microorganisms between planets in our Solar System appears to be possible via exchange of meteoritic material (Davies 1996; Horneck et al. 2008), however the exchange between stellar systems is statistically so unlikely, that the origin of life on Earth must be sought within the confines of our Solar System (Melosh 2003). Trace element composition in bacteria, fungi and higher organisms shows a strong correlation with the concentrations of these elements in sea water (Goldsmith and Owen 2003), which would support the origin of life in an aqueous environment on Earth. Deamer et al. (2002), proposed a plausible scenario for the origin of life in an aqueous environment with a moderate temperature ($<60°C$), low ionic strength, and pH values near neutrality (pH 5-8) with divalent cations at submillimolar concentrations. They based their conclusions on the following rationale: High salt concentration of the present oceans would exert a significant osmotic pressure on any closed membrane system, and divalent cations such as Ca^{2+} and Fe^{2+} (Fe^{2+} presence in the ocean because of the absence of atmospheric oxygen on early Earth) would have a strong tendency to bind to anionic head groups of amphiphilic molecules inhibiting them from forming stable membranes (Monnard et al. 2002). Only a better understanding of the possible habitats for the earliest life and the processes operating on the early Earth can lead to better insights into which type of environment the first assembly of a living cell took place.

3.5.3 Medium

The presence of a liquid medium is usually assumed for the origin of life on Earth, and indeed the presence of a liquid medium is very favorable. A liquid can provide a suitable medium in which atoms and molecules can move around relatively freely, encounter their reaction partners, and undergo chemical reactions in a reasonable time frame. Atoms are essentially fixed in place in a solid medium, and each atom can only react with its immediate neighbors, limiting severely the possibilities of complex reactions. Densities of atoms and molecules are usually low in the gas phase, and time periods between collisions and interactions between various constituents are large. Thus, complex molecules are not created or transformed in a reasonable time frame (before their disintegration). A liquid has the additional advantage that molecules present in some liquids such as water dissolve into charged ionic species, enhancing reaction rates by orders of magnitude. A liquid medium also allows easy transport of nutrients and disposal of wastes, although some nutrients such as N_2 or CO_2 can also be assimilated from the atmosphere by Earth organisms. Thus, under conditions currently prevailing on Earth, a liquid medium is clearly essential for living processes (for a more comprehensive discussion, see Chap. 7). However, on other planetary bodies a gas can be compressed by gravity or other forces to a similar or higher density than a liquid, thus making up some of the disadvantage compared to a liquid medium. A different scenario can be envisioned in a gaseous atmosphere where no ozone shield is present to drastically reduce the penetration of UV radiation and/or where the atmosphere is relatively thin to allow more ionizing radiation to penetrate. In that case, ions, radicals and electrons are created that are highly reactive, producing versatile chemical species (to some extent this is the case in Titan's atmosphere). Feinberg and Shapiro (1980) suggested that dense gases at high reaction-enhancing temperatures could be an equally convenient medium for chemically complex reactions and one which is much more common in the universe than liquid media. Sagan and Salpeter (1976) went so far as to envision specifically adapted organisms living in Jupiter's dense atmosphere. Evaluating the merit of these ideas is complicated by the fact that no distinct boundary exists between the liquid and gaseous medium at high temperatures and pressures. For example, water reaches the supercritical state at temperatures above 374°C and pressures above 215 bar, at which conditions it cannot be described adequately as either liquid or gas. While empirical observations suggest that life tends to thrive at boundaries between states of matter, there appears to be no theoretical obstacle to the persistence of life in the absence of such boundaries.

3.5.4 Minerals and Substrates

Whether life could arise from prebiotic precursors in the absence of boundary conditions is another matter. At the very least, encapsulation would appear to be necessary, to keep reactants concentrated sufficiently for self-sustaining (autopoeitic) reactions to be maintained. Whether life first arose under cold, warm, or hot conditions, the ability to concentrate reactants is coincident with the presence of solid substrates in contact with aqueous solutions, whether they be basins of tidal pools, the walls of water droplet inclusions in ice, or the ocean floor. While the spontaneous formation of protomembranous structures that could surround a pool of reactants could also serve to concentrate them, it isn't clear that the protomembranes themselves could form in the absence of a substrate.

The catalytic potential of substrates is the second argument for their likely involvement in any origin of life scenario. Theorists and experimentalists alike have repeatedly turned to the likely role of a substrate in catalyzing reactions that otherwise proceed with great difficulty (Miller and Orgel 1974; Srivatsan 2004). Minerals, in particular, have received close scrutiny for their catalytic properties (Huber and Wächtershäuser 1998; Wächtershäuser 1994, 2007), inasmuch as the mineral elements were available prebiotically and play a demonstrably important role in chemical catalysis generally.

The capacity of minerals for structural regularity, combined with their ability to attract and bind specific organic monomers, makes them prime candidates for a role in the ordering of organic constituents that could have led to the earliest, simple coding mechanisms. This role has been argued most thoroughly and persuasively by Cairns-Smith (1986) and Lahav (1994); and Lazard et al. (1987, 1988).

3.5.5 Implications for the Possibility of Life on Other Worlds

A consideration of what we know about the origin of life on Earth provides a list of constraints that is frustratingly short. Indeed, plausible arguments have been made that life could have emerged on Earth in different habitats at the full range of planetary temperatures using a variety of energy sources. Schemes for protometabolism, minimal cells, and primeaval coding mechanisms are numerous, with credible models and, in many cases, proof-of-concept data to back them up. Indeed, one is struck by the paucity of possible circumstances that can be ruled out at our current state of knowledge. The consequence of this is that, for now, the door to speculation on the conditions under which life could arise on other worlds needs to be kept open rather wide.

That said, there are virtually no proposals that life on Earth could have originated other than in water. This is natural enough, since Earth is a water world, and the organisms that comprise life on Earth are all aqueous systems at the cellular level. It does raise the question, however, of whether all life needs to originate in water. As we will argue in Chapter 7, while water is the most universal solvent, it is hardly the only one possible in which complex chemistry can occur. The more difficult question to answer is whether life can originate in any medium other than liquid. There are compelling reasons to doubt it (Ch. 7). Wherever in the universe where liquids exist, or existed at one time, therefore, would appear to provide a candidate habitat for the origin of a living system of some sort.

Since the atmospheres of the gas giant planets grade into liquids at increasing depths, the question may be asked whether life could arise in such habitats – in the lower reaches of the cloud layers of Jupiter or Saturn, for example. That prompts the next issue – whether a solid substrate, or at least discontinuous phase transition, is a further requirement for the origin of life. A more extreme constraint would be to posit that solid mineral surfaces are the most likely substrates for the first formation of life. While there appears to be no absolute, theoretical necessity for solid substrates in biogenesis, many theoreticians and experimentalists have found their models and data to be reconciled much more easily if solid substrates can be invoked. If substrates turn out to be necessary for the generation of living systems, we may expect to find life much more likely on differentiated, heterogeneous worlds, where interfaces between atmospheres, oceans, and land are more common.

3.6 Chapter Summary

Despite huge gaps in our knowledge of how life actually began on Earth (or an alien world prior to its transport to Earth), a vague but plausible outline of how it happened can be postulated. There is good reason to assume that prebiotic organic precursors were able to accumulate in the primeval oceans, generated from simple precursors with the abundant energy at hand. Self-sustaining (autopoeitic) reactions could have begun, with the advent of stable and reproducible macromolecules directing metabolic pathways, once membranous boundaries semi-isolated the protobiotic systems from the ambient environment. Over time, the original inorganic catalysts and scaffolds that provided reproducibility disappeared, as fully organic means of replication took over. Such a scenario, general though it is, has several implications for the generic origin of life anywhere. First, the most primitive organisms must be microbial in size. Remote detection from orbiters would therefore likely be restricted to visualizations of large aggregates of such organisms, while landers would need to be equipped with microscopes for a realistic view of individual organisms. Second, the early forms of life probably derive their energy heterotrophically, by consuming energy-rich molecules. Any other world with the chemical capacity for oxidizing hydrogen or harvesting chemical energy in some other way would be a candidate for the origin of life and its persistence to the present day. In fact, any world on which an energy gradient exists is potentially capable of supporting life. Finally, any genetic program for the encoding and transmission of information is based most likely on some form of macromolecular heterogeneity, possibly in concert with inanimate scaffolds such as clay or other minerals, prior to the transition to a wholly organic repository of information. While these inferences may be somewhat biased by the one case of life that we know – on Earth – we would close this chapter by noting that the composition of living matter resembles the composition of stars more closely than the composition of our planet, so terran life may be more typical for life in the universe than we think.

Chapter 4
Lessons from the History of Life on Earth

The discussion of life on other worlds is inevitably qualified by the phrase, "life as we know it." This customary and appropriate caution among scientists serves to (1) admit that all our speculations and extrapolations are based on a known sample size of only one, and (2) imply that the one form of life we know may be peculiar to the physical conditions under which it exists. While these constraints do place boundaries on the scientific latitude we should allow ourselves in speculating about unknown forms of life, the sample with which we are familiar does constitute a specific and robust example that has persisted through numerous crises in variable, changing, and often extreme environments. Assuming that the laws of physics and chemistry are universally operative, then life elsewhere might be expected to follow the same evolutionary and ecological principles that have characterized its history on Earth. Thus, rather than thinking of "life as we know it" in terms of constraints, this chapter explores the insights to be gained by regarding the one life we know as a harbinger and example of the life we can reasonably expect to exist on other worlds.

4.1 A Brief History of Life on Earth

The Earth is presumed to have formed about 4.55 billion years ago by accretion, like all concentrations of matter in the universe, through gravitational collapse and consequent rotation (Cassen and Woolum 1999). Recurrent bombardment continued for roughly 0.5 billion years, during which the Earth's interior differentiated and the atmosphere stabilized in composition, with N_2 and CO_2 as major constituents.

Based on dating of the earliest fossils, the first life on Earth appeared within 0.5 billion years after sterilizing bombardment had ceased (Chyba and McDonald 1995; Schopf 1999). While evidence for the ultimate ancestry of life on Earth is controversial at this time (Brasier et al. 2002; Mojzsis et al. 1996; Westall et al. 2001), few experts doubt that life was present by 3.5 billion years ago (Westall 2004), and some believe it is likely closer to 4.0 billion years old (Lazcano and Miller 1994).

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

The earliest life was unicellular, microscopic, and anaerobic (Schopf 1993) and this type of life still persists today. Though far more complex than any non-living particle of comparable size, its internal structure was relatively undifferentiated, lacking internal membranes or extensive subcellular segregation of function. Once the simple architecture of the prokaryotic cell emerged, it remained relatively unchanged for two billion years, or half of the history of life.

Based on fossil evidence photosynthesis arose fairly early, to harvest the abundant source of energy from the Sun (Cowen 1995; Margulis and Sagan 1995). Once oxygen began to be produced by photosynthesis, it was first consumed by the oxidation of minerals, then gradually began to increase in the atmosphere. At least a billion years of photosynthesis took place before the oxygen content of the atmosphere reached 10% of its current level (Walker 1977).

Gradually, subcellular specialization developed in concert with the availability of more efficient oxidative metabolism, enabling the enlargement of cells to the macroscopic size of eukaryotes (Han and Runnegar 1992; Margulis and Sagan 1995). Life persisted, however, exclusively as unicellular and water-borne for perhaps another half billion years, and unicellular descendants of early microbial life thrive to the present day.

After the mineral capacity of the Earth to absorb oxygen became saturated, and free O_2 began to accumulate in the atmosphere, oxidative metabolism became sufficiently available to support multicellular structures. These forms of life remained small and probably sluggish for close to a billion years (Cowen 1995). Widespread glaciation about 600 million years ago (Ma) was followed by a warming trend that coincided with an explosive diversification of structural forms and lifestyles between 500 and 600 million years ago, usually referred to as the Cambrian explosion (Cowen 1995). The diversification of animal morphology occurred quite sharply at the end of that glaciation. Peterson et al. (2004) points to the diversification of the bilaterian phyla as the signature event of the Cambrian explosion. Based on a molecular clock analysis using seven different amino acid sequences, the last common ancestor of bilaterians was estimated to have existed somewhere between 573 and 656 million years ago (the earliest unequivocally bilaterian fossils are about 555 million years old). Lowenstein (2006) argued that the rising oxygen concentrations at the end of the Precambrian period promoted macroorganisms, which fed on stromatolites. This led to a decreasing ability of stromatolites to fix Ca^{2+} from the ocean water. As the Ca^{2+} concentrations further increased, the ocean became toxic, which in turn led to evolutionary innovation in the form of shell producing organisms that represent the fossil record of the Cambrian explosion.

Either way, many of life's new experimental forms did not survive an environmental crisis 488 million years ago. Most of the extant higher order taxa of plants and animals were fixed at that time and have remained essentially unchanged to the present.

Life emerged with difficulty from the water less than 500 Ma (Margulis and Sagan 1995). Those organisms that did so, however, quickly radiated into a variety of forms that occupied niches above, on, and beneath the terrestrial surface, which affords a higher degree of environmental heterogeneity.

Life has been recurrently inventive, with a tendency toward increasing complexity in a minority of forms over time (de Duve 1995). Most of the diversions from basic forms and strategies have become extinct relatively quickly. A few innovations have proven highly adaptive, and have persisted with little modification once they became established (Eldredge 1985). The general rule for biomass as a whole, however, has been to remain simple.

The subsurface of the ocean, and subterranean habitats even more so, provide much more stable environments than the air or the surface of the water and earth. Much if not most of the Earth's biomass has evolved to occupy these niches, where it remains relatively simple, microscopic, and unchanged in basic form and function from the early days of life on Earth.

4.2 Lessons from the History of Life on Earth

A number of generalizations are suggested by a consideration of the history of life on Earth, as outlined above. While we lack evidence at the present time that any of these generalizations apply to life on other worlds, if that life is subjected to the same physical and chemical principles that apply on Earth, there is no reason to assume that the same patterns and principles would not apply to the trajectory of life wherever it occurs. Those generalizations and their implications are elaborated below.

4.2.1 Life Arises Relatively Quickly under Conducive Conditions

The fact that life arose or took hold relatively soon after the last heavy bombardment had subsided suggests that it is not a highly improbable phenomenon in relation to the time available for it to occur. Whether life originated on Earth or was transported here from another point of origin, the one example that we have shows the origin or colonization of life to be achievable within a few hundred million years of the opportunity for it to happen (de Duve 1995; Lahav 1999), and some have argued that as little as a few thousand years may be required (Lazcano and Miller 1994).

It follows that if life could take hold on Earth within tens to hundreds of millions of years, it could do so anywhere under comparable circumstances in the universe. Comparable circumstances (cessation of constant bombardment, presence of a liquid solvent, and reduced compounds or other forms of energy) probably existed on other planetary bodies in our Solar System at one time, and surely have existed abundantly throughout the universe over the 12 billion years or more since the first galaxies formed. Life itself may well have originated or existed for some time on other bodies in the Solar System, and almost surely is part of the extended fabric of the universe as a whole.

The criticism can be raised that the relatively sudden establishment of life on Earth is exceptional, rather than indicative of an intrinsic tendency. However, assuming the window of opportunity extended from 25 to 600 million years, Lineweaver and Davis (2002) calculated a probability of 0.13 at the 95% level of confidence for the origin or establishment of life on any suitable body with an age of at least one billion years. This amounts to saying that 13 out of every hundred suitable planetary bodies with an age of at least one billion years has a significant probability of harboring life. While the number of "suitable bodies" in the universe is not known, it has to be very large, even if only a small fraction of the trillions of stars in the universe contain such planetary bodies. While statistical probability cannot prove the actuality of specific events, it does provide a quantitative argument for the plausibility of the widespread existence of life in the cosmos. Specialists in the theory of complexity, in fact, suggest that given the proper materials, appropriate physical conditions, and a flow of energy, that matter will form itself inevitably into complex, self-organizing systems (Goodwin 1994; Kauffman 1995; Morowitz 1968). Once these systems become self-propagating, the basic criteria for life have been met.

4.2.2 Life Tends to Stay Small and Simple

Size and complexity are, of course, relative terms, but in relation to the size and complexity into which some forms of life have evolved, the vast majority of the biomass on Earth, even today, is microscopically small and no more complex than the solitary eukaryotic cell.

Physiology favors simplicity, and simplicity is aided by small size. The ratio of surface to volume decreases inversely as size increases. The simplest living functions (physiological processes) depend critically on exchange of materials across the boundaries of the system (external membrane). Not only does the high surface to volume ratio of small compartments favor exchange of materials, the ability of those materials to migrate to and from the center of the cell by diffusion, the simplest mode possible, depends on having a cell radius small enough for diffusion to be a practical mechanism for movement.

Ultimately, some advantages are gained by increased complexity. Multicellular organisms can achieve greater mobility and enhanced capacity to deal with a specific range of environmental fluctuations, but multicellularity requires specializations for distribution of materials, ingestion and excretion, and coordination of different body parts. This requires greater hereditary information for coding development and physiological coordination, consumes more energy, requires more space, and draws more resources from the environment. The density of such organisms is thereby reduced. Also, while advantages accrue for adaptation to specific niches, flexibility is diminished so that overall fitness to a broad range of changing conditions over time remain with the simpler structures and functions that require less coding, smaller size, and less elaborate cellular engineering.

It is not apparent whether life intrinsically requires 2 billion years to evolve into multicellular complexity, or if conditions on Earth simply precluded it from happening sooner. The lack of oxidative metabolic capacity has been cited as one characteristic that possibly was limiting. The constancy of the oceans, chemically and thermally, over the prolonged dawn of the history of life may have been another. Whatever the reason, there is no reason to assume that the tendency for life to remain simple and small on Earth would not be true of life on other worlds where conditions have long remained constant.

Also, we do not know how multicellularity started during Earth's history. There are some tantalizing hints of evolutionary convergence toward multicellularity. Examples are multicellular aggregates of magnetotactic bacteria (Keim et al. 2004) and microbialite structures that hint toward an analogue for the construction of a proto-macroorganism from loosely affiliated microbial cells (Turse et al. 2008).

4.2.3 Most Organisms Remain Relatively Unchanged over their Evolutionary Life Spans

While life may arise or take hold fairly quickly, it has little propensity to evolve very fast in general. It is perhaps surprising, in fact, that given the rapid pace of which evolution is sometimes capable, that little evolution at the macroscopic level took place for over half of the entire history of life on Earth. And when life did achieve multicellularity, it took many millions of years additionally for any of it to abandon the aquatic cradle of its birth and earliest nourishment (Margulis and Sagan 1995).

Every major group of organisms consists of some members whose lineage is easily traceable to a point early in the appearance of the taxon. Salamanders, turtles, crocodiles, armadillos, sturgeons, and sharks are vertebrate examples. Clams, lobsters, cockroaches, and jellyfish are just a fraction of the invertebrate examples. Within individual species, constancy is the rule, and extinction is much more common than gradual change (Eldredge 1985; Gould 1981).

In theoretical terms, we understand the tendency for living systems to retain their basic form and function for long periods of time in the context of *stabilizing selection* (Campbell 1996, p. 431). Under constant conditions, the mutations, genetic recombinations, and genetic drift that lead to deviations from the optimum phenotype are less adaptive and tend to be selected against. Those traits that are nearest the optimum are favored most strongly. So long as the environment remains stable, the optimal adaptations to it will remain the same. Outlying phenotypes will be selected against, and phenotypes conforming most closely to the optimum will be selected for, over time. The frequency distribution of traits will narrow and stabilize around the optimal, providing the highest proportion of organisms with the greatest adaptive advantage (Fig. 4.1a). Thus well adapted, the organisms will remain static as long as the environment does so.

Most of the planets and satellites in the Solar System have been static for long periods of time (Buratti 1999). It seems likely that all the planets except for Venus, Earth, and Mars assumed their current form and characteristics soon after their accretion. Of the sizeable satellites, only the Moon, Io, and possibly Titan have not

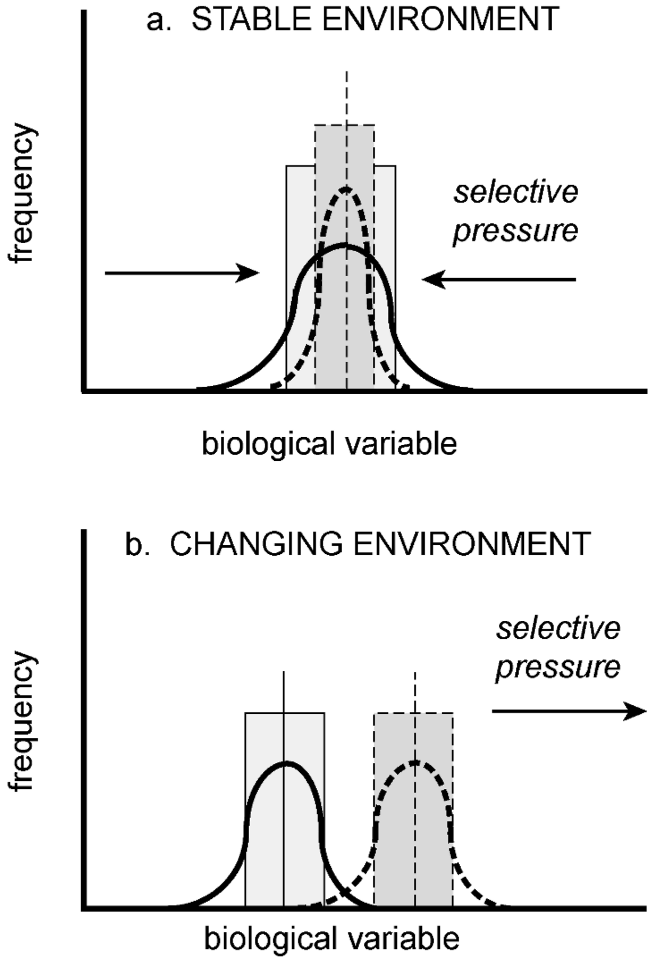


Fig. 4.1 Effect of selective pressure on biological characteristics, illustrated by changes in the frequency distribution of a quantitative biological trait in response to different forms of selective pressure. (a) In stable environments, stabilizing selection promotes elimination of peripheral values in the original population, reducing the range in the descendent population (dashed rectangle) without altering the mean value (dashed vertical line). (b) In changing environments, natural selection favors change in the direction that better adapts the organism to the new environment. The range for the majority of organisms from the original population (solid rectangle) and their mean value (solid vertical line) shift toward a different mean (dashed vertical line) without changing the range of the variable in the new population (dashed rectangle)

been ice covered for most of their existence. The barren surface of Mercury, the swirl of dense atmospheres on the gas giants, and the frozen worlds of the gas giant satellites all provide environments that have been constant for billions of years. Since the interiors of the “snowball” satellites are insulated by ice layers from the radiation, vacuum, and cold of outer space, whatever life may have gained a foothold there would be subjected to stabilizing selection in the extreme, unless changes in the flow of energy from the interior would have altered the course of physical conditions below the surface of those bodies, as might have occurred on the smaller satellites after their radiant cores expended their capacity for nuclear decay. On Venus and Mars, where irreversible changes have apparently transformed ocean bearing planets like Earth to an oppressive greenhouse on the one hand, and to a frigid desert on the other, stable environments may still be found beneath the surface of both, and possibly in the dense cloud layers of the lower atmosphere on Venus. In short, the dynamic nature of the Earth's biosphere appears to be exceptional in the Solar System. The role of the diurnal and annual cycles might have been important as they at least require storage of energy over shorter and longer periods of time. Most of the worlds close at hand provide environments of enduring constancy. If life on those worlds has followed the trajectory of life under constant conditions on Earth, we can expect that life on those bodies has been relatively unchanged from the ancient forms that characterized its beginnings.

Combining this point with the previous one above, whatever life exists on other worlds in our Solar System is likely to be microscopic, relatively simple, and basically unchanged from its earliest forms. Possibly Europa, and conceivably Titan and Triton could harbor exceptions, under circumstances to be argued later. The special histories of Venus and Mars may likewise raise alternative possibilities. But to the extent that our Solar System is typical of others throughout the universe, most life on other worlds is likely to be small, simple, and persistent in form and function from its early origins. Thus, while the possibility of some exceptions will be argued in subsequent sections, we concur in general with the view of Ward and Brownlee (2000) that most of the living fabric of the universe belongs in the province of microbiology.

4.2.4 Evolution is Accelerated by Environmental Changes

While the normal pace of evolution under stabilizing selection is negligible, changes in either the biotic or abiotic environment can alter the pace and direction of evolution relatively rapidly (Reznick and Ghalambor 2001). The macroevolutionary examples of greatest note include the major extinctions, followed by introduction of novel forms, at times of major environmental crisis, such as the end of the Cambrian, the Permian-Triassic boundary, and the Cretaceous-Tertiary boundary (Eldredge 1985). On a microevolutionary scale, industrial melanism is often cited as the definitive example. Cryptic coloration of moths changed over a few years in concert with changes in the color of tree trunks associated with increased soot production at the onset of the industrial revolution in England (Raven and Johnson 1999, p. 409). But very rapid evolution has been induced in the lab for a number of systems as well (Elena and Lenski 2003). Rapid evolutionary change illustrates the principle of *directional selection* (Campbell 1996, p. 432). When an environmental feature shifts in a particular direction (say the average habitat temperature gets colder), the optimum for the phenotype that is adapted to that feature (say thickness of fur) shifts to accommodate the change, so that formerly favorable phenotypes (short fur) become maladaptive and are selected against, while formerly maladaptive traits (thicker fur) become more favorable and are selected for. The frequency distribution for the phenotype, and its underlying genetic basis, shifts accordingly (Fig. 4.1b).

The more drastic and sudden the environmental change is, the quicker the evolutionary response needs to be in order for the organism to avoid extinction. In fact, extinction is more often the case, so the ones that survive are changed more radically in a briefer period of time. Over geological time spans, the fossil record thus appears to be discontinuous, with new forms arising relatively suddenly. This is the basis for the theory of "punctuated equilibrium" (Eldredge and Gould 1972).

4.2.5 Complexity Inevitably Increases but as the Exception rather than the Rule

Since geological and climatic changes are very slow in relation to the life span of all organisms, from one generation to the next, stabilizing selection is the more pervasive influence, and tends to favor constancy of biological form and function. Since, as argued above, simplicity is favored over complexity by the evolutionary process, most life remains stable, and the majority of biomass remains simple. But occasional episodes of directional selection and genetic drift inevitably give rise to some forms better adapted by adopting a greater level of complexity.

To a degree, increased complexity equates with increased size. Thus, the evolution of the more complicated eukaryotic cell from its simpler prokaryotic ancestor was the first great leap in size and complexity in the history of life (Margulis and Sagan 1995). The evolution of multicellular organisms from unicellular ancestors was another quantum leap in complexity (Cowen 1995). Within a given size range, however, the rule of preference for maintaining the status quo continues to hold. Only a small minority of mollusks developed complex nervous systems (the cephalopods). Only a minority of vertebrates developed the complex physiological regulatory mechanisms required for homeothermy. And only a small minority of mammals developed the refined sensorimotor coordination required for manual dexterity (primates) and eventually, complex language (humans).

But those levels of complexity did arise, and complexity theory argues in general that such complexity will arise eventually and inevitably (Gel-Mann 1994; Goodwin 1994; Kauffman 1995). This is because complexity enables specialization, and specialization sooner or later confers adaptive advantages under specialized circumstances. But specialization is difficult to reverse, as a host of interrelated organismic attributes become adapted to the specialized conditions. Once homeothermy evolves, as an example, other metabolic reactions adapt to narrow to optimal temperatures, and cease to function if the organism loses its ability to maintain the narrow thermal optimum. Thus the loss of thermal homeostasis would lead to extinction, so the specialization of homeothermy is retained as long as it provides an adaptive advantage.

Evolutionary biologists use the metaphor of a hilly landscape, where the altitude of a hill represents the degree to which its occupants are well adapted, or fit, to their particular biological niche (Dobzhansky 1951, adapted from Wright 1932). Complexity arises inevitably as time favors the "occupation" of higher points on the fitness landscape, but descent from the peaks of higher fitness is penalized by natural selection. While the overall landscape consists of fitness plains and valleys populated by less complex organisms with a broader range of general adaptations, the average level of complexity undergoes a net increase over time.

4.2.6 Biodiversity is Promoted by Heterogeneous Environments

Habitats can be relatively uniform over a large area (such as a desert) or volume (such as the interior of the ocean). The number of different varieties of organisms that occupy such environments is smaller than the number that occupy more diverse habitats, such as coral reefs or tropical forests (Brooks and McLennan 1991; Cowen 1995). This is because heterogeneous environments provide more niches to which different forms of life can become optimally adapted. The greater variety of living forms in turn creates more complex food webs and ecosystems. Thus, biodiversity, as measured by the overall variety of life and degree of interaction among components of the ecosystem, is greater where the habitat itself is more diverse.

By supporting a richer diversity of organisms, heterogeneous environments provide a more bountiful supply of progenitors for future evolution. Habitat fractionation thus becomes a spur to further evolution. With gradual changes in heterogeneous environments, biodiversity tends to increase even more. With sudden cataclysmic changes in such environments, biodiversity is reduced but survival of more forms is favored because of the numerical probability that more of them will be pre-adapted to persist through the cataclysm or thrive under the new environmental conditions. Thus, environmental heterogeneity not only promotes biodiversity but favors the persistence of life through challenging environmental changes.

These theoretical assumptions are well supported by the empirical evidence of life on Earth. The number of different species that occupy terrestrial habitats, which are inherently more complex than marine environments, is far greater than the number of marine species. On land, tropical rainforests provide the greatest habitat fractionation and support the greatest biodiversity. In the ocean a much greater diversity of species is found on the continental shelves, than in the deep ocean, and in the former, biodiversity is greater in coral reefs than in subtidal waters with smooth, sandy floors. The exception that proves the rule in the deep ocean is the proliferation of biodiversity around hydrothermal vents, where heated sulfur-rich effluents from encrusted "black smokers" create fragmented microhabitats with radical chemical and thermal gradients (Campbell 1996; Stetter 1985).

It follows that those other worlds in which the physical environment is heterogeneous and complex are likely to evolve a richer diversity of living forms than on those with more homogeneous habitats.

4.2.7 Individuals are Fragile, but Life is Hardy

Once life evolved on Earth, it proved to be extraordinarily resilient. Despite numerous global catastrophes and recurrent environmental crises – several of which wiped out a large proportion of the species in existence – life has persisted to occupy every suitable habitat on the planet. The widespread extinctions that accompany global catastrophes (Cowen 1995; Eldredge 1985) illustrate that individual organisms lack the capacity to survive radical changes. However, at the population, species, and higher taxonomic level, the capacity for survival is more robust, because the group has a wider range of survival mechanisms than the individual.

Macroevolutionary theory is based on the view that the large-scale patterns of evolution derive from differential survival of species (Gould 1981). The ability of the group to survive despite the fragility of the individual is attributed to the concept of inclusive fitness (Raven and Johnson 1999). Contributing mechanisms include altruistic behavior, spore formation, cannibalism, fluctuating sex ratios, and adjustable reproductive strategies. At the microbial level, spores and other dormant states such as the cryptogenic state in cold environments are of special relevance, because they allow organisms to stay dormant through harsh conditions until the environment becomes suitable for survival again. An especially intriguing example is provided by *Bacillus subtilis*, a common soil bacterium. Not only can it form spores, but under starvation conditions some of the cells resist sporulation by killing sister cells, enabling them to feed on the released nutrients for survival (González-Pastor et al. 2003).

4.3 Adaptations to Extreme Environments

Microbial life has proliferated into almost every environmental niche imaginable on Earth. These include extreme temperature, pressure, and pH environments, habitats exhibiting low nutrient and oxygen availability, and high salinity and radiation environments. From the human perspective, most of these environments are considered extreme, and the organisms living in them are considered extremophiles, This, however, is an anthropocentric characterization, as pointed out by Rothschild and Mancinelli (2001). A more suitable set of criteria might be based on certain conditions that destroy biomolecules, such as desiccation, radiation, and oxidation. From this perspective, all aerobic organisms including humans could be considered extremophiles, since oxygen forms reactive oxygen species which cause oxidative damage to nucleic acids, proteins, and lipids (Newcomb and Loeb 1998; Tyrell 1991). Regardless of which organisms are regarded as the extremophiles, the basic point is that life on Earth has adapted to the far edges of the range of niches available, and therefore could be expected to adapt to very different conditions on other worlds. Most renowned for their adaptation to extreme environments on Earth are the Archaea, but extremophiles occur in all domains including multicellular organisms and vertebrates (Islam and Schulze-Makuch 2007). A classification with examples of extremophiles is provided in Table 4.1.

Table 4.1 Known environmental limits for extremophiles for growth or tolerance (modified from Baross et al. 2007)

Environmental parameter	Bacteria and archaeans	Eukaryotes	Example environments
Temperature	113°C, *Pyrolobus fumarii*, 121°C, Strain 121 Bacterial growth at about −15°C	∼ 60°C algae (e.g. *Cynidium caldarium*) and some fungi Himalayan midge at −18°C	Submarine hydrothermal systems, geothermal hot springs, brine pockets in sea ice at about −30°C
pH	∼pH 0, acidophilic archaeans such as *Ferroplasma sp.* pH 13, *Plectonema*, pH 10.5 *Natrobacterium*	pH 0, fungi such as *Cephalosporium* pH 10, many species of protists and rotifers	Acid mine drainage, geothermal sulfurous sites (e.g. Yellowstone) Soda lakes, peridotite-hosted hydrothermal systems (e.g. Lost City vent)
Desiccation	Growth in 35% NaCl, archaeans and bacteria, such as halobacteria	Molds and yeasts such as *Zygosaccharomyces rouxi* (growth in high sugar content)	Deep-sea brines, soda lakes, evaporate ponds, dry soils and rocks, food with high solute content
Pressure	High diversity of bacteria and archaeans in deep ocean trenches including piezophiles	High diversity of invertebrates and fishes in ocean trenches	11,100 m deep Marianas Trench
Radiation	10,000 – 11,000 grays (gamma radiation), *Deinococcus radiodurans*	German cockroach (*Blatella germanica*) can survive exposure to radiation above 1,000 grays	No natural source of radiation on Earth at levels tolerated *by Deinococcus radiodurans*
Chemical extremes	Cd 2-5mM, bacterial and archaeans; Ni 2.5mM, Co 20mM, Zn 12mM, Cd 2.5mM, *Ralstonia eutrophus*	Algae, e.g. *Euglena* and *Chlorella* can grow in Cd, Zn, and Co at mM concentrations	Submarine hydrothermal vent fluids and sulfides; some high-metal containing lakes

4.3.1 Temperature Extremes

Temperature is a fundamental physical parameter that affects all life processes. First and foremost, it determines the liquidity of water. Secondary effects of temperature include its impact on the structure of biological macromolecules (e.g. proteins) and it's constraints on cellular processes, such as the fluidity of membranes (Charlier and Droogmans 2005). As temperatures increase, proteins denature, resulting in the loss of quarternary, tertiary, and even secondary structures, thereby eliminating all uses related to conformation (Rothschild 2007). Variations in temperature affect the optimum activity for enzymes, and when enzymes denature they loose their catalytic activity completely. DNA usually melts well below 100°C, and chlorophyll degrades above 75°C. In addition, the solubility of gases in water goes down as temperature goes up, creating problems at high temperatures for aquatic organisms requiring oxygen or carbon dioxide. At temperatures below the freezing point of water, membranes become dehydrated and rupture, and solute concentrations in unfrozen inclusions can create high osmotic pressures and possibly reach toxic levels. On a macroscopic level, ice crystals form and pierce cellular membranes.

4.3.1.1 Psychrophily

Low temperature environments are common on Earth. They include microenvironments within ice, cold terrestrial environments, the deep sea, and the troposphere. Ice environments include snow, glaciers, frozen lakes, sea ice, and permafrost. Examples of cold terrestrial environments include the Dry Valleys of Antarctica and Arctic polar deserts. Temperatures in the oceanic abysses are about 2°C at a maximum hydrostatic pressure of 110 MPa (1,100 bars or 10,660 m) in the Mariana Trench (Yayanos 1995). Temperatures in the troposphere can drop to −50°C, but life in cloud droplets, claimed to independently grow and reproduce (Sattler et al. 2001), may only extend to temperatures slightly lower than 0°C. There are a number of reports in recent years that have demonstrated that some microbes can metabolize, albeit slowly, at temperatures in the range from −17 to −20°C (Junge et al. 2001; 2004; 2006; Rivkina et al. 2000). These reports also include observations about active photosynthesis in Antarctic cryptoendolithic organisms at temperatures as low as −20°C (Friedmann and Sun 2005). These organisms include bacteria, lichens (a symbiotic association of algae and fungi), and fungi (yeasts) (Marion and Schulze-Makuch 2006). Also, metabolic activity in glacial ice has been inferred from anomalous concentrations of gases at temperatures as low as −40°C (Campen et al. 2003; Sowers 2001). Further, there is some evidence for the transfer of electrons and enzyme activity in a marine psychrophilic bacterium at a temperature of −80°C (Junge et al. 2006). Enzyme activity has been measured to occur in a mixture of methanol, ethylene glycol, and water at temperatures as low as −100°C (Bragger et al. 2000). Price and Sowers (2004) argued that there is no evidence of a minimum temperature for metabolism (growth, maintenance, or survival). However, active metabolism becomes much more challenging at very low temperatures, which is also due to the decrease in available water (water activity, see Section 4.3.3). An especially intriguing example of metabolic activity in ice was recently found by Rohde and Price (2007), which may open new doors in evaluating the limits of life. They found evidence of microorganisms in glacial ice metabolizing dissolved small molecules such as CO_2, CO, O_2, N_2, and CH_4 through diffusion into the ice lattice. They detected proteins associated with high concentrations of microbial organisms and determined via modeling the minimum amount of metabolism that has to occur to ensure survival of the organism as 1900 molecules per cell per year. This metabolic rate is about 6 orders of magnitude lower than that necessary for exponential growth and mobility. Nevertheless, Rohde and Price (2007) claim that an adequate supply of dissolved gases would meet the needs of this very slow metabolism rate for at least 10,000 years.

As the fluidity of membranes decreases with decreasing temperatures, organisms can maintain fluidity by increasing the ratio of unsaturated to saturated fatty acids (Rothschild and Macinelli 2001). Organisms adapt to temperatures below freezing by deploying mechanisms for either freezing avoidance or freezing tolerance. Freezing avoidance is often utilized by insects. For example, the super cooling point of the larvae of *Dendroides canadensis* decreases from a summer maximum of −2 to −7°C to a winter minimum of −20 °C or lower via the removal of highly active hemolymph and gut fluid ice nucleators along with the inhibition of residual nucleators by antifreeze protein (Olsen and Duman 1997). Freeze tolerance usually involves cryobiosis, a state in which all of the water within the cells of an organism freezes and the organism becomes dormant (no measurable metabolic activity) until warmer conditions reappear. The longer an organism remains in cryobiosis, the longer it takes for the organism to come out of that state (Keilin 1959). The common organisms of choice to study cryobiosis are tardigrades, which are known to survive freezing to near absolute zero. Another strategy often used in mammals is hibernation, which only involves a reduction of metabolic activity (see Islam and Schulze-Makuch (2007) for more details).

4.3.1.2 Thermophily

Microbes have been identified with temperature tolerances above 100°C in various environments such as submarine hydrothermal vents, the subterranean deep biosphere, and terrestrial hot springs (Marion et al. 2003). Microbes have been isolated from terrestrial hot springs that can tolerate temperatures up to 103°C (Stetter 1999). The highest temperature tolerances are found in microbes from marine hydrothermal vents and the subterranean deep biosphere; high pressures prevent these waters from boiling at 100°C, the normal boiling point of water at 1 atm (10^5 Pa, 1.01 bar) pressure. Kashefi and Lovley (2003) reported culturing microorganisms in the laboratory at a temperature of 121°C. Evidence has even been presented for microorganisms thriving in hydrothermal vents at temperatures exceeding 200°C (Schrenk et al. 2003), although this is controverisal. There may not be a reason in principle why microbial organisms would not be able to grow at temperatures as high as water's critical point as long as the water remains liquid. Hyperthermophilic organisms (microorganisms that grow best at temperatures above 80°C) are either bacteria or Archaea. Most eukaryotes have an upper temperature range of ~50–60°C, vascular plants of about 48°C, and fish of about 40°C, possibly a function of the low solubility of oxygen at high temperatures (Madigan and Marrs 1997; Nealson 1997; Rothschild and Macinelli 2001).

Hyperthermophilic microbes have fundamental changes in their macromolecular structures which compensate for the increased mobility and fluidity at high temperature (Charlier and Droogmans 2005). Protein structures are stabilized at high temperature through amino acid substitutions and the increased use of disulfide bonds (Beeby et al. 2005). Heat stable, ether-linked lipids are universal in hyperthermophilic archaeans and in some hyperthermophilic bacteria, and all hyperthermophiles studied have a reverse gyrase that positively supercoils DNA – the DNA of all other organisms being negatively supercoiled (Baross et al. 2007). Supercoiling with cationic proteins increases the thermal stability of DNA (Daniel et al. 2004b). Proteins of thermophilic organisms have evolved to cope with high temperatures by increasing ion-pair content, forming higher-order oligomers, and by utilizing monovalent and divalent salts enhancing the stability of nucleic acids (Rothschild and Macinelli 2001). Also, external factors such as high pressure appears to increase the thermal stability near the known upper temperatures of life (Holden and Baross 1995). Microbes are not the only thermophilic organisms. The most thermophilic metazoan is the Pompeii worm capable of withstanding temperatures as high as 105°C (Chevaldonne et al. 1992). The worm uses both physical means (e.g., circulation of cold water over its exterior) and biochemical means to achieve this feat. One biochemical adaptation is the use of the most thermostable fibrillar collagen known (collagens are extracellular proteins with triple-helical domains). While the interstitial collagen of coastal polychaete worms (e.g., *Arenicola marina*) is denatured at 28°C, the collagen of the Pompeii worm remains stable at 45°C (Gaill et al. 1995). Its collagen is adapted to the hydrothermal vent environment by its stability at higher temperatures, high pressures, and associated enzymatic processes, which appear to be optimized under anoxic conditions. Thermophilically-inclined terrestrial organisms also include the desert snail *Sphicterochila boisseri*, which can survive in the desert at temperatures of up to 50°C (Schmidt-Nielsen et al. 1971) and the desert ant *Proformica longiseta*, which forages on sand surfaces when temperatures reach as high as 60°C (Wehner 1989).

4.3.2 Extreme pH-Conditions

Acidity is typically quantified using the pH scale:

$$\mathrm{pH} = -\log_{10}(a_{\mathrm{H}+}) \tag{4.1}$$

where $a_{\mathrm{H}+}$ is the hydrogen ion activity. Bacteria, Archaea, fungi, and algae have all been demonstrated to tolerate pH values ≤ 1.0 (Bachofen 1986; Johnson 1998;

Schleper et al. 1995; Huber and Stetter 1998; Schrenk et al. 1998; Edwards et al. 2000; Robbins et al. 2000). For example, the red alga, *Cyanidium caldarium* can live at a pH ~ 0 (Seckbach 1999) and *Ferroplasma acidarmanus*, which was isolated from acid mine drainage, can grow at a pH of 0 (Edwards et al. 2000). The Archaea *Picrophilus oshimae* and *P. torridus* can grow at a pH of -0.06 (Schleper et al. 1995). There are fewer studies of high alkalinities (pH >10) than of extreme acidities (pH <1.0), probably because high alkalinity environments (e.g., soda lakes) are rarer in nature. The challenge for organisms living at a high pH is that they must either pump protons to maintain an intracellular pH close to neutrality or use an alternative genetic structure different from standard DNA. Also, the hydroxide anion, arising from water at high pH, is a powerful nucleophile and destroys many molecules which are essential parts in metabolic reactions (Baross et al. 2007). Nevertheless, there are reports of organisms tolerating pH values >11, and even as high as 12.5–13 (Bachofen 1986; Duckworth et al. 1996). A diversity of organisms, from bacteria to cyanobacteria and rotifers have been reported to live at pH 10.5 (Martins et al. 2001) and microbial communities have been reported to live at pH 12.9 in the soda lakes of Maqarin, Jordan (Pedersen et al. 2004). Kelley et al. (2005) reported about a marine environment (Lost City hydrothermal field) with a pH of up to 11 and temperatures of up to 90°C that was teeming with microorganisms. The Vinegar eelworm (*Turbatrix aceti*) is probably the most pH-tolerant multicellular organism. It can grow at a pH range of 3.5 to 9, and tolerate a range of 1.6 to 11 (Wharton 2002).

Low pH-values are challenging for organisms, because a surplus of hydrogen ions can enter the cell and disrupt its internal biochemistry. For example, proteins denature under very acidic conditions. On the other hand, a high pH is challenging for organisms due to a lack of hydrogen ions which are needed for the proton pumps in the cell. Most organisms living at moderately extreme pH-values maintain a near neutral pH in their cytoplasm. In general, acidophiles evolved efficient proton pumps and low proton permeabilities, and alkaliphiles evolved an efficient proton transport system (Rothschild 2007). Active mechanisms to achieve this adaptation may also involve secondary proton uptake mediated by membrane-associated antiporters (Rothschild and Macinelli 2001). Other mechanisms include specially adapted bioenergetics and permeability properties, surface charges, high internal buffer capacity, overexpression of proton export enzymes and unique transporters for acidophilic organisms (Pick 1999), and negatively charged cell-wall polymers in alkaliphilic organisms (Krulwich et al. 1998).

4.3.3 Low Availability of Water

Life processes on Earth are mediated in water as a solvent. The availability of water is referred to as water activity and is defined as the vapor pressure of water divided by that of pure water at the same temperature. Pure water has a water activity of exactly one. A higher water activity in the medium tends to support more microorganisms. No bacteria or Archaea have been found to date that can grow at a water activity lower than 0.7 in their natural environment, while fungi have a somewhat greater tolerance (Marion et al. 2003). Diverse populations of microorganisms have been shown to undergo cell division in saturated NaCl brines at a water activity of about 0.75 (Grant 2004), but no microbial reproduction has been demonstrated in Dead Sea brine dominated by $CaCl_2$ and $MgCl_2$ (Special Regions Science Analysis Group 2007), which has a water activity of about 0.67 (Kis-Papo et al. 2003). The record holder as of this writing is the food spoilage fungus *Xeromyces bisporus*, which can grow in a sugar solution at a water activity of 0.61 (Grant 2004). Values for liquid water activity in equilibrium with ice decrease with temperature. Ice has a water activity of 0.82 at $-20°C$, and a water activity of 0.67 at $-40°C$, respectively. Thus, the lack of available water at low temperatures will greatly affect the survival ability of psychrophilic microorganisms (Section 4.3.1.1).

In a dormant state, without biological activity occurring, some organisms can even survive a 99% loss of water and about 0 water activity (Mazur 1980). A drop in water activity or desiccation causes DNA to break, lipids to undergo permanent phase changes, and proteins to crystallize, denature, and undergo condensation reactions (Potts 1994). One strategy of organisms to survive in an environment with low water activity is to match their internal water activity with that of the surrounding environment. Microbes can accomplish this feat by accumulating compatible solutes such as potassium ions or low molecular weight soluble organic compounds that do not interfere with the normal physiological functions of the cell (Mueller et al. 2005). Some microbes employ a different adaptation strategy and go dormant, for example forming spores or cysts, while others such as the bacterium *Deinococcus radiodurans* employ mechanisms to repair their DNA (Cox and Battista 2005).

A very powerful adaptation to desiccation is anhydrobiosis, which allows organisms to survive up to 99% of water loss. It is defined as the state of an organism in which there are no visible signs of life and metabolic activity is unmeasurably low or non-existent. Anhydrobiosis is exhibited by many forms of life ranging from unicellular organisms such as yeast, bacteria, protozoans, and fungal spores, to nematodes, rotifers, tardigrades, springtails, cysts of primitive crustaceans, and resurrection plants. Anhydrobiosis is commonly identified by morphological changes such as the coiling of the body observed in tardigrades. Trehalose, the disaccharide of glucose, plays a major role in protecting anhydrobiotic unicellular organisms, invertebrates, and resurrection plants, while other disaccharides, mainly sucrose, are present in seeds and pollen of higher plants (Crowe et al. 1992). In addition to trehalose, heat shock proteins and the so-called LEA (late embryogenesis abundant) proteins appear to be involved in conveying protection to organisms in the anhydrobiotic state. A summary of anhydrobiosis and its biochemical changes is provided in Islam and Schulze-Makuch (2007).

If salt concentrations become too high, organisms have to cope with a lack of water availability and high osmotic stress. The higher the salinity, the more energy an organism has to expend to maintain a favorable osmotic balance (Marion and Schulze-Makuch 2006). Measures of salinity include salt %, molality, or the thermodynamic activity of water. Seawater has a water activity of 0.98, but most bacteria and fungi can tolerate much higher salinities than sea water. Organisms best adapted to high salt conditions are usually from the domain Archaea. However, cyanobacteria and the green alga *Dunaliella salina* are also able to withstand periods in saturated sodium chloride solutions (Rothschild and Macinelli 2001). Microbes tend to respond to increases in osmolarity by accumulating osmotica (compounds used to attain an osmotic balance) in their cytosol to protect them from cytoplasmic dehydration and desiccation (Yancey et al. 1982). Halobacteriaceae use K^+ as their osmoticum (Larsen 1967), while glycine betaine is the most effective osmoticum in most other prokaryotes (Le Rudulier and Boillard 1983). However, there is evidence that environments that have $MgCl_2$ at concentrations greater than 2.3 M may inhibit life due to the ability of $MgCl_2$ to denature biological macromolecules (Baross et al. 2007). Brine shrimps (*Artemia*) are the best known multicellular organisms to withstand high salt concentrations in their natural habitat of terminal inland salt lakes and coastal salterns. Adaptation to high salt conditions can involve a cessation of metabolism as observed in the nematode *Steinernema feltia* (Chen et al. 2005), and is referred to as osmobiosis. Encysted embryos of the primitive crustacean *Artemia franciscana* appear to be most resistant to high salt concentrations. *Artemia's* survival abilities are enhanced by a protective cyst wall, the accumulation of trehalose and glycerol, the protein artemin, and the involvement of heat-stress proteins, which act as molecular chaperons.

4.3.4 Low Oxygen Availability

It could be argued that all aerobic organisms are extremophiles, because oxygen forms reactive oxygen species which cause oxidative damage to nucleic acids, proteins, and lipids (Rothschild and Macinelli 2001). In fact, with the advent of the cyanobacteria and the production of oxygen more than 2.5 billion years ago, oxygen concentration increased in Earth's atmosphere sharply (Kasting 2006). This must have resulted in the largest mass extinction in Earth's history, as oxygen and oxygen species are potent toxins for the then anaerobic organisms of the earlier Earth. However, given that Earth's atmosphere has been oxygen-rich for at least 1.5 billion years, and that aerobic respiration is the metabolic pathway of highest energy yield and the one to which Earth's fauna has fully adapted, it is informative to explore how aerobic organisms on Earth have adapted to a lack or temporal unavailability of oxygen.

Oxygen has become essential for any life based on aerobic respiration. Anaerobic energy sources can supply the requisite ATP to maintain cellular functions for a limited time only, before substrate depletion, energy shortfall, or end-product poisoning threaten the survival of the organism (Islam and Schulze-Makuch 2007).

Tolerance to anoxia is on the order of minutes for many vertebrates, because of the immediate dependence of the heart, central nervous system, and brain on a continuous supply of oxygen. A particularly effective way for an organism to withstand oxygen deficiency is the state of anoxybiosis, during which metabolism comes to a standstill. For example, brine shrimps have been stored in anoxic conditions for 4 years and then hatched successfully without using any of their food reserves, such as trehalose, glycogen, or glycerol (Wharton 2002). Recent research indicates that the protein p26 and Gp4G molecules are associated with biochemical changes during the anoxybiotic state (Clegg 2001).

An especially remarkable example of adaptation to a lack of oxygen is exhibited in the Crucian carp (*Carassius carassius*). It is known that some turtles can survive without oxygen for a long period of time by inactivity at low temperatures. The carp, however, remains active during anoxic conditions. When water temperatures are dropping in its habitat in Northern Europe, the carp begins to store vast amounts of glycogen in the brain, which enables the carp to make the switch to anaerobic metabolism. Stored glycogen in the body of the carp is then broken down into glucose and ethanol providing sufficient energy to survive (Vornanen and Paajanen 2006). Its survival is very temperature dependent though. The Crucian carp can survive anoxia for several months at 0°C during the winter when the small lakes and ponds in which it thrives become oxygen depleted, but it can survive only a few days without oxygen at room temperatures (Nilsson and Lutz 2004).

4.3.5 Pressure

Pressure affects living processes by determining the liquidity ranges of water, and by forcing changes in volume. Pressure compresses the packing of lipids, resulting in decreased membrane fluidity (Bartlett and Bidle 1999), and alters gene expression (Nakasone et al. 1998). Most chemical reactions produce increases in volume, and pressure counteracts this increase (Rothschild and Macinelli 2001).

High pressures occur in both deep-earth and deep-sea environments, but there are some fundamental differences between these two habitats. In the deep sea, hydrostatic pressures on organisms are strictly a function of depth. For example, 1 atm = 1.01325 bars = 0.101325 MPa = 9.816 m (Yayanos 1995). Deep in the terrestrial subsurface, the confining pressure could be atmospheric with organisms growing in air pockets or, in contrast, very high as in brine pockets, where the organisms may be subjected to both hydrostatic and lithostatic pressures (Marion and Schulze-Makuch 2006). Another significant difference between the two habitats is that temperatures underground increase with depth, but deep-sea environments decrease in temperature with increasing depth. Microorganisms have been recovered from the Mariana Trench in the Pacific (10,660 m depth) where pressures reach 110 MPa (Abe et al. 1999; Kato et al. 1998; Yayanos 1995) and temperatures are about 2°C. Two bacteria similar to *Moritella* and *Shewanella* are apparently obligately barophilic; they grow optimally at 70 MPa and do not grow at all below 50 MPa (Kato et al. 1998). There are some Archaea associated with deep-sea hydrothermal vents that can survive at pressures as high as 890 bars (Pledger et al. 1994). The high pressure of hydrothermal vents appears to have a compensatory effect that allows stabilization of molecules at high temperatures (Marion and Schulze-Makuch 2006). Piezophilic bacteria have been obtained from the Marianas Trench, which can grow at 70–80 MPa, but not below 50 MPa (Bartlett 2002). Using a diamond anvil cell in the laboratory, it was demonstrated that *Shewanella oneidensis* and *Escherichia coli* strains remain physiologically and metabolically active at pressures of 68–1680 MPa for up to 30 hours (Sharma et al. 2002). At pressures of 1200–1600 MPa, living bacteria resided in fluid inclusions in Ice VI crystals (Fig. 7.2) and continued to be viable when pressure returned to 1 bar – 1% of the total population survived (Sharma et al. 2002). The rate of change in pressure may be significant in that experiment as organisms are extremely sensitive to sudden pressure changes. Nevertheless, it demonstrates that pressure may not be much of an impediment for some forms of life.

Organisms may be more sensitive to low pressures, however, since low pressure leads to rapid desiccation. It is difficult to envision how an organism would hold on to its environmental substrate on a planet with no or only a thin atmosphere. It has been shown that for terrestrial organisms under Martian surface conditions, the low pressure is at least as much of an environmental obstacle as UV irradiation (Diaz and Schulze-Makuch 2006).

4.3.6 Radiation

The types of radiation that have a detrimental effect on life include high-energy electromagnetic radiation (ultraviolet, x-ray, and gamma radiation) and high-energy alpha and beta particles. Ultraviolet radiation is the most abundant form of damaging radiation on the Earth's surface and probably also the most common natural mutagen. Ultraviolet light can also kill cells as a result of dimerization of thymidine residues in the DNA, preventing replication (Baross et al. 2007). Ionizing radiation, including x-rays, gamma rays, alpha and beta particles, and also part of the UV spectrum is detrimental to cells because it causes multiple breaks in the double-stranded DNA (Obe et al. 2001). Direct damage to DNA or indirect damage due to the production of reactive oxygen species creates modified bases and single and double-strand breaks (Rothschild and Macinelli 2001). While the major source of UV irradiation is the Sun, sources of ionizing radiation include cosmic rays, x-rays, and radioactive decay. Most organisms have mechanisms for protection from damaging radiation such as radiation-absorbing pigments and DNA repair mechanisms, but resistance to one form of radiation does not necessarily convey protection from other forms (Marion and Schulze-Makuch 2006).

Deinococcus radiodurans is the most well-known organism for radiation resistance. This resistance is thought to have evolved initially as an adaptation to desiccation (Mattimore and Battista 1996). The mechanism for conveying this resistance is thought to be attributable to the ability of *D. radiodurans* to quickly repair DNA damage with high fidelity (Bachofen 1986; Kushner 1981; Smith 1982; Zahradka et al. 2006). However, hyperthermophilic archaeans recovered from a submarine hydrothermal vent environment were found to also withstand radiation levels of up to 8000 Gy (Jolivet et al. 2004). There are also some multicellular organisms that are quite resistant. For example, the tardigrade *Milnesium tardigradum* in its desiccation-resistant “tun” state can survive high levels of x-ray exposure, and the German cockroach (*Blatella germanica*) can withstand ionizing radiation levels of up to 1,000 Gy. Microbial mechanisms to limit radiation damage include photorepair, excision repair, and homologous recombinational repair, avoidance behavior, and the production of antioxidants and detoxifying enzymes (Petit and Sancar 1999; Rothschild 1999; Smith 2004; Yasui and McCready 1998). Mechanisms to protect organisms from UV radiation also include the development of iron-enriched silica crusts (Phoenix et al. 2001), habitation beneath protective layers of soil or water (Pierson et al. 1987; Wynn-Williams and Edwards 2000), specialized organic pigments such as carotenoids and scytonemin (Wynn-Williams et al. 2002), self-shading (Smith 1982), and shielding by organic compounds derived from dead cells (Marchant et al. 1991).

4.3.7 Low Nutrient Availability and Chemical Extremes

Life on Earth requires or interacts with 70 elements (Wackett et al. 2004), and Sixteen elements (nutrients) are considered essential for life. These Sixteen elements are carbon, oxygen, hydrogen, nitrogen, potassium, calcium, phosphorus, magnesium, sulfur, iron, chlorine, copper, manganese, zinc, molybdenum, and boron (Marion and Schulze-Makuch 2006). The first nine elements (carbon to sulfur) are macronutrients because they are needed in large amounts (on a percentage basis), while the last seven elements are micronutrients (iron to boron) that are needed in trace amounts, in a ppm range (Raven and Johnson 1999). Any one of these nutrients may limit life. The macronutrients are likely the more limiting nutrients in any environment because they are needed in larger amounts than micronutrients. Nitrogen, phosphorus, and potassium are usually the most critical elements in this regard, hence their inclusion in fertilizers for agricultural purposes.

There are many toxic elements that can limit life including mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As). On Earth, high toxic element concentrations are often associated with high acidities because strong acids are very effective in dissolving primary minerals and releasing heavy metals into the environment (Fernandez-Remolar et al. 2003; Lopez-Archilla et al. 2001; Robbins et al. 2000). Thus, organisms that tolerate strong acidity usually also tolerate high levels of heavy metals. However, several of the toxic elements are also essential nutrients (Marion et al. 2003). There is often a delicate balance between adequate nutrients and excess toxins. Interestingly, some of the elements that are generally toxic, such as arsenic and selenium, are used by some bacteria in their metabolic pathways as a source of energy (Stolz and Oremland 1999).

4.4 Questions Unanswered by the History of Life on Earth

While a great deal of insight can be harvested by studying historical evolution and the adaptation of Earth's organisms to extreme environments, there are some questions critical to anticipating the nature and history of life on other worlds that the history of the one life we know cannot answer.

Though life arose relatively quickly on Earth, it isn't certain that it would inevitably arise as quickly, even under the same conditions as on Earth. All we know for certain is that it *can* arise endogenously, or take hold following importation, within a half billion years of the appearance of a suitable environment.

There are no theoretical reasons or empirical observations compelling us to think that the biochemistry of life on Earth, at the molecular genetic or metabolic level, is based on the same or even similar biomolecules as on other worlds. While it could be that some or all of the nucleotides, sugars, amino acids, and other metabolic intermediates that have evolved with life on Earth are so favored by physicochemical and thermodynamic selection that the same molecular configurations will inevitably evolve elsewhere, this by no means is apparent. In fact, the existence of alternative amino acids in meteorites that are not found commonly in living organisms (Cronin et al. 1988), argues against such a premise. Life on Earth shows us one form of molecular architecture that is possible, but does not rule out alternatives.

The duration of evolutionary episodes cannot be predicted from a sample size of one. While it took two billion years for eukaryotes to evolve from prokaryotes, and a billion years for macrofauna to evolve from microscopic multicellular forms, were these lengths of time necessary? The one sample we know cannot tell us whether these qualitative changes in the nature of life inherently require such long periods of time, or simply took that long for reasons that were either fortuitous, or peculiar to conditions on Earth.

The details of form and function that a different history of life would take cannot be predicted. Will taxa with calcified exteriors, such as the shells of bivalve mollusks, inevitably arise in marine environments? Will photosensitive receptors such as eyes inevitably arise if light is available? Will metabolic mechanisms for detoxifying, then utilizing oxygen for energy production, inevitably arise in the presence of oxygen? The fact that systems such as these have evolved independently under appropriate circumstances on Earth suggests the possibility that they would or at least could do so elsewhere (Morris 2003), but such an extrapolation is not warranted by the observation of a single case.

We have pointed out numerous examples of astonishing adaptations to extreme environments. Indeed, there is virtually no habitat anywhere near the surface of the planet, however extreme the temperature, pressure, dryness, salinity, or pH, that hasn't been found to harbor life. Thus, the one case of life in the universe provided by the example on Earth gives very little evidence of limiting conditions that have been reached.

We are left with the conclusion that life *could* arise quickly on other worlds, *possibly* using similar molecular and metabolic machinery to our own; that it *might* take as long to undergo revolutionary changes in form, size and complexity as it did on our planet, that it *conceivably* could follow macroevolutionary trajectories that mimic the history of life on Earth, and that it *might not* be limited by any physical or chemical conditions, short of those that lead to molecular destruction. That any of these things is true cannot be ascertained from the one limiting case we have before us. It is tempting, however, to speculate that given the number of other worlds in the universe, a fraction of them could be like Earth, and that a fraction of those could have harbored life with a history similar to our own. For the vast majority of other worlds, which are dissimilar to Earth, other forms of life are clearly possible, as subsequent chapters argue. Whether similar to life as we know it on Earth or not, life as we do know it provides a suite of expectations about the nature of life throughout the universe, and there is no reason to doubt the validity of these general expectations.

4.5 Chapter Summary

Life arose relatively quickly on Earth, suggesting that it could do so elsewhere under appropriate conditions. Without defining (since we don't know) precisely what those conditions are, the vast number of worlds in the universe makes it virtually certain that conditions suitable for life exist on a large number of them. Therefore, life is almost surely highly redundant throughout the universe, well adapted to its environment, and as diverse as the habitats that it occupies – as the one example from Earth demonstrates. Given the harshness and volatility of conditions at most planetary and satellite surfaces, more stable environments are to be found beneath their surfaces where the constancy of conditions favors simplicity, and stabilizing selection favors stasis of form and function. The majority of the biomass across the universe is likely, therefore, to be microscopic, simple, subsurface, and similar to its early forms. However, the range of physical and chemical conditions over which those forms of life could survive is great. Where the physical history of the planetary body has been complex, or where the physical environment is relatively heterogeneous with a variety of boundary conditions, life can be expected to have evolved into more complex forms. This would be particularly true on worlds where environments are extremely variable. In proportion to the total number of worlds harboring life, however, these are likely to constitute a distinct minority.

Chapter 5
Energy Sources and Life

An external energy source is a necessary condition for life, because living systems require a flow of energy to organize materials and maintain a low state of entropy (Morowitz 1968). Energy is also needed to perform work. Life on Earth can be distinguished by the external energy source that it uses. Photoautotrophic life derives energy from sunlight and uses CO_2 as a carbon source. Chemolithotrophic life uses redox reactions involving abiological compounds and chemolithoautotrophic life uses CO_2 (or other small carbon compounds) as a carbon source. Chemoheterotrophic life uses high-energy organic molecules, produced in general by autotrophic life, as a source of energy and carbon. On other worlds, where other forms of energy may be more abundant, or where the primary sources for energy on Earth may be lacking, life may have evolved to depend on different forms of energy. In this chapter, we critically analyze the various forms of energy that are potentially available to living systems, consider other factors that bear on the evolution of energy harvesting mechanisms, and evaluate the apparent availability of different forms of energy at different sites in our Solar System.

5.1 Life As We Know It

The National Research Council (Baross et al. 2007) defined terran life as a form of life that (1) uses water as a solvent, (2) is built from cells and exploits a metabolism that focuses on the carbonyl group (C=O), (3) is thermodynamically dissipative, exploiting chemical-energy gradients, and (4) exploits a two-biopolymer architecture that uses nucleic acids to perform most genetic functions and proteins to perform most catalytic functions. Terran organisms store energy in two principle ways, either in a molecule that has a high free energy of reaction under the conditions that prevail inside the organism (e.g., ATP), or as a gradient of concentrations of chemical species across a physical structure (e.g., a biological membrane). The term “terran” was used to denote a particular set of biological and chemical characteristics that are exhibited by all life on Earth. Thus, any alien life could be terran or nonterran depending on its characteristics. With regard to energy, terran life has evolved to use

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics, © Springer-Verlag Berlin Heidelberg 2008

light, organic molecules, and oxidizable inorganic chemicals as abundant sources of energy on Earth, so living systems have evolved specialized adaptations to use these energy sources.

5.1.1 Oxidation-Reduction Chemistry as an Energy Source for Life

Energetically favorable redox-reactions are the basis for life on Earth. The best known and most common types of metabolism are based on hydrogen oxidation and methanogenesis, sulfur reduction and oxidation, iron and manganese reduction, denitrification, and aerobic respiration. However, many other energy-yielding redox-reactions are known that involve the reduction or oxidation of relatively rare elements such as arsenic, selenium, copper, lead and uranium. Thus, there does not appear to be a basic limitation on which elements or redox-reactions can be used. Rather, the reactions that occur will likely be dictated by the abundance, availability and suitability of a specific element in a certain type of environment. The diversity of arsenic and selenium respiring bacteria thriving in playas (alkaline salt lakes) and mining tailings is a good example (Stolz and Oremland 1999).

As pointed out in Chap. 3, the oxidation of hydrogen may be one of the most ancient and basic metabolic pathways for life on Earth, and possibly elsewhere. The oxidation of the most common element in the universe yields an appreciable amount of energy, 2.5 eV per reaction (or 237.14 kJ/mole, 56.68 kcal/mole) assuming standard conditions (25°C, 1 atm)

$$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O \tag{5.1}$$

The metabolic pathway is called methanogenesis if the oxidation of hydrogen is coupled with the reduction of carbon dioxide to methane.

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{5.2}$$

Methanogenesis as defined here does not imply that the hydrogen has to be supplied in molecular form, but it may also derive from an organic source. The reduction of carbon dioxide to methane requires the expenditure of energy, but due to the production of two water molecules the reaction is energy-yielding (1.4 eV energy yield at standard conditions, 474.28 kJ/mol). This reaction powers autotrophic life at hydrothermal vents and also some of the endolithic life present in the cracks and pores of the basaltic ocean floor. In addition to providing energy for metabolism, this pathway has the advantage of fixing carbon dioxide that can further be used for organic synthesis reactions. Another important redox reaction is the oxidation of molecular hydrogen coupled to the reduction of iron.

$$H_2 + 2\,Fe(III) \rightarrow 2\,H^+ + 2\,Fe(II) \tag{5.3}$$

The energy yield from this reaction is 1.6 eV (148.6 kJ/mol). Examples of terrestrial organisms that use this reaction are *Pseudomonas* sp. (Balashova and Zavarzin

1980) and *Shewanella putrefaciens* (Lovley et al. 1989). There are many other compounds that can be coupled to the oxidation of hydrogen. One intriguing example is the reaction of hydrogen peroxide (H_2O_2) with molecular hydrogen to water, which is performed by *Acetobacter peroxidans* (Doelle 1969; Tanenbaum 1956) . This can serve as a model pathway for highly oxidized environments not commonly found on Earth.

Sulfur metabolism appears to be very ancient, as many terrestrial microbes are thermophilic and are associated with expressions of volcanic activity such as hot springs. One of the reasons that sulfur is so widely used is that it occurs in a wide variety of oxidation states including fractional nominal oxidation states. Oxidation states for sulfur of +7, +5, +4, $+3^1/_3$, +3, +2.5, +2, −0.4, −0.5, $-^2/_3$, −1 are known, leading to a complex inorganic sulfur cycle, much of which is mediated by microbes (Amend and Shock 2001). Sulfur reducing bacteria are quite commonly observed to populate anoxic sediments of bottom fresh waters, and marine and hypersaline aquatic environments including submarine hydrothermal vents. Many sulfate reducers prefer molecular hydrogen or hydrogen from an organic source such as acetate or lactate, which is used as an electron donor. Some of the sulfur reducing bacteria live symbiotically with green sulfur bacteria that photooxidize hydrogen sulfide to elemental sulfur (early photosystem). Sulfur oxidizing microbes are common in oxygen-rich aquatic ecosystems and ground-water systems, often in close proximity to sulfur reducing microbes (Schulze-Makuch 2003). Sulfur oxidation may be coupled to the reduction of iron as in the case of *Thiobacillus thiooxidans* or the thermophilic microbe *Sulfolobus acidocaldarus* (Brock and Gustafson 1976; Lovley 1991).

$$S^\circ + 6\,\mathrm{Fe(III)} + 4\,H_2O \rightarrow HSO_4{}^- + 6\,\mathrm{Fe(II)} + 7\,H^+ \tag{5.4}$$

This reaction yields a high amount of energy, 2.6 eV per reaction under standard conditions and occurs in acidic environments.

Iron and manganese reduction occur in those environments associated with hydrothermal vents in the oceanic basalt crust as well. Iron reduction is coupled to the oxidation of hydrogen (see Eq. 5.3) or the oxidation of organic sources such as glucose, lactate, formate and organic acids. Under oxygen-rich conditions the energetically favorable reaction is the oxidation of iron, which can already occur under slightly oxidizing conditions.

$$\mathrm{Fe(II)} + \frac{1}{4}\,O_2 + H^+ \rightarrow \mathrm{Fe(III)} + \frac{1}{2}\,H_2O \tag{5.5}$$

This kind of reaction is performed on Earth, for example, by *Gallionella* and *Thiobacillus ferrooxidans* (note that *T. ferrooxidans* can grow by oxidizing sulfur as well as iron). The net gain of energy is 0.5 eV for each Fe^{2+} that is oxidized. Schulze-Makuch (2002a) suggested an iron cycle between anaerobic ocean bottom water and oxidized upper ocean water for ice-covered planetary oceans (such as the one suspected on Europa) as a possibility for a primitive microbial ecosystem.

Denitrification and metabolism using molecular oxygen are metabolic pathways that likely developed later as the Earth's atmosphere became enriched in nitrogen and oxygen. Thus, they don't relate directly to the primordial stages of life. However, denitrification and metabolism using molecular oxygen are among the highest energy-yielding metabolic pathways, and thus are extremely important for the later evolution of life. Heterotrophic organisms that use pre-existing, energetically rich organic macromolecules are usually considered to have evolved later as well. However, speculation has long held that the very earliest organisms on Earth were heterotrophic rather than autotrophic (Fox and Dose 1977; Haldane 1929; Oparin 1938), based on the assumption that energetically rich organic macromolecules may have been supplied on the early Earth in abundance by prebiotic synthesis (Miller and Orgel 1974) and/or by comet delivery (Chyba et al. 1990).

5.1.2 Light as an Energy Source for Life

Probably one of the most important factors in the success of life on Earth is the use of a narrow band of electromagnetic radiation (visible light) emitted from the Sun at a high intensity. The evolution of photosynthesis allowed life to tap into a practically unlimited source of energy. Sometime early in the history of the Earth, photosynthesis developed as a favorable energy capture mechanism.

The free energy that can be provided by photoautotrophy can be calculated by multiplying the frequency (f) of the light that is used by Planck's constant (h).

$$\mathrm{W} = \mathrm{h}\, f \tag{5.6}$$

The frequency varies inversely with wavelength, and somewhat different wavelengths are used by different organisms. For example, bacterial chlorophyll uses a wavelength of 800 to 1,000 nm, while carotenoids in plants absorb wavelengths ranging from 400 to 550 nm. The average energy gain across the visible spectrum is about 2 eV (190 kJ/mol, 45 kcal/mol). It is interesting to note that this value is very similar to the free energy provided by hydrogen-oxidizing prokaryotes thought to represent early chemoautotrophic organisms. Thus, from a purely energetic viewpoint, light energy and chemical energy are equally competitive.

5.2 Life As We Don't Know It

Light, organic molecules, and oxidizable inorganic chemicals are abundant sources of energy on Earth. Thus, living systems on our planet have evolved to use these forms of energy. However, living cells make biological use of other forms of energy as well. Organisms can sense heat (Viswanath et al. 2003), pressure, stretch, movement of air and fluids, gravity, and electric and magnetic fields (Blakemore 1982; Schmidt-Nielsen 1990). All these stimuli generate responses through membrane transductions, either by altering the gating of ions that change transmembrane potentials, or by initiating metabolic changes through secondary messenger systems.

Thus, they indicate the capacity of living systems to use energy in a variety of forms to affect biological processes.

The accumulation of high-energy intermediates such as adenosine triphosphate (ATP) depends on the generation of proton gradients across membranes. Since the molecular machinery of cell membranes mediates most sensory transductions, it is reasonable to assume that natural selection could have favored the evolution of membrane mechanisms that transform heat, pressure, stress, magnetic fields, or kinetic energy into high-energy covalent bonds, either directly or indirectly by coupling to ion or proton pumps. Perhaps these mechanisms have failed to evolve in living systems on Earth only because of the lack of a need for them. On other worlds where light is unavailable, natural selection would be expected to favor the evolution of alternative energy harvesting mechanisms (Schulze-Makuch and Irwin 2002a).

How much energy is needed to power a living system? We do not know, but we can get a rough idea by calculating the amount of energy used by living organisms on Earth. First, as mentioned before, both light energy (in the visible spectrum) and chemical energy (hydrogen oxidation) provide about the same amount of energy (2 eV per photon or hydrogen molecule oxidized). Second, we know how much energy is required to assemble energy-storing compounds used on Earth. For example, an energy of about 7 kcal/mol or 0.304 eV per molecule (4.86×10^{-23} kJ or 1.16×10^{-23} kcal) is required to form the terminal phosphate bond in ATP. While the chemical storage form of energy used by another form of life would not necessarily be ATP or anything like it, the amounts of energy required for ATP phosphorylation on Earth provide a known benchmark. Given the required bonding energy of 0.304 eV, it follows that a photon of light or the oxidation of a molecule of hydrogen to water provides in theory sufficient energy to convert 6 to 8 molecules of ADP to ATP, if the conversion is close to 100% efficient. With this benchmark in mind, we can speculate whether other energy sources could be as efficient as chemical energy or light on Earth to provide sufficient energy for a living organism under a different set of environmental conditions.

5.2.1 Electromagnetic Waves (other than Visible Light)

The wavelength of light used by phototrophic organisms lies in the visible and near-infrared spectrum. The fact that these specific frequencies are used may merely reflect adaptation by Earth organisms to the most prevalent wavelengths of electromagnetic radiation emitted from the Sun. These wavelengths are also transmitted through our atmosphere well, making them readily available to life on the surface of our planet. On other worlds the same may be true, even though many habitable worlds could be associated with other types of stars such as F, K or M dwarf stars. Kiang et al. (2007) suggested that photosynthetic organisms on a planet surrounding an F2V star would likely exhibit peak absorbances in the blue, on a K2V star in the red-orange, and on an M star in the near infrared. Most atmospheres would absorb far less UV radiation, and absorb wavelengths below near-infrared to a great extent. However, in principle other wavelengths could be harvested. The problem with more energy-rich radiation such as that in the ultraviolet range, is its detrimental effect on many biogenic molecules such as proteins and DNA (Rettberg and Rothschild 2002). Thus, any organism using UV or more energy-rich radiation would need some kind of protection to harvest this type of electromagnetic wavelength, or would have to be based on a very different type of biochemistry. Alternatively, organisms may be able to take up a greater amount of less energy-rich radiation from near-infrared wavelengths. This radiation is plentiful in the universe, as any body or substance above 0° K will radiate infrared light. A prime example is hydrothermal vents on the ocean floor of Earth that emanate infrared light at a depth where photons from the Sun cannot reach (Van Dover et al. 1994; White et al. 2002). Analysis of a green sulfur bacterium from a deep-sea hydrothermal vent indicated that geothermal radiation and associated reduced sulfur compounds are sufficient to at least enhance the survival of green sulfur bacteria in the otherwise dark oceanic depths (Beatty et al. 2005). This organism, which was not found to be present in the surrounding water, thus expands the range of possible environments that could harbor life dependent on electromagnetic energy to drive endergonic biochemical reactions. However, more photons of infrared radiation than of visible light would have to be harvested to obtain a comparable energy gain. Experimental evidence has also been provided by Gusev and Schulze-Makuch (2005) that microbes may be capable of converting radio waves into chemical energy to supplement their energy needs. They hypothesized that protons in liquid water could be excited at their natural resonance frequencies by the Sun's and Earth's natural magnetic field through Langmuir oscillations, generating enough kinetic energy to charge the transmembrane potential of a cell. Even less energy would be available from this source. The hypothesis is very controversial, however, and has not yet been independently confirmed by other research groups.

5.2.2 Thermal Energy

Radiogenic elements decay in planetary interiors and produce heat that drives all major processes in the interior of planetary bodies. Examples for Earth include keeping the outer core liquid, establishing a protective magnetic field, and driving plate tectonics. Tidal flexing can also cause heat to emanate as observed on Io, the volcanically most active planetary body in the Solar System. The tidal flexing is caused by the changes in gravitational attraction to Jupiter and to some minor degree to the other Galilean satellites. Heat released by tidal flexing is also observed in the Earth-Moon system, but to a lesser degree.

This geothermally produced heat results in thermal gradients on which thermotrophic organisms could feed. We have named these putative organisms "thermotrophs" by analogy with phototrophic and chemotrophic organisms that use light and chemical energy as basic energy sources, respectively (Schulze-Makuch and Irwin 2002a). A relatively straightforward possibility would be to harvest energy from the thermal gradients at hydrothermal vents. Thermotrophic life could harvest energy from the high heat capacity of water, which is about 4 kJ/kg K between 0 and 100°C and 0 and 100 MPa pressure. If we assume a cell mass of 10^{-12} g comparable to that of microbes on Earth (Brock 1979), and further assume that one tenth of the cell mass is a vacuole of water from which the thermotrophic organism could extract energy, about 2.5×10^{6} eV would be obtained from cooling the vacuole by 1°C. If a microbe were able to use the Carnot cycle, the organism could extract about 9,000 eV of usable energy for a temperature change from 5°C to 4°C (Schulze-Makuch and Irwin 2002a); upon larger decreases the potential free energy gain would increase proportionally. High-energy metabolites within the organism could be produced via conformational changes if a temperature gradient between vacuole and cell plasma were present. For a cell as large as the giant pantropical alga, *Valonia macrophysa* (Shihira-Ishikawa and Nawata 1992), containing a water vacuole of approximately 10 g, the potential energy yield could be close to 1 Joule.

Thermal gradients could also be harvested directly. In a series of papers Muller (Muller 1985, 1993, 1995, 2003) and Muller and Schulze-Makuch (2006a) suggested thermosynthesis as a plausible metabolic pathway. Thermosynthesis, just as a steam engine, would make use of a phase transition (Muller and Schulze-Makuch 2006b). Membranes undergoing the thermotropic phase transition would increase the mobility of the molecules within the membrane (Muller and Schulze-Makuch 2006a). Due to a change in dipole potential, such a transition would quite plausibly result in a change in potential across the membrane (Muller 1993). Although this potential change has not been measured directly, similar potential changes that undergo the thermotropic phase transition have been measured across monolayers of lipids at the water/air interface. The changes can easily reach 100 mV - high enough to drive ATP synthesis (Muller and Schulze-Makuch 2006a). Electrogenic ATP synthases might be capable of converting the electrical energy gained by thermosynthesis into ATP if their activity and stoichiometry were properly regulated (Muller 1993). If correct, thermosynthesis could be a plausible basic pathway of metabolism for early organisms on Earth, possibly a progenitor of bacterial photosynthesis (Muller 1985, 1995, 2003), and an option for possible life on other worlds.

A potential drawback to the use of thermal energy is its inefficiency. The most efficient thermodynamic system known – the Carnot engine – is very inefficient, especially for small temperature differences. Because of the low efficiency, most of the energy in a thermal gradient would be dissipated as heat without being captured by chemical bonds, and would readily degrade the thermal gradient itself. A possible solution to the problem would be a thermotrophic organism that could shuttle back and forth across fairly sharp environmental gradients, or a thermotrophic organism that possesses an elongated body and makes use of convection to dissipate the unusable entropy-related energy.

Based on these principles, Muller and Schulze-Makuch (2006a) visualized four different physiological versions of a possible thermotrophic organism (Fig. 5.1). In the first type, a water vacuole would be warmed when the thermotroph moved into the vicinity of a hydrothermal vent. It could then float into the colder ocean, using the buoyancy of the warm vacuole, and harvest the free energy released by heat flow down the internal thermal gradient between the vacuole and the surrounding cell.

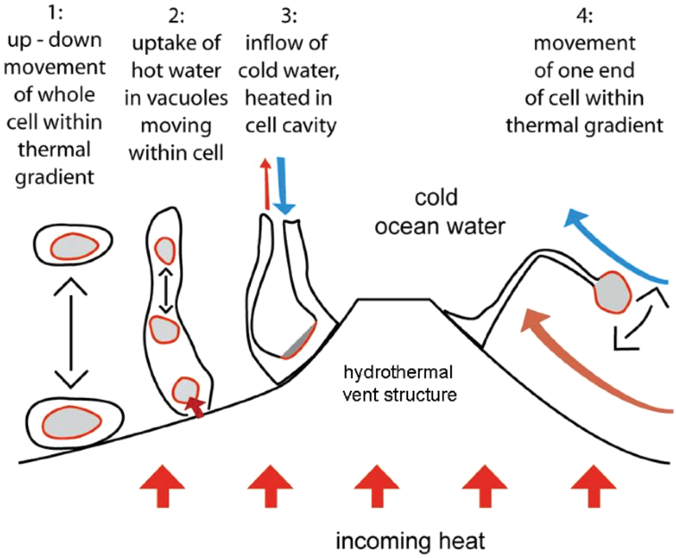


Fig. 5.1 Four types of thermotrophs that could be present near a hydrothermal vent. Areas within the organisms where the thermal gradient is tapped are marked in grey, hot water areas are red, and cold water areas are blue (modified from Muller and Schulze-Makuch 2006a)

The other three types of thermotrophs are envisioned as sessile, with one end remaining anchored to the surface of the hydrothermal vent. The second thermotroph is a filamentous-type of organism that spans the thermal gradient between the hot structure and the cold ocean. Near the structure it could take up hot water in a vacuole, and then gain free energy as the vacuole moves inside the cell to the cooler distal part. The third type of thermotroph would take up cold ocean water in a vacuole or cavity, and eject warm water from its base, not unlike the pattern of water flow seen in sponges, barnacles or mussels. While this process is used for filter feeding by these contemporary organisms, it may hint at an ancestral mechanism for the direct harvesting of energy from heat (Muller and Schulze-Makuch 2006a). Interestingly, mussels are still commonly found near vent structures today (Van Dover and Lutz 2004).

The fourth type of anchored thermotroph would have a distal end that moves freely in the cold ocean water, similar to the large sulfur bacteria (Gundersen et al. 1992) and giant tubeworms (Van Dover and Lutz 2004) present in the deep ocean environment today. Since the heat flux would vary on time scales as short as minutes (Tivey et al. 2002), water flow would be turbulent, and significant thermal fluctuations near the surface would therefore be expected, which could be harvested by the organisms, especially at summits of microscopic roughness that stick out above the boundary layer. Similar thermal fluctuations have been observed on top of bacterial mats in these environments (Gundersen et al. 1992). This type of thermotroph, can be compared to an organism that ‘filters’ temperature fluctuations from water, possibly sharing important characteristics of a direct progenitor of water filtering organisms such as the sessile protist ciliate *Vorticella*, with its long, quickly contractable stalk (Moriyama et al. 1998; Muller and Schulze-Makuch 2006a). It has to be emphasized that there are no known contemporary organisms that use thermal gradients as an energy source for metabolism, though such organisms conceivably could have existed on the early Earth, to be later outcompeted by phototrophic and chemotrophic organisms. But they could exist on an alien world. One possible example would be within the likely subsurface ocean of Europa, where light as an energy source is not readily available, but thermal gradients are likely to exist.

5.2.3 Kinetic Energy

The kinetic energy of convection cells or tidal currents could be harvested directly and used to sustain life. Organisms could contain pili or cilia much like ciliated bacteria or protozoa and adhere to a substrate at the ocean bottom or on the underside of an ice ceiling, where they are exposed to currents of moving water that cause the cilia to oscillate through bend and flex cycles that extract energy from the convection current (Fig. 5.2). The cells could enclose protein-like macromolecules that induce an electrical polarity across the membrane through a Donnan equilibrium. The hair cells could be surrounded by Na^+ channels whose permeability is proportional to the deflection of the hairs, with properties like those of sensory hair cells in the vestibular membrane of vertebrates or lateral line organs of fish (Fig. 5.3).

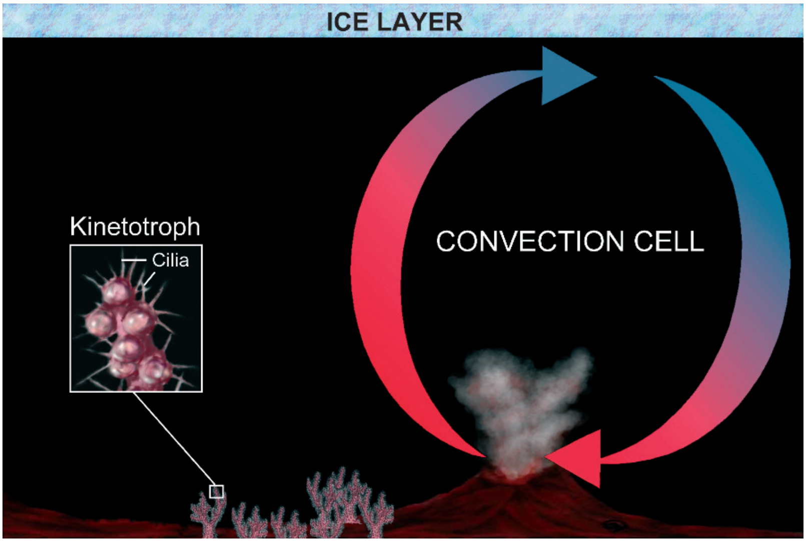


Fig. 5.2 Kinetotrophic organism in an oceanic environment, schematic. Convection currents can bend cilia leading to the opening of Na^+ channels, allowing Na^+ to flow into the cell passively down its concentration gradient. Art provided by Chris D'Arcy, Dragon Wine Illustrations, El Paso, Texas

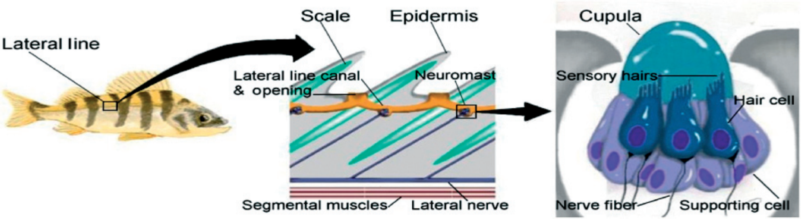


Fig. 5.3 Lateral line organ in fish, illustrating the role of cilia in transducing fluid movement into electrogenic signals. Cilia bend from the movement of fluid, allowing ions to move through the open channels. Art provided by Chris D'Arcy, Dragon Wine Illustrations, El Paso, Texas

By bending the cilia, the convection currents could open the ion channels, allowing ions to flow into the cell passively down their concentration gradients. This thermodynamically favored process could be coupled to the direct formation of high-energy phosphate bonds or to a H^+ transporter across another internal membrane, by analogy with mitochondrial membranes (Schulze-Makuch and Irwin 2001). The ionic gradient would be maintained by extrusion of the ions via exocytosis. The ions could bind, for example, to intracellular macromolecules whose tendency to fuse with the external membrane and disgorge their ionic ligands is thermodynamically favored, once the number of ions bound to the carrier reaches a concentration greater than the concentration of the ions outside the cell (Schulze-Makuch and Irwin 2002a). Alternatively, the ions could simply be precipitated as salts. A steady convection current with a velocity in the mm/s range would certainly be able to provide the requisite molecular distortion. Since this system works essentially like a battery that is charged over time, all that is needed is a minimal ionic gradient and enough time to charge the system high enough to form energy-storing chemical compounds.

5.2.4 Osmotic or Ionic Gradients

Osmotic gradients can be an enormously powerful source of energy. The osmotic pressure can be calculated by the van't Hoff formula.

$$\prod = c\,R\,T \tag{5.7}$$

where $\prod$ is osmotic pressure (atm), c is the molar solute concentration (mol/L), R is the universal gas constant (0.08206 L atm/mol K), and T is the absolute temperature (K). Some halophilic strains of cyanobacteria are known to tolerate salt concentrations of up to 2.7 M NaCl (Hagemann et al. 1999). Marine teleosts (bony fishes) retain a strong osmotic differential of roughly 0.7 osmoles between their intercellular fluids and their surrounding environment (Wilmer et al. 2000), where 1 osmole is one mole of osmotically active particles. Using this conservative figure as a first estimate at a temperature of 25 C (298 K), the osmotic pressure would be 16.9 atm (1.7×10^6 Pa). The force that acts on one water molecule along its concentration gradient is then

$$\mathrm{F} = \prod \mathrm{A} \tag{5.8}$$

where A is the cross-sectional area of one water molecule. This force is about 10^{-13} N. Further, assuming this force moves the water molecule through a membrane channel that couples the movement to the formation of a high-energy covalent bond, the energy available for bond formation is given by

$$\mathrm{W} = \mathrm{F\,s} \tag{5.9}$$

where s is the distance the water molecule moves down its density gradient (assumed to be 10^{-8} m for a biomembrane). Using the above figures, the calculated potential energy yield is 10^{-21} J, or 0.007 eV. Thus, one ATP could be phosphorylated from ADP for about every 45 water molecules entering the cell by osmosis. This is about two orders of magnitude below the energy yield for chemoautotrophs or photoautotrophs on Earth. The 0.007 eV may be a conservative estimate, because the osmotic differential calculated here is based on those of fish that have adapted from their freshwater origin to their marine environment rather than microbes adapted to use osmotic gradients. Halophilic microbes as described above, if adapted not only to tolerate but to use osmotic gradients, might easily be able to more than quadruple this energy yield.

The direct coupling of water movement to phosphorylation reactions is not known for living systems on Earth. However, evolution could have favored the origin of membranes in which water movement yields energy, where osmotic gradients were readily available and other forms of energy were not. A plausible mechanism would involve tertiary structural changes in a channel-associated protein that catalyzes formation of high energy bonds, much as ligand-induced conformational changes in membrane receptors lead to a series of steps culminating in the synthesis of high-energy cyclic AMP (Schulze-Makuch and Irwin 2002a). As in the case of thermal gradients, degradation of the osmotic gradient is a potential drawback to their use for generating free energy. The influx of many water molecules would either significantly increase the cell volume, or increase counteracting pressure in rigid cells that cannot expand in volume. This could be mitigated, however, by a compensatory loss of solutes, such as efflux of Na^+ (and Cl^- for electrical balance) powered by the rise in intracellular pressure. Either the extrusion of solutes, or the pressure itself, could be coupled to conformational changes that could catalyze high energy bond formation. Alternatively, cell volume could be reduced by reverse osmosis upon movement of the organism to a more hypertonic level of the liquid medium. The zone close to the ocean bottom would be expected to be high in total dissolved solids due to persistent dissolution of the mantle and a higher density of salt water compared to fresh water. Solute gradients would be present both at the ocean bottom and in higher regions, but in opposite directions if not much water circulation is occurring. For example, a membrane water channel could be coupled to a reaction that forms a high-energy bond inside the cell as the water moves inward

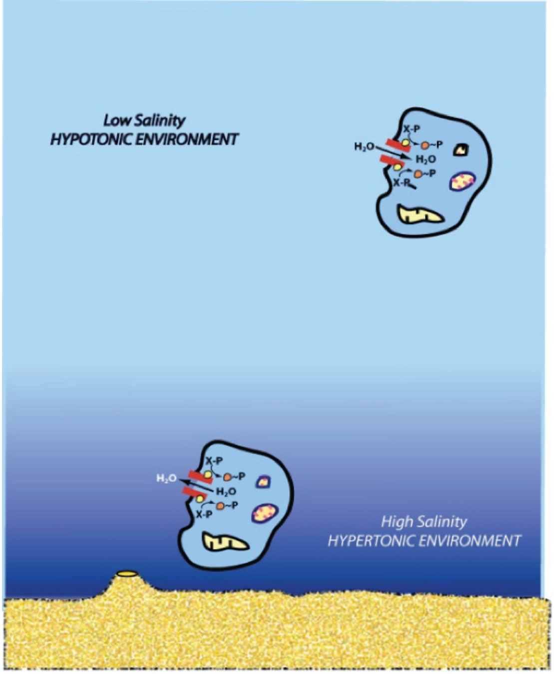


Fig. 5.4 A hypothetical osmotroph that harvests energy from osmotic gradients. Movement of water would be coupled to a reaction that forms a high-energy covalent bond through variants of a membrane molecular complex that are energized by the entrance or exit of water, depending on the direction of the osmotic gradient (P_i = inorganic phosphate, ATP formation is used as an example, not necessarily implying that ATP would be used by a hypothetical osmotroph. Redrawn from Schulze-Makuch and Irwin (2002a)

from hypotonic surroundings, while a similar channel oriented in the opposite direction could harvest energy when water leaves the cell in hypertonic surroundings. The hypothetical organism could thus move between two layers of different salinity, using both to harvest energy (Fig. 5.4).

Ionic gradients and H^+ gradients conceivably could also provide energy. For a 100-fold ionic gradient between the cytoplasm of an organism and its external environment – a differential observed in halobacteria on Earth (Brock 1979) – the amount of potential energy can be calculated from the Nernst equation

$$E = (RT/nF)\ln([\mathrm{ion}]_{\mathrm{ext}}/[\mathrm{ion}]_{\mathrm{int}}) \tag{5.10}$$

where n equals the number of charges transferred in the reaction, F the Faraday constant (J/mV mol) and R and T as above. The potential energy yield, $\Delta G = -nFE$, equals 0.12 eV, when $[\mathrm{ion}]_{\mathrm{ext}} = 100 \times [\mathrm{ion}]_{\mathrm{int}}$ at 298 K. This could drive the diffusion of about 3 ions, which could provide the energy for the phosphorylation of one ATP molecule. This might well be an underestimate of the potential energy yield since some bacteria achieve ionic distribution ratios as high as 10^6 across their membranes (Neidhardt et al. 1990).

Thus, the harvesting of osmotic or ionic gradients for bioenergetic purposes appears to be feasible in principle. Both types of gradients would often coexist, allowing for the possibility of reciprocal cycling between the two. On other planetary bodies where strong chemical concentration gradients are likely present, as in the putative liquid ocean on Europa (Kargel et al. 2000) and possibly other icy satellites, the use of osmotic or ionic gradients as bioenergetic sources must be considered a reasonable possibility, especially where other energy-yielding strategies may not be feasible. Irwin and Schulze-Makuch (2003) have modeled a putative multilevel ecosystem, based on the assumption of a hypertonic ocean bottom and a hypotonic ocean ceiling on Europa. Their calculations indicate that organisms the size of brine shrimp could be supported at a density of several hundred per cubic meter at the ocean bottom. While such an ecosystem is purely hypothetical at this point, their calculations point to the theoretical feasibility of an ecosystem in which the producer level is powered purely by osmotic or ionic gradients.

5.2.5 *Magnetic Fields*

Charge separation and extractable free energy can be generated from magnetic fields in theory. Magnetic fields can yield energy based on the Lorentz force, the movement of a charge within a magnetic field, or by induction from a periodically changing magnetic field. The Lorentz force can be expressed by

$$\mathrm{F_L = q\,(E + v \times B)} \tag{5.11}$$

where E is the electric field acting on the charge (Newton/Coulomb; N/C), v is the velocity (m/s) of the charge in the magnetic field, and B (T) is the magnetic field strength. The cross product $\mathrm{v \times B}$ is reduced to vB in the special case of a perpendicular movement of the charge with respect to the direction of the magnetic field B. If the movement of the charge occurs parallel to the direction of the magnetic field, the cross product is zero, and thus in the absence of an electric field no force acts on the charge q. A somewhat analogous directional dependence is observed for induction. In the absence of a magnetic field ($\mathrm{B=0}$), a charge is accelerated parallel to the electric field such that

$$\mathrm{F = q\,E} \tag{5.12}$$

with E being the magnitude of the electrical field (N/C).

5.2.5.1 Possible Biogenic Use of the Lorentz Force

The amount of energy that can be extracted via the Lorentz force depends on the strength of the magnetic field of the particular planetary body. The strength of

Earth's magnetic field at the surface is about 0.3 gauss, or 3×10^{-5} Tesla (T). There are planetary bodies that have a far larger magnetic field strength than Earth, such as Jupiter (4.3 gauss at the equator) and Saturn. Earth's magnetic field can be described in a first approximation as a magnetic dipole. Any charged particle moving in a conducting liquid at a direction perpendicular to the magnetic field line would experience the Lorentz force. Protons inside of organisms are charged and Earth's oceans consist of salt water, which is a conducting liquid. But would the Lorentz force be sufficiently strong to yield a significant amount of energy? Let us assume a hypothetical organism the size of an Earth microbe that is transported by the current of the convection cell at a rate of 1 m/s perpendicular to the magnetic field lines. Then the potential energy yield can be calculated from

$$\mathrm{W} = \mathrm{F_L}\ \mathrm{s} \tag{5.13}$$

where W is the energy yield (J or eV), $\mathrm{F_L}$ is the Lorentz force as given above, and s is the distance where charge separation can occur. If it is assumed that the total length of the microbe (10^{-6} m) can be used for charge separation, then the Lorentz force that can act on a unit charge (electron or proton, $q = 1.6 \times 10^{-19}$ C) is about 5×10^{-24} N. This charge separation can be imposed if the magnetic field is perpendicular to the line of movement of the charge and released if the magnetic field is oriented parallel to the movement of the charge. It follows that the energy obtained from the Lorentz force is 3×10^{-11} eV, 11 orders of magnitude lower than the energy that could be obtained by chemoautotrophy (assuming hydrogen-oxidizing metabolism) or photoautotrophy. However, there is no conceptual reason why charge separation of only one electron or proton can be harvested at one time; several or thousands of reactions could occur in parallel. Also, the available energy yield could be increased by many orders of magnitude, if the microbe is an analog to hair cells on Earth with lengths in the millimeter or centimeter range instead of being ball- or pancake-shaped in the micrometer range. A plausible energy-harvesting mechanism could be that H^+-ions are driven across a one-way channel against their concentration gradient into an internal organelle, where they accumulate to a higher concentration gradient than on the outside of the organelle. Then, the H^+-ions can diffuse back out of the organelle through a different channel coupled to a phosphorylation reaction that produces a high-energy organic phosphate (similar to how mitochondria work). A more elaborate scheme would be if the Lorentz force is used to separate one electron and one proton from the center of the cell in opposite directions toward the respective ends of the hair cell. When the magnetic field lines are oriented parallel to the hair cell, the energy could be released and the proton and electron would move toward each other producing H_2 (Fig. 5.5). The efficiency of both types of model organisms could be increased if its cells contain magnetite crystals that would orient themselves to the external magnetic field to optimize the harvest of magnetic energy (Schulze-Makuch and Irwin 2001).

In addition to the model organisms discussed, there is another interesting possibility: charge separation would not necessarily have to occur within the microbial cell. Organisms of microbial dimensions could be envisioned that would cling to

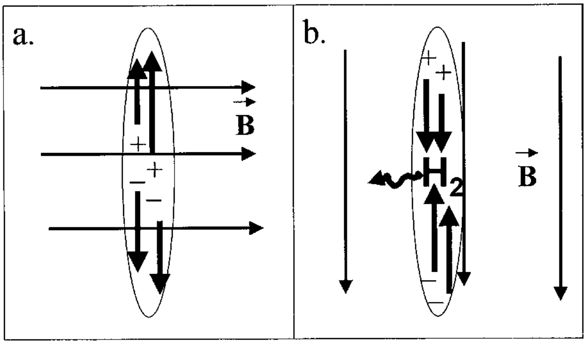


Fig. 5.5 Scheme for magnetotrophic organism to obtain energy, a. Lorentz force separates protons and electrons, b. magnetic field lines are oriented parallel to long axis of microbe and protons and electrons form molecular hydrogen

strips of inanimate conducting material and harvest energy from the magnetically induced electron flow in their substrates. That possibility would depend, in part, on whether a suitable mineral or aggregate of conducting matter would be present under the environmental conditions in question. Mineral assemblages including silicates, zeolites, albite, sphene, and illites, plus the iron minerals pyrite and hematite, have been identified at deep hydrothermal systems on Earth (Gonzalez-Partida et al. 2000) and could constitute suitable materials. Although not impossible, it would take a considerable effort to overcome a difference of 11 orders of magnitude in energy gain. Thus, it is not surprising that we don't encounter magnetotrophic life on Earth. However, sensitivity to magnetic fields, as in magnetotactic bacteria, is a well-established phenomenon (Blakemore 1982; Frankel et al. 1979), and there is strong evidence that some animals use magnetospheric orientation for navigation (Aekesson et al. 2001; Ioale et al. 2001). This implies the presence of cellular mechanisms for detecting magnetospheric energy. In the absence of more concentrated or effective sources of free energy, it seems plausible to assume that a cellular mechanism for transducing magnetospheric energy into a biologically useful form could evolve.

5.2.5.2 Possible Biogenic Use of Induction

The second physical option for harvesting energy from a magnetic field is by induction. The possibilities and problems associated with that option will be examined using Jupiter's moon Europa as an example (Schulze-Makuch and Irwin 2002a): It seems highly likely that Europa has a liquid subsurface ocean beneath its icy surface (Kivelson et al. 2000), which may be a suitable environment for microbial life. Jupiter's magnetospheric plasma corotates with Jupiter at a corotational velocity of 118 km/s at the orbit of Europa (Beatty and Chaikin 1990). Thus, Europa moves with respect to Jupiter's rotating field lines at a relative velocity of 102 km/s. However, the force exerted by this magnetic field cannot be used by an organism in the ocean. Europa's thick insulating layer of ice concentrates induced charges that produce an electric field that exactly cancels the Lorentz force. However, it was observed that Jupiter's magnetic field creates charge separation in a global conducting layer, which was interpreted as a shell of a salty ocean with a high electrical conductivity (Zimmer et al. 2000). Thus, the option remains that energy can be obtained from magnetic fields based on the induction from a periodically changing magnetic field (the Lorentz force, however, would still apply, as a charge can move perpendicular to the induced magnetic field, but it would be at a much lower magnitude). The alternating magnetic field that is experienced by Europa's ocean can be described as follows: Europa is subject to an oscillatory magnetic field

$$\mathrm{B} = \mathrm{B_o} \sin(\mathrm{w\,t}) \tag{5.14}$$

with an amplitude $\mathrm{B_o}$ of about 200 nT. Thus, the rate of change is

$$\mathrm{dB/dt} = \mathrm{w\,B_o} \cos(\mathrm{w\,t}) \tag{5.15}$$

with a maximum value of $2\pi\ \mathrm{B_o}/10\,\mathrm{hrs}$, which corresponds approximately to 2nT/min (Khurana et al. 1998). The work W performed on a charge q (e.g. an electron or proton) is then given by

$$\mathrm{W} = \mathrm{U_{ind}\,q} \tag{5.16}$$

where $\mathrm{U_{ind}} = \mathrm{A\ (dB/dt)}$ with A being the microbial cross-sectional area ($\mathrm{m^2}$), dB/dt the change of the magnetic field strength (T/s), W is work or energy (J), and q is a unit charge of 1.602×10^{-19} C per electron or proton.

Assuming a microbial diameter of 1 μm, and the above figure for a reasonable maximum temporal magnetic field change in Europa's ocean, the amount of energy per reaction that can be extracted via induction is about 4×10^{-42} J or 3×10^{-23} eV per electron, which is 23 orders of magnitude lower than the energy that can be harvested via chemosynthesis or photosynthesis on Earth. Even if many of those reactions would occur simultaneously, the energy gain is much too low. Thus, induction does not appear to be a feasible option for living systems to capture energy in Europa's ocean, and would only be very unlikely anywhere else.

5.2.5.3 Concluding Remarks on the Biogenic Use of Magnetic Energy

Life based on magnetic energy does not appear to be very promising in an Earth-type environment. However, magnetic field strengths much larger than on Earth would present certain possibilities. The gas giants Jupiter and Saturn have much larger magnetic field strengths, and neutron stars have magnetic field strengths millions of times stronger than the Sun or planets that surround a star like our Sun (Lattimer and Prakash 2004). Although life on gas giants or a neutron star itself would be very unlikely due to other considerations that are discussed in the following chapters, some moons that orbit the gas giants, and especially planets that orbit neutron stars, may provide an opportunity for organisms to harvest magnetic energy. For example, the neutron star SGR 1806-20, a magnetar, has been reported to have a magnetic field strength of about 10^{15} Gauss, or 10^9 T (Ibrahim et al. 2003). Energies from these huge fluctuating magnetic fields could become competitive for organisms on planets orbiting neutron stars, depending on the magnetic field strength of the particular star, distance of the planetary body from the neutron star, environmental conditions on the planet or moon, and the availability of suitable niches below the planetary surface for protection from radiation intensity, among other factors. Refined adaptive strategies by organisms that would have evolved in such an environment presumably would have increased the efficiency of magnetic energy to make it competitive with light and chemical energy, even under planetary conditions similar to our Solar System; but the strategies would have to be highly refined in a more efficient direction to make up for the generally low energy yield.

5.2.6 Gravitational Forces

Gravitational energy could be harvested in a direct fashion by the movement of protons or molecules through a gravitational field. The effects of gravity on a large scale are readily seen on Earth by the tidal amplitudes in the oceans caused by gravitational interactions between the Earth, Moon and Sun. Tidal flexing is more dramatic on Io, the volcanically most active planetary body in our Solar System, due to strong tidal interactions between Jupiter inside Io's orbit and the other three major moons beyond its orbit. But gravity is the weakest of the fundamental forces known in nature, and the free energy that it yields on a small scale is very slight. That value can be calculated by assuming a simple model in which a proton is moved a micrometer (assumed microbial diameter) against a defined gravitational attraction.

$$W = m_{H+} g\ h \tag{5.17}$$

On Earth, the energy would be about 10^{-13} eV and thus much smaller than the energy than can be harvested via chemotrophy and phototrophy. If large macromolecules ($\sim 10^6$ a.m.u.) instead of protons were moved, the energy yield could be as high as 10^{-7} eV. Even allowing for a planetary body the size of Jupiter, chemotrophy and phototrophy would still out-compete gravitational energy. Thus, gravitational forces seem unlikely as a useful direct basis for bioenergetics in our Solar System, because gravity is simply far too weak. However, the *indirect* effects of gravitational forces, such as convection currents in the oceans could be used to power living systems, as discussed before (see Sect. 5.2.3). It should also be pointed out that organisms are sensitive to gravity on Earth. Even single cell organisms can orient themselves in a gravitational field through the use of intracellular receptors located in the cell membrane (Bräucker et al. 2002).

5.2.7 *Tectonic Stress*

Meteorite impacts and fractures within a planetary crust release energy that could be used by organisms for obtaining energy. Meteorite impacts are common occurrences as can easily be observed on our Moon, Mercury and Mars. The meteorite's kinetic energy is converted upon impact into electrical potential, while the mechanical disruption of the impact causes the release of stress energy in the form of light, heat, electrical fields and magnetic fields (Borucki et al. 2002). While the impact only occurs in a short time period that can be measured in milliseconds, melted slurry pools under impact sites can persist for as much as a million years, depending on the size of the impact, as shown by Thompson and Sagan (1992) for Titan. Additional energy supplied from crustal stress to the subsurface regions after the impact could increase the lifetime of the melted impact zone and provide suitable conditions for microbial life. While the energy released from the immediate impact of the meteorite would dissipate relatively fast, energy provided by the piezoelectric effect could be provided for a very long time. Piezoelectric energy is a form of electricity generated when a pressure is applied to an ionic solid as a result of strain. A charge across the crystal is produced because a dipole moment is created by the deformation of the otherwise non-polar molecular structure. The polarization of the crystal faces parallel to the direction of strain converts the crystal into a capacitor, which temporarily stores an electrical charge. A good example for demonstrating this effect is a planar molecule of any ionic solid. Its structure has 3 electric dipoles at 120 degrees to each other, which cancel and give a net dipole moment equal to 0. Applying a pressure or a voltage to this molecule will result in deformation of the molecule, and the generation of a dipole moment as a result of this deformation. The piezoelectric effect will immediately cease if the pressure or current is removed from the structure of the crystal. Piezoelectric energy, although somewhat "exotic," could thus provide a possible avenue for life. It could be associated not only with meteorite impacts but also with other geological events such as plate tectonics on Earth. However, it is restricted to 20 of the 32 crystal classes, ionic crystalline solids that lack a center of inversion such as quartz, perovskite, sodium chlorate, and Rochelle salt. Similar to the other alternative energy sources, no indication of its energetic use by microbial organisms has been observed on Earth. It is doubtful whether this process can provide a sufficient or sufficiently constant amount of energy. At the very least, it does not appear to be competitive with chemical or light energy.

5.2.8 *Pressure Gradients*

Life based on energy harvested from a pressure gradient is another theoretical possibility. There are three principal opportunities. Energy could be harvested from atmospheric, fluid or subterranian pressure gradients.

Pressure gradients exist in the vertical column of any atmosphere held by gravity. However, the capacity of such a pressure gradient to be used as an autotrophic energy source is questionable. Atmospheric pressure is the sum of the forces of all the molecules striking a surface area, and thus a measure of the linear momentum of the gas molecules. A pressure gradient is established if the molecules do not move randomly, but in a preferred direction. It is difficult to see how a microbial organism suspended in the atmosphere could utilize the pressure gradient. The organism would just be carried along with the wind, unable to maintain a consistent orientation within the pressure gradient, which in any event would be miniscule over the linear dimensions of the organism. This does not exclude the atmosphere of planets and large moons as habitable environments, but other metabolic strategies such as chemoautotrophy or photoautotrophy would have to be employed, as suggested originally for the Jovian atmosphere (Sagan and Salpeter 1976) and more recently for the Venusian atmosphere (Grinspoon 1997; Schulze-Makuch and Irwin 2002b).

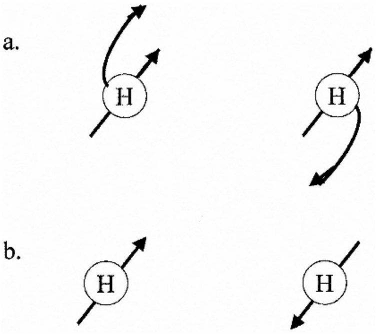
Large pressure gradients can also exist in fluids. For an organism suspended in the fluid, the same problem would be faced as that of an organism suspended in an atmosphere. If the organism were attached to a fixed substrate, it could at least maintain a consistent orientation within a localized pressure gradient. Such localized pressure gradients exist, for example, at hydrothermal vents on the ocean floor. However, the wide fluctuations in pressure likely arising at the vents would represent a practical problem. Furthermore, how an organism could stay attached to a substrate at these pressures and at the same time harvest the pressure gradient is unclear.

Tremendous pressures are present in the vertical rock column of a planetary body's lithosphere. Since microbial organisms are known on Earth to live at considerable subterranean depths, there is precedence for assuming that life on other worlds would occupy this habitat. Although the absolute pressure is high, the pressure gradient is not, especially with respect to microbial dimensions. Thus, life based on pressure gradients in the subsurface does not appear likely.

5.2.9 Spin Configurations

Atoms in molecules can revolve and rotate in various ways. For example, the two atoms of hydrogen gas, H_2, perform a vibrational motion in the direction of the line joining the nuclei, and a rotational motion around a direction perpendicular to the molecular axis in addition to the translational motion. The vibrational and rotational motions are in quantum states resulting in two different modifications of hydrogen, parahydrogen molecules that have antiparallel nuclear spins and even rotational quantum numbers, and orthohydrogen molecules that have parallel nuclear spins and odd rotational quantum numbers (Fig. 5.6). The two sets of molecules do not easily convert into each other but can be considered as two gases differing from each other in certain optical and thermal properties (Farkas 1935). The o-hydrogen is the higher energetic state but is relatively stable kinetically. For example, although at 20 K equilibrium hydrogen consists practically of pure parahydrogen, simply cooling the hydrogen to this temperature or transitory liquefaction or solidification does not cause equilibrium to be established.

Fig. 5.6 Motions of o-hydrogen and p-hydrogen, a. o-hydrogen atoms revolve around a common center, while their nuclei rotate around their own axis at the same time, b. In the simplest version of p-hydrogen the atoms do not revolve and the nuclei rotate in opposite directions. Modified from Feinberg and Shapiro (1980)



The two states of hydrogen could provide a source of energy in very cold environments with abundant hydrogen. For example, one could envision a mechanism to retrieve energy by having o-hydrogens on a cell boundary collide with o-hydrogen molecules in the environment. Both o-hydrogens would convert to p-hydrogen and a relative high energy yield of about 700 J/g would be obtained. P-hydrogens could then be converted back to o-hydrogens by allowing rotating p-hydrogens to collide with magnetic impurity molecules (such as oxygen), which would catalyze the formation of o-hydrogens. The potential of spin configurations as an energy source was first realized by Feinberg and Shapiro (1980), who suggested the possibility of life based on spin configurations on a very cold and dark planet, just a few 10s of degrees above absolute zero. Although energy based on spin configurations represents an intriguing idea, it is doubtful that at these low temperatures energy could be transferred into chemical energy usable to organisms at a high enough rate. Energy from spin configurations may rather present an interesting engineering opportunity and challenge to obtain energy for space probes on cold and dark planetary bodies.

5.2.10 Radioactivity

Radioactivity is one of the most basic processes in our universe. Radioactive nuclei of atoms decay with time and release particles and electromagnetic radiation. Forms of high-energy radiation include alpha (helium nuclei) and beta particles (electrons or positrons), gamma rays (short wavelength, high-energy photons), X-rays, neutrons, and heavy ions. This type of radiation is very destructive to life as we know it because it destroys biologically important molecules, especially the sensitive machinery for molecular replication. Biological effects depend on the spatial density of ionizations produced per unit absorbed dose in the irradiated tissue. For example, particles with high atomic numbers and high energy (HZE particles) cause the greatest damage for a given dose (Baumstark-Khan and Facius 2002). Nuclear processes are the ultimate source of energy for life on Earth, since the Sun emits photons as a byproduct of the fusion of hydrogen into helium at its core. And heating produced by radioactive decay in the Earth's core could serve as the energy source for possible thermoautotrophic organisms. The question remains, however, whether radioactivity can be tapped directly by living organisms. This may be too destructive for organic synthesis and reproduction. Due to the presence of many radioactive isotopes with short half-lives, radioactive material was much more common on the early Earth, when life originated or first became established. Yet, today high-energy radiation does not serve as an energy source for any form of life as far as we know. Gamma radiation and X-rays may have been too rich in energy and too difficult to control. Or, was the visible light of our Sun simply more accessible and easier to use? How about the alpha and beta particles? They possess ample amounts of kinetic energy over the short distance of cellular dimensions. From an energetic viewpoint they would be a preferential energy source. Yet, they are not used as far as we know either. Again, the basic problem may be control, as well as insufficient frequency, and inconsistency. Radiation and particle emissions occur in a random fashion from a decaying atom. The frequency, direction, and precise level of energy are all unpredictable. It is difficult to envision how any organism could control the decay in a way to obtain energy on a consistent basis. On Earth, organisms have developed mechanisms to avoid, tolerate, and repair damage caused by ionizing radiation. A prime example is *Deinococcus radiodurans*, which possesses a high redundancy of repair genes to cope with ionizing radiation and organic pigments to cope with UV radiation.

5.3 The Question of Entropy, Uniformity, and Origin

A qualitative and quantitative assessment of the various energy sources indicates the theoretical plausibility that several of them potentially could power living organisms on other worlds. From a purely energetic view, a thermotrophic organism appears to be most favored. Such an organism may have in fact developed on Earth, and may be the progenitor of the photoautotroph as suggested by Muller (1995). His proposed thermosynthesis scheme is certainly simpler than photosynthesis, and heat is a ubiquitous energy source. However, we do not observe the presence of thermotrophic life on Earth, even though it appears to be favored on the basis of theoretical energetic considerations. It may be present and yet undiscovered on Earth, but terran life definitely prefers chemical and light energy. What is the basic difference between thermal gradients on one hand, and chemical and light energy on the other hand that could account for this observation? Thermal energy has a high degree of entropy – it is highly disordered. Chemical and light energy are highly ordered forms of energy. According to the 2nd Law of Thermodynamics, the degree of disorder in a system as a whole has to increase spontaneously with time. Any form of life is highly ordered and complex, and living processes increase the order of the system further. In order to maintain the highly ordered state of a living system, some free energy has to be expended to increase the degree of disorder, because the overall entropy of the system and its environment has to increase. In terran organisms this increase in entropy is achieved by giving off heat and waste products, which are highly disordered. Thus, using a highly disordered energy source to begin with is very inefficient. Much less of the total amount of energy obtained from a more highly ordered source has to be converted into the disorder required to obey the 2nd Law of Thermodynamics. Clearly, then, entropy is a factor that needs to be considered when assessing whether alternative energy sources can be used to power an organism.

Another factor that needs to be considered is uniformity of intensity. An alternative energy source has to provide its energy in quanta suitable and manageable for the organism to use. High-energy particles as emitted from decaying atoms are inconsistent and unpredictable, for instance. It may be that living systems can evolve a capacity to harvest energy more easily when that energy comes in the specific and consistent quanta appropriate for the control of metabolic reactions in a reliable way.

One other factor that needs to be considered is the question of pre-biotic evolution. How difficult was it for the earliest organisms to develop a mechanism for harvesting a specific energy source? The molecular machinery that has survived in chemoautotrophs and photoautotrophs today is very complicated, hence highly unlikely to have been the earliest mechanism for energy extraction. At the origin of life, the mechanisms for harvesting energy must have been simpler, and quite possibly were dependent on sources other than those that are used today. Chemoautotrophy and photoautotrophy are now the dominant basis for life on Earth, presumably because of the abundance and efficiency of those sources of energy. However, there may have existed early bioenergetic mechanisms that possibly were outcompeted over evolutionary time by more efficient mechanisms.

5.4 Survey of Energy Sources in our Solar System

Energy sources are ubiquitous in our Solar System. Solar radiation providing light and thermal energy is one of the dominant energy sources for the interior terrestrial planets, and still significant for the Jovian and Saturnian systems. Heterogenous surface colorations such as on Venus and many of the icy outer satellites imply the presence of chemical energy. Geothermal energy is indicated by volcanism and a high-density interior that would imply radiogenic heating on planetary bodies such as Venus, Mars, Io, and Enceladus. Pressure is an energy source for planets with thick atmospheres such as the gas giants and Venus. Kinetic energy is a force on any planetary body with strong convection cells such as the gas giants, and possibly Europa. Tidal flexing is an energy source commonly found in the Solar System, for example at Io, Europa and Triton. Strong radiation and magnetic fields emanating from Jupiter and Saturn affect their satellites. Tectonic stress is definitely observable on Io, and osmotic gradients may be present on icy moons with a subsurface liquid ocean as proposed for Europa, Ganymede, and Titan. Observations indicating the presence of various energy sources on the major planetary bodies of our Solar System are listed in Table 5.1. This does not mean that the potentially available energy sources are actually used by putative organisms, but only that they are present based on our current knowledge. A discussion on the suitability of life on those planetary bodies based on energy sources plus other geoindicators is provided in Chap. 11.

Table 5.1 Energy sources in the Solar System that would be available in principle for other possible forms of life

Body	Observations	Energy source
Mercury	Thermal gradients pass through range for liquid water at slowly moving terminator. Possible water ice at poles. High density and electromagnetic field ⇒ metallic core	Solar radiation, Geothermal
Venus	Extensive resurfacing ⇒ geological activity and chemical recycling. Very dense atmosphere ⇒ pressure gradients	Solar radiation Geothermal, Chemical, Pressure
Moon	Extensive cratering ⇒ old surface. Evidence of past volcanism. High density ⇒ metallic core. Strong sunlight. Minor amount of frozen water at poles	Geothermal, Solar radiation
Mars	Daily to seasonal temperature fluctuations above melting point of water at some latitudes, volcanoes. High density and weak electromagnetic field ⇒ metallic core. Surface erosion by flowing water. Likely aquifer beneath permafrost	Solar radiation, Geothermal, Chemical?
Jupiter, Saturn, Uranus, Neptune	Gas giants with indistinct high-pressure atmosphere/liquid transitions, extensive turbulence. Strong magnetospheres and radiation output	Pressure, Convection, Magnetism, Radiation
Io	Volcanism, extensive resurfacing, large size, and density >3.5. Surface coloration ⇒ complex chemistry. Strong Jovian radiation. Weak intrinsic electromagnetic field	Geothermal, Tidal flexing, Chemical, Stress (tectonic), Magnetic
Europa	Extensive resurfacing, density > 3. Surface coloration ⇒ complex chemistry and chemical recycling. Water ice surface, liquid subsurface water. Strong Jovian radiation. Projected high salt contents in subsurface liquids	Geothermal, Tidal Flexing, Magnetic, Chemical, Convectional, Radiation Osmotic Gradients
Ganymede	Extensive resurfacing ⇒ geological activity, subsurface liquid water. Rippled surface, low density, weak magnetic field. Surface coloration ⇒ complex chemistry. Strong Jovian radiation	Geothermal, Tidal Flexing, Chemical, Radiation, Magnetic
Callisto	Low density⇒ mostly water-ice. Strong Jovian radiation. Extensive cratering, lack of magnetic field ⇒ little internal energy	Magnetic, Radiation
Enceladus	Very low density and high albedo ⇒ mostly water-ice. Strong Saturnian radiation. Heavily cratered but resurfaced in part, with evidence of ice geysers and volcanic activity ⇒ internal energy	Geothermal, Tidal flexing, Radiation, Magnetic, Convectional
Iapetus	Low density and moderate albedo ⇒ mostly water-ice. Dark leading edge ⇒ possible hydrocarbon chemistry. Heavily cratered: little internal energy	Chemical

Table 5.1 (continued)

Body	Observations	Energy source
Titan	Dense, colored atmosphere ⇒ complex chemistry. Density $\simeq$ 1.8 ⇒ organic liquids and water-ice, with solid core. Atmospheric protection from radiation	Chemical, Geothermal
Triton	Surface coloration ⇒ complex chemistry, unusual surface features ⇒ internal energy. Density $\simeq$ 2 ⇒ rocky core. Elliptical, retrograde orbit ⇒ tidal flexing and seasonal temperature fluctuations; volcanism. Possible subsurface ocean	Chemical, Geothermal, Tidal flexing, Stress (tectonic)
Pluto Charon	Density $\sim$2.1 ⇒ rock/ice mixture. Mix of light and dark features⇒ complex chemistry	Tidal Flexing, Chemical

5.5 Chapter Summary

We have used relatively straightforward evaluations and calculations to show that life does not need to be restricted to energy from chemical bonds and light as a basis for bioenergetics, as it apparently is on Earth. While light and chemistry do indeed represent cosmically abundant and efficient sources of energy, on many worlds other sources of energy may be more practical. Thermal, ionic, and osmotic gradients, as well as the kinetic energy of fluids in motion, appear to be the most promising alternatives to light and chemistry on worlds where the latter energy sources are available. But in specialized circumstances, other exotic forms of energy could be favored. Life evolving under those alternative conditions would be pressured by natural selection to make use of the forms of energy available. The numerous alternative options that are plausible within our own Solar System are shown in Table 5.1. Even though life on Earth may not use any energy source other than chemistry and light, the sensitivity of terran organisms to many other forms of energy provides a hint of other bioenergetic possibilities elsewhere in the universe.

Chapter 6
Building Blocks of Life

Life is based on complex chemistry yet only a few of all the available elements participate in most life-supporting reactions on Earth: carbon, nitrogen, oxygen, hydrogen, phosphorous, and sulfur. Of these, the most characteristic element of biological systems is carbon. In this chapter we will discuss why carbon is so favored by life on Earth and whether other elements could replace carbon in its dominant role on other worlds.

6.1 The Uniqueness of Carbon

Carbon is the universal building block for life as we know it. Its ability to form complex, stable molecules with itself and other elements, particularly hydrogen, oxygen, and nitrogen is unique. Organic chemistry involves millions of compounds. The simplest are the alkanes, with the general formula C_nH_{2n+2} (for $n = 1$, the compound is CH_4, or methane). Alkanes are converted to other compounds by replacing a hydrogen atom with other functional groups. The most important substitutions for biochemistry are -OH (alcohol), -CHO (aldehyde), -COO-R-(ester, R = alkyl group), -COOH (carboxylic acid), $-PO_4$ (organic phosphate), and $-NH_2$ (amine). An organic acid with both amino (NH_2) and carboxyl (COOH) groups is an amino acid, and polycondensation of amino acids leads to proteins, whose virtually infinite variety of shapes provide a vast repertoire of macromolecular complexity. Carbon atoms can also be arranged in a ring, as in cycloalkanes and aromatic hydrocarbons, rather than a chain. The basic structure of the aromatic hydrocarbons is the benzene ring, a resonant ring held together by π-bonding. This structure forms the basis for cholesterol and steroids, which are vital biochemical compounds for many cellular structures (such as membranes) and functions (such as hormone signaling). Rings are also formed by -O-bridges between carbon atoms (Fig. 6.1). The stability of these structures accounts for the fact that sugars occur naturally in this form.

The great variety of structures formed from carbon, from chains and rings to three-dimensional macromolecules, are mostly stable within a broad temperature range. The versatility of carbon is further enhanced by its ability to form double and triple bonds, which alters the chemistry and geometry of the molecule as well as its

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

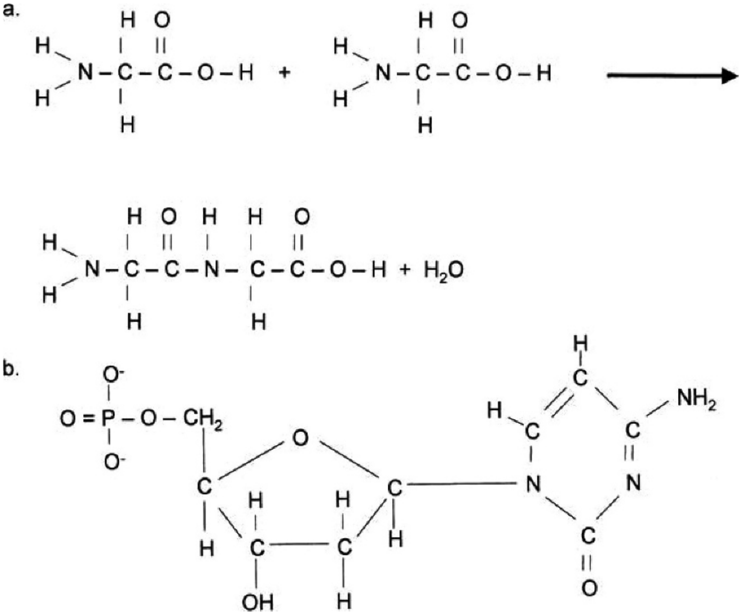


Fig. 6.1 Some selected important carbon molecules: (**a**) two glycine molecules (a simple amino acid) combine to form a peptide bond with the release of water as an important first step in the formation of proteins, (**b**) sugar (deoxyribose) – phosphate backbone and the base cytosine as one chain link of DNA (the next link of the chain would be the bonding of the upper oxygen of the phosphate group to the next sugar at the OH location)

temperature-dependent fluidity. This ability of carbon to build an almost unlimited range of molecules can be attributed to various factors: (1) the stability of carbon macromolecules due to a carbon-carbon bond energy that is higher than that of any other non-metal, and is comparable to the strengths of carbon-hydrogen and carbon-oxygen bonds; (2) carbon's mid-range value of electronegativity that promotes the formation of primarily covalent bonds; and (3) high activation energies for substitution and bond cleavage reactions due to the absence of lone pairs or empty valence orbitals, thus enhancing the stability of hydrocarbons and halocarbons to water and oxygen (Sharma et al. 2002).

Chirality is an important property of life-supporting carbon compounds. With several exceptions, only right-handed carbohydrates and left-handed amino acids are used in Earth's organisms. Enzymes, which regulate a variety of biological processes, have the ability to recognize the desired chirality of a substrate. This further enhances the versatility of carbon (though chirality is not limited to carbon compounds and occurs in most macromolecules).

The ability of carbon to form the backbone of long-chain polymers is central to its contribution to the chemical complexity of living systems. The hydrocarbons that make up the long chain and cyclic skeleton of lipids consist exclusively of covalent carbon-carbon bonds. The backbones of proteins are repeating units of two carbon

Table 6.1 Typical bond energies for carbon and silicon with some other elements, as enthalpy of bond formation (kJ/mol)

Atoms	with Silicon	with Carbon
Hydrogen	393	435
Oxygen	452	~ 360
Nitrogen	322	~ 305
Chloride	381	351
Carbon	360	368
Silicon	340	360

Note: Bond strengths are highly variable depending on which compounds are involved and on whether single, double or triple bonds formed. Data above indicate enthalpies of single bond formation, from Greenwood and Earnshaw (1984).

atoms followed by a nitrogen atom. These chains are made possible because of similar bond strengths between a carbon-carbon bond and a carbon-nitrogen bond (Table 6.1). The backbone of nucleic acids is formed by repeating units of three carbon atoms, one oxygen atom, one phosphorus atom and another oxygen atom (Fig. 6.1). The capacity for each of these backbones to exist in a myriad of sizes and shapes, and to be modified by the placement of a great variety of reactive functional side groups, while maintaining the stability of the skeletal framework, provides living systems with an almost endless repertoire of stable but variable and interchangeable molecular forms.

Energetically favorable redox-reactions are the basis for metabolism. Carbon can be converted fairly easily between its fully reduced state (methane, CH_4) with a valence of -4 and its fully oxidized state (carbon dioxide, CO_2) with a valence of $+4$, which makes it a favorable element for use in metabolism. It is a considerable advantage that both products are gases under a fairly broad temperature range including Earth environmental conditions (Table 6.2). These compounds are the end products of metabolic activity – carbon dioxide for aerobic respiration and methane for methanogenesis – and because they are gases they can be disposed of readily as metabolic end products. Furthermore, they continue to be available

Table 6.2 Some physical properties of the fully reduced and fully oxidized forms of carbon and silicon

Property	CH_4	CO_2	SiH_4	SiO_2
Molecular Weight	16.04	44.01	32.12	60.09
Melting Point (°C)	-182.5	-56.6^1	-185	1713^3
Boiling Point (°C)	-161.5	-75^2	-112	2950
Density (g/cm^3)	0.424 (at −164°C)	1.03 (at −20°C, 1.97 MPa)	0.68 (at −186°C)	2.65 (solid)

Note: 1. at pressures above 5.1 bar, 2. sublimation temperature at 1 bar, 3. SiO_2 as β-cristobalite. Data from Greenwood and Earnshaw (1984), Christen (1984), CRC (2001), and Air Liquide (2003).

Table 6.3 Some elemental abundances in the universe (as mass percent) and Earth. The elemental abundance of the Sun can be used as an approximate elemental abundance for the universe

Atom	Sun	Earth	Earth's crust	Earth's atmosph.	Ocean	Microbe
Hydrogen	91	< 0.1	0.14	< 0.001	11	63
Oxygen	0.08	50	46	21	86	26
Carbon	0.03	< 0.1	0.02	0.04	0.003	6.4
Nitrogen	0.010	< 0.1	0.002	78	5×10^{-5}	1.4
Silicon	0.003	14	28	< 0.001	2×10^{-4}	< 0.1
Sulfur	0.002	1.6	0.035	< 0.001	0.09	0.06
Phosphorus	3×10^{-5}	0.08	0.11	< 0.001	6×10^{-6}	0.12

Note: Data are from Goldsmith and Owen (2003) and CRC (2001).

for reactions. CO_2 dissolves easily in water and dissociates when exposed to short-wave UV radiation, and methane reacts with oxygenated compounds in the Earth's atmosphere.

Carbon appears to fit ideally with water as a solvent. Of the common elements, carbon has the strongest bond enthalpy to hydrogen and also forms a strong bond to oxygen (Table 6.1) – the constituents of water. Further, many biochemical reactions involve the dissociation or production of water, such as photosynthesis and the polycondensation of sugars, lipids, nucleic acids, and proteins. Carbon is also a relatively abundant element in the universe (Table 6.3), and thus no shortage of carbon as a universal building block of life should be expected in many types of planetary environments. Also, many complex carbon compounds have been found in the interstellar medium (Table 6.4) and meteorites, further strengthening the dominance of carbon as a building block for life. The Murchison meteorite contained an especially rich inventory of carbon compounds (Table 6.5) including adenine and guanine and their hydrolysis products, uracil, and ribitol and ribonic acids (the reduced and oxidized form of ribose), but not ribose itself (Cooper et al. 2001).

Table 6.4 Some complex carbon compounds detected in the interstellar medium and meteorites

Number of Atoms				
6	7	8	9	> 9
C_5H, HCH_2OH	CH_3C_2H	CH_3OCHO	$(CH_3)_2O$	$(CH_3)_2CO$
NH_2CHO, CH_3CN	CH_3CHO	CH_3C_3N	CH_3CH_2OH	HC_9N
CH_3NC, CH_3SH	HC_5N, C_6H	C_7H, H_2C_6	CH_3CH_2CN	$HC_{11}N$
H_2C_4, HCC_2HO,	CH_3NH_2		HC_7N	C_6H_6, C_{60}^{+}
C_5H, C_5N, C_5O	CH_2CHCN		CH_3C_4H, C_8H	PAHs,
	C_2H_4O		CH_3C_4N	glycene?

Note: Based on data from Chièze (1994), Goldsmith and Owen (2003), Ehrenfreund and Menten (2002), and http://www.spie.org/app/publications/magazines/oerarchive/july/jul97/ extrater.html. PAHs= Polycyclic Aromatic Hydrocarbons.

Table 6.5 Some complex carbon compounds detected in the Murchison Meteorite

Compounds detected at concentrations of			
> 1000 ppm	100-1000 ppm	10-100 ppm	1 –10 ppm.
Sulfonic acids	Carboxylic acids Polar hydrocarbons	Amino acids Dicarboxylic acids Hydroxy acids Amides Alcohols Aldehydes Ketones Aliphatic hydrocarbons Aromatic hydrocarbons	Phosphonic acids N-heterocycles Purines Pyrimidines Amines

Note: Data from Cronin (1988); ppm = parts per million

6.2 An Alien Carbon Biochemistry?

The ability of carbon to form the backbone of long-chain polymers is central to the chemical complexity of living systems on Earth. The carbon compounds that make up the long chain and cyclic skeleton of lipids consist exclusively of covalent carbon-carbon bonds. However, the make-up of the lipids is directly related to the solvent with which the lipids interact. Thus, a different make-up would be required for example in a non-polar solvent (Schulze-Makuch and Irwin 2006). The genetic code is also dependent on the solvent. For example, the solubility of DNA in water is beneficial to its stability (Westheimer 1987). However, even with water as solvent a variety of possibilities exist. Benner et al. (2004) pointed out the importance of phosphate linkages to molecular recognition in DNA and offered the following three hypotheses: (1) the repeating charges in the backbone force inter-strand interactions away from the backbone, causing the strands to contact at the edge of the heterocycles (without the polyanionic backbone, inter-strand contact could be anywhere (Steinbeck and Richert 1998), (2) the repeating monopoles in the backbone keep DNA strands from folding, and (3) the repeating backbone charges allow DNA to support Darwinian evolution by generating inexact copies, with the inexactness itself being replicable. The repeating element of RNA and DNA is a monopole (a charge) rather than a dipole. The backbone of DNA and RNA is formed from repeating units of three carbons, one oxygen, one phosphorus, and another oxygen. Benner et al. (2004) suggested that the polyanionic backbones dominate the physical properties of DNA, and that replacing a nucleobase by another would thus have only a second-order impact on the physical behavior of the molecule. Thus, different types of nucleotides could be expected in alien forms of life. Miller et al. (1981) and Reddy and Bruice (2003) even suggested that a polycationic backbone may work as well as a polyanionic backbone. Thus, the biochemistry of a genetic code in an alien organism may be quite different even though the same solvent (water) is used.

Proteins are essential to life on Earth. The backbones of proteins are repeating units of two carbon atoms and one nitrogen atom. These chains are made possible because of similar bond strengths between a carbon-carbon bond and a carbon-nitrogen bond (Table 6.1). Proteins are made up of amino acids connected by peptide bonds. Only 20 standard amino acids are used, but experiments with unnatural amino acids using the natural ribosome to incorporate them into proteins have expanded the amino acid repertoire of proteins (Bain et al. 1989; Hohsaka and Masahiko 2002; Noren et al. 1989). It is important to note that the functionality of proteins is based on their efficient catalytic properties, which is related to their folding capacity. The folding capacity requires dipolar repeating elements, so that the positive ends of one dipole can interact with the negative end of another dipole, inducing the tertiary structure of the protein. If that functionality is preserved, as found in polyamides, sulfonamides, or phosphoesters, there appears to be no reason why alternative sets of polypeptide chains and amino acids should be excluded from hypothetical proteins in putative alien forms of life (Benner et al. 2004).

6.3 Alternatives to Carbon as the Universal Building Block of Life

There has long been speculation about whether some other element could replace carbon as a universal building block for life (Reynolds 1906; Spencer 1940). Boron, nitrogen, silicon, phosphorus, and sulfur are other common non-metallic elements that are known to form heat-resistant polymers. Macromolecules are required to address the essential needs of living entities as we have defined them in terms of compartmentalization, energy, and information (see Chap. 2: Definition of Life). Therefore, a key feature of the functional structure of biochemistry is the presence of highly specific non-repetitive macromolecules and their smaller components or interaction mediators (Bains 2004). Polymeric chemistry and macromolecules will still be required for life, even if it is based on building blocks unknown to us (Schulze-Makuch and Grinspoon 2005).

As a possible alternative to carbon as a building block, we will first discuss silicon, which has many properties similar to carbon and probably is the most promising substitute for carbon. Then we will discuss briefly other elements that form polymers, which could alone or with other elements together form the backbone for polymeric molecules. It will be hard for any other element to match the complexity and versatility of carbon, but we have to keep in mind that (1) the research on polymeric chemistry is carried out overwhelmingly under Earth environmental conditions and many polymers that are stable below the freezing point or above the boiling point of water are unknown, and (2) life may not in principle require any particular element to be as dominant as carbon is in terran biochemistry. Chains composed of just one element may not be necessary; chains of alternating atoms constructed from two or more different elements may work just as well (e.g. sequential units of B-N or Si-O). Proteins and nucleic acids already provide examples of structures that incorporate other elements into their backbones, as described above. Furthermore, in some other variety of carbon-based life, many of the carbon atoms could be replaced by silicon. The C-Si bond has about the same strength as the C-C bond (Table 6.1). Pure carbon-based and pure silicon-based forms of life may merely be the limiting cases, with a variety of transitional alternatives in between (Firsoff 1963). Some work on proteins and nucleic acids, where C atoms are replaced by Si atoms but functionality is attained, seem to support that assertion (Chen et al. 2001; Furusawa 1994).

6.4 The Possibility of Silicon-Based Life

6.4.1 Physical Properties of Silicon

Silicon is the most obvious potential substitute for carbon. It is also a p-block element of group IV (Group 14), just below carbon in the periodic table. With four electrons in its outer shell, it has somewhat similar physical properties to carbon (Table 6.6). Silicon and carbon are both small elements with small atomic weights and small atomic numbers, with carbon being the smaller of the two. Both elements have very high melting and boiling points, with carbon having the higher of the two (Table 6.6). Both elements are in the mid-range of electronegativities, but again carbon is higher. Both are solids at standard temperatures and pressures (STP) (298 K, 10^5 Pa) and both are semi-metallic. They both form sp^3 hybrid orbitals with tetrahedral structures in many of their compounds.

Silicon has a larger radius and therefore forms relatively weak bonds with the light elements that are abundant in the universe (Tables 6.1 and 6.3). The electrons in carbon are closer to the nucleus, and thus form stronger bonds that can retain light elements much better. This increases carbon's chance of forming complex compounds. The Si-Si bond strength is lower than the C-C bond strength, thus carbon is much more likely to bond with itself than silicon. The smaller Si-Si bond energy is also reflected in silicon's lower energy of vaporization (Table 6.6). Silicon rarely forms any double or triple bonds, but double bonds and triple bonds are common and of great biological significance for carbon (Koerner and LeVay 2000). For example, amino acids, fatty acids, and nucleotides frequently have double bonds

Table 6.6 Physical properties of carbon and silicon

Physical properties	Carbon	Silicon
Molecular Weight	12.011	28.086
Melting Point (in °C at 1 bar)	∼ 3500	1414
Boiling Point (in °C at 1 bar)	∼ 3900	3265
Density (g/cm^3 at 20°C)	2.27[1]	2.34
Electronegativity	2.55	1.90
Single Bond Covalent Radius (pm)	77	118
Heat Capacity (J/g L at 25°C)	0.709	0.705
Enthalpy of Fusion (kJ/mol)	0.00[2]	50.6
Enthalpy of Vaporization (kJ/mol)	394[3]	383

Note: 1. measured as alpha-graphite, 2. defined as standard state, 3. enthalpy of combustion. Data from Greenwood and Earnshaw (1984), Christen (1984); and CRC (2001).

between carbon and oxygen. The fully oxidized form of silicon forms four single bonds with four oxygen atoms resulting in a relatively inert mineral. Carbon dioxide, the fully oxidized form of carbon, forms double bonds with two oxygen atoms, resulting in CO_2, a reactive gas. Double and triple bonds are also used by organisms to store varying amounts of energy.

The homogeneous bond length of silicon is 235 pm compared to 144 pm for carbon, due mostly to silicon's larger electron cloud, which provides a greater magnitude of shielding and results in weaker Si-Si bonds compared to C-C bonds (Linn 2001). The larger size of silicon results in larger bond angles than for carbon (Zeigler and Fearon 1989), which has a great effect on which compounds can bond with silicon. For example, silicon cannot duplicate carbon's π-bonding, which is necessary to stabilize the delocalized electrons in resonant ring structures like benzene (Linn 2001). Thus, there is no set of aromatic compounds for silicon as there is for carbon.

Due to silicon's strong bond enthalpy with oxygen, it will be oxidized if oxygen is present. The high abundance of silicates on many of the rocky planets is caused by the bonding of silicon with oxygen when the planets formed. When silicon is fully reduced, it forms silane, a compound analogous to methane in the carbon system. Silanes burn spontaneously when in contact with oxygen to form a silicate and molecular hydrogen. Silane decomposes in the presence of water vapor to SiO_2, which explains why no SiH_4 has been detected in the hydrogen-rich atmosphere of Jupiter (though H_2O, CH_4, NH_3, and PH_3 were detected) even though it has been detected in the interstellar medium (Goldsmith and Owen 2001). The much higher reactivity of silanes compared to the corresponding carbon compounds cannot be attributed only to lower bond strengths. Other factors include (1) the larger radius of silicon which is thought to facilitate attack by nucleophiles, (2) the great polarity of silicon bonds, and (3) the presence of low-lying d orbitals which permit the formation of 1:1 and 1:2 adducts (unbounded association of 2 or 3 molecules in which a molecule of one compound, is either wholly or partly locked within the crystal lattice of one or two molecules of the other compound), thereby lowering the activation energy of the reaction (Greenwood and Earnshaw 1984). The affinity of silicon to oxygen is so strong that if silicon is placed in water, it will form a silica shell, stripping the oxygen from the water (LeGrand 1998). Thus, water is not a compatible solvent for silicon-based compounds. Methane, ethane, or any compounds that contain methyl groups are more compatible solvents for a silicon-based system. Under surface conditions on Earth, the most stable silicon polymers are silicones, organic silicon polymers with a Si-O backbone. Silicon-silicon bonds are not stable under these conditions, but can be produced in the laboratory under conditions vastly different from those of the Earth's surface.

Silicon does occur with variable valences (4, 5, and 6), and forms stable covalent bonds with itself, carbon, germanium, nitrogen, phosphorus, oxygen, sulfur, halogens, and many metals (Muller et al. 1998; Walsh 1981). Some of the compounds that silicon can form include (1) stable tetra-, penta-, and hexa-coordinate compounds with N, C, and O bonds, with or without overall charge on the molecule (Bains 2004), (2) branched and unbranched chains, and ring systems such as cyclohexasilanes (Schulze-Makuch and Irwin 2006), (3) highly polarized systems where rapid, reversible chemistry occurs (Sharma and Pannell 1995), (4) cage systems such as silsesquioxanes that provide for complex core structures, which may be surrounded with other groups that are oriented precisely in space (Feher 2000; Harrison 1977) and may protect the core from degradation. Benner et al. (2004) pointed out that oligosilanes having up to 26 consecutive Si-Si bonds are known that can be (1) chiral, (2) support a variety of functionalized and non-functionalized side chains, (3) have alkyl side chains that are generally soluble in non-polar solvents, (4) carry carboxylic acid groups that are soluble in water, and (5) self-aggregate into amphiphilic structures in water, creating vesicles and micelles. Silanes cannot form a π-conjugated system, hence do not form aromatic compounds. However, silicon can form sigma conjugated polysilanes (Maxka et al. 1991) with electronic properties similar to those of the carbon containing π-conjugated system (Benner et al. 2004). When considering biochemical alternatives to carbon, the key is to look for functional rather than structural analogues. For example, Bains (2004) demonstrated this principle by elaborating on the possibility of photosynthesis in a silicon biochemistry. He pointed out that silicon's sp^2 structure is disfavored over carbon's sp^3 structure in its ability to delocalize charge over a large structure. However, sp^3 silicon can delocalize electrons via s-orbital overlap to a degree that carbon cannot, to the extent that polysilanes are semiconducting (Tokito and Okazaki 1998; West 2001). Electron delocalization could therefore occur readily in appropriate silicon compounds, and light-activated electronic effects (the basis of photosynthesis as observed on Earth) could also occur (Fujino 1987). Dahn et al. (1993) pointed out that layered silanes synthesized from calcium silicide of the general formula $(SiH)_n$ have a layered structure and are electroluminescent. A more thorough discussion of the polymeric chemistry of silicon and its possibilities for "exotic life" is provided in later sections of this chapter after we discuss the use of silicon by organisms on Earth.

6.4.2 Role of Silicon for Life on Earth

Silicon is not the basis for life on Earth, but it is still a very important component of living organisms. Without silicon, most of the plant and animal life on Earth would not exist as it does today. Plants use silicon as silica within the walls of the stems to provide rigidity so that the stem can remain erect, yet still remain flexible enough to not become brittle (Sangster and Parry 1981). Large amounts of silicon dioxide are used in the plant kingdom to form the rigid, defensive protrusions on plants. The silicon content of some plants such as the cucumber increases following fungal infection, and appears to exert a protective effect (Samuels and Glass 1991). Silicon, as silicic acid (0.1–0.6 mM), can be regarded as a plant nutrient (Birchall 1995; Epstein 1994). In the animal kingdom, silicic acid is a major constituent of the cells of the connective tissue where it is found in hair, nails, and the epidermis. Among vertebrates, silicon is essential for growth and bone development and for collagen and glycosaminoglycan synthesis (Carlisle 1981). When a bone is broken, high levels of silica are found around the break as it heals. The aorta, muscles, and tendons contain as much as 0.1% silicon, and the kidneys, heart, and liver contain about 0.05% silicon (Tacke and Wannagat 1979).

There is some evidence that silicon is an important nutrient for microbial life, and that it may even be used as a direct energy source for metabolism, or as a catalyst (Wainwright 1997). For example, Yoshino (1990) found that 100 µg/mL of silicon has a remarkable stimulatory effect on the growth of *Staphylococcus aureus*. Chakrabarty et al. (1988) and Das et al. (1992) showed that *Mycobacterium* and *Nocardia sp.* can grow in the absence of carbon, provided that silicon compounds are present. Similar observations were made by Tribe and Mabadje (1972) and Parkinson et al. (1989). They found that certain fungi grew in ultra-pure water only when silicon compounds were added. Wainwright et al. (1997) showed that silicic acid stimulates the growth of fungi, including *Penicillium* species, when growing in ultra-pure water as well as nutrient-rich media. A possible explanation for these observations was provided early in the twentieth century. Reynolds (1906) suggested that silicon takes the place of carbon in some types of microbial metabolisms, and Bastian (1914) suggested the existence of some form of silicon-based autotrophy, which, however, could not be confirmed. Lauwers and Heinen (1974) proposed that a silicon cycle operates in the environment involving microbial transformations between insoluble and soluble forms, which may in part be based on an earlier finding by Henderson and Duff (1965) that a wide range of bacteria and fungi can solubilize insoluble silicates by producing mineral and organic acids, and chelating agents.

One of the best examples of silicon use by a carbon-based form of life is the presence of silicates in the diatom (Fig. 6.2). Diatoms may account for as much as one-fourth of the world's entire net primary production of biomass, and serve as the basis for marine food webs. Although diatoms have a carbon-based energy metabolism, their shells are composed of silicon dioxide, and diatoms are absolutely dependent upon silicon for growth and development (Lewin 1954; Richter 1906). Diatoms require silicon in the form of $Si(OH)_4$ for their metabolism. Werner (1967) concluded that silicon affects (1) the citric acid cycle between acetyl-CoA and alpha-ketoglutarate, (2) the synthesis of special proteins, (3) the regulation of respiration, and (4) chlorophyll synthesis. Another example of the essential nature of silicon for diatoms is provided from an experiment conducted by Darley and Volcani (1969) in which DNA replication was stopped prior to mitosis by maintaining the newly divided cells of the diatom in a $Si(OH)_4$-free medium. The presence of silicon in the organelles of diatoms may indicate the possibility that it participates in the biochemistry of subcellular structures (e.g. Azam 1974; Mehard et al. 1974).

Silaffins, a type of unique peptide, and long-chained polyamines are constituents of the biosilica of diatoms and can precipitate silica nanospheres (Kröger et al. 2002). The formation of the biosilica occurs within a membrane-bound compartment (silica deposition vehicle), which acts as a casting mold (Pickett-Heaps et al. 1990).

Thus, carbon compounds do interact with silicon compounds in diatoms to build a distinct organism. In diatoms the carbon compounds appear to act as a template for

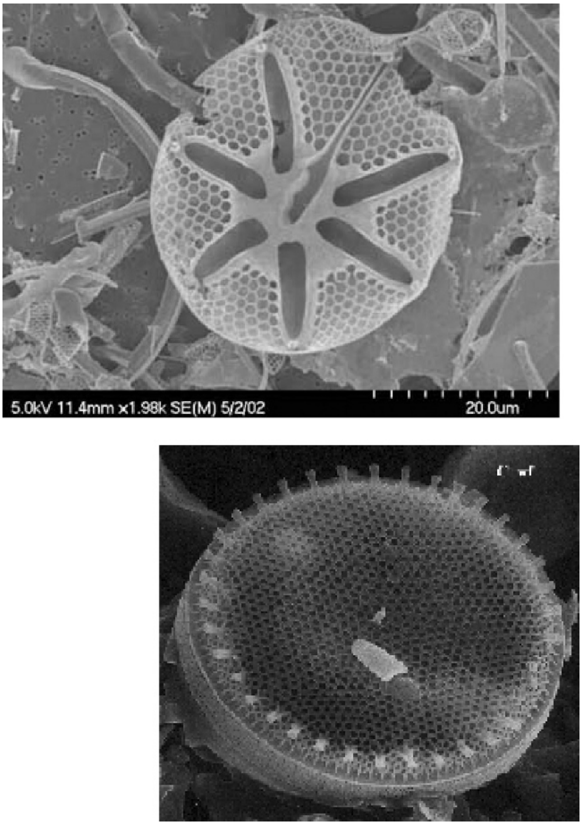


Fig. 6.2 Image of diatom *Asteromphalus hyalinus* provided by Tawnya Peterson, University of British Columbia (*top*), image of unknown diatom provided by Daniel Scheirer, Northeastern University (*bottom*)

silicon structures. Cairns-Smith (1982, 1985) and Cairns-Smith and Hartman (1986) suggested that silicon compounds may have provided the first templates for carbon-based life, noting that the first carbon compounds may have received their initial handedness from clays or silicate minerals that also had handedness. For example, alpha-quartz, the thermodynamically most stable form of SiO_2 at Earth's surface conditions, forms tetrahedra that are interlinked to helical chains. Due to two slightly different Si-O distances of 159.7 pm and 161.7 pm and a Si-O-Si angle of 144°, the helices in any one crystal can be either right-handed or left-handed. A close association between minerals and the first forms of life is consistent with a variety of mineral characteristics (e.g. Table 2.1). Dessey (1998) suggested that silicon started the evolutionary process for carbon-based life on Earth. This is not impossible as conditions on Earth were quite different early in its history from today. Silicon could have played a vital role in the origin of life on Earth in its pre-biotic stage, but if so, its role was replaced by carbon relatively quickly as conditions became less harsh and more carbon friendly. If indeed silicon compounds were involved in molecular replication, this assembly alone must still have been far from the phenomenon that we call life, since this process meets only one of the characteristics of life as stated in Chap. 2.

6.4.3 Polymeric Chemistry of Silicon

Silicon hydrides or silanes have the generic chemical composition Si_nH_{2n+2} and occur both as branched and unbranched chains. They form direct analogs to hydrocarbons in the carbon-based world (Fig. 6.3). For example, a ring of six silicon atoms is called a cyclohexasilane, which has a direct analogy to a ring of six carbon atoms (Zeigler and Fearon 1989). However, because the silicon atom is larger than the carbon, it cannot duplicate carbon's π-bonding, which is essential for stabilizing the electron cloud in C_6H_6 and sustaining the benzene resonant ring structure. Thus, silanes do not form benzene analogs (siloxene has a ring of six silicon atoms but some of the Si-Si bonds are reinforced with oxygen bridges (Firsoff 1963), and thus are not an aromatic series analog). Because the bond energy between hydrogen and silicon is relatively weak compared to the bond energy to oxygen, silanes are much more reactive than their corresponding carbon compounds, and are readily oxidized into silicates in the presence of oxygen. The thermal stability of silanes decreases with increasing chain length. However, if hydrogen is replaced by organic groups, stable compounds are obtained. For example, polysilanes with molecular weights of above 10^6 have been synthesized (Sharma and Pannell 1995). Traces of alkali metals catalyze the hydrolysis of silanes, which is rapid and complete, to yield silicates and hydrogen molecules (Greenwood and Earnshaw 1984). Polysilanes are not stable at the temperature and pressure conditions of Earth's surface (with the exception of silane), but are fairly stable at low temperatures, especially at higher pressures.

Replacing the hydrogen in silane with organic groups produces an analogue to hydrocarbons that eventually leads to silicon polymers, possibly resembling a reaction pathway to very complex silicon compounds. Organosilicon compounds (silicones) have considerable thermal stability (many up to about 400°C) and chemical inertness reflecting the strength of both the Si-O bond and the Si-C bond (comparable in strength to the C-C bond) in the polymer backbone. Silicone polymers are relatively stable to oxidation, repel water, have good dielectric properties, and show a prolonged resistance to ultraviolet radiation (Greenwood and Earnshaw 1984). Hydroorganosilanes, organic compounds with silicon and hydrogen, have bonds that are thermodynamically more stable than other silanes, but become unstable

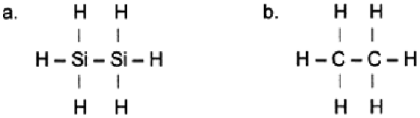


Fig. 6.3 Structural analogy between (**a**) disilane and (**b**) ethane

at temperatures over 25°C. The organosilicon reactions, for the most part, form directly without radical formation, while carbon tends to form radicals in the intermediate stages. Organosilicon compounds also more readily undergo nucleophilic substitutions when compared with their carbon equivalents. Yet, even with silicon's ability to produce complex molecules and carbon analogs, to more readily undergo reactions without the formation of radicals, and to take more direct routes in the formation of organic compounds, silicon accounts for less than one percent of all known organic compounds. Furthermore, the organic compounds of silicon that are known have all been produced in the laboratory but have not been found in nature (Pawlenko 1986). And while a very large number of compounds have been synthesized that involve multiply bonded silicon (DeLeeuw et al. 1992; Sekiguchi et al. 2004; Stone and West 1994; West 1986, 1987), stable compounds containing double or triple silicon bonds are difficult to form because of the larger atomic size and bond angles required (Zeigler and Fearon 1989). Silicon forms stronger bonds to nitrogen and the halogens than carbon does, but forms weaker bonds to hydrogen, phosphorous, and sulfur. The strong Si-O bond can be avoided and the carbon scenario reproduced if oxygen is replaced by sulfur. Then the resulting ratio of bonding energies of Si-Si to Si-S is comparable to the ratio of the C-C to C-O bonding energies (Firsoff 1963). Also, silicon polymers have been obtained with nitrogen instead of oxygen, where nitrogen acts as an electron donor. In hydrogen-poor environments, hydrogen is often replaced by a halogen such as chloride, and long linear chains of silicon and chloride are formed. Large labile molecules based on a Si-O-Si or Si-NH-Si backbone, with halogens as side-groups, could provide a basis for complex chemical systems.

Due to the strength of the Si-O bond, silicon forms a silicon tetrahedron in the presence of oxygen with the silicon in the center and a single bond to each of the four oxygens (Fig. 6.4). The tetrahedra can combine into chains, double-chains,

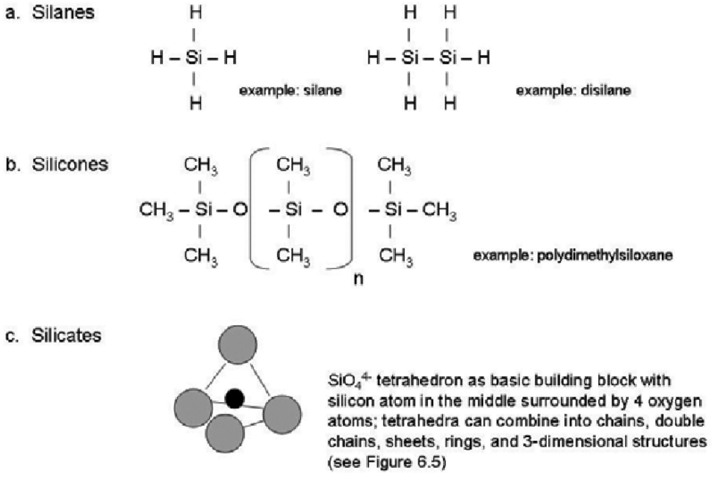


Fig. 6.4 Structure of (**a**) silanes, (**b**) silicones and (**c**) silicates

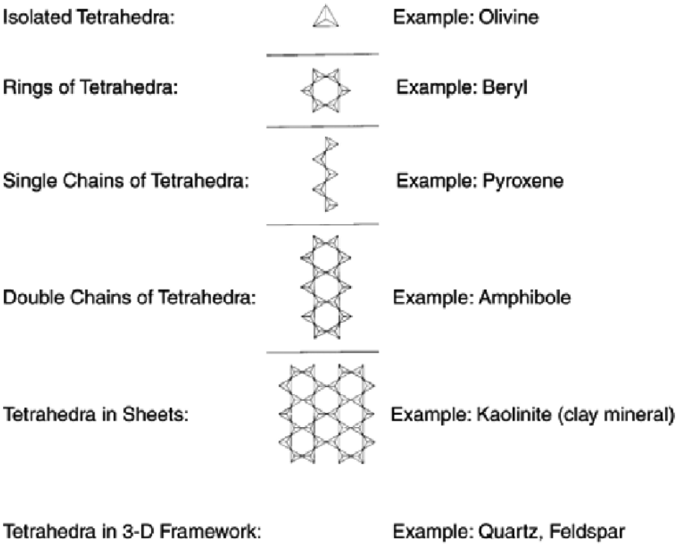


Fig. 6.5 Some silicate structures

rings, sheets and three-dimensional structures depending on the mineral formed. Neso-silicates consist of discrete SiO_4 tetrahedrons, sorosilicates of discrete Si_2O_7 units with one oxygen atom shared, cyclo-silicates of closed ring structures with two oxygen atoms shared, ino-silicates of continuous chains or ribbons with two oxygen atoms shared, phyllo-silicates of continuous sheets with three oxygen atoms shared, and tecto-silicates consist of continuous three-dimensional frameworks with all four oxygen atoms shared (Fig. 6.5). All silicates have in common high melting points (e.g. SiO_2 (β-cristobalite) at 1713°C) and are therefore a major constituent of Earth's crust. Aluminum can substitute for silicon in the silicate network. At the surface conditions of Earth silicon dioxide is a tough, unreactive polymer (Koerner and LeVay 2000). However, at temperatures above 1000°C complex silicate structures become more labile, partially melt and react with each other.

6.4.4 Environmental Conditions for the Possibility of Silicon-Based Life

Based on the previous discussion, the prospect of silicon-based life under any conditions resembling those on Earth does not appear encouraging. Carbon can form a vast variety of complex compounds, not only from organic molecules on Earth, but also from material found in the heads of comets, inside meteorites, within the nebulae, and among the interstellar matter of the universe (Fegley-Jr. 1987; Gladstone et al. 1993; Hanon et al. 1996; Llorca 1998; Varela and Metrich 2000). While polymeric carbon compounds seem to be ubiquitous, polymeric silicon compounds do not. Silicon, on the other hand, is found overwhelmingly as silicates making up the structure of the shell of the rocky planets, meteorites, and moons within our Solar System. A very dense polymorph of silica has been discovered in the Martian meteorite Shergotty (Sharp et al. 1999), but this polymorph could not support life and still raises the question of what compounds silicon can and cannot form when subjected to conditions other than the constraints of Earth's surface. More recently though, Bains (2004) noted that in the protostellar disc W33A 1/250 to 1/40 of all infrared-visible silicon atoms seem to have a hydrogen directly bonded to them. Thus, there is a need to discuss the chemical pathways of possible silicon-based life and the environmental conditions that could make it possible. Our approach is to distinguish between silanes, silicones, and silicates on the basis of the different environmental conditions at which these polymers are reactive. We start with silanes, because they present the closest analog to hydrocarbons, which are so important to life processes as we know them on Earth.

6.4.4.1 Life Based on Silane?

Silicon forms a series of hydrides, the silanes, consisting of Si-H and Si-Si single bonds (Fig. 6.4a). If silanes could be a basis for life as hydrocarbons are for carbon-based life, it would not be under the conditions found on present-day Earth, where silanes turn instantly into a silicate rock. A list of conditions can be derived that would have to be met as a minimum to make silane-based life a possibility (Table 6.7).

First, the atmosphere has to be reducing, with only minor amounts of oxygen available to avoid turning the silane polymers into silicate rocks. This kind of environment could exist if most of the original oxygen of a planetary body has been removed, for example by the precipitation of iron as iron oxides (as on early Earth). Oxygen could have also been lost to space due to fractionation during the early history of the formation of a planetary body and its atmosphere. Oxygen has a relatively high molecular weight of 32, but it dissociates to an atomic state in the outer atmosphere where the escape occurs. However, if the oxygen had escaped, then the much lighter hydrogen would also be expected to be severely depleted unless there was a specific mechanism to retain it. An oxygen-free atmosphere would allow the retention of free silicon instead of the formation of silicates.

Second, water is another compound that has to be scarce for silane-based life to form, because silicon is easily oxidized by water. Alkali-metals would likely be

Table 6.7 List of minimum conditions for silane-based life

1. Little or no atmospheric or lithospheric oxygen
2. Little or no water in liquid form
3. Low temperatures (at least below 0°C) and/or high pressures
4. Solvent suitable for silane-based complex chemistry
5. Restricted abundance of carbon

in solution catalyzing silane polymers into silicon dioxide and hydrogen gas. As for condition 1 (Table 6.7), the atmosphere would have had to undergo an extreme fractionation process to shed all lighter atmospheric gases with a molecular weight of up to 18 at least (H_2O =18g/mol), or alternatively temperatures on the planetary body would have to be much below the freezing point of water to immobilize nearly all the water in the frozen state.

Third, temperatures far below the freezing point of water would be needed to make the silane-reactions that are so volatile at surface conditions on Earth controllable and accessible for life processes. A high-pressure environment would slow the silane-reactions as well, and thus have a complementary effect.

Fourth, and very importantly, a suitable solvent would be essential to foster the chemical reactions essential for life. Methane would be a good solvent for a silane-based system, and would have the additional advantage that it stays liquid at fairly low temperatures. However, methane has a relatively low molecular weight (16g/mol) and would be degassed if the atmospheric depletion of oxygen and possibly water is required (conditions 1 and 2; Table 6.7). Thus, in such an environment, heavier methyl-compounds such as methyl alcohol remain about the only alternative solvents.

Fifth, the availability of carbon should be restricted, because carbon may be able to outcompete silicon for building complex macromolecules due to its greater chemical versatility. Other opinions on this issue have been offered, however. For example, Feinberg and Shapiro (1980) argued that the great versatility of carbon could also be considered a disadvantage because life-supporting molecules would have a very difficult time finding each other during the origin-of-life phase. Either way, some carbon may be an asset to silane-based life due to the possible formation of silicon-carbon bonds, but too much carbon appears to be a disadvantage.

The conditions imposed on the availability of silane polymers that could lead to a living system thus are very restrictive: a non-oxidizing, nonhydrous, extremely cold, high-pressure world where carbon is not abundant. While some of these restrictions are mutually compatible and commonly found in the universe, in their totality they are rarely found in our Solar System and are not likely to be common elsewhere in the universe. The Saturnian moon Titan comes closest in our Solar System to meeting all the criteria, except for a low abundance of carbon, where the opposite is true. Still, there is some chance that under the extremely cold, reducing conditions on Titan, carbon would lose its competitive advantage over silicon. Processes and environments suggested by Bains (2004) for the creation of silanes include (1) serpentization reactions in a cryogenic environment, (2) meteorite impacts on cold planetary bodies, and (3) ice/silicate grains exposed to UV radiation and 1 MeV protons in a hydrogen atmosphere.

The conclusion that silane-based life, if it exists, is not common in the universe is based on chemical reasoning, but is also supported by observational evidence. The apparent lack of silane polymers and the abundance of carbon polymers in meteorites would suggest that carbon-based life is much more probable than silicon-based life (Tables 6.4 and 6.5). There are significant variations in chemical abundances in our galaxy and the universe (e.g. In regard to metallicity), but no evidence seems to suggest that our Solar System is extraordinary. However, the possibility that life could exist in very exotic planetary environments based or partially based on silane-chemistry, as discussed above for Titan, should not be overlooked. The general failure to detect large amounts of silanes in space (the exception being the protostellar disc W33A), may just mean that silanes are very rapidly oxidized to silicates under the conditions of interstellar space.

6.4.4.2 Life Based on Silicone?

A silicone is an organo-silicon polymer with a silicon-oxygen framework. Its simplest fundamental unit is $(R_2SiO)_n$ (Fig. 6.4b). Carbon atoms can be included in the chain. Silicones are thermally stable at much higher temperatures than silane, even at temperatures where hydrocarbons are not stable. Silicones are also resistant to oxidation and prolonged exposure to UV radiation, thus are durable polymers under Earth's surface conditions and at higher temperatures. However, they repel water and would need a solvent such as methane or a methyl-compound to exhibit polymer activity. There is no suitable solvent for silicone in appreciable amounts on Earth, thus carbon with its excellent solvent partner – water – undoubtedly had the edge for the evolution of life on Earth. This holds true even though silicon and oxygen are the most common compounds in the Earth's crust (Table 6.3). The fact that silicone-based life did not develop on Earth – or was outcompeted very early in the origin-of-life phase – dims the prospects for silicone-based life elsewhere. However, the main problem for silicone-based life on Earth may have been the abundance of water and the lack of a suitable solvent in appreciable quantities. An Earth-type world with methane as a major solvent is certainly imaginable, but whether this scenario would result in a silicone-based life form is very uncertain. Other planetary conditions that would make silicone-based life more likely are high pressures, higher temperature (50 – 400°C), higher abundances of silicon than carbon, and a reducing atmosphere. A niche could exist at the temperature range of 200 – 400°C, because carbon-based macromolecules generally disintegrate at about 200°C and would not be competitive. But a solvent that would be liquid at that temperature is difficult to envision. Complex chemistry in a semi-molten state that would resemble life is conceivable, but the structural stability required for the low entropy requirements of a living system under such conditions seems improbable. Thus, the chemical properties of silicones render a silicone-based evolutionary pathway to biology unlikely.

6.4.4.3 Life Based on Silicate?

Silicates are salts containing anions of silicon and oxygen with the silicon-oxygen tetrahedron being the basic building block (Fig. 6.4c). At the surface conditions of Earth, silicates are inert, very slowly reactive polymers; but some silicates melt at temperatures beyond 500°C, and most melt above 1000°C where they become reactive. Feinberg and Shapiro (1980) suggested the existence of lavobes, organisms that could exist in lava flows, and magmobes, organisms that could exploit thermal gradients or chemical energy sources within the molten rock. These organisms could make use of the chemical complexity of silicate rocks in which aluminum could replace silicon in the tetrahedrons and cation exchange reactions could occur in interlayer sites between the tetrahedral and octahedral sheets. For this to occur, silicates would have to be in the form of sheets, such as the clay minerals smectite and montmorillonite. Information could be represented as irregularities in the crystal lattice of minerals. A particularly intriguing example is the clay mineral amesite, which has a helical structure. Information could be encoded by substitution of silicon with aluminum (Fig. 2.1).

It would be difficult to imagine how life could sustain itself at such high temperatures. Reactions at 1000°C or above happen so fast that it would be difficult for an organism to control them. However, some silicates start to partially melt at much lower temperatures, such as zeolites. Recently, organic-inorganic hybrid zeolite materials have been synthesized where siloxane bonds (Si-O-Si) have been replaced with methylene frameworks ($Si\text{-}CH_2\text{-}Si$) (Yamamoto et al. 2003). Zeolite minerals could provide a suitable silicate membrane, because they have been shown to act as semi-permeable membranes comparable to cell membranes, preferentially filtering some molecules but not others (Falconer and Noble 2002). Thus, they possibly would be able to maintain disequilibrium conditions that are so crucial for life. They also may provide a durable enough membrane that would be needed as a boundary between the interior of the organism and the outside environment. Herron (1989) suggested that zeolites may also be used by silicon-based life as enzyme mimics. Still, the problem of a suitable solvent at these temperatures, as discussed for silicone, remains.

All inner planets of our Solar System have magmatic activity in their interiors, as do some of the moons of the gas giant planets. For example, Io is the planetary body with the most volcanic activity in our Solar System (Matson and Blaney 1999). All these bodies could present favorable environments for silicate-based organisms. However, given the environmental conditions of Earth's crust and its composition (46% oxygen, 28% silicon) with abundant silicate melts, Earth should be more favorable than most other planets and moons in our Solar System for such a form of life. Yet no fossilized remnants or structures consistent with such an organism have been found, even though outcrops of igneous and volcanic rocks are abundant. Thus, the existence of such organisms seems very unlikely.

6.5 Other Alternatives as Building Blocks of Life

A few other potential substitutes for carbon deserve consideration as candidates for polymer-based complex chemistry. In order to be a viable alternative to carbon, the element should be a non-metal and be able to form at least the alkane-equivalent to the hydrocarbons. The possible choices are boron from group III of the periodic table, nitrogen and phosphorous from group V, sulfur from group VI, and possibly germanium from group IV (in addition to silicon).

Boron, like carbon and silicon, has a marked propensity to form covalent, molecular compounds, but it has one less valence electron than the number of valence orbitals. Thus, it has somewhat different chemical properties from carbon (Greenwood and Earnshaw 1984). Boron forms many different structural varieties of hydrides, but the boron atoms are linked indirectly through hydrogen bridges and are therefore not direct analogs to hydrocarbons. Boron has a high affinity for ammonia rather than water. It forms bonds with nitrogen that resemble the carbon-carbon bond. Two electrons of the nitrogen are donated in addition to the covalent electron sharing (Fig. 6.6). Boron-nitrogen compounds reproduce the physical and chemical properties of alkanes and aromatic hydrocarbons to a great extent, but with higher melting and boiling points. Borazole especially bears a strong resemblance to ordinary benzene in both physical and chemical properties (Firsoff 1963; Fig. 6.6). Borazole and its derivatives have a higher reactivity than the corresponding benzene group and thus would fit with the lower temperature range at which ammonia is a liquid solvent. Reactions at this lower temperature range would be at a more controllable pace. Also, boron has an affinity for nitrogen and ammonia as solvents that would fit into a low-temperature biological scheme. Many B-N compounds, furthermore, exhibit high thermal stability. However, boron is an element of low abundance, with an average of about 10 ppm in Earth's continental crust (CRC 2001), thus a biological scheme based on boron without a strong fractionation mechanism appears unlikely.

Nitrogen can form long chains at low temperatures with a liquid solvent such as ammonia or HCN. However, the major drawback of nitrogen as a backbone for large molecular structures is that the energy of the triple bond in N_2 is much greater than that of the single bond, thus nitrogen-nitrogen bonds tend to revert back to elemental nitrogen. However, nitrogen can form longer molecular structures with boron as described above as well as with carbon, phosphorous, and sulfur. Nitrogen can also form hydrides for which hydrazine is an example. Phosphorus forms hydrides and has some merit as a potential building block with phosphine (PH_3) as compatible solvent. Sulfur forms hydrides as well, and could be of organic importance in a sulfur-rich environment with liquid solvents such as H_2S or H_2SO_4. Sulfur compounds with sulfur chains are known. However, given the poor variety of phosphorus and sulfur hydrides and the restricted environmental conditions, it is hard to imagine that either one of those elements would be a major building block

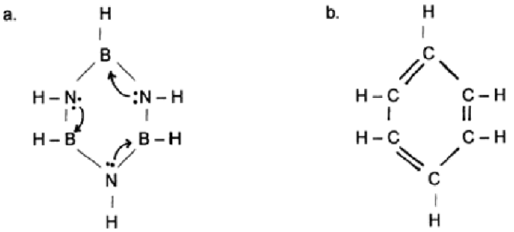


Fig. 6.6 Structure of (**a**) borazole and (**b**) benzene. The benzene ring is held together by π-bonding

of life. At best, they could form chains together with other elements such as carbon, silicon, or nitrogen. Sulfur, however, is unique in another way. It has more oxidation states than carbon, including fractional nominal states (e.g., +7, +5,+4, +3.33, +2.5, +2, −0.4, −0.5, −0.67, −1; Amend 2001), and thus can form a huge variety of different compounds. Germanium is not a suitable backbone element due to its large size, metallic character, and low abundance.

6.6 Chapter Summary

Carbon exhibits many characteristics that make it uniquely suited for life-supporting processes. Its usefulness for life derives primarily from (1) the versatility that enables it to form millions of complex polymers, including single-, double- and triple-bonded compounds, chiral compounds, and resonant ring structures, (2) the ease with which it changes from one valence state to another, thereby suiting it well for energy-transferring redox reactions, and (3) its compatibility with water (and ammonia) as a liquid solvent. The only other element that approaches the versatility of carbon and is common enough to be a universal building block is silicon. Silicon can form long chains as silanes, silicones, and silicates. Some of these compounds could present a possible alternative to carbon for the construction of polymers under very restricted environmental conditions. These are (1) little or no oxygen, (2) little or no liquid water, (3) temperatures above 493 K (silicones, silicates) or below 273 K (silanes), (4) pressures greater than on the surface of Earth, (5) presence of a solvent such as methane or methanol, and (6) relative lack of available carbon. Other elements would likely not be suitable as backbones for the building blocks of a living system. However, it is not clear that polymeric skeletons have to be built from one element only. Polymers can also be assembled as chains of alternating elements such as Si-C, Si-O, and B-N. Alternation with carbon is used to some extent in terran organisms (such as C-C-N in proteins and C-C-C-O-P-O in nucleic acids), and silated compounds play important structural roles in the cells of many organisms on Earth. But no comprehensive bioenergetic metabolism is known to arise from non-carbon complex chemistry, despite the high abundance of oxygen and silicon on Earth, and the relative concentration of silicon on other terrestrial planets. Thus, if elements other than carbon constitute the building blocks for any living system on other worlds, they almost surely exist under conditions far different from those on Earth, including temperatures and pressures where water could not be the solvent. Titan provides the best natural laboratory in our Solar System for investigating this possibility.

Chapter 7
Life and the Need for a Solvent

Life as we know it consists of chemical interactions that take place in the liquid state, yet the requirement that life be liquid-based is not normally part of anyone's definition of a living system. Thus, we cannot state categorically that life in either a solid or gaseous state is impossible. There are, however, compelling theoretical advantages for the complex chemical interactions that compose the living state to occur in a liquid medium. These include (1) an environment that allows for the stability of some chemical bonds to maintain macromolecular structure, while (2) promoting the dissolution of other chemical bonds with sufficient ease to enable frequent chemical interchange and energy transformations from one molecular state to another; (3) the ability to dissolve many solutes while enabling some macromolecules to resist dissolution, thereby providing boundaries, surfaces, interfaces, and stereochemical stability; (4) a density sufficient to maintain critical concentrations of reactants and constrain their dispersal; (5) a medium that provides both an upper and lower limit to the temperatures and pressures at which biochemical reactions operate, thereby funneling the evolution of metabolic pathways into a narrower range optimized for multiple interactions; and (6) a buffer against environmental fluctuations.

For a substance to be an effective solvent for living processes, its physical properties in the liquid state must be matched to those of the environment in which it occurs. Those relevant properties include the requirement that it be liquid at the prevailing temperatures and pressures on the planetary body in question. These properties include the melting and boiling point of the solvent, but also its critical temperature and pressure. The critical temperature of a compound is that temperature beyond which the liquid phase cannot exist, no matter how much pressure is applied to it. The critical pressure of a substance is the pressure required to liquefy a gas at its critical temperature. A suitable solvent must also have sufficient physical buffering capacity, which can be specified by its enthalpy of fusion (melting) and vaporization (kJ/mol) describing the amount of energy needed to change 1 mol of the substance from solid to liquid at its melting point and from liquid to gas at its boiling point, respectively. A large temperature range for the liquid state is favorable. For those reactions that depend on the making and breaking of ionic and hydrogen bonds, and for maintaining appropriate macromolecular configurations, a measure of the solvent's polarity is important. The common

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

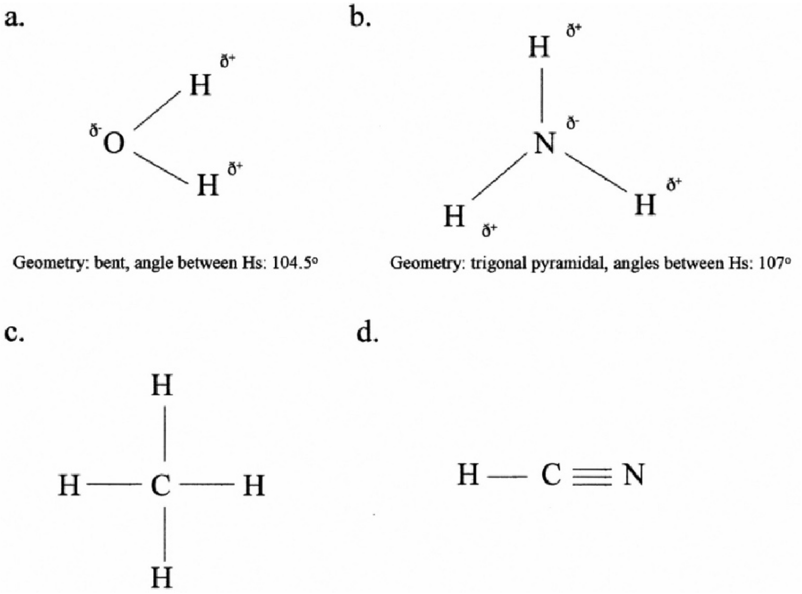


Fig. 7.1 Structure of some molecules that are discussed here as a solvent; **a.** water, **b.** ammonia, **c.** methane, and **d.** hydrocyanic acid

measure is the dipole moment in debye (D, $1\,\text{D} = 3.335 \times 10^{-30}\,\text{Cm}$), which describes the polarity of a molecule and is dependent on charge and distance. The more polar the compound the higher is its dipole moment, but if the geometry of the molecule is symmetrical (e.g. CH_4, Fig. 7.1c), the charges are balanced and the dipole moment equals zero. The maintenance of appropriate diffusion rates depends on both density and viscosity. Viscosity, the quantity that describes a fluid's resistance to flow, is very much dependent on temperature and is measured in poise (P, dyne s/cm^2) or pascal seconds (Pa s; $1\,\text{Pa s} = 10$ poise). To the extent that electrical conductivity is relevant to a particular living process, the dielectric constant is also pertinent. The dielectric constant (dimensionless) is the ratio of the permittivity of a substance to the permittivity of free space and describes the extent to which a material concentrates electric flux (permittivity is the proportionality constant between electric displacement and electric field intensity). The physical properties for a variety of inorganic candidate solvents are provided in Table 7.1.

First, we will discuss why water is such an excellent solvent for the environmental conditions of Earth. Then, we will discuss other possible solvents that could replace water under environmental conditions either similar to or vastly different from those existing on Earth. Finally, we will discuss how the nature of a solvent could determine the chemical characteristics of a living system, including the nature of its origin and evolution.

Table 7.1 Some physical properties of water and other polar compounds relevant to their solvent capabilities

Property	H_2O	NH_3	HCN	HF	H_2S	H_2SO_4	H_2O_2	N_2H_4
Molecular Weight	18.02	17.03	27.02	20.01	34.08	98.08	34.01	32.05
Density (g/ml)	0.997	0.696	0.684	0.818	1.393	1.831	1.443	1.004
Melting Point (°C at 1 bar)	0.00	−77.73	−13.3	−83.4	−85.5	10	−0.4	1.6
Boiling Point (°C at 1 bar)	100.0	−33.33	26.0	20.0	−59.6	337	150.2	113.5
Liquid Range (°C at 1 bar)	100	44.4	39.3	103.4	25.9	327	151	111
Critical Temp. (°C)	374	132	184	188	100	NA	455	380
Critical Pressure (bar)	215	111	54	64.8	88	NA	215	14.2
Enthalpy of Fusion (kJ/mol)	6.0	5.7	8.4	4.6	2.4	10.7	12.50	12.7
Enthalpy of Vaporization (kJ/mol)	40.7	23.3	25.2	30.3	18.7	NA	51.6	41.8
Dielectric Constant (ε)	80.1	16.6	115	83.6	5.9	101	89(?)	51.7
Viscosity (10^{-3} P)	9.6	2.7 (at-34°C)	2.0	~ 4.3	4.3	260	11.4	9.8
Dipole moment (D)	1.85	1.47	2.99	1.83	0.98	2.7	2.01	1.9
Surface Tension (10^{-3} J/m^2)	71.99	19.8	18.1	NA	NA	NA	79.7	66.39
Relative probability of occurrence[a]	1	0.25	0.14	NA	1.31	0.42	NA	0.26

Note: Data from CRC (2001); Firsoff (1963); Merck Research Labs (1996); Moeller (1957); http://www.trimen.pl/witek/ciecze/old_liquids.html and http://www.flexwareinc.com/gasprop.htm. NA = not available

[a] Relative probablitiy of liquids on bodies > 1000 km in diameter around any star in our stellar neighborhood as provided by Bains (2004).

7.1 Water as the Universal Solvent for Life on Earth

Water is usually portrayed as the universal solvent for life as we know it, because of various properties that make it a very good solvent for the environmental conditions of Earth. Probably, the most important property of water is its polar structure (Fig. 7.1a). This polarity allows liquid water molecules to stick to each other via hydrogen bonding, providing it with polymer-like properties. The hydrogen bonding also raises the freezing and boiling point of water to much higher temperatures than would otherwise be expected from a molecule with a molecular weight as low as 18 g/mol. Water is a liquid in a temperature range of 0 °C to 100 °C (at 1 bar pressure). The triple point of water at which all three phases – solid, liquid, and gas - coexist is also located within this temperature range, very close to Earth's average temperature (Fig. 7.2). Thus, water in the liquid form allows for the wide variety of climatic conditions, differentiated habitats, and complex chemical and physical interactions found on Earth. And because life on Earth has evolved as a system that operates in liquid water, the temperature at which water is a liquid determines the range of temperatures at which living processes can proceed normally. The dynamic properties of life cease below the freezing point of aqueous solutions, and are destroyed at temperatures above their boiling point. This empirical fact lends credence to the supposition that life is fundamentally a liquid-based process. Some tardigrades (hydrophilous micrometazoans) have been recorded to survive temperatures below −250°C and as high as 151°C (Cavicchioli 2002), but this kind of survival occurs only in a dormant state.

The superiority of water as a good solvent for ionic and polar covalent bonds is a function of its high dipole moment (1.85 D), which quantifies the electric charges at its poles. Thus, water readily dissolves molecules such as salts that serve as cofactors for many metabolic reactions and mediate bioelectrical processes, as well

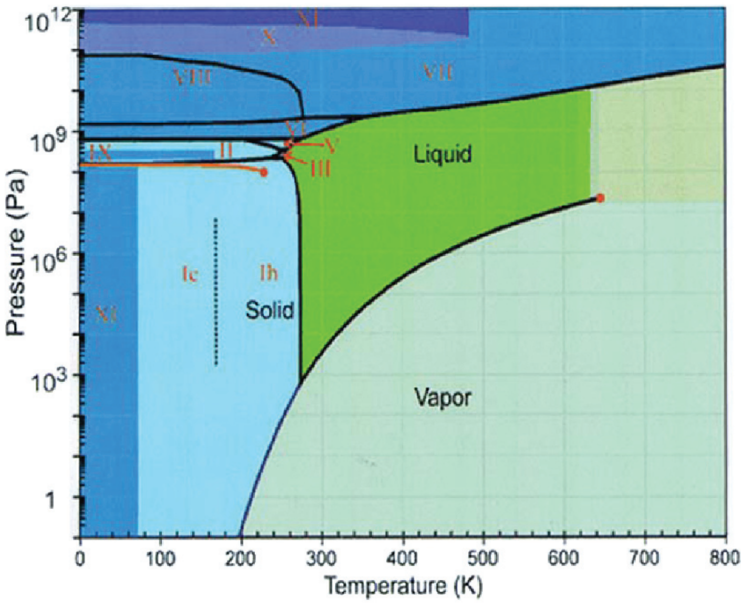


Fig. 7.2 Phase diagram for water. Stability fields for the solid, liquid, and gas phases as shown. All the different solid phases of ice involve hydrogen bonding of water molecules to four neighboring water molecules (from Chaplin 2003). Notice that the triple point is located very close to Earth's average temperature allowing all three phases to coexist under a wide variety of climatic conditions

as monomeric organic compounds with abundant polar groups such as sugars and amino acids that need to be capable of intracellular and transcellular mobility. On the other hand, water is not a good solvent for molecules with non-polar covalent bonds, such as those of hydrophobic organic molecules like lipids, which serve as the core of cellular membranes, and proteins embedded in the membrane core. Large biomolecules are thus able to maintain stable stereochemical configurations – a property essential for their biological activity – because of the stability of covalent carbonyl, peptide, glycosidic, phosphatidyl, and disulfide bonds in an aqueous solvent. Another advantage of water is that it offers organic non-polar compounds a way to be concentrated.

There are challenges, however. First, many organic synthesis reactions involve dehydration, which is inhibited in the presence of water, hence requiring energetically expensive and elaborately catalyzed reactions. Secondly, water is very reactive and therefore damaging to many biomolecules, including high-energy phosphatidyl compounds that break down easily, and many cellular macromolecules, particularly the nucleic acids (Feinberg and Shapiro 1980). Water does not support protein folding, because it disrupts the hydrogen bonds (Baross et al. 2007). Specific repair mechanisms have evolved to counter the damaging reactivity of water with DNA, and metabolic evolution has evolved generally under the limitations imposed by water on biochemical processes.

One of the most biologically favorable properties of water is its role as a thermal moderator. The reason is that (1) water's high heat capacity allows it to be available over a wide range of temperatures (from 0°C to 100°C at 1 bar pressure), and (2) water is a good heat insulator. For example, the heat of vaporization, the amount of energy required to change from the liquid into the vapor phase, requires 40.7 kJ/mol (at a pressure of 1 bar), compared to 23.3 kJ/mol for ammonia and 18.7 kJ/mol for H_2S (Table 7.1). This high heat of vaporization stabilizes an organism's intercellular temperatures and promotes consistent chemical reaction rates. This same property also accounts for the cooling capacity of water evaporated from the surface of animals living in air, a mechanism important in the dissipation of excess heat.

The property of water to act as a heat insulator can be quantified by its dielectric constant, which is relatively high compared to most other potential solvents (Tables 7.1 and 7.2). Taken together, the wide temperature range at which water stays liquid and its insulating properties allow organisms immersed in liquid water to be very well protected from temperature fluctuations. This property is readily observable in the tendency of the oceans of the Earth to maintain moderate temperatures and counteract extreme temperature climatic fluctuations (though the floating of water ice on top of liquid water is counterproductive). Water also provides stability against environmental fluctuations in a chemical sense. Water dissociates into a proton ($H+$), which is usually attached to a water molecule as a hydronium ion (H_3O^+), and an anion (OH^-), providing acid and base characteristics further increasing the solubility of compounds immersed in water. Drastic changes in pH, which could easily be detrimental to life, can be prevented by the presence of naturally and widespread occurring buffers such as carbonate and phosphate. The

Table 7.2 Comparison of physical properties for water, organic, and non-polar compounds relevant to their solvent capabilities

Property	H_2O	CH_4	C_2H_6	CH_3OH	$HCONH_2$	N_2
Molecular Weight	18.015	16.04	30.07	32.04	45.04	28.01
Density (g/ml)	0.997	0.426 at −164°C	0.572 at −107°C	0.793	1.13	0.85
Melting Point (°C at 1 bar)	0.00	− 182	− 172	−94	3	−210
Boiling Point (°C at 1 bar)	100.0	− 161.5	− 89	65	211	−196
Liquid Range (°C at 1 bar)	100	18	65	159	208	14
Critical Temp. (°C)	374	− 82.6	+ 32.3	240	NA	−147
Critical Pressure (bar)	215	45.4	47.8	78	NA	33.3
Enthalpy of Fusion (kJ/mol)	6.0	0.94	2.7	2.2	8.44	0.71
Enthalpy of Vaporization (kJ/mol)	40.7	8.2	14.7	40.5	60.1 at 25°C	5.56
Dielectric Constant (ε)	80.1	1.7	1.9	354 at 13°C	110	1.45
Viscosity (10^{-3} P)	9.6	0.009 at 20°C	0.011 at 20°C	5.9	33	2.04
Dipole moment (D)	1.85	0.0	0.0	1.6	3.4	0
Surface Tension (10^{-3} J/m^2)	71.99	NA	NA	22.1	57.03	10.53
Relative probability of occurrence[a]	1	0.62	1.25	NA	NA	1.96

Notes: Data from CRC (2001); Goldsmith and Owen (2003); Firsoff (1963); Moeller (1957); Merck Research Labs (1996); http://www.trimen.pl/witek/ciecze/old_liquids.html and http://www.flexwareinc.com/gasprop.htm.

NA = not available

[a] Relative probability of liquids on bodies $>$ 1000 km in diameter around any star in our stellar neighborhood as provided by Bains (2004).

presence of acid and base possibilities also leads to neutralization reactions, in which the cation of the base combines with the anion of the acid to form a salt, and the anion of the base combines with the cation of the acid to form a molecule of the solvent. Salts dissociate in their solvent, in this case water, into charged ions, increasing the reactivity of the solution as well as its conductivity. The usefulness of this electrolytic property is enhanced by the low viscosity of water. Ions can flow within and circulate efficiently through the solvent and participate in reactions within a reasonable time frame.

The role of water as a climatic stabilizer is an immensely important property for all organisms. Associated with that property is its unusual capacity to decrease in density as it freezes below its maximum density at 4°C. This has obvious advantages for life in Earth's oceans and lakes, because the lighter water ice floats and acts as insulator for organisms beneath its surface and prevents the complete freezing of a body of water from the bottom to the top. This advantage is more important for multicellular forms of life than for microbial life, because microbes can more easily employ adaptive strategies against freezing such as surviving in a spore state. This peculiar property of water has a disadvantage as well, in that ice crystals pierce the cellular membranes due to the expansion of water as a solid. This is the basis for frost damage to plants, for example. However, this property is only valid for ice I (Fig. 7.2), while ice II or any other form of ice is denser than liquid water (Baross et al. 2007). Thus, on a planet much more massive than Earth, ice would sink in water. Another peculiar property of water is its high surface tension, which reflects the tendency of water to form droplets due to greater cohesion among adjacent water molecules than between water and the molecules of air with which it is in contact. The surface tension of water is very high with a value of 71.99 mN/m at 25°C (CRC 2001), compared to most other liquids. The surface tension of other potential solvents at their respective temperature of liquidity is not very well known though. This property is not directly related to the solvent's ability to transport nutrients, but is likely to be relevant to the origin of life. Organic compounds may have been concentrated in small water droplets that enhanced the probability of a reaction sequence leading to prebiotic molecules (Gusev 2002).

One important environmental advantage of water is that in an Earth-type environment it is self-shielding against ultraviolet radiation. Ultraviolet photons dissociate water molecules, releasing oxygen and hydrogen into the atmosphere. If that happens, some of the oxygen atoms will form ozone molecules, which are an excellent absorber for UV radiation, thus shielding the planetary surface from this detrimental form of high energy.

Another important property for any candidate to be qualified as a vital solvent in a scheme of organic chemistry leading to biology is that it has to be related to that scheme (Firsoff 1963). A solvent may be as good as water in an Earth-type environment, but if it does not form any ions that could advantageously enter into biochemical reactions, it is of little interest. With respect to water, hydration and dehydration reactions are widespread in the biochemistry of Earth's organisms. Examples include the formation of peptide bonds between amino acids via dehydration synthesis reactions and the breakdown of complex sugars by hydration hydrolysis.

If life requires proteins, which are essential biomolecules for life on Earth, water is an ideal solvent. Proteins fold to a unique, globular conformation, which tightly packs over 80% of the peptide groups and non-polar side chains. This marginally higher stability of proteins in the folded state, which allows both stability and solubility, would be very difficult to reproduce in alternative solvents (Pace et al. 2004). However, Benner et al. (2004) pointed out that many organic molecules that are parts of a carbon-based metabolism display problematic reactivity with water, citing the difficulty with carbon dioxide cycling as an example. At a more recent symposium on the biological importance of water, Daniel et al. (2004a) wondered about the biological functions of water at the molecular level and whether water is truly irreplaceable for the function of living systems. Terran organisms are very well adapted to water and other solvents are usually very toxic to them. The toxicity of these solvents is determined by their ability to permeate the cell membrane, which results in the leakage of macromolecules, including proteins and RNA (Isken and de Bont 1998). However, some bacteria tolerate other solvents at very high concentrations by membranes that limit the diffusion of solvents into the cell and by specialized efflux mechanisms that remove solvents that have diffused into the cell (Baross et al. 2007).

Perhaps the most important property of a life-sustaining solvent is that it has to occur in large quantities on the planetary surface or wherever the life-sustaining reactions are to occur. With oxygen the most common element on Earth, and hydrogen the most common element in the universe, water would be expected to be common on Earth. Water is also known from spectral analysis to be a common molecule in the universe, and thus may be the obvious choice as a solvent elsewhere as well. However, many properties that make water such a good solvent are directly linked to the environmental conditions existing on Earth as discussed above. Thus, considering environmental conditions unlike those on Earth may require the participation of some other types of solvents. This notion will be explored in the coming sections.

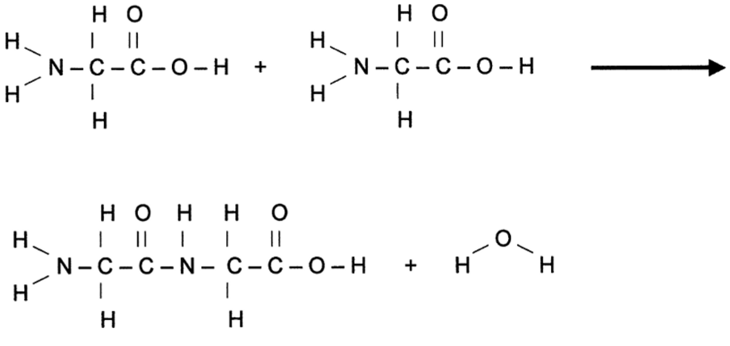
7.2 Polar Inorganic Solvents as Alternatives to Water

In their assessment of the limits of organic life in planetary systems, the National Research Council (Baross et al. 2007) found no compelling reason to limit the environment for life to water as a solvent, although terran life is constrained to use carbon as the scaffolding element for most of its biomolecules. Several potential candidates could replace water as a polar solvent on other worlds. For example, Benner (2002) suggested sulfuric acid (H_2SO_4) as a possibility for Venus, and ammonia (NH_3) as a possibility for Jupiter. Most of the potential solvent candidates are liquids at lower temperatures than water. Hydrazine, N_2H_4, which is a liquid from 2°C to 114°C at 1 bar pressure, is one of the few exceptions. There is, however, overlap with the thermal range of liquidity for water in some cases (e.g. HCN, HF). Chemical reactions occurring within these solvents would proceed at a much slower pace than on Earth, typically by a factor of 2 for every 10°C decrease in temperature (Jakosky 1998). However, the key to developing a suitable chemistry at a given temperature lies in selecting chemical reactions suited to that temperature. For example, those reactions involving unstable and highly reactive free radicals have very low activation energies (Feinberg and Shapiro 1980) and would be suited for low temperature organisms. Also, lower temperatures and an abundance of nitrogen could open up new possibilities, such as polymeric chains of nitrogen atoms. Bonds of nitrogen to nitrogen are weaker than carbon to carbon bonds, and are less abundant on Earth. Some of them are very reactive under Earth conditions (e.g. hydrazine). At lower temperatures, however, these compounds would be more stable and may be suitable for the construction of complex molecules. Many planetary bodies within our Solar System have much colder surface temperatures than Earth, and planets and moons at these temperature ranges may be much more common than Earth-type bodies in the universe.

In order to qualify as a suitable candidate for a polar solvent, the solvent has to be easily available and plentiful, as well as suitable for at least a hypothetical scheme that could lead to prebiotic chemisty. If not plentiful in the universe, there has to be some kind of fractionation mechanism that could conceivably enrich the particular solvent on a planetary body. In the following we discuss the polar solvent candidates ammonia, hydrocyanic acid, hydrofluoric acid, methanol, hydrogen peroxide, hydrazine and possible sulfur-based and organic solvents, which we rank according to the likelihood that they could replace water as the life-supporting solvent in certain types of environments.

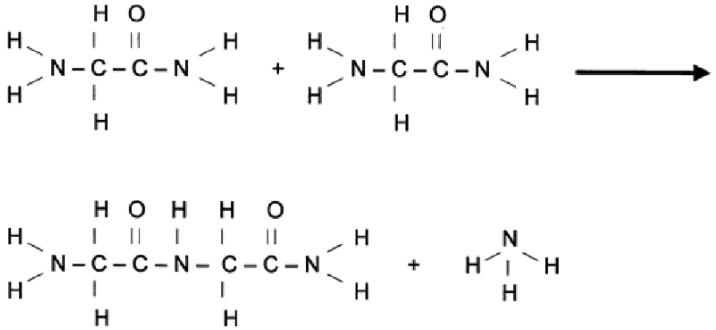
7.2.1 Ammonia

The idea of life based on ammonia as a solvent has received a considerable amount of attention. For example, Haldane (1954) pointed out ammonia analogues to water and suggested the possibility of building proteins, nucleic acids and polypeptides within a liquid ammonia solvent. Raulin et al. (1995) suggested that "ammono" analogues of terran biomolecules in which oxygen atoms are replaced by NH groups might yield an equally viable pseudo-biochemistry. Life on Earth exploits compounds containing the C=O carbonyl unit. In ammonia, C=O units would have to be replaced by C=N units, but given this adjustment Benner et al. (2004) argued that metabolism in liquid ammonia is easily conceivable. Baross et al. (2007) argued that the C=N bond would be equally satisfactory for supporting carbon-carbon bond forming reactions. Firsoff (1963) went into some detail showing similarities of synthesis reactions in water-based, ammonia-based and water-ammonia mixtures. An especially interesting example provided by him is the synthesis of proteins from amino acids through a peptide bond. In a water system two glycine molecules combine with the release of water (Eq. 7.1):



$$H_2N-CH_2-C(=O)-O-H + H_2N-CH_2-C(=O)-O-H \longrightarrow H_2N-CH_2-C(=O)-NH-CH_2-C(=O)-O-H + H_2O \qquad (7.1)$$

If reaction (7.1) would take place in a water-ammonia mixture the COOH group would be replaced with a $CONH_2$ group and reaction (7.2) would be the result. In this reaction (7.2) the peptide bond is preserved and ammonia is released instead of water:



(7.2)

Firsoff (1963) speculated that the preservation of the peptide bond may be a relic of an ammono-organic scheme on Earth in the early stages of evolution.

In a pure ammonia solvent without the presence of oxygen, the carboxyl group could be replaced with a -$CH(NH_2)NH_2$ group and the peptide bond with a –$CH(NH_2)$-NH- group. Similar analogues can be shown for the phosphate bonds in the nucleic acids (Firsoff 1963). A further parallel is that ammoniation reactions in ammonia as solvent are directly analogous to hydration reactions with water in which a salt and the solvent are produced. This leads to an important environmenttal consequence that minerals in a near-surface or subsurface "hydrosphere" would contain ammonia in their crystal structure just as Earth's rocks contain water. Although there appear to be chemical pathways leading from ammonia to prebiotic macromolecules, water is a more powerful solvent than ammonia based on its physical and chemical properties. Ammonia has a structure comparable to water (Fig. 7.1b) but a lower dipole moment and is thus less efficient at dissolving polarized compounds. Ammonia's heat of vaporization and heat of fusion are lower than that of water (although the heat of fusion is nearly equal, Table 7.1). Thus, ammonia is not as good at moderating temperature as water, but is still sufficient to have a stabilizing effect on climatic conditions. The surface tension of ammonia is only about one third of water; thus ammonia is not likely to concentrate organic macromolecules in microscopic interfaces as well as water. Ammonia dissociates into nitrogen and hydrogen, and does not afford any protection from UV light when compared to the dissociation of water. Thus any origin of life in ammonia would have to occur in some kind of protected environment. Ammonia, however, makes up for this disadvantage by its ability to dissolve alkali metals without reaction, which is of biological relevance because alkali metals can act as catalysts. Also, salt solutions in liquid ammonia have usually a greater electrical conductivity than an aqueous solution of the same salt (Mee 1934). Ammonia is about four times less viscous than water, thus dissolved particles and ions have a less difficult time to find and react with each other. Ammonia self-dissociates as water does but to a much lower degree (1.9×10^{-33} at -50°C compared to 10^{-14} at 25°C for water). Ammonia dissociates to NH_4^+ (equivalent to H_3O^+ of water) and the anion NH_2^-. It can further dissociate to form two more base anions, NH^{2-} and N^{3-}, thus acid-base reactions do occur in an ammonia system but to a much lower degree.

Ammonia is liquid at lower temperatures than water and has a smaller range in which it stays liquid, thus life would have to adapt to a smaller temperature window to survive on such a world. However, the temperature range over which ammonia is liquid for some relevant planetary surface pressures is greater than for water. For example, at a pressure of 60 bar ammonia is liquid from 196° to 371°K (Baross et al. 2007). Since solid ammonia is denser than liquid ammonia, there is no mechanism for preventing liquid ammonia from completely freezing during a cold spell. This is no problem for microbial life since it could have adapted to survive any cold spell or cyclic freezing in a spore state. However, survival of multicellular organisms in such an environment would be less likely. Further, chemical reactions would generally be expected to progress at a slower pace, lengthening life spans, and therefore decreasing the rate at which competition and adaptive radiation would drive evolution (Schulze-Makuch and Irwin 2006). Microbial life in ammonia might not be as differentiated or as well adapted compared to water-based life on Earth. Further, liquid ammonia cannot co-exist with free oxygen, thus aerobic metabolism would be inconsistent with ammonia as a solvent.

Liquid ammonia could, on the other hand, present an opportunity for microbial life on the more numerous colder bodies in the Solar System as well as for Jovian type planets where the boiling point of ammonia could be as high as ammonia's critical temperatures of $+132.4°C$ (given the extreme pressures). Ammonia and water are definitely related solvents, as indicated by the fact that life sustaining organic macromolecules such as proteins, amino acids and nucleic acids contain both OH and NH_2 functional groups in various combinations and proportions with which ammonia could easily interact. Aspinall et al. (2002) suggested that phosphate, a vital element for life on Earth, can be replaced by ammonophosphate analogues that are stable in water and ammonia, can lose protons to hold multiple negative charges, and can form stable amide-like bonds with carbon molecules. Bains (2004) hypothesized that movement of electrons ("electricity") rather than protons ("proticity") would be a reasonable energy transaction for ammonium supported life. Different hydrocarbons become miscible with ammonia depending on temperature and pressure conditions. The formation of ammonia-philic and ammonia-phobic phases (analogous to hydrophilic and hydrophobic phases in water) is clearly conceivable in liquid ammonia at temperatures well below its boiling point at standard pressures (Baross et al. 2007).

Interestingly, several enzymes of terran organisms remain active down to temperatures of about $-100°C$ (Bragger et al. 2000). In the likely subsurface oceans of the Galilean satellites, and possibly also at Titan and Triton, some ammonia dissolved in water may act as antifreeze, lowering the temperature at which water can stay liquid and thus possibly support life (Fortes 2000). Alternatively, any ammonia solvent in this type of environment should not be expected to be pure either. Water in the form of ice or icebergs would dissolve in liquid ammonia, thus the occurrence of water groups such as OH^- and O^{2-} should be expected within an ammonia solvent, if it indeed is capable of supporting life. Any ammonia-water mixture would be very basic, though. A 1.7% ammonia solution has a pH of 11.6 (Budavari et al. 1996) and it isn't clear how well life could adapt to this high basicity. On Earth, life is much more capable of withstanding and adapting to extreme acidities than basicities. However, there are not many natural environments on Earth with high pH-values (mostly soda lakes); thus there may have been no need for the evolution of organisms on Earth to develop this type of adaptation. Therefore, high pH may not be a fundamental obstacle for life. There is certainly enough ammonia in our Solar System, and in comets and the interstellar medium of the universe in general, to sustain the possibility that living systems could thrive in a solvent of ammonia, or an ammonium-water mixture, within the appropriate thermal limits.

7.2.2 Hydrocyanic Acid

The structure of hydrocyanic acid, with a triple bond between the carbon and the nitrogen, is quite different from the structure of water, ammonia and methane (Fig. 7.1d). It is an excellent ionic solvent with a dipole moment of 2.8 D compared to 1.85 D for water and 1.47 D for ammonia. Also, as a thermal moderator it is about equal to water and superior to ammonia, with (1) a heat of fusion of 8.41 kJ/mol and heat of vaporization of 25.2 kJ/mol, and (2) a dielectric constant of 114.9. The range of temperature at which HCN remains a liquid is somewhat small, but it extends up to 26°C allowing chemical reactions to proceed at a reasonable pace. Hydrocyanic acid dissociates into H^+ and CN^- with sulfuric and hydrochloric acids remaining acids in liquid HCN while cyanides are bases (Firsoff 1963). Cyan compounds are generally toxic to aqueous life in Earth's oceans and fresh water reservoirs. However, the toxicity only indicates the occurrence of reactions that are competitive with water-based biochemistry and the ease with which water groups can be replaced by CN. CN bonds are of fundamental importance in proteins and other organic substances, and the substitution of CN for OH would yield HCN-analog compounds. Some compounds valuable for life such as metals are insoluble or only soluble to a small extent in HCN, while other compounds such as certain salts (e.g. potassium thiocyanite, permanganate) are highly soluble and give highly conductive solutions (Moeller 1957).

Hydrocyanic acid is not as abundant as water in the universe but has been detected in comets and at planetary bodies such as Jupiter and Titan, and in the interstellar medium (Brown 1984; Lunine et al. 1999). Hydrocyanic acid not only offers protection from UV radiation, but can even combine with itself in alkaline solutions to form amino acids with the assistance of UV photons (7.3).

$$3\,\mathrm{HCN} + 2\,\mathrm{H_2O} + \mathrm{UV\,light} \rightarrow \mathrm{C_2H_5O_2N} + \mathrm{CN_2H_2} \qquad (7.3)$$

In addition to glycine, this reaction produces cyanamide (CN_2H_2), which can link amino acids together as the first step in the formation of proteins. Another promising pre-biotic pathway was offered by Matthews and Moser (1966), who suggested the direct synthesis of protein ancestors (heteropolypeptides) from hydrogen cyanide and water without the intervening formation of amino acids. Also of interest is that the important purine adenine ($C_5H_5N_5$) is a pentamer of HCN. A biochemistry based on hydrocyanic acid would likely be quite different from one based on either water or ammonia, and that is perhaps the primary reason why HCN did not receive much consideration as a solvent for life. HCN cannot interact as well with Earth-type organic macromolecules as ammonia. Its relatively small thermal window of liquidity, and its limited ability to dissolve some biologically important compounds are disadvantages for HCN as a solvent for living systems. However, it is intriguing that when dissolved in water HCN spontaneously reacts to form heterogeneous oligomers, which upon standing hydrolyze to release a variety of molecules of biological significance such as purines, pyrimidines, urea, and amino acids (Cleaves et al. 2008). To the extent that Earth provides a natural laboratory for comparing HCN with H_2O, with temperatures covering the range at which both compounds are liquid, HCN clearly is not competitive with water as a solvent, either because of its lower abundance, or because the nature of biomolecules that would be stable and reactive in a hydrocyanic acid medium are not metabolically competitive with those that function in water. However, with its relatively high molecular weight of 27 g/mol, it could be the solvent of choice on a planetary body where most of the lighter molecules may have steamed off at some stage of atmospheric evolution. In such an atmosphere, cyanogen (C_2N_2) could be expected as an atmospheric constituent, which might provide energizing reactions analogous to oxidation in Earth's atmosphere (Firsoff 1963).

7.2.3 Hydrofluoric Acid

The solvent properties for hydrofluoric acid and water are very similar. The dipole moment and the dielectric constant are basically the same, while the heat of fusion and heat of vaporization of HF is only slightly lower (Table 7.1). Thus, hydrofluoric acid is an excellent temperature moderator and solvent. The temperature range at which HF remains liquid is a bit larger than for water and extends much lower (−83°C to +20°C). Two hydrofluoric acid molecules dissociate into HF_2^- and H^+. Due to their non-polar nature most hydrocarbon compounds are insoluble in hydrofluoric acid, but many of them are polymerized, decomposed or lead to conducting solutions with complex cations, where the organic molecule bonds to the proton of HF (Firsoff 1963). Conceivably, F^- or HF_2^- could replace OH^-, and F_2^{2-} could replace O^{2-} in oxides. Fluorination could thus replace oxidation as the primary energy-yielding reaction, and would be more efficient due to the greater bonding energy of fluorine. As a result, free fluorine would be one of the atmospheric gases, and would likely have the same fate as oxygen had in the early Earth atmosphere (being such a very reactive element it would quickly be bound to surface rocks and removed from the atmosphere). The primary problem with hydrofluoric acid as a primary solvent is the low cosmic abundance of fluorine. Its abundance in the Solar System was estimated to be about 1000 times less than that of carbon, nitrogen or oxygen (Anders and Grevesse 1989). It is difficult to envision any fractionation mechanism that could enrich hydrofluoric acid to such a sufficient extent to become the primary solvent on a planetary body. One possibility is that all molecular oxygen could be used up in oxidation reactions on the planetary surface and that fluorine gas would be released from F-rich magmas later in the history of the planetary body. However, due to its low cosmic abundance and the unlikelihood of an efficient fractionation mechanism, we rank HF as an alternative solvent lower than ammonia and hydrocyanic acid in spite of the advantageous properties of the hydrofluoric acid molecule.

7.2.4 Hydrogen Sulfide, Sulfur Dioxide and Sulfuric Acid

Hydrogen sulfide remains a liquid at colder temperatures than any other candidate solvent introduced in Table 7.1, but its temperature range as a liquid is only 26°C. Hydrogen sulfide does not moderate temperatures very well, given its low heat of fusion, heat of vaporization and dielectric constant. It is not particularly efficient as an ionic solvent, given its low dipole moment, but it does dissolve many substances, including many organic compounds. Similarly to water hydrogen sulfide dissociates into H^+ and SH^-. In a biochemical scheme with H_2S as solvent, the SH^- anion could simply replace the hydroxyl group in organic compounds. Hydrogen sulfide is a relatively common compound in the universe, usually associated with volcanic activity on planetary bodies. H_2S could be a conceivable solvent on Io, the volcanically most active planetary body in the Solar System. A subsurface layer of hydrogen sulfide could turn liquid when overhead lava warms the subsurface layer up to its range of liquidity (Table 7.1), then "spores" could become activated, reproduce, and perpetuate an exotic subsurface microbial ecosystem.

In this type of environment another sulfur solvent, sulfur dioxide, may compete with hydrogen sulfide. Sulfur dioxide is a solvent with a dipole moment of 1.6, remains a liquid at temperatures from -75°C to -10°C, and could be retained preferentially on massive planetary bodies due to its high molecular weight of 64 g/mol. However, due to the double bond in sulfur dioxide the development of a biochemical scheme would be more complicated for SO_2 than for H_2S, because rearrangements would be needed. Also, SO_2 is not a proton-based solvent. Proton-based solvents have the advantage that organic macromolecules such as nucleic acids are constructed via hydrogen bonds and are able to exchange materials with the solvent or change their formation for biological purposes without having to overcome a high-energy barrier. Interestingly, sulfates including sulfuric acid (H_2SO_4) are insoluble in sulfur dioxide, and would thus be rock material in a pool of sulfur dioxide.

Sulfuric acid has been suggested as a possible candidate for a life-supporting solvent within 1 AU (astronomical unit) of a star like our Sun (Fig. 7.3). Benner (2002) suggested sulfuric acid (H_2SO_4) as a possibility for Venus, where the atmosphere is rich in it. Sulfuric acid has a huge liquidity range, from 10°C to 337°C, a dielectric constant and dipole moment larger than water, and an extremely high viscosity (Table 7.1). The prospect of pure sulfuric acid as a life-sustaining solvent would

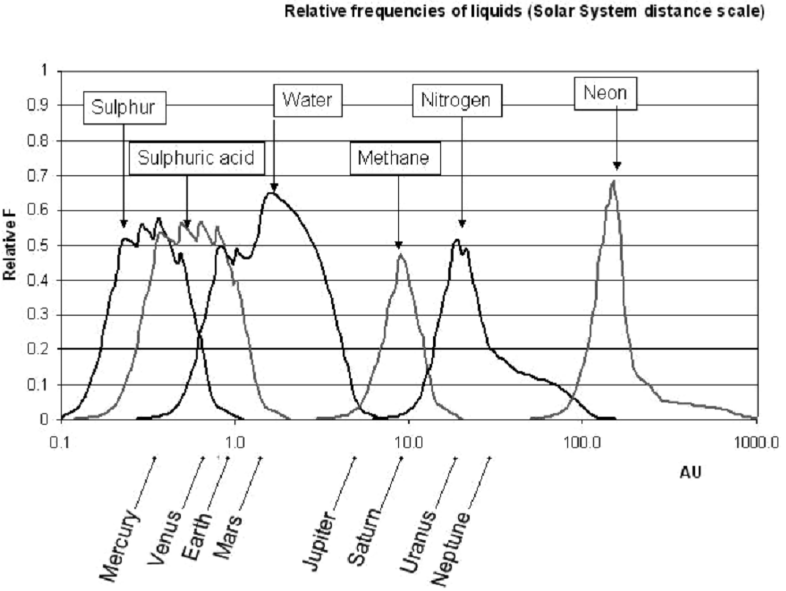


Fig. 7.3 Probability distribution for occurrence of different liquids as a function of distance from a Sun-like star. The x-axis represents distance and the y-axis represents the added probability of surface and subsurface liquid. Figure courtesy of William Bains, following the method described in Bains (2004).

require a biochemistry very different from the one with which we are familiar. The C = C bond is reactive as a base in strong acids and could support metabolism as an analog to the C = O unit (Baross et al. 2007), a reactivity shown to work in some terran biochemistry like that used by plants to synthesize fragrant molecules (Kreuzwieser et al. 1999). Sulfuric acid mixes well with water, and if life exists in the atmosphere of Venus (Sagan 1961; Grinspoon 1997; and Schulze-Makuch et al. 2002b; 2004), it would be expected to be adapted to a sulfuric-acid water mixture. This possibility is explored further in Chap. 8.3.

7.2.5 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) has a larger liquidity range than water (from −0.4 to 150.2°C), but mirrors water in many other properties (Table 7.1). As a pure compound, hydrogen peroxide does not qualify as a good solvent for life, because it is a strong oxidizer and would oxidize most carbon compounds rapidly to carbon dioxide. Thus, it is not compatible with biochemistry as we know it. However, mixtures of H_2O_2 and H_2O present an intriguing possibility, as recently suggested by Houtkooper and Schulze-Makuch (2007). Such a mixture would freeze at temperatures significantly below the freezing point of water, because the lower eutectic point lies at −56.5°C for a mixture with 61.2 weight % H_2O_2 (Foley and Giguère 1951). Also, mixtures with a high H_2O_2 concentration tend to supercool (Giguère and Secco 1954), and would thus not produce icy crystals that could pierce cellular membranes. H_2O_2-H_2O mixtures are slightly acidic, with a pH of 4.5 for the 60 weight % mixture. Because of the lower water vapor partial pressure in equilibrium with the liquid, H_2O_2-H_2O mixtures tend to be hygroscopic compared to water alone, which would offer the opportunity for an organism to scavenge water molecules from the atmosphere in an arid environment. Houtkooper and Schulze-Makuch (2007) hypothesized that organisms on Mars might use a H_2O_2-H_2O mixture as a mechanism of adaptation to Martian environmental conditions. They pointed out that such a biochemistry would explain the observations made during the Viking life detection experiments amazingly well (see also Chapt. 12.1). There are various terrestrial analogs for the utilization of H_2O_2, including microbes that use H_2O_2 in their metabolic pathways, such as *Acetobacter peroxidans* (Tanenbaum 1956). Of course, the tendency for peroxides to form free radicals that are highly reactive would require the evolution of counteractive mechanisms for protecting cellular material in a peroxide-rich environment.

7.2.6 Hydrazine

Hydrazine (N_2H_4) is a liquid at a temperature range from 2°C to 114°C and thus one of the very few solvent candidates that has a larger temperature range and a larger absolute temperature at which it stays a liquid than water. Hydrazine is an excellent polar solvent with a dipole moment of 1.9 comparable to water. Its dielectric constant (51.7) and viscosity (9.8×10^{-3} P) are also very similar to water. Based on its physical properties it would be an excellent solvent candidate as an alternative to water. Hydrazine, however, is a very reactive molecule and decomposes extremely fast in the presence of oxygen, making it an ideal rocket fuel. This property suits it poorly to serve as a solvent in the presence of oxygen. Because of its high reactivity, it would be expected to make a better solvent at low temperatures in an anoxic environment, for driving biochemical reactions at a reasonable speed. However, at temperatures below 2°C hydrazine is a solid and therefore not a suitable solvent. Furthermore, hydrazine is not an abundant molecule, and thus does not appear to be a promising solvent candidate despite its favorable physical properties.

7.2.7 Supercritical Fluids: Carbon Dioxide

Supercritical fluids could also play a role as a life sustaining solvent on other worlds. The properties of supercritical fluids are usually quite different from those of regular fluids. Supercritical water, for example, is relatively non-polar and acidic. There are some advantages to supercritical fluids, especially for carbon dioxide and water, which include: (1) high solubility of gases within supercritical mixtures, (2) miscibility of gases such as O_2 and H_2 in supercritical fluids, (3) high diffusion rates and variable density, and (4) high dissolving power (Baross et al. 2007). Ikushima (1997) advanced the case for supercritical fluids as an appropriate medium for chemical and biochemical processes under certain conditions. One cited example was the synthesis of esters from acryl donors and terpene alcohols by lipase in *Candida cylindracea*, which in supercritical carbon dioxide caused drastic conformational changes that enabled active sites to catalyze stereoselective synthesis. Reactivity was found to be susceptible to small changes in pressure or temperature near the critical point of the supercritical fluid. Shkrob and Sauer (2001) showed that high-mobility CO_2-multimer anions in supercritical carbon dioxide form stable complexes with water, aliphatic alcohols, alkyl halides, and alkyl nitriles.

An example of how supercritical CO_2 might support living processes can be seen in the recent discovery of subsurface accumulations of liquid carbon dioxide under Earth's oceans (Inagaki et al. 2006). The low density liquid CO_2 has been found to be trapped by a surface pavement and subpavement cap of CO_2 hydrate ($CO_2 \times 6H_2O$). As the density of liquid CO_2 increases with depth, it becomes denser than sea water, opening up the possibility of many reservoirs of liquid carbon dioxide on the sea floor (House et al. 2006). Most amazing was the detection of 10^7 cells/ml at the liquid CO_2/CO_2-hydrate interface (Inagaki et al. 2006), which is quite remarkable given the potentially hostile nature of CO_2 (Nealson 2006). Carbon dioxide is usually described as a non-polar solvent, given the zero molecular dipole moment and its low dielectric constant. However, strong theoretical and recent experimental evidence indicates that CO_2 can participate in hydrogen-bonding interactions, and thus has polar attributes (Raveendran et al. 2005). Industrially, supercritical carbon dioxide is increasingly promoted as an environmentally benign alternative to conventional organic solvents (Raveendran et al. 2005). Carbon dioxide is a very common compound on many planets, including our neighbors Venus and Mars. Supercritical carbon dioxide could occur in a number of these extraterrestrial locations, such as in the subsurface of Venus. It certainly deserves more attention as a potential life-sustaining solvent.

7.3 Organic and Non-Polar Solvents

Organic and non-polar compounds are usually not considered good candidates as alternative biological solvents. However, Carrea et al (1995), Cabral (2001), and Klibanov (2001) have shown that terran enzymology can operate in a variety of non-aqueous solvents, and even in completely non-polar solvents such as benzene, diphenyl ether, or straight-chain hydrocarbons from heptane to hexadecane. Furthermore, the fungus *Fusarium alkanophilum* is known to be able to thrive in a hydrocarbon environment, extracting metabolic water from light hydrocarbons (Marcano et al. 2002). Also, many organic reactions fundamental to biochemistry can occur in nonaqueous solvents (Benner et al. 2004; Bragger et al. 2000). Table 7.2 provides some solvent-related physical properties of polar and non-polar hydrocarbons, and the non-polar compound dinitrogen. These compounds are relatively common in the universe, and some of them are primary liquid compounds on at least one planetary body of our Solar System (e.g., methane and ethane on Titan, dinitrogen on Triton). Except for formamide ($HCONH_2$) and methanol (CH_3OH), these compounds are liquid at temperatures much lower than water (as most of the polar substitutes for water are).

7.3.1 Organic Non-Polar Compounds

Traditionally, it has been assumed that liquids other than water are unsuitable for the complex catalysis that is essential for biochemistry, especially organic compounds which are mostly non-polar (Bains 2004). Membranes of terran organisms, which are submerged in the polar solvent, water, are amphiphilic with their polar (hydrophilic) heads exposed to the solvent and their non-polar (hydrophobic) tails oriented toward each other, away from the solvent. They interact with the polar solvent to take up nutrients, respond to intracellular signals, and discard wastes. If a non-polar solvent could support life, the chemical orientation of membranes would have to be fundamentally different. In this case, the heads immersed in the solvent would have to be non-polar in order to interact with the hydrocarbon solvent. However, broad empirical experience has demonstrated that organic reactivity in hydrocarbon solvents is no less versatile than in water, and many enzymes derived from organisms on Earth are believed to catalyze reactions by having an active site that is not hydrophilic (Benner et al. 2004). Also, a hydrocarbon solvent may actually improve chances for the origin of life, inasmuch as extensive experience with organic synthesis reactions has shown that the presence of water greatly diminishes the chance of constructing nucleic acids. Thus, the assemblage of organic macromolecules that could give rise to life appears to be much more straightforward in a hydrocarbon environment. A hydrocarbon solvent would also provide protection against UV radiation, as hydrocarbon smog emanating from the liquid solvent would absorb some of the UV radiation and thus offer a significant degree of protection. Hydrocarbons as the primary solvents on a planetary body are not beyond the realm of possibility. Saturn's moon Titan may provide a strong case in point. Spectroscopic results indicate the presence of methane rain on Titan (Lorenz 2000; Lunine et al. 1983) and the presence of liquid lakes on Titan's surface has been confirmed by the Cassini-Huygens mission (Stofan et al. 2007). In a non-polar hydrocarbon solvent such as methane or ethane, cellular membranes would likely be hydrophobic on the outside and hydrophilic at their cores. Thus, if a hydrocarbon liquid such as methane or ethane, or a mixture of both, could support life as a primary solvent, the resulting organisms would likely be quite different from those on Earth. In a solvent such as ethane a putative organism would be able to use hydrogen bonding more effectively, because the bonds would have the appropriate strengths for low temperatures.

Methanogenesis could be an energy-yielding strategy in this type of environment. For example, photochemically produced acetylene, which is a solid under Titan's surface conditions (Lorenz 2000), could be reduced with the help of hydrogen in the atmosphere to methane (Eq. 7.4)

$$C_2H_2 + 3H_2 \rightarrow 2CH_4 \tag{7.4}$$

In fact, methane is detected at a lighter isotopic fractionation than would be expected from Titan formation theory (Lunine et al. 1999), which could indicate activity of living organisms (Abbas and Schulze-Makuch 2002; Schulze-Makuch and Grinspoon 2005). Essential building blocks of life such as sugars, proteins and nucleic acids could exist in such organisms as well. However, given the vastly different environment from which that form of life would originate, it appears more likely that another solution to the make-up of life would have been found. Baross et al. (2007) suggested that the environment of Titan meets the absolute requirements for life, which include thermodynamic disequilibrium, abundant carbon containing molecules and heteroatoms, and a fluid environment – further concluding that "this makes inescapable the conclusion that if life is an intrinsic property of chemical reactivity, life should exist on Titan."

7.3.2 Organic Polar Compounds

Hydrocarbon compounds are generally non-polar but can be made into polar molecules by replacing H with an OH group in a hydrocarbon molecule. For example, methyl alcohol or methanol (CH_3OH) is an excellent polar solvent with a dipole moment of 1.68 D compared to 1.85 D of water and 1.47 D of ammonia. It is also a better temperature moderator than water based on its extremely high dielectric constant and heat of vaporization (Table 7.1), and remains a liquid in the wide temperature range from $-94°C$ to $+65°C$. It may also be a relatively common compound in the universe as it has been found in the interstellar medium and in comets (Goldsmith and Owen 2003). Liquid hydrocarbon compounds are known to exist on Titan in large quantities, but methanol has not been found there. However, Tang et al. (2006) suggested the presence of pools or even oceans of methanol on early Mars. They pointed out that the gray hematite found on Mars could have been produced in a thermal system of organic compounds such as methanol that was generated from the photochemical oxidation of methane, since methane is thought to have been abundant in the early Martian atmosphere.

Another excellent possibility is formamide ($HCONH_2$, Table 7.2). This compound has more than double the liquidity range of water and stays liquid at much higher temperatures. It has a high surface tension to concentrate solutes, and a higher dipole moment and a larger dielectric constant than water. Benner et al. (2004) pointed out that many chemical species that are thermodynamically unstable in water with respect to hydrolysis, are spontaneously synthesized in formamide.

This includes ATP from ADP and inorganic phosphate, peptides from amino acids, and even oligoribonucleotides (Schoffstall et al. 1982; Schoffstall and Liang 1985). Formamide itself is hydrolyzed by water and can thus only exist in a dry environment. However, desert environments have been proposed as potential sites for the prebiotic synthesis of ribose (Ricardo et al. 2004) and many synthesis reactions of organic macromolecules would be thermodynamically favorable in desert pools of formamide (Baross et al. 2007). However, though formamide is formed by the reaction of hydrogen cyanide and water, both of which are abundant, formamide itself does not appear to be abundant in the Solar System, nor probably elsewhere in the universe.

7.3.3 Inorganic Non-Polar Compounds

Liquid nitrogen is probably the most promising non-polar inorganic compound. Liquid nitrogen boils at $-196°$C and thus can occur in our Solar System in the liquid state only on the icy satellites of the outer Solar System (Fig. 7.3). Temperature and pressure conditions should be right for Triton to have liquid nitrogen in its subsurface. Even a liquid nitrogen ocean may be a possibility (Bains 2004). Though it is very abundant, dinitrogen does not have properties that would be considered as suitable for life from a terran perspective (Table 7.2). However, Bains (2004) hypothesized that silanols could dissolve in liquid nitrogen on very cold planetary bodies at concentrations sufficient to be precursors of life. Nitrogen may also occur in mixtures such as many of the other solvent candidates. While the surface liquids on Titan are a mixture of methane and ethane, substantial amounts of nitrogen from the atmosphere are thought to be dissolved into the hydrocarbon mixture, which would alter its properties significantly (Bains 2004; Lorenz and Lunine 1997; Thompson et al. 1992).

7.4 Quantitative Assessment of Solvent Candidates

In this section we will attempt to make a quantitative assessment regarding the suitability of a compound as an alternative solvent for life. There are some properties that are advantageous for life independently of the biochemistry of the living organism. Abundance is a definite advantage and may be the primary reason why life on Earth uses water as the universal solvent. Local abundance is most important for the solvent to be available for life processes, but overall cosmic abundance is relevant as well. If a compound is cosmically very rare a suitable fractionation mechanism has to be available to provide the compound in sufficient quantity. Aside from abundance, the most important property is being in a liquid state at the prevailing temperature of the local environment. The enthalpy of fusion and vaporization indicates how good a heat insulator the solvent is, and the dipole moment of the compound gives a general measure of its ability to dissolve other compounds (for life based on non-polar polymeric chemistry this criterion would be applied differently; for the present analysis that possibility will be disregarded).

A quantitative estimate of the feasibility that a given solvent could be effective in a particular planetary environment is shown in Table 7.3. The metric is obtained by assigning +1 to four favorable characteristics – cosmic abundance, local abundance, enthalpy of vaporization, and dipole moment; by assigning −1 for unfavorable instances of the same characteristics; and by assigning 0 to cases that fall between clearly favorable and unfavorable characteristics. A fifth property – liquid at prevailing local temperature – is of such obvious importance that +2 is assigned for favorable cases, −2 for cases in which the solvent cannot be liquid at the prevailing temperature, and 0 for intermediate or unknown situations. The range of temperatures at which a solvent candidate is in the liquid state (at a pressure of 1 bar) is given in Fig. 7.4. Adding the assigned points for each of the five characteristics yields a single composite value for each solvent on each planetary body shown in Table 7.4.

This estimate is obviously crude and speculative to a large degree, and we certainly have not considered all possible solvents. A more precise and systematic analysis may emerge from further research, a consideration of other relevant variables,

Table 7.3 Feasibility of selected solvents for particular planetary environments

Solvent	Earth					Icy satellites					Gas giants				
	C	L	T	E	D	C	L	T	E	D	C	L	T	E	D
H_2O	+	+	++	+	0	+	+	0	+	0	+	−	0	+	0
NH_3	+	−	−−	0	0	+	−	++	0	0	+	+	0	0	0
HCN	0	−	++	0	+	0	−	−−	0	+	0	−	0	0	+
HF	−	−	0	0	0	−	−	++	0	0	−	−	0	0	0
H_2S	−	0	−−	−	−	−	−	++	−	−	−	0	0	−	−
CH_3OH	0	−	++	0	+	0	−	++	0	+	0	−	0	0	+
C_2H_6	0	−	−−	−	−	0	−	++	−	−	0	−	0	−	−

Solvent	Io (near subsurface)					Titan surface					Titan subsurface				
	C	L	T	E	D	C	L	T	E	D	C	L	T	E	D
H_2O	+	−	0	+	0	+	0	−−	+	0	+	0	−−	+	0
NH_3	+	−	0	0	0	+	0	−−	0	0	+	+	++	0	0
HCN	0	−	−−	0	+	0	0	−−	0	+	0	0	−−	0	+
HF	−	−	0	0	0	−	−	−−	0	0	−	−	0	0	0
H_2S	−	+	++	−	−	−	0	−−	−	−	−	0	++	−	−
CH_3OH	0	−	0	0	+	0	0	0	0	+	0	0	++	0	+
C_2H_6	0	−	0	−	−	0	+	++	−	−	0	+	++	−	−

Cosmic Abundance (C): + = major component on planetary bodies or in interstellar space; − = found only in trace amounts

Local Abundance (L): + = major constituent in local environment; − = trace amounts or less in local environment

Thermal Range (T): ++ = liquid at prevailing local temperature; −− = liquid outside of prevailing local temperature

Enthalpy of Vaporization (E): + => 40 kJ/mol; − =< 20 kJ/mol

Dipole Moment (D): + => 2; − = <1

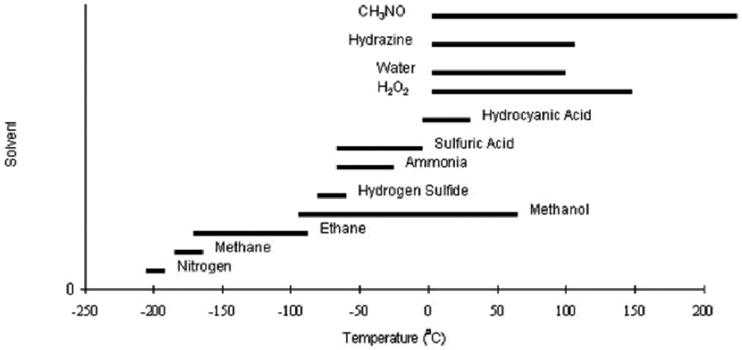


Fig. 7.4 Temperature ranges for solvent candidates to occur in the liquid state (at 1 bar)

and a more highly differentiated system of weighting the different factors. Nonetheless, some generalizations can be gleaned from even this preliminary analysis. These include the inference that water is the best solvent on warmer bodies, but methanol may be superior on some colder worlds; that ammonia or ammonia-water mixtures (with ammonia being the "antifreeze" for water) may be an important solvent on the colder worlds as well (also supported by Leliwa-Kopystyski (2002)); and that despite some favorable properties, hydrocyanic acid, hydrofluoric acid, and hydrogen sulfide do not appear particularly advantageous under any conditions.

With respect to specific planetary bodies, Table 7.4 suggests the following: (1) water is clearly the best solvent for Earth; (2) water is also the best solvent, perhaps in combination with ammonia and methanol, beneath the surface of the icy satellites; (3) the gas giant planets do not favor any particular solvent except possibly water and ammonia within a particular thermal and pressure range; (4) the special circumstances of Io make it difficult for any solvent to function there, though some combination of water and H_2S might work beneath the surface; (5) Titan's surface is inhospitable for any other than organic solvents; while (6) the subsurface of Titan could function with a combination of organic solvents, ammonia, and water.

In conclusion, Table 7.4 suggests that other solvents may be more favorable under the many environmental conditions likely to be found on other worlds that differ

Table 7.4 Summary assessment of selected solvent candidates for certain planetary environments

Solvent	Earth	Icy Satellites	Gas Giants	Io (near subsurface)	Titan Surface	Titan Subsurface
H_2O	+4	+3	+1	+1	+1	0
NH_3	−1	+1	+2	0	0	+3
HCN	+1	−1	0	−1	0	0
HF	−2	−1	0	−2	−3	0
H_2S	−4	−3	−3	0	−4	−2
CH_3OH	+1	+1	0	0	+1	+2
C_2H_6	−4	−2	−3	−3	0	0

from those on the Earth's surface. A good example is Titan, where water is in the solid state and ethane and methane are liquids, making them more suitable solvents. Over a large range of circumstances, however, it does appear that water is an adequate if not preferred solvent. Nevertheless, many more possibilities are worthy of investigation, such as the solvent dinitrogen, which would receive a favorable rating for Triton, a very cold icy satellite.

7.5 Some Additional Thoughts

Except for the fundamental thermodynamics of its constituent molecules, there is probably no property of a living system that is more important for determining its characteristics than the nature of the solvent in which the system originated and evolved. Since the solvent determines the thermal limits within which chemical reactions can take place, the type of molecules that dissolve and do not dissolve, and the nature of the chemical interactions that can occur, both among the molecules and between them and the solvent, it follows that the total chemical makeup of the living system is a consequence of the solvent in which it occurs.

If our Solar System is any indication, Earth-like planets are relatively rare, while planetary bodies that are either smaller and much colder, or larger and gaseous, are more frequently occurring. Both conditions render water useless as a solvent, but raise the prospects that an alternative solvent could be an effective medium for energy flow through chemically complex systems. Among the candidates are compounds that are not rare. Even those that are cosmically uncommon, like the sulfur-based solvents, may occur at critical densities under specialized circumstances (as on the volcanic planetoid, Io). In each case, however, the alternative solvent will almost surely foster a very different biochemistry from that which thrives in an aqueous environment. It is by no means apparent that exotic biochemical systems unfamiliar to us are less plausible under exotic conditions. As defined earlier, the essence of life has to do with complexity, energy flow, and information – none of which is limited in principle to the biochemical system with which we are familiar on Earth. In searching for life beyond Earth, we would therefore be well advised to expect the unusual.

The possibility does remain that the thermodynamic properties of any molecule that could undergo complex reactions and be assembled into stable macromolecular form is strictly constrained to conditions under which only water is an adequate solvent. Until research on complex chemical interactions in solvents other than water becomes more common, this possibility cannot be ruled out. If it should turn out that only water is an adequate solvent, the implication would be that life is likely to be restricted to water-abundant planetary bodies such as Earth, Mars and Europa. Even if this were the case, the astronomical number of planetary bodies that surely exist in the universe, combined with the abundance of water throughout the cosmos, makes it possible that life even as we do know it may be widespread. Our hunch, however, is that the nature of life is broader and more pervasive than most of us imagine.

7.6 Chapter Summary

Water is an ideal solvent for the complex chemical systems that constitute life on Earth, because of its broad thermal range of liquidity corresponding to Earth's average temperature and atmospheric pressure, and because of other characteristics that make it both an excellent physical buffer and advantageous medium for complex chemical interactions among the biomolecules that have evolved under the physicochemical conditions prevailing on Earth.

On other worlds where temperatures and pressures are different, other solvents are more likely to be found in the liquid state. Many of them have properties that make them adequate, if not advantageous, as solvents for complex chemical systems. This includes, in particular, polar solvents like ammonia, hydrocyanic acid, and methanol. Under specialized conditions, others such as hydrogen sulfide and sulfur dioxide, could serve as solvents as well. Likewise, non-polar solvents like methane and ethane can be stable liquids under some conditions. While each of these could in principle host complex biochemical interactions, the nature of the molecules that would thrive in a given solvent would be dependent on the nature of that solvent. On worlds where the physicochemical conditions require that a solvent other than water provide a liquid medium, the conditions for the origin of biomolecules and the evolution of their variations and transformations would be different, and likely would result in the elaboration of a biochemical system different from that known to us from the one example of life on Earth.

Chapter 8
Habitats of Life

There are four principal habitats in which life may exist – the surface of a planetary body, its subsurface, its atmosphere and space. From our own experience we know that life does exist on the surface of a planet, in its subsurface and transiently at least in the atmosphere. Where it is present, it exists in a surprising diversity and in a variety of microhabitats, from deep caverns (Hose et al. 2000; Melim et al. 2001) to hydrothermal fluids and hot springs of various chemistries (Jannasch 1995; Rzonca and Schulze-Makuch 2002), to the frozen deserts of Antarctica (Friedmann 1982; Sun and Friedmann 1999). In this chapter we will elaborate on the principle habitats, the constraints they impose on life, and the possibilities they provide.

8.1 Life on the Surface

We live on the surface of our planet, which makes us biased towards it being the common case. However, there are various factors that make life on the surface of a planetary body challenging. Life on the surface is much more exposed to environmental extremes of temperature, wind, radiation and humidity than, for example, life thriving in the subsurface protected by thick layers of soil and rock. A planet or moon with life on its surface requires an atmosphere to keep essential liquids on the surface from evaporating into the vacuum of space, to protect life on the surface from harmful cosmic and UV radiation (the degree of protection depending on the composition and thickness of the atmosphere), and to protect the surface to some degree from potentially devastating meteorite impacts. Smaller meteorites burn up in the atmosphere and the effect of larger ones is mitigated. However, meteorites still pose a grave threat to life on the surface of any planet. For example, the surface of our planet may have been sterilized several times early in Earth's history (Sleep and Zahnle 1999). In that case life could have only survived deep in the crust and then resettled the surface again after the effects of the impact were diminished with time. Life on the surface is also very susceptible to large-scale climatic fluctuations. Earth experienced several episodes of global freezing ("Snowball Earth") events (Hoffman et al. 1998; Kirschvink et al. 2000), when it substantially or perhaps completely froze over. Mars is currently a cold, arid planet with little or no

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

Table 8.1 Total carbon content in 10^{15} g of carbon

Ecosystem	Plants	Soil and aquatic prokaryotes	Subsurface prokaryotes
Terrestrial	560	26	22-215
Marine	1.8	2.2	303
Total	561.8	28.2	325-518

Note: Data from Whitman et al. (1998)

liquid water on its surface, though it probably had oceans on its surface earlier in its history (Dohm et al. 2000; Head et al. 1998). Venus, probably wet and somewhat Earth-like early in its history, experienced a run-away greenhouse effect with current surface temperatures above 400°C. If life as we know it ever existed on the surface of Venus, it does not anymore.

However, life on the surface does provide two critical advantages: (1) the use of visible light as an energy source and (2) space to expand. Life on Earth without photosynthesis would be much more limited and may have remained in the microbial evolutionary stage. The biomass contribution via photosynthesis is immense; the total carbon content of plants is estimated to be 560 Pg ($1\,\mathrm{Pg} = 10^{15}\mathrm{g}$) for terrestrial plants and 1.8 Pg for marine plants (Schlesinger 1997, Table 8.1). Space to expand may not be very important to microbial life, because most microbial life easily fits into the pore spaces of rocks. However, for complex multicellular life the surface does provide a challenging but suitable environment for growth and development to macroscopic forms. Thus, it is not a surprise that we as macroscopic organisms populate a planet in a climatically fairly stable environment with enormous amounts of liquid water. However, life remains very vulnerable on a planetary surface. Threats include a large meteorite impact that could destabilize the climate or sterilize the surface of the planet, a cosmic disaster such as a nearby supernova-explosion that showers the surface with radiation, or exhaustion of fuel in the planet's central star, leading to the engulfment of the planet, similar to our Sun which will expand to become a red giant.

8.2 Life Beneath the Surface

Microbes, fungi, and small animals have lived in the upper layers of the soil since their first expansion from water onto the land. More recent evidence suggests that microbial life penetrates to great depths, beneath the surface of both the land and ocean bottom, deep into the crust (Johnson and Party 2003; Pedersen and Ekendahl 1990). Estimates indicate that the total amount of carbon in subsurface organisms may equal that of all terrestrial and marine plants (Table 8.1).

Microbial life appears to be abundant in various types of subsurface habitats such as the oceanic crust, and continental sedimentary and igneous rocks. While the

Table 8.2 Total number of prokaryotes in unconsolidated subsurface sediments

Depth Interval (m)	Cells/cm^3, x 10^6	Deep Oceans (no. of cells, x 10^{28})	Continental Shelf and Slope (no. of cells, x 10^{28})	Coastal Plains (no. of cells, x 10^{28})
0.1–10	220	66.0	14.5	4.4
10–100	45.0	121.5	26.6	8.1
100–200	6.2	18.6	4.1	1.2
200–300	19.0	57.0	12.5	3.8
300–400	4.0	12.0	2.6	0.8
400–600	7.8	NA	10.1	3.2
600–1200	0.95	NA	3.7	1.2
1200–2000	0.61	NA	3.2	1.0
2000–3000	0.44	NA	2.6	0.9
3000–4000	0.34	NA	NA	0.7

Note: Data from Whitman et al. (1998); NA = not available.

overall number of organisms generally decreases with depth (Table 8.2), because of the huge amount of volume, the total subsurface biomass is enormous (Gold 1992).

Some distinct advantages over life at the surface can readily be appreciated. Temperatures and vapor pressures are stable, and protection from damaging radiation is afforded. The obvious disadvantages are the unavailability of sunlight as an energy source, and limitations on organismic size. The latter restriction results from the fact that pore spaces that serve as habitats are generally small in size, and become smaller with increasing depth. Thus, life at any substantial depth is probably restricted to microscopic dimensions, but this allows for a great range of living systems, as evidenced by the variety of microbial life within the crust of the Earth. Microbes indigenous to crustal rocks have been isolated from a depth of 2,800 m in continental sedimentary rocks (Onstott et al. 1999) and 5,300 m in igneous rocks (Pedersen 2000). Temperature increases with depth and imposes an absolute limit on the temperature and pressure conditions under which water can remain in the liquid state. The amount of dissolved solids in the ground water also tends to increase with increasing temperature adding osmotic stress to any organism. Thus, there is an absolute limit to the depth at which organisms can thrive. The absolute limit of this depth, however, is very variable due to the heterogeneous conditions in the crust and variable geothermal gradients.

While sunlight is not available to provide energy in a subsurface environment, other sources of free energy are readily available. Chemical energy, both inorganic and organic, may be found in abundance, depending on the planetary body in question. Other energy sources such as those discussed in Chap. 5 may also be an option for certain subsurface environments. Availability of energy should not be a problem, if the planet or moon is large enough to have a metallic core and decaying radioactive elements as an energy source. In principal, energy in many forms can be transformed into biologically usable energy. If the availability of energy, then, is not an issue, and the living system is microscopic in size, the advantages of the subsurface habitat become overwhelmingly favorable for the persistence of life.

Although the subsurface clearly favors microbial life, there are a few niches and possibilities for macroscopic life. A bizarre example of a macroscopic subsurface organism is a fungus of the *Armillaria* family, which is pathogenic to trees (Armillaria root disease). These fungi are incredibly large, with one *Armillaria ostoyae* organism of genetic uniformity detected at a size of 9.65 km^2 (Ferguson et al. 2003). A subsurface niche particularly favorable for macroscopic forms is the cave environment, to which various types of animals on Earth are ideally adapted. Caves do not occur only where karstic sedimentary rocks are present, but also commonly form in cooling lava flows. Thus, they can be expected to be common on other planetary bodies as well. Several locations have been suggested for Mars (Fig. 8.1). Due to the relatively low gravity on Mars, lava tube caves can be expected to be larger and more common than on Earth.

On all the terrestrial planets and all the larger satellites, subsurface strata probably exist where thermal stability and some solvent in liquid form can exist. Thus, the presence of at least microbial life at multiple sites beneath the surface of planets and some of their satellites throughout the Solar System is distinctly possible. The larger icy satellites that show evidence of tidal flexing or other energetic perturbations, such as Europa, Ganymede, Enceladus, Iapetus, Titania, and Triton, have at least the potential for liquid water beneath their icy crusts (Carr 1986; Chyba 1997; Coustenis and Lorenz 1999; Khurana et al. 1998; McKinnon and Kirk 1999). Evidence for a substantial amount of ground water within the upper crust of Mars is

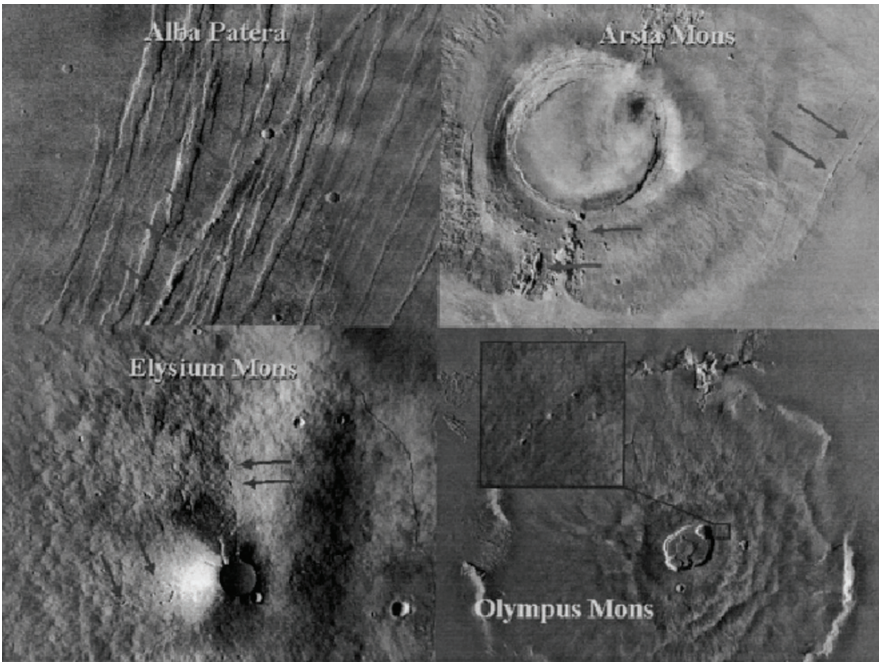


Fig. 8.1 Collapsed lave tubes on Mars highlighted by arrows (composite image provided by R.D. "Gus" Frederick, Silverton, Oregon, based on data from NASA)

now compelling (Boynton et al. 2002; Carr 1996; Malin and Edgett 2000a; 2000b; Schulze-Makuch et al. 2004). Thus, aquatic life approximately as we know it on Earth is even possible in those situations. While the surface of Io is normally frozen, periodic lava flows heat it from above, and tidal flexing heats this rocky planetoid from below. Titan is colder still, but as the second largest satellite in our Solar System, it is obviously large enough for radiogenic heating to possibly liquefy mixtures of ammonia, water, and organic compounds which may be sequestered beneath its surface (Coustenis and Lorenz 1999). Both of these satellites represent more unusual but certainly possible subsurface habitats for life. Even Mercury and the Moon, both of which show evidence of some polar ice (Showstack 1998; Slade et al. 1992), and even Venus, where liquid silicates or water in a supercritical state could exist beneath the surface, cannot be completely ruled out as sites of possible subsurface life (Schulze-Makuch et al. 2002b). "Run-away" planets that were ejected from their Solar System and are now moving through empty space represent another theoretical possibility (see Chap. 9.5).

Stabilizing selection, which tends to narrow variation and optimize adaptive advantages (Chap. 4), is particularly effective in relatively constant habitats over long periods of time. Thus, life that has been optimized by stabilizing natural selection for a subsurface existence should be extremely durable and persistent. It also tends to be static, evolving little from the form and function that characterized it upon its introduction to the stabilized habitat. Subsurface environments may thus be repositories for early forms of life that have changed little since conditions made life on the surface untenable. On Earth, the microbes that are found at the greatest depths beneath the surface tend to be members of the evolutionarily ancient Archaea, or Eubacteria with ancestral forms of chemoautotrophic metabolism, and may include some types of nanobacteria. It follows that life on other worlds is most likely to be found beneath the surface of those worlds, where it is probably microscopic and relatively unchanged from an ancestral state.

8.3 Life in the Atmosphere

The possibility that the gaseous envelope of planets and those satellites that hold an atmosphere could serve as a suitable environment for life is generally viewed with skepticism. This probably derives from our familiarity with the nature of the atmosphere and of life on Earth. We are aware of the diversity of terran life, both in the subsurface and on the surface of Earth, but no organism that spends its entire life cycle in the atmosphere has been documented. The lack of green clouds is visual evidence for the absence of concentrated airborne photosynthesis. And even the smallest organism has a higher density than air. Nevertheless, it has been recognized for some time that bacteria exist in cloud aerosols on Earth (Gislén 1948) and that rain and fog water rich in nutrients may provide a good substratum for microorganisms (Fuzzi 2002; Herlihy et al. 1987). While the dispersal of microorganisms by wind is well accepted (Schulze-Makuch et al. 2003) and may even occur within the stratosphere (Imshenetsky et al. 1978), the claim that microbes independently grow and reproduce in Earth's atmosphere is controversial. Dimmick et al. (1979) reported the division of bacteria on airborn particles and more recently Sattler et al. (2001) analyzed condensing clouds at the Sonnblick Observatory in Austria at an altitude of 3106 m, and suggested growth and reproduction of microbes in supercooled cloud droplets.

However, in general the atmosphere of Earth is a poor analogy for atmospheric habitats where life would be more likely; namely that of planetary bodies or satellites where gases are denser, and liquids are found in larger aggregates with longer survival times. Also, any particles in the Earth's atmosphere have typically a short residence time in the range of several days only. Most atmospheres of other planetary bodies we know are dynamically much more stable in the vertical direction and particles do not precipitate out as frequently (e.g., Venus), thus particle residence times are much longer. On other planets various chemical compounds might serve as nutrient sources, such as H_2S in the case of Venus (Schulze-Makuch and Irwin 2002b) or complex carbon compounds in the case of gas giants like Jupiter (Boston and Stoker 1983; Stoker et al. 1990) or carbon-rich moons like Titan. The composition of some planetary atmospheres is provided in Table 8.3.

If, instead of the unstable and thin atmosphere of Earth, the denser atmospheres of Venus, Titan, and the gas giant planets are taken as a prototypical atmospheric habitat where life could exist, some positive advantages can be noted. For instance, many of the denser atmospheres are more stable and more richly endowed with organic molecules. Sunlight, especially in the ultraviolet frequencies, breaks apart simple organic molecules in the planetary atmosphere, producing ions, free radicals,

Table 8.3 Composition of some planetary atmospheres (modified from Lewis 1995)

Planetary body	Major compounds	Minor compounds	Trace compounds
Venus	CO_2 (96.5%), N_2 (3.5%)	SO_2, Ar, CO, H_2O, He, Ne, H_2S	HCl, Kr, HF, COS
Earth	N_2 (78.1%), O_2 (20.9%), Ar (0.9%)	H_2O, CO_2, Ne, He, CH_4, Kr	H_2, N_2O, CO, Xe, O_3, NH_3, SO_2, H_2S, CH_2O, NO_2, NO, HCl,
Mars	CO_2 (95.3%), N_2 (2.7%), Ar (1.6%)	O_2, CO, H_2O, Ne,	Kr, Xe, O_3, CH_4
Jupiter	H_2 (82%), He (18%)	CH_4, H_2O, NH_3, C_2H_6, PH_3	H_2S, C_2H_2, CH_3D, HCN, CH_3NH_2, N_2H_4, GeH_4, CO
Saturn	H_2 (94%) He (6%)	CH_4, H_2O, NH_3, C_2H_6, PH_3	H_2S, CH_3NH_2, C_2H_2, CH_3D, HCN, N_2H_4, GeH_4, CO
Titan	N_2 (94%), CH_4 (6%)	Ar, H_2, CO, C_2H_6, C_3H_8, C_2H_2	C_2H_4, HCN, CH_3CCH, HC_4H, HC_3N, NCCN, CO_2

Note: Major compounds are defined here as those compounds that have a mole fraction larger than 0.005 in the respective atmosphere, minor compounds as having a mole fraction between 0.005 and 10^{-6}, and trace compounds as having a mole fraction smaller than 10^{-6}.

and other highly reactive molecules that combine to form complex, energy-rich compounds. These heavier molecules sink until they reach a level where they are destroyed by temperature and pressure, as likely occurs on the gas giants, or they accumulate on the planetary surface, as on Titan. Sagan and Salpeter (1976) suggested that life could exist at a level of the Jovian atmosphere where descending organic molecules could be captured and used for energy. The organic rich atmosphere of Titan, with a density 50% greater than that of Earth, conceivably could support life in the same way.

Several challenges to life in an atmosphere must be met. A main problem is that the density of gas molecules in an atmosphere is much lower than on a planetary surface, so to achieve the level of interactions between molecules required for living processes, the density of the organism is inevitably going to exceed that of its surroundings, and buoyancy will be a problem. However, atmospheres can be very dense, achieving liquid-like states at sufficiently high pressures. And just as fishes evolved air bladders to give them buoyancy in water on Earth, an airborne microbe conceivably could evolve a gas-filled organelle that radically increases its volume to a point where its average density is sufficiently low to keep it afloat in the air. Another potential problem could be exposure to high radiation levels, thus conditions that would promote the survival of atmospheric organisms would favor the evolution of radiation protection mechanisms.

A critical problem for indefinite survival in the atmosphere is the question of a suitable solvent for the support of life-sustaining reactions. Both liquids and solids are generally present in an atmosphere, such as liquid water and aerosols in Earth's clouds. But their abundance in the atmosphere compared to the planetary surface is very low. To be effective solvents, the liquids need to be condensed into droplets of sufficient size and longevity to provide a transiently stable pool of airborne liquid. Such droplets do appear to exist in the upper atmosphere of Venus (Grinspoon 1997), and perhaps in other dense atmospheres elsewhere.

Another potential problem is the scarcity of a solid substratum. The interface of a liquid solvent with a solid surface is presumed to provide a much more likely circumstance for the development of complex chemistry, simply because the degrees of freedom for interacting components is reduced from three dimensions to two. Thus, the origin of life in particular, seems much more likely to come about at interfaces than in three-dimensional volumes of gasses or liquids. Once underway in its confined cellular compartments, life would have an easier time of surviving in three-dimensional volumes, as many organisms in water, and some forms in air, do on Earth. The plausibility of life in an atmosphere is thus higher on those planetary bodies where conditions at the surface were amenable for the origin or early cultivation of life on a solid substrate. This would mean that Venus and Titan, for example, would have experienced a greater chance for the origin of surface (or subsurface) life that eventually evolved adaptations for an airborne existence, than would the gas giant planets, where a solid substrate may never have existed under conditions appropriate for life to originate or take hold. For an alternative view, see Feinberg and Shapiro (1980) who consider that the absence of a surface might be an advantage, because it would allow free motion between different environments, making it possible for an organism to invent its own disequilibrium by moving from one condition to another.

As an instructive example, we will consider the case of Venus in more detail. There is evidence for an early ocean on Venus while the early Sun was fainter than it is now. Life on Earth developed very fast once conditions became appropriate (Chap. 4). The same could have occurred on Venus. Alternatively, life may have been transplanted from Earth or Mars to Venus via meteorite impacts. Either way, life may have become established on Venus at an early point in its history. We know that conditions on the surface of Venus are now inhospitable to life as we know it, with temperatures around 733 K ($\sim$ 450°C) and extreme desiccation. The change in planetary surface conditions was presumably caused by a run-away greenhouse effect as the Venusian atmosphere moved toward its present composition of 97% CO_2. If the environmental transformation occurred slowly enough, microbial life could have adapted to life in the clouds of Venus by directional selection (Schulze-Makuch et al. 2003).

Several factors would support such a life style in the atmosphere of Venus: (1) The lower atmosphere is thick, so under liquid-like conditions microbial transport between the surface and the cloud layer would be easier than in Earth's atmosphere. (2) The clouds of Venus are much larger, providing more continuous and stable environments than clouds on Earth. (3) Current conditions in the lower cloud layer of Venus are relatively benign at 300-350 K, 1 bar pressure and a pH of 0 – conditions of temperature, pressure and pH under which thermoacidophilic microbes are known to thrive on Earth (these are also some of the oldest known forms of life on Earth!) (4) Cloud particles are projected to last for several months in the Venusian atmosphere compared to only days on Earth (Grinspoon 1997). (5) The Venusian atmosphere is super-rotating, thus cutting the nighttime significantly and thereby allowing for more photosynthesis. (6) Water vapor is reasonably dense in the lower cloud layers of Venus. (7) Oxygenated species such as SO_2 and O_2 coexist and are in thermodynamic disequilibrium with reducing species such as H_2S and H_2 in the Venusian atmosphere.

An ultraviolet absorber has been detected in the Venusian atmosphere that may be related to microbial UV protection and possible photosynthesis (Schulze-Makuch et al. 2004b; Fig. 8.2). These and other aspects of the possibility of life in the clouds of Venus have been raised by different authors over the years (Sagan 1961; Feinberg and Shapiro 1980; Grinspoon 1997), and have been discussed more recently in the context of a proposed sample return mission to Venus (Schulze-Makuch et al. 2003; 2004; 2005a). These authors concluded that Venus provides one of the best possibilities for harboring atmospheric life in the Solar System. Since it is also the most accessible planetary body beyond the Moon a sample return mission lies within the capabilities of existing technology.

Venus illustrates nicely the theoretical potential for atmospheric life. Nonetheless, the problems for persistence of living systems in an atmospheric habitat are formidable, so their existence warrants a lower probability than life on the surface, and much lower than life beneath the surface, on other worlds.

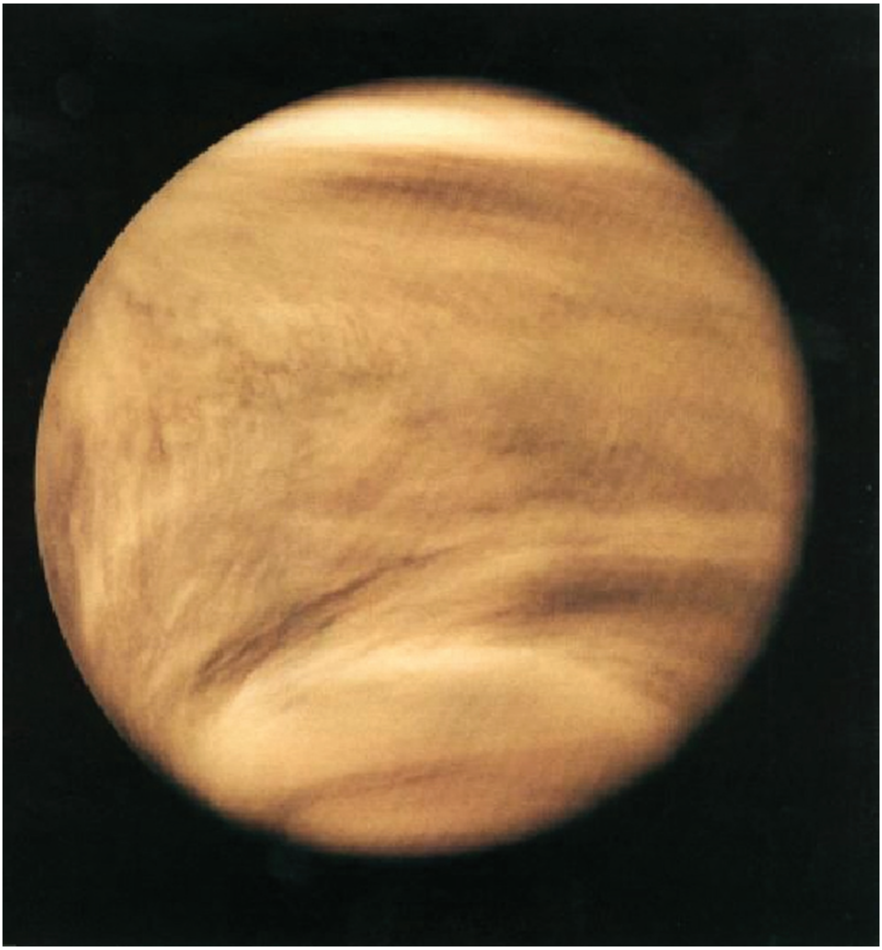


Fig. 8.2 Ultraviolet image of the clouds of Venus as seen by the Pioneer Venus Orbiter (5 February 1979). The dark streaks are produced by absorption of solar UV radiation. Source: NSSDC, http://nssdc.gsfc.nasa.gov/photo_gallery/photogallery-venus.html, image pvo_uv_790205

8.4 Life in the Space Environment

If the low density of matter would make life-supporting interactions between molecules in a gaseous atmosphere difficult to maintain, the problems are much more severe in space. The damaging potential of ultraviolet and particle radiation, the extremely low temperature and nonexistent vapor pressures, and the homogeneity of empty space further add up to such a hostile environment that outer space can not be regarded as a likely habitat for life. However, the possibility that life could survive interplanetary travel through space in the protective sanctuary of meteorites or even dust particles cannot be discounted. There is increasing evidence that microbes, especially when in the dormant spore form, can survive space conditions fairly well (Horneck 1981; Koike et al. 1991; Nicholson et al. 2000; Horneck et al. 2008). This is especially the case if the microbe is surrounded by a thin layer of solid material that would shield it from cosmic and UV radiation. The effect of space vacuum is another constraint. Some space experiments have shown that up to 70% of bacterial and fungal spores survive 10 days exposure to space vacuum, even without any protection (Horneck 1993). Survival rates increased when *Bacillus subtilis* spores were embedded in salt crystals or if they were exposed in thick layers (e.g. 30% spore survival after nearly 6 years when embedded in salt crystals (Horneck et al. 1994). Spores from thermophilic bacteria are generally more resistant to heat than mesophilic spores (Ashton and Bernard 1992). Other studies showed that bacterial survival rates decreased by 2 to 4 orders of magnitude when exposed to space vacuum and short wavelength UV radiation (Saffary et al. 2002), but confirmed the protection provided by salt crystals (Mancinelli 1989). An intriguing example of microbial survival under space conditions was the reported recovery of living bacteria from the Surveyor 3 spacecraft after three years of exposure on the lunar surface (Mitchell and Ellis 1971), although this claim has been disputed. Nevertheless, microbes do apparently have the possibility to survive for extended periods in space. *Deinococcus radiodurans* appears to accomplish its resistance to radiation and desiccation by having multiple copies of DNA, large organelles, a large nucleus, a thick membrane, having the DNA in a ring-like structure (Levin-Zaidman et al. 2003), and by possessing a high redundancy of repair genes, but most microbes accomplish this feat by sporulation. During sporulation cytoplasm and genetic material is sealed off by the inner cell membrane. The DNA is then protected by thick layers of protective membranes (Fig. 8.3), which are only permeable to nutrients that the organism needs for germination.

Microbes can survive in this type of dormant phase for extremely long time. Cano and Borucki (1995) isolated a strain of *Bacillus sphaericus* from an extinct bee trapped in 25-30 million year old amber, while Vreeland et al (2000) claimed to have isolated a 250 million year old halotolerant bacterium from a salt crystal.

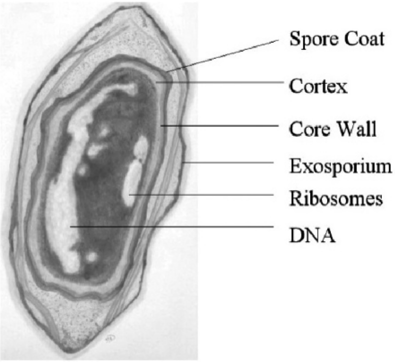


Fig. 8.3 Bacillus subtilis spore, schematic. The DNA is contained in the nucleoid (light regions) within the spore core. The core is surrounded by the protective cortex. The long axis of a *B. subtilis* spore is about 1.2 micrometers (Nicholson et al. 2000). Drawing provided by Chris D'Arcy, Dragon Wine Illustrations, El Paso, Texas

Findings such as these lend new credibility to the idea of panspermia (Arrhenius 1903; Arrhenius 1908), the transfer of organisms between planetary bodies. However, any organism taking this type of journey would have to survive a series of hazards, including (1) survival of the meteorite impact that ejects the organism into space from the planet of its origin, (2) maintenance of viability for long durations of time inside the meteoritic material, (3) intense UV and cosmic radiation, cold, and vacuum, and (4) the shock and heat of impact on the planetary body to which the organism is transferred. Mileikowsky et al. (2000) and Clark (2001) provided estimates on the likelihood of microbial survival for the different steps. Davies (1996) analyzed this scenario for the Mars-Earth case and concluded that it is a plausible scenario. A critical parameter is travel time, which can be as little as 2 months for microscopic particles from Mars to Earth (Moreno 1988). Boulder-size rocks, however, have been estimated to need a mean travel time of several hundred thousands to millions of years for the same distance (Melosh 1988). Nevertheless, interplanetary travel from one planetary body to another within a Solar System is a definite possibility. However, panspermia between different Solar Systems is extremely unlikely given the great distances between Solar Systems and the low statistical probability for a life-transporting meteorite to intersect with a habitable planet.

It should be pointed out that viability in the space environment very likely involves only dormant forms of life. Active forms of life as speculated by Hoyle (1959; see Chap. 9.2) could not exist due to the harsh radiation environment, cold vacuum conditions and low density, plus the problem of origin. The idea that an ancestor of such an organism would have originated on a planetary surface and later adapted to life in space similar to marine animals and plants that conquered the land during Earth's history, seems unreasonable. There are many transitional habitats between land and sea, but not between a planetary atmosphere and space. Evolutionary pressure would have had to push certain types of organisms to adapt to life in the atmosphere, then pressed it to higher and higher levels of the atmosphere until finally the organism would have to be capable of living in space. Over Earth's history of immense evolutionary pressure during certain time periods, only a tiny fraction of terrestrial organisms adapted even to a life style involving the atmosphere. The major problem appears to be that chemical nutrients that are needed for growth in addition to light are not present in high enough concentrations in the higher atmosphere and certainly not in space.

8.5 Cosmic Biogeography

The possibility of worlds beyond our own has been appreciated since the speculations of the early Greeks. In 1584, Giordano Bruno asserted that there were "countless Suns and countless earths all rotating around their Suns," but confirmation of other Solar Systems with rotating, planar clouds of dust and gas that could lead to planet formation was not made until infrared observations were conducted of such a disk of dust surrounding the star Beta Pictoris, in the 1980s (Smith and Terrile

1984). Today we know of many extrasolar planets and even many star systems with multiple planets, but are they habitable? As pointed out by Cockell and Westall (2004), the assessment of actual or past habitats on other planets poses a variety of problems for different reasons: (1) it is logistically difficult for scientists to visit extraterrestrial sites of interest, (2) data are limited and may have been acquired by just a few spacecrafts or by ground observations from Earth, (3) the data gathered may not have an astrobiological focus, because that might not have been the focus of the mission in the first place, and (4) environmental conditions on other planetary bodies are often very different from conditions known to support life on Earth, thus inhibiting any analog parallels that can be used to assess the possibility of life.

The traditional approach to habitability is to define a "Habitable Zone (HZ)". The concept of the HZ of a star is based on equating the possibility of life with the existence of liquid water on the surface of a planet orbiting the star. This is motivated by the fact that liquid water is thought to be an important precondition for most, if not all forms of life (Bennett et al. 2003; Goldsmith and Owen 2003). The position and extent of the HZ depends on the stellar luminosity, even though the exact boundaries of circumstellar HZs vary from system to system because planets have different volatile inventories, albedos, and masses, which affect the rate of atmospheric escape of water near the inner edge and the rate of global refrigeration near the outer edge. The limits of the solar HZ often quoted are those of Kasting et al. (1993) obtained by a radiative-convective model for the Sun-Earth system. However, life may also be present outside of a traditionally defined HZ, such as in the putative subsurface ocean of Jupiter's moon Europa (Figueredo et al. 2003; Schulze-Makuch and Irwin 2002a), or in the clouds of Venus (Schulze-Makuch et al. 2004). A life style between dormant and proliferative forms may expand the outer edge of the HZ, as it requires only periodic stability of liquid water on a planetary surface (Schulze-Makuch et al. 2005b). Also, life may be based on a novel biochemistry with different HZ requirements around a star.

However, following the traditional approach, the inner edge of the current HZ of our Solar System lies between 0.95 AU, where the Earth's stratosphere would become moist, and 0.84 AU, where the surface temperature would climb dramatically because of a positive feedback loop (Kasting et al. 1993). The outer edge of the HZ is determined by the formation of CO_2 clouds, which cool a planet's surface by increasing its albedo and by lowering the convective lapse rate. Thus, the outer edge of the HZ would be between 1.40 and 1.46 AU (or up to 2.0 AU for a larger planet than Mars), where clouds would snow out on to the ground causing atmospheric CO_2 levels and surface temperatures to decrease irreversibly (Forget and Pierrehumbert 1997; Williams and Kasting 1997). Work by Mischna et al. (2000) argues that the HZ of the Sun might extend up to 2.0 AU or more, allowing Mars at 1.52 AU to be well inside the HZ if it had a thick atmosphere with a strong greenhouse effect.

By analogy to the circumstellar habitable zone, the term of a Galactic Habitable Zone (GHZ) has been suggested as well (Gonzalez et al. 2001). The GHZ is defined as that region in the Milky Way where biogenic elements are available and where any life would be far enough away from the galactic center to not be exposed to disruptive gravitational forces or to too much radiation. The GHZ has been quantified by Lineweaver et al. (2004), who modeled the GHZ as an annular region between 7 and 9 kiloparsecs from the galactic center that widens with time and is composed of stars between 4 and 8 billion years old. Their assumptions for the presence of a GHZ were based on (1) the presence of a suitable host star, (2) enough heavy elements to form terrestrial planets, (3) sufficient time for biological evolution, and (4) an environment free of life-extinguishing supernovae. The concept of a GHZ has the same advantages and drawbacks as the concept of a circumstellar habitable zone. While these concepts are useful in prioritizing astrobiology targets, especially in a search for life as we know it, they do not take into account any life based on a different biochemistry, or life that simply utilizes adaptative mechanisms that don't require permanent liquid water on the planetary surface.

Much of the search for extrasolar planets (see Chap. 11.4) is motivated by the quest for terrestrial planets, for the common-sense reason that we are better qualified to recognize life as we know it, and therefore more likely to find it on smaller, rocky planets such as our own. It is important to consider, however – as we argue at numerous points in this book – that life in forms unfamiliar to us could flourish under conditions alien to the life with which we are familiar. There may thus be specialized niches for some forms of life on gas giants, or on their satellites, or on brown dwarfs or orphan planets, within radiation fields of high intensity, in liquids other than water, using metabolic systems and energy sources unlike anything we have ever seen. We have already been surprised to find, for example, that our closest star belongs to a triple star system (Alpha Centauri A, Alpha Centauri B and Proxima Centauri), and we are just starting to explore other Solar Systems. The broader mandate for space and planetary science should therefore be to characterize the full range and variety of Solar Systems, and seek in the pattern of their distribution the clues that will lead us to consider how exotic our consideration of life on other worlds should remain.

One example of where research should be expanded is the possibility of habitable planets around M stars rather than G stars like our Sun (Tarter et al. 2007). The smallest extra solar planet detected as of this writing is about 5.5 Earth masses, orbiting an M dwarf star (Beaulieu et al. 2006). M stars (also known as red dwarfs or dM stars) are the most common stars in the universe. Furthermore, because of their longevity and constant luminosities they may be hosting many habitable planets (Guinan et al. 2007). Heath et al. (1999) even suggested higher plant habitability for red dwarf planets based on possible moderate climates and global water cycles on these bodies. They also pointed to the availability of photosynthetically active radiation in the sunlight of M stars. Some properties of red dwarf stars and their relationship to planetary habitability are listed in Table 8.4.

Finally, the notion of cosmic habitability could be expanded even further. Recent research efforts, especially into the cosmological idea of inflation, suggest the highly speculative possibility of many universes existing in parallel with ours, all with different values for the cosmological constants such as the Boltzmann constant, Newton's constant, the charge of the electron, electric permittivity, magnetic permeability, the speed of light, Fermi's constant, the Planck constant, etc. If that speculation is correct, many universes could exist which would be essentially

Table 8.4 Properties of red dwarf (dM) stars and their relationship to planetary habitability (modified from Guinan et al. 2007)

M star property	Astrobiological assessment
Nearly constant luminosities over tens of billions of years	M star planets provide a stable environment for life to form and evolve within fixed habitable zones
M stars are ubiquitous, comprising >70% of stars	High chance for at least some habitable planets
Long life times (> 50 Gyr)	Especially beneficial for evolution of complex/intelligent life, because of greater evolutionary time span (compared to 4.5 Gyr for evolution on Earth)
There are many old M stars (> 5 Gyr) in our galaxy	Very old, metal poor, M stars would likely not be able to form rocky planets because of the paucity of metals. A low metal environment would also be problematic for the development of life
Theoretical studies by Boss (2006) indicate that "Super Earths" can easily form in the proto-planetary disks of M stars	Planets hosted by M stars should be at least as common as those hosted by solar-type stars. Even without much effort, several M stars have been found to host planets
HZ is located very close to the host star at <0.1–0.4 AU	The planet would easily become tidally locked, reducing likelihood of global habitability
Unlike solar-type stars, M stars have essentially no photospheric continua in the UV (<2500 Å), because of their low temperatures	While generally harmful to organisms, UV irradiation is a powerful force in evolutionary adaptation, and may also play a role in the origin of life
M stars have very efficient magnetic dynamos resulting in strong coronal X-ray, transition region FUV & chromospheric FUV-UV emissions	While generally harmful, these types of radiation are easily filtered out by planetary atmospheres and may be evolutionarily beneficial

unrecognizable to us, as, of course, would be any life existing within them. Another suggested alternative is that the fundamental constants have changed with time (Olive and Quian 2004), which, if true, would tie habitability in the universe closely to time. At the core of this problem lies a version of the anthropic principle: our universe, however unique among all the possibilities, harbors a form of life that can see it because that life evolved under those same unique constraints. Whether our universe is only a random chance event within an incredibly large number of other universes, a kind of bubble in a multiverse (Leslie 1996; Linde 1986; Rees 2001; Susskind 2005), and whether life can exist only in our type of universe, cannot currently be answered, and is perhaps not resolvable by the scientific method at all.

8.6 Chapter Summary

The human perspective of life as a planetary surface phenomenon is deceiving. The surface provides a heterogeneous environment conducive for the diversification of life over time as conditions change. It is just these circumstances, in all probability, that have given rise to macrobiological complexity on Earth. But the part of the biosphere that lies beneath the surface provides for a more stable and secure abode for life, and may even on Earth harbor a greater total biomass than is found above ground. Thus, life in the subsurface is much more likely to be the rule than the exception on other worlds. If this is so, there are compelling theoretical reasons for believing that in the vast majority of cases, such life is microscopic and relatively ancestral.

The gaseous atmosphere that surrounds planetary bodies is a much less favorable habitat for living systems. But at high densities with an appropriate mixture of chemicals and available free energy, atmospheres could harbor life. Like their subsurface counterparts they would probably be microscopic for reasons having to do with buoyancy, but because of the peculiar evolutionary trajectory that likely led to their adaptation to an aerial existence, they are more likely to be highly derived in form and function from their ancestors. Active life in space is highly improbable due to the harsh radiation environment, cold vacuum conditions and low density, relative homogeneity, and the problem of origin. However, organisms have developed protective mechanisms that allow them to travel passively through space for some time.

Habitable worlds might be widespread and would likely include planets that orbit M stars. A first attempt to search for habitable planetary bodies would consist of defining habitable zones around stars and by quantifying galactic habitable zones within our own galaxy. However, the traditional approach of the habitable zone concept is to consider only those planetary bodies as habitable that exhibit stable liquid water on their surfaces. This approach most likely omits many habitable worlds.

Chapter 9
Ideas of Exotic Forms of Life

Science and speculation have converged at the boundaries of human imagination to conceive of some very exotic states of matter and/or energy that have been claimed by their authors to represent alternative forms of life or to exhibit life-like characteristics. Those ideas have been advanced by serious thinkers and thus deserve to be evaluated in the context of our assumptions about the fundamental nature of life. We will briefly mention some of the most important ideas proposed and critically examine them in light of our proposed definition advanced in Chap. 2 that living entities are (1) composed of self-organizing, local bounded environments in thermodynamic disequilibrium with their surrounding, (2) capable of transforming energy to maintain a low-entropy state and perform work, and (3) capable of information encoding and transmission through indefinite cycles of replication. Only if all of those three criteria are met, does the proposed idea constitute a viable alternative form of life in our view.

9.1 Life Based on Spin Configurations

In Chap. 5.2.9 we discussed the possibility of obtaining energy from spin configurations. Feinberg and Shapiro (1980) took this idea a step further and speculated on the possibility of life based on spin configurations of p-hydrogen and o-hydrogen (Fig. 5.7). They suggested an organism with a helium interior, an inner o-hydrogen layer and an outer p-hydrogen layer, which would be capable of controlled processes and obtaining energy by the process described in Chap. 5.2.9. The living environment envisioned was a very cold and dark planet, just a few 10s of degrees above absolute zero. In this type of environment solid hydrogen would be floating in a sea of liquid hydrogen. An input of energy, most suitably from a faint star with emissions in the weak infrared and microwave wavelengths, would be absorbed by hydrogen, thereby transferring some of the hydrogen into the energy-rich ortho-hydrogen state. The energy stored in the o-hydrogen state would then be released when the atoms are transformed into the p-hydrogen state. Feinberg and Shapiro (1980) suggested that for such life to form, a precise arrangement of o- and p-hydrogen would need to be established.

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

However, it is difficult to envision how such an organism could perform work efficiently without chemical reactions. Second, the force that would hold the unbounded organism together against the tendency toward entropy is unclear. Specifically the inner energy-rich o-hydrogen molecules would have to be kept apart from each other to avoid catalyzing their own destruction. The function of the helium interior is unclear as well.

Feinberg and Shapiro (1980) do address the issue of replication (though not in direct association with the proposed organism). Information encoding and transmission would not need to occur chemically, but rather could be based on magnetic orientation (Fig. 9.1). The starting point would be a chain of atomic magnets with their magnetic moments aligned in variable directions. A randomly directed magnet approaching the chain would line up with its direction parallel to that of the nearest magnet. If that process were continued for many magnets, a new chain would eventually be formed that duplicates the original chain in the directional arrangement of its magnets. If the magnets in place along the chain retained their alignment and could be protected, for example from re-magnetization from an exterior field, then such an informational string would be a realistic possibility for replication and transmission of biological information. However, for such a code to be consistent with our definition of life, the code-bearing material would need to be distinct from the living entity that harbors it. Such a distinction is not made, nor is it clear how the information in such a magnetic string would be transformed into physical or chemical operations associated with living processes.

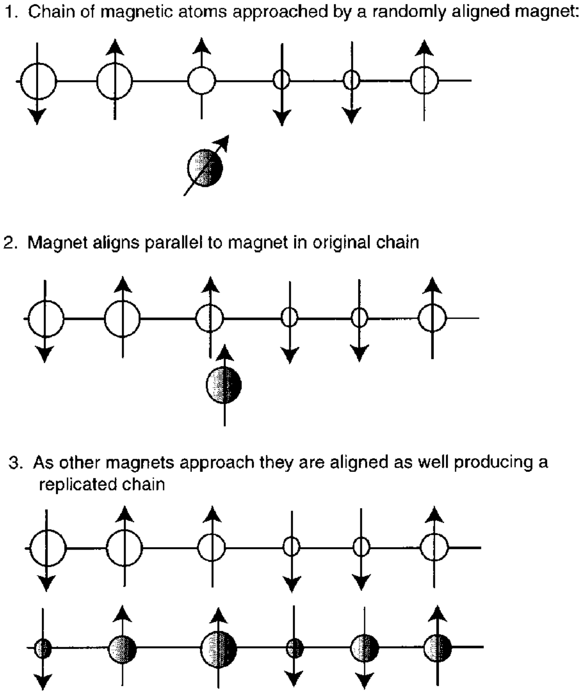


Fig. 9.1 Hypothetical replication mechanism of an ordered chain of magnets. Notice that identical components are replicated rather than complimentary and that the chain of magnets is only sensitive to the direction of magnetization, not to magnet size (modified from Feinberg and Shapiro 1980).

Thus, while this is a stimulating and intriguing idea for an exotic form of life, especially under conditions of extreme cold, which are common in the universe, we consider the existence of such an organism as extremely unlikely.

9.2 Fred Hoyle's Black Cloud and Similar Ideas

The Black Cloud organism envisioned by Hoyle (1959) is portrayed as a formless mass living in space, obtaining energy from the light of stars, and communicating with itself and other forms of life by radio waves. It has an organization analogous to that of complex terrestrial animals, such as gas that has the function of blood, an electromagnetic heart and kidneys, and a complex neurological system that can be understood as a brain. In his novel Fred Hoyle entertains the fiction that a gaseous being in the universe would have definite advantages compared to organisms living on a planetary surface, because it (1) would be free of constraints from large gravitational forces, and (2) would be able to absorb much more energy from starlight than the minute amount harvested by organisms confined to a planetary surface.

An organism like this is imaginable in principle (Goldsmith and Owen 2003). However, while such an amorphous and anthropomorphic creature is a worthy character of fiction, its potential for scientific credibility is severely limited. The major problem with this idea is the difficulty of envisioning how it could arise from an inanimate origin in the space environment. Being unbounded, the "proto-organismic" matter would have a low density, and be exposed to cosmic radiation. Low density and radiation would counteract any tendency for the matter within such an organism to become organized. Furthermore, no mechanism of replication is envisioned.

A somewhat similar concept was proposed by Arvidas Tamulis and co-workers (Tamulis et al. 2001; 2003), in the form of a molecular quantum computing cloud that could absorb magnetic and light energy from planets and stars, compute information, and move in space by using light pressure. Tamulis et al. (2003) pointed out the similarity to molecular quantum computers that use photoactive molecules converting light energy to magnetic flops interacting and controlling the central generating element of 10 quantum bits. An essential requirement for quantum computing life would be long lasting coherent quantum states, which would only be possible at extremely low temperatures found in interstellar dust clouds and on very cold planets. Basically, this idea suffers from the same problems as Hoyle's Black Cloud – an intriguing idea, but it lacks key fundamental characteristics of living systems.

9.3 Life on a Neutron Star

Life based on the strong interaction (strong nuclear force) rather than electromagnetic energy has been suggested as a possible basis for life as well (Feinberg and Shapiro 1980; Goldsmith and Owen 2003). The strong interaction affecting quarks, antiquarks and gluons (carrier particle of the strong interaction) holds together the nuclei of atoms, but it is a force that is only strong at extremely short distances. Thus, if atoms are (for us) in their usual state with electrons orbiting the nucleus, the individual nuclei are too far apart for the strong atomic force to result in significant interactions between different nuclei. However, given the situation that electrons are ripped off from their nuclei, protons and neutrons from various nuclei come into close proximity. This requires immense gravitational forces, and occurs naturally in neutron stars, which have one to two solar masses concentrated in a body with a diameter of 10 to 20 km and a magnetic field of about 10^{12} gauss. Given the high density and temperatures, interactions between protons and neutrons occur much more frequently than electromagnetic force interactions. These interactions occur because of incredible gravitational and magnetic forces present on the surface of a neutron star. Ruderman (1974) pointed out that the magnetic forces would reshape the "normal" atoms into strange configurations exhibiting long polymer-like chains in which the nuclei lie along a central line and the electrons in elongated bands. Magnetically formed polymers could then even align to form larger structures.

Life on a neutron star based on the strong interaction is one of the most extreme applications of energy in a conceivably biological context. The idea provides some conceptualization of how dynamic complexity can be established, but falls far short of constituting a comprehensive model of a living system, including any meaningful definition of life such as the one offered in Chap. 2. Neutron stars, however, might have planets, and possible life on such a planet could use the extremely strong magnetic field of their star as a primary energy source (see Chap. 5.2.5). In fact, the first extrasolar planets were discovered around a neutron star, the pulsar PSR $1257 + 12$ (Wolszczan 1994; see also Chap. 11.4).

9.4 Life on a Brown Dwarf

Brown dwarfs are accumulations of gas that have not been able to increase their mass and temperature sufficiently to sustain hydrogen fusion and become a star. Low-mass brown dwarfs may contain liquid water, and could possibly be capable of supporting life (Shapley 1958). Energy on a brown dwarf could be provided from the body's own intrinsic infrared spectrum, though this form of energy is much weaker than light in the visible and near-infrared spectrum. If life could adapt to use the low infrared spectrum to obtain energy instead of the visible and near-infrared spectrum as used on Earth, organisms relying on photosynthesis would have a nearly unexhaustible supply of energy. Such organisms, however, would have to adapt to the strong gravitational field of brown dwarfs, perhaps 100 times stronger than on Earth. That may not be a problem though. Mastrapa et al. (2001) tested *Deinococcus radiodurans* and *Bacillus subtilis* by exposing them to extreme acceleration ($4.5 \times 10^6\,\mathrm{m/s^2}$) and jerks ($1.5 \times 10^{11}\,\mathrm{m/s^3}$) in a compressed-air pellet rifle and noted survival rates between 40 and 100%. Also, Sharma et al. (2002) observed physiological and metabolic activity of *Shewanella oneidensis* strain MR1 and *Escherichia coli* strain MG1655 at pressures of 68 to 1680 MPa in diamond anvil cells. However, other major problems would include the lack of available surfaces for chemical reactions, suitable temperatures, and the relative lack of heavier elements such as potassium, calcium, and iron, which are necessary for living processes with which we are familiar. A more conventional possibility would be life on planets that are orbiting brown dwarfs. Andreyeschchev and Scalo (2002), for example, modeled habitable distances and time scales for planets orbiting brown dwarfs. Near-infrared observations indicate that young brown dwarfs probably possess proto-planetary disks (Muench et al. 2001; Testi et al. 2002), thus life could conceivably exist on a planet in a brown dwarf system.

9.5 Life on a Rogue Planet

Rogue planets are planets that have been ejected from their parent stars soon after accretion (Stevenson 1999). Bada (2001) pointed out that many of these rogue planets could be Earth-like with an inventory of radioactive elements sufficient to heat and melt their interiors. These worlds could have retained their initial dense hydrogen atmosphere, thus the heat leaking out from their interiors would not be rapidly lost into space, but instead water could condense and oceans could form (Bada 2001). With a highly reducing atmosphere which would likely include methane and ammonia, these planets could be a laboratory for prebiotic chemistry. It is even imaginable that primitive life could form under these conditions. Perhaps, rogue planets could constitute a universal mechanism for spreading prebiotic molecules or even primitive life from one Solar System to another. Unfortunately, rogue planets are very difficult to detect, though they ought to be very common on theoretical grounds, and based on the history of our own Solar System, in which Pluto, Charon, and Triton arguably represent captured rogue planetesimals.

9.6 Some Other Ideas on Forms of Exotic Life

Some other ideas of exotic life have been proposed in the past. They include speculations of plasma life inside a star, which was first advanced by Maude (1963) and later elaborated on by Feinberg and Shapiro (1980). The idea is based on replication of certain patterns of magnetic force and the dynamic activities within a star. The idea was revived more recently by Lozneanu and Sanduloviciu (2003), who created blobs of gaseous plasma that replicated by splitting into two, grew by taking up neutral argon atoms and splitting them into ions and electrons to replenish their boundary layers, and "communicated information" by emitting electromagnetic energy, which made the atoms within the other spheres vibrate at a particular frequency. We consider these possible interactions as interesting examples of dynamic complexity arising from relative chaos similar to forest fires and hurricanes on Earth, but do not consider them alive by any meaningful definition of the term.

Other speculations of exotic biology include life based on pure energy and life based on topological effects in quantum space rather than atoms as suggested in a novel by Egan (2002). As intriguing as these speculations are, any ideas not involving atomic matter are farfetched and have to remain in the realm of science fiction for now. Further, unlike matter, where two atoms or two planets affect each other's behavior through collisions, two independent flows of radiation will usually pass through each other without having any significant effect on each other. Thus, these ideas are imaginative examples of exotic physics, but, in our view, do not have a recognizable relationship to any meaningful definition of life.

9.7 Chapter Summary

We have given these brief examples of other, more exotic notions about forms of life that transcend even the basic chemical and physical laws that operate within usual planetary dimensions, because they have been advanced by serious thinkers who force us to critically examine our assumptions about the fundamental nature of life. In no case, however, do we feel that any of these examples constitute a plausible argument for an alternative form of life. They embody some imaginative alterations of state, matter, and energy, and bear some resemblance to some characteristics of life – particularly those having to do with the organizing capacity of energy flow and the tendency to create low-entropy states of disequilibrium. But in their totality, they do not come close to meeting the criteria for living systems set forth in Chap. 2. They do not prescribe bounded environments, nor specify a mechanism for reproduction, nor identify informational storage mechanisms that persist in unitary form from one generation to another. It perhaps could be argued that the flaw in our analysis lies in the definition of life, rather than its application. In other words, perhaps we lack the imagination to envision all the possibilities by which living systems could be manifested. However, we believe that in this book we have already pushed the limits of what it means to be alive, and to push beyond those limits at this point in our understanding would take us into the realm of a speculative physics that has no recognizable relationship to life in the universe.

Chapter 10
The Future and Fate of Living Systems

The future of life on Earth and elsewhere in the universe is the least studied of the three fundamental questions posed by NASA's Astrobiology Roadmap (Des Marais and Walter 1999; Des Marais et al. 2003). A lack of focus on this question raises two concerns. First, in a sense, the future of life is the question that has the greatest practical significance, since an ability to anticipate the consequences of human actions for the biosphere on Earth and wherever humans may come in contact with alien life in the future, should be a critical consideration in formulating policies for human activities on Earth at present and exploratory strategies for the future. The only one of the Roadmap's seven Goals and Objectives (#6) that relates to the future of life focuses narrowly on the fate of ecosystems and the evolution of microbes on Earth and in alien environments. The biosphere is now being changed so rapidly by anthropogenic forces, though, that the bigger and more immediate question is the general fate of groups of organisms, including especially those with the greatest environmental impact (Tong 2000; Woodruff 2001). Secondly, on planetary systems older than the Solar System, there is little reason to doubt that life has emerged in some cases, and therefore had longer to evolve than on Earth. The question may then be asked whether the history of life on Earth provides insights into the fate of living systems that have had longer to unfold.

10.1 Evolutionary Alternatives

We propose that the history of life on Earth reveals consistent patterns that can be grouped as a working formalism into one of three scenarios: taxonomic groups either (1) reach a stable *plateau* from which they do not deviate for a long to indefinite period of time; (2) they *collapse* into near or total extinction; or (3) they undergo *transition* to a form of life with dramatically new features—after which a new round of evolution radiates into new forms, each of which again follows one of the three scenarios. These interrelated possibilities are shown in Fig. 10.1. Each of these scenarios is considered below, with examples from the history of life as we know it.

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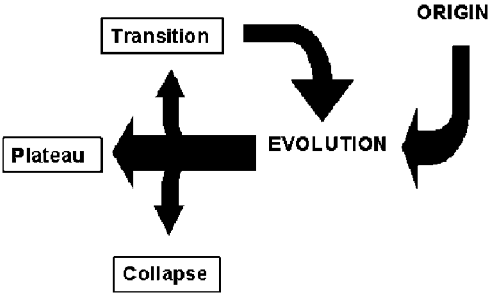

Fig. 10.1 Generic scheme for the cycle of evolution. The point at which life begins is a matter of definition. Once underway, life diversifies through evolution, with different taxa progressing ultimately to either collapse and extinction, a plateau phase leading to prolonged stability, or a radical transition to a new precursor that itself then radiates into a variety of forms, each with the same set of potential fates

10.1.1 Plateau

Organisms that occupy stable environments are subjected to stabilizing selection, which minimizes variation and optimizes adaptation over time (Campbell 1996). So long as the environment remains constant, form and function persist relatively unchanged. Hence, over geological time spans characterized by relatively constant environmental conditions, organisms tend to show little modification from the ancestral forms that emerged when they first arose. If that origin occurred as the consequence of punctuated equilibrium (Eldredge and Gould 1972), emphasis over the vast majority of the taxon's life span will be on equilibrium. Even in changing environments, highly successful and robust biological features may be retained. Evolutionary plateaus are the result.

The most obvious examples of the plateau scenario are life's most ancient surviving organisms, the bacteria and Archaea (Altermann and Kazmierczak 2003). Many microbes are likely unchanged from very early in their history. Cyanobacteria, though doubtlessly possessing a more elaborate photosynthetic machinery than the earliest versions, have remained virtually unchanged ecologically and morphologically for over two billion years (Altermann and Schopf 1995). Once plants invaded the land, bryophytes quickly developed a morphology and physiology that has remained constant for at least 360 million years (Hueber 1961; Karssilov and Schuster 1984).

Among the invertebrates notable for their evolutionary longevity are crustaceans such as the horseshoe crab (Xia 2000), insects such as ants (Grimaldi and Agosti 2000), and mollusks such as the nautilus (Landman 1987). Among the vertebrates, the sharks emerged during the early Devonian and developed some unusual physiological features that have remained relatively stable for 400 million years (Lisney and Collin 2006; Miller et al. 2003; Speers-Roesch et al. 2006). Likewise, the turtles emerged in the late Triassic with a highly successful defensive morphology that has preserved them relatively unchanged for 200 million years (Krenz et al. 2005; Pritchard 1979).

The history of life on Earth leaves several unanswered questions about the Plateau scenario. First among them is whether evolutionary plateaus remain stable indefinitely as long as the environment does not change. Can genetic drift give rise to change even in unchanging environments? What are the critical factors that promote survival of some forms through global catastrophes, such as the persistence of bryophytes and sharks through the Paleozoic-Mesozoic (P-M) boundary, and the survival of turtles through the Cretaceous-Tertiary (K-T) transition?

10.1.2 Collapse

Biologists have long recognized that most taxa have finite life spans; hence the majority of species that have ever lived have become extinct (Eldredge 1985; Woodruff 2001). Collapse, therefore, is the ultimate fate of most forms of life. This presumably reflects the fact that even optimal adaptations are essentially irreversible, and sooner or later circumstances will change to the point that the basis for past evolutionary success becomes maladaptive. Alternatively, previously well-adapted forms may simply be displaced by more highly adapted competitors. Or, precipitous events may lead to a relatively sudden collapse, as in the global catastrophes that mark several prominent paleobiological boundaries.

The stromatolites dominated the biosphere for three billion years, but disappeared at the end of the Proterozoic (Cowen 1995) except in a few scattered niche environments such as Shark Bay, Australia. The Ediacaran fauna provided numerous experiments in animal morphology over a 40 million year period just prior to the Cambrian, but few representatives survived into the Paleozoic (Cowen 1995). With the advent of the jawed fishes, the placoderms came to dominate the early Devonian seas, but were displaced entirely by unarmored but more resilient competitors by the end of the Devonian. Dinosaurs rose to prominence during the Mesozoic but were exterminated precipitously by the K-T catastrophe. It has been estimated that extinction is now occurring on an unprecedented scale, accelerated by the impact of human activity on the biosphere (Tong 2000; Woodruff 2001). The relatively sudden disappearance of the mammalian megafauna in North America has been attributed to the arrival of humans, though the precise role played by human-megafaunal interactions remains controversial (Barnosky et al. 2004; Brook and Bowman 2002; Diniz-Filho 2004; Johnson 2002; Remmert 1982). And the human species itself is the lone survivor of a number of hominids that appear to have been unable to compete with *Homo sapiens* during the late Pleistocene and early Holocene (Kaifu et al. 2005; McBrearty and Brooks 2000).

The question of causation is the one most relevant to the Collapse scenario. What is the relative importance of maladaptation and competition in precipitating extinction? Does collapse ever occur due to genetic drift, absent precipitating competition or abiotic changes? How common is Collapse, even in relatively stable environments?

10.1.3 Transition

According to the punctuated equilibrium model of the origin of species (Eldredge and Gould 1972), most new taxa come into existence through relatively rapid transitions from ancestral forms. The power of directional selection to drive adaptive change when either the biological or abiotic environment is altered compels often drastic and rapid evolutionary changes (Eldredge 1985; Elena and Lenski 2003; Reznick and Ghalambor 2001). Transition thus represents a third scenario among the fates that befall life.

Major transitions in the history of life that emphasize information transfer and hierarchical organization have been outlined by Szathmáry and Smith (1995). Highlights that affect the nature and biodiversity of life on Earth include the emergence of a metabolic machinery for photosynthesis, the endosymbiotic creation of eukaryotic cells, the origin of calcified exoskeletons, and reproductive innovations that drove protistan diversification in the late Proterozoic (Cowen 1995; Margulis and Sagan 1995). The Cambrian explosion generated several major transitions, the most successful of which appear to have been the origin of the arthropods and mollusks. The vertebrates represent a somewhat later but equally successful transition. Among the vertebrates, transitional innovations include the development of jaws, leading to the formulation of more complex food webs with larger and more active animals; the evolution of lungs, leading ultimately to the colonization of terrestrial niches by organisms with higher metabolic rates supported by the richer supply of oxygen; development of the amniotic egg that freed reproduction from restriction to aquatic habitats; and endothermy, which enlarged the range of climates and niches which animals could occupy.

The Transition scenario raises questions as well. Is transition inevitable, given enough time under hospitable conditions? Is transition even possible for most forms of life, especially for macrobiota, if the environment changes radically over a short time span, as appears to be occurring now in the global biosphere? A study of the survivors of past mass extinction events may lead to instructive insights in that regard (Ward 2001).

In rare cases, the transitions have been great enough to transcend biology. The evolution of photosynthesis altered the global atmosphere, while redirecting the course of evolution itself. Multicellularity transformed life from an exclusively microscopic domain, to macroscopic and megascopic dimensions. The evolution of nervous systems gave rise to “neural individuals” (Jablonka and Lamb 2006), which evolved intelligence to varying degrees. The combination of intelligence and sophisticated communication with manual dexterity enabled humans to develop technology, which has so amplified biological capabilities that the Earth in its entirety is being transformed.

10.2 Evolution of Intelligence

Intelligence has evolved independently several times during the evolution of life on Earth (Irwin and Schulze-Makuch 2008). Four specific examples of the independent evolution of a transforming degree of intelligence are provided by the social insects, cephalopods, cetaceans, and primates.

Insects evolved on land during the Silurian, though the eusocial ants, wasps, and bees apparently did not diversify until the Mesozoic, ∼150 million years ago (Moreau et al. 2006; Schultz 2000; Wilson 1980). Biologists do not rate the social insects as intelligent in the conventional sense, and as individual organisms they certainly do not meet the usual criteria for intelligence. But in the aggregate, they display some of the features that would suggest intelligence, were they a single organism. They build elaborate housing, divide labor, communicate symbolically (in the case of bees), radically modify their microenvironment, grow food (in the case of fungal cultivating ants), domesticate other species, wage war, and cooperate for the good of the whole (Brady 2003; Mueller et al. 1998; Wilson 1980). As such, they represent a case of meta-intelligence, which obviously has been subject to strong group selection.

Cephalopods have achieved the pinnacle of intelligence among all the invertebrates (Young 1964). They diverged from other mollusks in the late Cambrian, became numerous in the Ordovician, and suffered a cataclysmic decline during the Permian crisis, with only the octopi, squids, cuttlefish and a few nautiloids surviving to the present day (Cowen 1995; Landman 1987). Those forms, however, are active benthic foragers and predators, with highly developed tactile and visual sensory abilities, and elaborate motor systems for the control of jet-like propulsion, complex mouth part movements, and fine manipulation of each of their eight appendages.

The Cetaceans probably diverged from their terrestrial ancestors near the start of the Cenozoic 65 million years ago, since the oldest fossil whale has been dated from the early Eocene, ∼55 million years ago (Bajpai and Gingerich 1998). Whales have the largest brains that have ever evolved, the brain of the blue whale measuring nine times the size of the human brain. By the Miocene (∼20 Ma), cetacean brains had achieved essentially their modern size (Jerison 1973). Most of the enlargement of the brain in cetaceans reflects a huge elaboration of the neocortex beyond the sensorimotor primary projection areas (Hof et al. 2005; Lilly 1978). While cetaceans have essentially lost their olfactory sense, the pyriform cortex has not been reduced, perhaps reflecting compensatory enhancement of their gustatory sense. Anatomical changes have enabled the sound production that forms the basis of a sophisticated echolocating capability and a communication system whose full complexity is not yet known (Herman 1986).

Primates diverged from ancestral insectivores early in the great mammalian radiation at the start of the Cenozoic, about 65 million years ago (Cowen 1995). The evolution of hominids shows a relentless increase in brain size, characterized mainly by expansion of the neocortex, and in humans by increase in the prefrontal lobes in particular (Byrne 1995). The evolutionary acceleration in brain size occurred in the anthropoids much more recently than in the cetaceans—the qualitative expansion of the human brain over that of the chimpanzee occurred within the last 6 million years, while neocortical expansion in the Cetacea exceeded that of humans probably 20 Ma earlier (Jerison 1973). The acceleration of neural complexity in these two very distantly related mammals has thus been a completely independent event. By 4 million years ago, humans had split from chimpanzees, and begun to diversify into a number of species (Cowen 1995). *Homo sapiens* is the sole survivor of several competing human lineages, achieving modern morphology and brain size $\sim$200,000 years ago (Jerison 1973; McBrearty and Brooks 2000).

From an astrobiological perspective, the relative infrequency with which intelligence has arisen is noteworthy. Even among those species that have developed the capacity for insight such as chimpanzees, that ability appears to be underutilized in their natural habitat (Byrne 1995). It may be that high intelligence has sufficient negative attributes that its evolution is not commonplace. Thus, if and when complex living entities are found on other worlds, it should not be taken for granted that intelligent forms will be among them.

10.3 The Rise of Technological Competence and its Fate

An equally compelling though lesser mystery is why technology has developed so rarely among species that have the intellectual capacity for it. Technology (the use of energy, tools, material, and information to amplify the impact of a species on its environment) has emerged fully in only the human species. Crude prototypes can be seen in other species, but only among the primates and some birds. The social insects show limited forms of meta-technology, in the construction of elaborate housing and limited domestication of other species. But only humans have fully exploited technology to the point of significantly changing their environment beyond their purely biological impact. A particularly pertinent issue raised by the human example is whether any technologically capable form of life will inevitably metamorphose into something else—perhaps (a) custom-designed, genetically engineered organic beings, (b) totally mechanized forms with artificial intelligence, or even (c) virtual (non-material) entities.

Technology for the first alternative is advancing rapidly. The pace at which humans create genetically modified species, perhaps to the point of giving rise to new species, and/or enabling their own custom-designed genetic transformation, at this time appears to be constrained more by social, political, and moral attitudes than by technological capabilities. Inasmuch as social, political, and ethical views change over time, the trend to engineer new organic beings – non-human, human, or both – is likely to continue if not accelerate.

The second alternative leads to the question of the relationship between evolving machines and their human innovators. A symbiotic fusion is one possibility, and is already in the early stages of occurring (Clark 2003). Artificial limbs, sensory aids, and implanted mechanical devices such as pacemakers reflect this trend. An alternative relationship would be an ongoing co-evolution of humans and machines, with increasingly comparable capabilities of organic and mechanical forms but without significant fusion between the two. The advancement of robotic technology illustrates this trend. In this case, the ultimate possibility of replacement of organic by mechanical beings clearly looms. How rapidly (and how peacefully) the mechanical entities will replace their organic predecessors, is clearly a compelling question. The ability of machines to compete with humans depends ultimately on the capacity of the former for feature extraction, abstract processing, and anticipation – in short, to be intelligent. While it is commonplace to argue that computer intelligence is merely decades away, fundamental arguments that digital computers can never be intelligent have been advanced (Chyba and McDonald 1995; Hawkins and Blakeslee 2005; Searle 1984).

The third possibility is reflected in the growing sophistication of human-engineered virtual reality. As human biology becomes increasingly dominated by and subservient to cognitive experience, the motivation to manipulate that experience by artificial means is likely to grow. Once the ability to create enriching and satisfying virtual realities becomes feasible, and the logistical problems of sustaining sufficient other (social, economic, and political) requirements of the material world to support the virtual world are solved, organic humans would become progressively superfluous. The argument has been pushed even further by Bostrom (2003), who suggested that humans may have reached a "posthuman" stage capable of running a significant number of simulations of their own evolutionary history (or variations thereof), and that we might already be living in one such simulation.

In the event that technologically-capable species spawn mechanical adjuncts to their own biology, the nature of life and the forces that influence its evolution may be radically altered. In such cases, depending on the nature of the descendent forms, an adjustment in those definitions of life that emphasize organic complexity and evolution by natural selection may be required (Grinspoon 2003; Lwoff 1962), as indicated in Fig. 10.2.

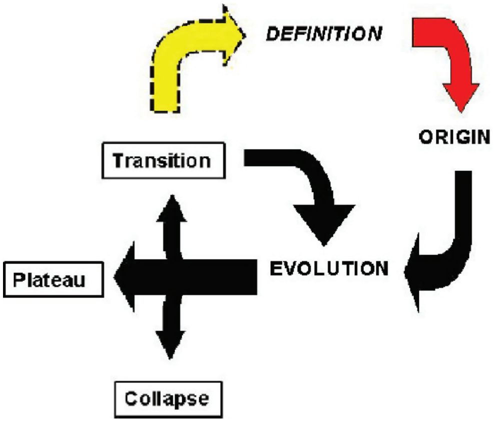

Fig. 10.2 The cycle of evolution with a redefinition of life. In the case where life evolves technological capabilities, the prospect of non-organic organisms and artificial intelligence requires a reconsideration of the definition of life

The benefits of considering the fate of life in a formal way may thus be not only to determine whether the scenarios observed over the course of life on Earth represent exhaustive examples of the fate that can befall living organisms anywhere, but to reexamine clearly the definition of life itself.

10.4 Application to the Possibility of Life on other Worlds

We and others have argued previously that if life exists elsewhere in our Solar System – and we rate the probability that it does so moderately high (Irwin and Schulze-Makuch 2001) – it almost surely exists in a microbial to small and relatively ancestral form. This is because conditions on the surfaces of all the other planets and satellites, with the possible exception of Titan (Campbell 1996; McKay and Davis 1999; Schulze-Makuch and Grinspoon 2005), are not favorable for complex liquid-based biochemistry. Whatever life may have arisen on (or been transported to) them, it would be expected to have become sequestered in stable, environments once life on the surface became untenable. Since subsurface habitats favor small organisms (Chap. 8.2), life on such bodies would likely be microbial to small, and probably near its ancestral state, or whatever state it was in when subsurface existence became mandatory.

Lack of knowledge about the nature of planetary bodies in other Solar Systems that could harbor life severely constrains informed speculation about the nature of living systems beyond our own Solar System. Of the over 300 extrasolar system planets now recognized, almost all are giant planets orbiting near their central stars (Marcy and Butler 1998), presenting formidable challenges to the existence of life. Because there are surely other Solar Systems with planets more distant from their central stars, perhaps containing water or other liquids at temperatures where complex biochemical reactions can proceed, the chances are greater on bodies such as those that complex ecosystems could develop, leading to multiple trophic levels, hence complex macrobiota. To the extent that many planetary bodies resemble the cold arid surface of Mars, or the icy satellites of the outer planets, life on them would likely be subterranean, rendering the plateau scenario most likely.

If the conditions that enabled the evolution of complex life on Earth are indeed as rare throughout the universe as they are in our own Solar System, so too might be the prevalence of complex life. However, we do not yet know that complex life *cannot* arise under conditions exotic by Earth standards (Schulze-Makuch and Irwin 2006), so a generalization about the rarity of complex life throughout the universe (Ward and Brownlee 2000) is not yet justified.

We have previously defined life in a way that avoids limitation to the carbon-based, water-borne form of living organisms that currently inhabit Earth (Schulze-Makuch 2002b). At the same time, our analysis of physicochemical constraints suggests that carbon-based, water-born life is by far the most likely form for life to take (Chapters 6 & 7). In as much as numerous planetary bodies in our Solar System have, or have had, conditions for the origin and evolution of life as we know it (Irwin and Schulze-Makuch 2001), we suggest that space exploratory missions continue to "follow the water" in subsurface habitats on Mars, Europa, and the other satellites of the outer planets, where ecosystems may be found to persist largely in a plateau stage of evolution. At the same time, the atmosphere of Venus (Grinspoon 1997; Schulze-Makuch et al. 2004) and the surface or subsurface of Titan (McKay and Smith 2005; Schulze-Makuch et al. 2005) may offer habitats for forms of life quite unknown to us.

Where extreme geophysical transformations have occurred over the history of a planetary body, as on Venus and Titan, forms of life quite different from those known on Earth could be the outcome. Thus, the definition of life that guides our search for it needs to be generic enough to consider all the possibilities, including those difficult to envision by analogy with life on Earth.

10.5 Chapter Summary

With robotic missions to Mars and the outer planets increasing our knowledge of other potential habitats for life, and with astrobiology becoming an institutionalized interdisciplinary field of study, the time has come to formalize models for the life history of biospheres in their entirety. We propose a generic framework for considering the history and fate of life wherever it occurs in the universe. Using analogs from the history of life on Earth, we extrapolate to a variety of circumstances likely to be encountered by life on other planetary bodies. The most common fate of life is evolution to a "plateau" state in which life stabilizes into forms optimally suited for persistently unchanging environments. Assuming that life on other worlds is most often microbial and ancestral, this is likely the most widespread scenario. "Collapse" occurs when evolutionary changes produce forms incapable of adapting to altered biotic or abiotic conditions. Total extinction is a special case of collapse, but near extinction leading to survival of only a few, significantly altered descendent forms is another, perhaps more common outcome of the collapse scenario. "Transition" occurs when evolution leads to biotic or environmental changes sufficient to generate radical transformations. The climactic evolution of neural complexity and manual dexterity, leading to symbolic language and technology in humans raises the question of whether any technologically capable form of life will inevitably be transformed through codependency with machines and external data processing and storage, into entities that require a redefinition of life. If the fate of living systems as we propose here holds generally for other worlds, it is most reasonable to expect that life will be found to be simple and near its ancestral state on worlds that solidified into a constant, constraining physical condition early in their history, such as the icy satellites in our Solar System. The transition to complex life, with the possible evolution of intelligence and rise of technology, is likely to be found only on worlds which have experienced a history of multiple physical transformations and persist in a heterogeneous state.

Chapter 11
Signatures of Life

In this chapter we will elaborate on how evidence for life on other worlds can be sought, and if present, possibly detected. The best evidence for extraterrestrial life, of course, would be recovery of actual specimens or their fossils. For the next one or two decades, the possibility of obtaining such direct evidence is almost surely restricted to samples from Mars and Venus. So detection of life beyond our nearest neighbors will be dependent for the near future on remote sensing. As technology of robotic exploration and remote sensing improves, the possibility of detecting extraterrestrial life will grow. While the size of individual organisms makes their detection at a distance virtually impossible, organisms in the aggregate alter their environments, generating signatures of their functional processes. These direct consequences of biological activity are referred to as "biosignatures". Other effects of the presence of living systems may be detected in global or geological features. These alterations of the geological environment due to life processes, we call "geosignatures". Even on worlds too remote, small, or difficult for whatever reason to monitor for the existence of explicit signatures of life, certain planetary characteristics can be detected that are more likely to be consistent with the presence of life than others. These we refer to as "geoindicators." They consist of parameters that are consistent with life as defined in Chap. 2, and the requirements for life as described in subsequent chapters, including a flow or gradient of energy, presence of an appropriate solvent, and availability of complex polymeric chemistry. While geoindicators point to the potential for supporting life, they do not confirm its existence. Most geoindicators can be detected by remote sensing methods with relative ease, however, and thus can be used in assessing the plausibility of the existence of life. At the end of the chapter, we apply our discussion of signatures and indicators of life to assess the relative plausibility for the existence of life on other bodies in our Solar System, and discuss recent results on extrasolar planetary detection and their implications for astrobiology.

11.1 Searching for Signatures of Life

Biosignatures and geosignatures of life are currently not known to exist from any planetary body of our Solar System other than Earth. Examples of signatures of life

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Table 11.1 Some examples of biosignatures and geosignatures of life

Observation	Signature
Organic macromolecules larger than 500 daltons	Biosignature
Atmospheric gas composition, such as O_2 and CH_4, resulting from biogenic processes	Geosignature
Rocks and sediments produced by biogenic processes such as the banded-iron formation (BIF) and stromatolite deposits of early Earth	Geosignature
Known biogenic substances such as chlorophyll not explicable by naturally occurring inorganic chemical processes	Biosignature
Rate and type of erosion consistent with biological processes	Geosignature
Structural complexity, such as geometric regularity (roads, canals) or unnatural local aggregates (cities) not explicable by natural geological processes	Geosignature
Distribution and magnitude of emitted heat inconsistent with an abiotic origin	Biosignature
Energetic emissions such as radiowaves, which are neither highly regular, as from a pulsar, or highly random, as in the universal background radiation	Biosignature

are given in Table 11.1. Thus, there is presently no available evidence for life as we know it elsewhere in the Solar System. Life could exist nonetheless, either in a form known or unknown to us, that does not give rise to any of the biosignatures or geosignatures indicated in Table 11.1, if it (1) occurs beneath an opaque surface, (2) is too small to cause environmental transformations extensive in magnitude or spatial extent, or (3) is insufficiently complex to generate complex phenomena, such as roads or radiowaves. Other difficulties are that extraterrestrial life may involve dynamic processes that occur on (1) a spatial scale too small to be detected by current remote technology, and (2) a time scale too prolonged to be sampled feasibly (Schulze-Makuch et al. 2002a). Nevertheless, there are several signatures of life that may become relevant for the detection of life in the near future, either for life in our Solar System or in another Solar System. These signatures are discussed below.

11.1.1 Atmospheric Composition of a Planetary Body

An often cited geosignature of life is the presence of molecular oxygen and particularly the presence of ozone in an atmosphere. For example, Akasofu (1999) suggested the use of the green oxygen line at 557.7 nm from auroral emissions to search for extraterrestrial life. Ozone was suggested to be more suitable than molecular oxygen because its abundance increases nonlinearly with the abundance of molecular oxygen (Leger et al. 1993) and ozone absorbs UV radiation known to be detrimental for terran life on extrasolar planets. Any such spectroscopic remote observation has two major technical challenges: the weak signal and the huge background from the parent star (Frey and Lummerzheim 2002). However, for the detection of the habitability of planets in other Solar Systems this may be the only reasonable approach for the near future. In our view, an oxygen atmosphere or ozone layer alone, in the absence of other abnormal concentrations of gases such as methane, should be regarded only as a geoindicator consistent with the presence of life, not as a geosignature. For example, Jupiter's moon Europa currently has a thin oxygen atmosphere from interactions of radiation with surface ice (Hall et al. 1995) and it can easily be envisioned that it had a much thicker oxygen atmosphere and possibly an ozone layer for part of its geological history. When the Solar System formed Europa most likely had oceans of water on its surface and a water vapor atmosphere. Given the high radiation environment of the Jovian system, water would have split into hydrogen and oxygen with the hydrogen escaping to space and the oxygen being retained for longer time periods because of its higher molecular weight. Thus, the presence of a high amount of molecular oxygen and even ozone for some time period is absolutely plausible based on physical means alone (Europa likely experienced global re-melting events for which the above scenario may be valid as well).

However, the atmospheric composition of Earth is a prime example of a signature of life (Table 11.1). Earth's atmosphere is the peculiar product of a particular biological process: photosynthesis. Oxygen by itself could not be considered a signature, but the high amounts of oxygen (about 20%) combined with the presence of hydrogen (H_2), methane (CH_4), ammonia (NH_3), methyl chloride (CH_3Cl), and methyl iodide (CH_3I), along with various sulfur gases can best be explained by the continuous metabolic production of these compounds faster than they can react with each other (Sagan 1994). These gases, highly reactive when mixed, would not coexist at such high concentrations unless their levels were being actively maintained. It is this type of disequilibrium, in combination with high amounts of oxygen that can be used as an indicator for oxygen producing photoautotrophs.

11.1.2 Geological Evidence

Particular signatures also exist for chemoautotrophic organisms. An example are the limestones and ironstones produced by biological activity on the early Earth. Both types of rocks can form from inorganic processes. The large quantities produced during Earth's early history, however, can hardly be explained by abiotic processes. For example, microbial life dominated the ecosystems of Precambrian shallow marine environments, and is likely to be implicated in widespread carbonate formation, and possibly also in the precipitation of other evaporates (Wrights and Oren 2005). The large amounts of deposited Banded Iron Formation (BIF) rocks are even less imaginable without microbial participation. Similar processes might be occurring on Mars. For example, Parro et al. (2005) described the development of technology to detect iron-powered chemosynthetic microbes. Chemosynthesis generates various chemical end-products depending on the exact metabolic process. Nevertheless, the chemical end-product may provide a useful marker, especially if produced in a large enough amount over an extended period of time to make it a signature of chemotrophic life. The biochemical end products often exhibit large-scale geomorphological characteristics such as stromatolite colonies and coral reefs, some of them large enough to be observed with the naked eye from the Moon such as the Great Barrier Reef.

The high rates of erosion and types of erosion observed on Earth due to biological and chemical weathering induced by living organisms provide another example of a geosignature. The biomass of fungus-lichen rock dwellers is estimated to be enormous, by one account 13×10^{13} tons (Margulis 1998). Thus, the effect of these rock dwellers on chemical weathering from metabolic by-products is immense. Rates and types of erosion can be inferred from the visible and microwave wavelengths of the electromagnetic spectrum (Schulze-Makuch et al. 2002a), but are traditionally not considered as a signature of life. Dietrich and Perron (2006) suggested the search for a topographic signature of life based on the quite apparent impact of life on rock weathering, soil formation and erosion, and slope stability and river dynamics, even over short time scales. But even for a topographical signature of life, high-resolution images are necessary to have confidence in the detection, and at present this type of resolution is only available for the inner planets of our Solar System. It would not be expected to be available for any extra-solar system planets, particularly not for any encased by an atmosphere.

11.1.3 Fossil Evidence

Fossil remnants and isotopic fractionation caused by biotic processes are other examples of biosignatures. One controversial example is the Martian meteorite ALH84001 in which McKay et al. (1996) claimed to have found evidence of fossilized microbes. However, these claims have come under intense scrutiny as have some of the oldest known records of life such as stromatolites and microfossils (Pasteris et al. 2002; see also Chap. 12). Isotopic signatures of carbon, sulfur, nitrogen, hydrogen, iron and other elements are another form of fossil evidence (Schidlowski et al. 1983). Observations from terran organisms show that chemically lighter isotopes are preferred resulting in a net fractionation of lighter isotopes. A carbon isotope fractionation, typical for biological processes, has been found in the geological record for the last 3.5 - 3.8 billion years of Earth's history (Schidlowski 1988).

A robotic mission would be needed to detect these signatures of life unless a rare fortunate circumstance would bring a meteorite from that world to Earth where it can be analyzed by in-situ methods. However, microbial biofilms that become preserved on rock surfaces could possibly be identified with remote sensing methods if (1) spectroscopically identifiable compounds exist that display unique adsorption, diffraction, and reflection patterns characteristic of biogenerated organic compounds (e.g. chlorophylls, carotenes, melanins), (2) biogenic geomorphological features are exhibited (e.g. biopitting, biochipping, bioexfoliation), and (3) biominerals are detected that are produced in association with biofilms that occupy rock surfaces such as oxalates and certain types of carbonates and sulfides (Gorbushina et al. 2002).

11.1.4 Macromolecules and Chirality

Among the most powerful biosignatures are macromolecules that are directly linked to biogenic metabolism or other cellular functions. Chlorophyll is the prime example and can be identified by radiance spectra in the visible region (Gordon et al. 1980; Hovis et al. 1980) and by advanced very high resolution radiometer (AVHRR) measurements (Gervin et al. 1985; Tucker et al. 1985). Methylhopanoids have also been suggested as biomarkers and have the additional advantage of distinguishing between cyanobacteria (2-methyl) and methanotrophic (3-methyl) bacteria (Farrimond et al. 2004). Proteins, polypeptides and phospholipids are other examples of macromolecules that are linked to life. In general, any macromolecule of a size larger than 500 daltons (protein-size) can be considered a biosignature (Table 11.1).

Chirality, or non-racemic handedness, is a fundamental property of biogenic molecules on Earth and thus may be used as an indicator of possible extraterrestrial life detectable by remote sensing in the near future. Large macromolecules are not symmetrical and thus inevitably exhibit chirality. Plaxco and Allen (2002) pointed out that all terran life uses well-structured, chiral, stereo-chemically pure macromolecules of 500 or more atoms as their metabolic catalysts. Xu et al. (2003) argued that all life would employ these types of macromolecules irrespective of the specifics of their chemistry. They pointed out that these molecules strongly absorb at terahertz frequencies and exhibit significant circular dichroism, which they consider an unambiguous biosignature. Left- and right-handed circularly polarized light interacts differentially with chiral molecules, especially at blue-green and shorter wavelengths (Van Holde et al. 1998). Salzman et al. (1982) found that organisms also scatter circularly polarized light differentially, with angular and wavelength spectra somewhat characteristic of particular organisms or strains. Evidence presented by these authors and by Nicolini et al. (1991), Diaspro et al. (1991) and Lofftus et al. (1992) indicates that the configuration of DNA in organisms strongly affects their differential scattering. Winebrenner et al. (2008) has developed a first experimental system for the detection of biogenic molecules by means of circularly polarized light scattering with a polarization-dependent resonance at 436 nm. This indicates that macromolecules and their resulting chirality have a great potential as useful biosignatures.

11.1.5 Presence of Metabolic By-Products and End-Products

Metabolic by-products and end-products are well known for organisms on Earth. They include various biochemical compounds such as ATP and lipids, but also electron donor and acceptor pairs such as Fe^{3+}/Fe^{2+}, NH_3/N_2, and H_2S/S enriched in lighter isotopes. This isotope enrichment or fractionation occurs as part of the metabolic reactions for organisms on Earth and may also occur for life elsewhere. While biochemical macromolecules such as ATP are very specific signatures for certain biological processes, using isotopically light electron donors or acceptors as signatures for life is more challenging. An endless number of possible electron donor/acceptor pairs could potentially be used for energy-harvesting reactions on other worlds, and there are also numerous inorganic processes that lead to isotopic fractionation, many of them poorly understood. One promising approach might be the use of the oxygen isotopic ratio of phosphate, which was suggested as a means for detecting enzymatic activity since the exchange of oxygen isotopes between water and phosphate requires enzymatic catalysis at low temperatures (Blake et al. 2001). Also, the presence of gaseous electron acceptors and donors (e.g. H_2S, COS, CH_4) enriched in lighter isotopes may constitute a signature of life that can be screened readily by remote sensing methods. One example is the presence of CH_4 on Titan, which is isotopically lighter than would be expected from Titan formation theory (Lunine et al. 1999). However, any such interpretation is limited by our understanding of the physical and chemical processes occurring on a planetary body as foreign to us as Titan.

A related biosignature may be the metabolic multistep pathways that run close to equilibrium for some internal steps, but are coupled to a last step, which is energetically downhill, thus pulling the whole reaction to completion (Voet and Voet 2004). Baross et al. (2007) considered this feature as a possible universal biosignature as it exploits most economically a surrounding chemical disequilibrium.

11.1.6 Production of Biogenic Heat

Another possible signature of life is biogenic heat that may be detectable in the future by more advanced technologies. Living systems exist in thermodynamic disequilibrium by drawing energy from their environments. A consequence of the biochemical reactions that an organism needs to carry out to sustain itself is the production of “unorganized energy”, commonly in the form of heat. The production of heat follows as a consequence of the 2nd Law of Thermodynamics. Organisms by their very nature have to be structured and organized. However, in order to conform to the tendency of the physical world toward a state of greater disorder, any organism has to give up a portion of its energy in the form of heat or other type of disorganized energy. The distribution and magnitude of heat produced by living systems or colonies of living systems may be possible to detect by in-situ monitoring or remote sensing techniques in the near future, thereby serving as a biosignature if an abiotic origin can be ruled out.

11.1.7 Signatures of More Advanced Life

Signatures of life also include structural complexity produced by biogenic processes ranging from termite mounds to artificial constructions such as streets and evidence of an advanced civilization such as a Dyson Sphere (a constructed spherical shell centered around a star absorbing most of its visible and shorter wavelength radiation; Dyson 1959), that would imply the presence of designed, dynamic activity known only to living systems. Energetic emissions, such as radiowaves, which are neither highly regular, as from a pulsar, nor highly random, as in the universal background radiation, are currently used by SETI (Search for Extraterrestrial Intelligence) to scan the skies for signs of extraterrestrial intelligence. These kinds of signatures, of course, would be linked directly to the presence of more technologically advanced forms of life than microbes, but, if present, would also imply the presence of microbial life based on the presumption that more complex organisms would have to have evolved from simpler ancestors.

11.2 Geoindicators of Life

With the exception of Mars and Venus, the detection of life elsewhere in the universe for the foreseeable future has to focus on remote detection given our current state of technology (Schulze-Makuch et al. 2002a). Retrieval of samples for direct analysis for years to come will be limited to meteorites, comet or asteroid material returned to Earth, and Venusian atmospheric samples and Martian surface samples possibly retrievable within the next decade or two. Thus, for the foreseeable future it is not feasible practically and economically to send robotic landers to each planetary body of our Solar System and beyond. Further, even on a planetary body with life the detection may be unsuccessful if (1) the site is unsuitable or sparsely populated, or (2) life detection experiments are not set up appropriately to detect life thriving in that particular environment.

Under these circumstances, the more sophisticated and abstract definitions of life alluded to in Chap. 2 may provide the basis for a set of parameters that could point to conditions favorable for generic forms of life, either known or unknown to us. Specifically, (1) the maintenance of disequilibrium from the environment requires the availability of energy flow (hence gradients of energy) for sustaining low entropy states; (2) the level of chemical complexity required to transform and store energy appears to require a fluid medium where concentrations can be high but molecular mobility can be maintained; and (3) the storage and transmission of information appears to require polymeric chemistry that can involve the making and breaking of covalent bonds with relative ease. Parameters that indicate the presence of any of these conditions, and therefore imply that life could be present though not confirming its existence, are defined here as geoindicators. Based on the forgoing discussion primary geoindicators of life would include evidence of (a) an atmosphere or ice shield, (b) thermal gradients and chemical disequilibrium conditions, (c) internal differentiation of the planetary body, implying the capacity for radiogenic heating, (d) complex polymeric chemistry, (e) energy flow or gradients, and (f) a liquid medium as a solvent. The advantage of these geoindicators is that remote sensing can detect all of them readily in principle.

11.2.1 Presence of an Atmosphere or Ice Shield

It is difficult to envision the presence of life on the surface of any planetary body that is not shielded by an atmosphere. Without an atmosphere any liquid or gaseous compound will vaporize into the vacuum of space. Aside from the gas giants, relatively dense atmospheres exist only on Earth (1 atm), Venus ($\sim$ 90 atm) and Titan ($\sim$ 1.5 atm). However, for life to thrive at planetary surface temperatures on Venus (very hot) and Titan (very cold) would require a biochemistry with properties unfamiliar to life forms on Earth. The surface of both Venus and Titan is obscured from visual light penetration by a thick atmosphere. On Titan, organic compounds such as methane and ethane are present in the atmosphere (Coustenis and Lorenz 1999; Lorenz 1993), and Titan is also the only planetary body with a significant atmosphere other than Earth known to have nitrogen as the most abundant atmospheric gas. The high nitrogen content in Earth's atmosphere has been interpreted to result from biological processes (Lovelock 2000). Since Titan's atmosphere can only be penetrated by narrow frequency windows between bands for methane and radar with current remote sensing technology (Griffith et al. 1991; Lorenz and Lunine 1997), probes have to be sent to explore the physical conditions and chemistry of the surface (e.g. the Huygens probe which descended through Titan's atmosphere in January of 2005). On Titan a warmer subsurface could be a suitable habitat for microbial life. Venus, on the other hand, would provide very little hospitality for microbes in the subsurface habitat, unless they were able to use water that might possibly be present in a supercritical state. Instead, if life evolved on Venus, it may have retreated toward cooler conditions in the atmosphere (Schulze-Makuch and Irwin 2002b). Mars has a much thinner but still significant atmosphere dominated by CO_2. The Martian atmosphere would not provide much protection for any life on its surface, but life would be possible in protected niches such as caves or beneath the surface (Boston et al. 1992).

The Jovian moons Europa and Ganymede, and possibly Callisto as well as Neptune's moon Triton, do not have significant atmospheres, but suitable conditions for life in a planetary ocean, if it exists, would be shielded by an ice crust. This ice crust would act as a shield preventing subsurface compounds from evaporating into space and would also provide a shield against cosmic rays. Planetary oceans capped by an ice shield may in fact be much more common in the universe than "naked" or "near-naked" oceans as on Earth (Schulze-Makuch 2002).

11.2.2 Internal Differentiation

Life is easier to envision on any planetary body that is differentiated into a radioactive core, a mantle and a crust. Internal differentiation is a sign of endogenic activity that is powered by radioactive decay. The likelihood of internal differentiation, in turn, is directly related to global mass, and that can be deduced by a planetary body's influence on orbiting or passing probes and by the gravitational attraction it exerts on other planetary bodies or light.

To the extent that the evolution of life on Earth is a typical example, plate tectonics, which are driven by the internal heat of Earth, or some other effective recycling mechanism for minerals and nutrients appears to be important for the persistence of living systems. Nutrients and minerals would otherwise be quickly exhausted and evolving life, especially when still in its infant stage and not well established, would not be able to meet its nutrient demands within a relatively short time frame (on a planetary time scale). On Earth and probably early Mars the recycling mechanism has been plate tectonics (Connerney et al. 1999; Sleep 1994). Plate tectonics on Earth have also constantly produced greenhouse gases that have acted as a global thermostat providing stability for the evolution of life (Ward and Brownlee 2000). The presence of plate tectonics can be identified with remote sensing methods based on measured magnetic properties of the rock, visible symmetry along a spreading axis, and specific patterns in fracture orientation and propagation.

11.2.3 Polymeric Chemistry

Chemical complexity is based at the molecular level on polymeric molecules joined by covalent bonds (Lwoff 1962). For reasons elaborated in Chap. 6, other life in the universe, except under very exotic conditions, is likely to be based on polymers of carbon. Polymeric organic compounds are in general detected by their absorption spectra.

On an active planet, polymeric organic compounds will be subject to chemical cycling. This can be inferred from spectra and gradients in surface coloration, and it appears to be widespread in our Solar System. Io, Europa, Enceladus, Iapetus, and Triton, in addition to all the planets, provide examples. On Earth, chemical cycling occurs through oxidation-reduction reactions that are actively maintained by organisms, though they can occur inorganically as well.

11.2.4 Energy Source

A flow of energy is required to organize the material of the living state and to maintain its low entropic state (Morowitz 1968), thus an external energy source is a minimal requirement for life. Light and the oxidation of inorganic compounds provide the energy for the Earth's biosphere, so wherever light and a means for sustaining oxidation-reduction cycles can be demonstrated, the possibility for maintaining life is present. Light is a highly effective form of energy on Earth, and phototrophic organisms are responsible for the high oxygen content in the Earth's atmosphere. Light from the Sun could serve as the principle energy source for living systems on all the inner planets of our Solar System, and possibly as far as the Jovian and Saturnian systems. Light is directly measurable using remote sensing and thus a good indicator for the theoretical possibility of photosynthesis. In general, energy gradients can fairly well be detected by remote sensing as detailed in Table 11.2. On Earth, all these energy sources are present. However, the availability of certain energy sources, such as heat, motion or pressure, does not necessary imply that life

Table 11.2 Remote detection of energy gradients (modified from Schulze-Makuch et al. (2002a)

Type of energy	Examples within the Solar System	Examples of remote detection
Light	Mercury to Saturnian system	Directly measurable
Chemical Cycling	Io, Europa, Iapetus, Triton	Molecular absorption spectra, surface reflectance spectra, imaging spectroscopy, polarimetry, radar measurements, detection of alteration minerals, gradients in surface coloration
Thermal	Mercury, Titan, Jovian satellites, Triton	Gradients of infrared radiation, thermal radiometry, infrared to visible spectral imaging, distance to Sun, mass sufficient for internal differentiation of planetary body (gravitational measurements), microwave radiometry to detect geothermal heat flows
Motion	Venus, Mars, Enceladus, Jovian satellites, Triton, Titan	Doppler imaging, radar interferometry, electromagnetic indications of a conducting liquid (e.g. Europa), thermal and infrared imaging (volcanic movement)
Gravitational Tides	Jovian and Saturnian satellites, Triton	Visible evidence of surface fragmentation and resurfacing, microwave radiometry
Pressure	Venus, Titan, Gas Giant planets	Visible clouds, changing atmospheric patterns (e.g. Red Spot on Jupiter), direct measurement by robotic probes
Electromagnetism	Jovian and Saturnian system	Measurement of electromagnetic field fluctuations, detection of energetic particles

relies on them, but merely that the planetary body in question is active and meets one of the prerequisites for life.

Thermal gradients are commonly available energy sources throughout the inner Solar System, and also among some larger satellites as shown from gradients of infrared and thermal infrared radiation (e.g., Io and Titan). Thermal energy can be derived from solar emissions or from radioactive heating if the mass of a planetary body is sufficient for differentiation into a radioactive core, as in the major Jovian satellites, and in Titan and Triton. Multispectral remote sensing methods are suitable for detecting rocks altered by hydrothermal heat and solutions, because their reflectance spectra differ from those of unaltered host rock. Thermal radiometry has been used, for instance, to determine that night-time temperatures on Europa are colder at the equator than at mid-latitudes for some longitudes, apparently due to latitude-dependent thermal inertia (Spencer et al. 1999; Spencer et al. 2001). Thermal radiometry has also been used extensively on Io (Spencer et al. 2000) and Mars (Christensen et al. 2003).

Kinetic energy is possible wherever gas or fluids exist. Atmospheric motion can be detected directly from visible clouds that move, such as those of Mars, Venus, the gas giant planets, and Titan from visible and reflected infrared images. Speed and direction of moving objects can be determined by Doppler imaging at various wavelengths in an atmosphere or on a planetary surface. Active faults on which earthquakes may occur can be identified by observation of topographical features from space using radar (Tapponnier and Molnier 1977). Changes in the shape of a volcano caused by an expanding or contracting magma chamber can be determined by radar interferometry. Increased emissions of gas and heat of volcanoes can be identified with thermal infrared images and movements of plumes by images in the visible or infrared wavelengths. Electromagnetic measurements with the magnetometer instrument on board the Galileo orbiter were used to infer a conducting liquid in Europa's interior (Khurana et al. 1998; Kivelson et al. 2000).

Gravitational tides are exhibited by planetary bodies and major satellites that are in periodic alignments such as the Earth-Moon system, the Neptune-Triton system, and Jupiter and its four major moons. Significant tidal fluctuations in these sufficiently massive bodies are visible by the evidence of surface fragmentation and resurfacing of the planetary or lunar surface. For example, arcuate lineaments of vast extension on Europa have been interpreted as surface expressions of these enormous tidal forces (Hoppa et al. 1999).

Pressure gradients in an atmosphere can be inferred from banded cloud patterns and measurements of their rotational velocities by large storm systems such as Jupiter's famous Red Spot and less dramatic but similar examples on the other gas giants. Also, stratification as measured at Jupiter is another indicator of pressure gradients. Osmotic pressure gradients may also exist in planetary oceans that could be conducive for the support of life (Schulze-Makuch et al. 2002a). Those gradients are difficult to confirm directly, but could be inferred by a subsurface probe analyzing ocean chemistry, or possibly by remote determination of the solute content of a liquid eruption to the surface.

Electromagnetism is another energy source that occurs wherever eletromagnetic fields are traversed or induced (Schulze-Makuch and Irwin 2001). Jupiter's magnetospheric plasma corotates with the planet at a velocity of 118 km/s, thereby creating a strong magnetic field (Beatty and Chaikin 1990). Energetic ion and electron intensities throughout the Jovian magnetosphere were measured by the Galileo orbiter using an energetic particle detector. Saturn generates a less massive but still large magnetosphere that will be mapped in detail by the Cassini orbiter. More benign electromagnetic fields and their fluctuations can be measured directly using a magnetometer.

11.2.5 Liquid Medium

Finally, a liquid medium appears to be favorable for living processes because macromolecules and nutrients can be concentrated within a bounded internal environment without immobilizing interacting constituents. This assumption is usually taken to mean an aqueous medium, though organic compounds and water mixtures with ammonia and other miscible molecules can exist in liquid form at temperatures well below the freezing point of water. The possibility that life could exist in dense atmospheres has also been suggested (Grinspoon 1997; Sagan and Salpeter 1976;

Schulze-Makuch and Irwin 2002b). There is for example both experimental and observational evidence for organic synthesis in Jupiter's atmosphere (Guillemin 2000; Raulin and Bossard 1985; Sagan et al. 1967). However, it is difficult to envision how the boundary conditions necessary for compartmentalizing the flow of energy and restraining the population of interacting molecules could be established under such conditions. However, once originated in a liquid medium, life could adapt to thrive in a gaseous environment (Schulze-Makuch and Irwin 2002b; Schulze-Makuch et al. 2002b).

Major amounts of liquid water are known for certain only on Earth, but very likely exist as subsurface water on Mars in underground aquifers (Carr 1996; Greeley 1987; Malin and Edgett 2000a; Malin and Edgett 2000b; Malin et al. 2006), and on Europa and Ganymede, where subsurface oceans are inferred from electromagnetic measurements from the Galileo orbiter (Khurana et al. 1998; Showman and Malhotra 1999) and from the presence of hydrated salt minerals on the surface (Kargel et al. 2000). Mixtures of water-ammonia-organic compounds are another possibility on cold planetary bodies, since these mixtures are liquid at much lower temperatures than water (Jakosky 1998). Theoretical models indicate the presence of subsurface stores that are liquid at extremely cold temperatures on Titan (Coustenis and Lorenz 1999; Fortes 2000) and possibly some of the satellites of Uranus and Neptune. Liquid water at or close to the surface can easily be detected by radar, gamma-ray spectrometry, and the absorption spectrum of water, but not when it is present in the deep subsurface or shielded by a thick layer of ice.

Liquid ethane and methane are assumed to be present on Titan's surface (Lorenz et al. 2003), and could provide an alternative solvent for life (Schulze-Makuch and Grinspoon 2005). Liquid sulfur compounds are inferred to exist on Io (Kieffer et al. 2000), and sulfur dioxide or hydrogen sulfide could play a role as solvent as well. Liquid compounds on a planetary surface can most easily be identified by visible and radar images of the erosional features that they cause.

11.3 Geoindicators for Life in our Solar System

Neither biosignatures nor geosignatures have been identified unambiguously on any planetary body beyond Earth to date, though the search should continue as resolution improves. Mars and Venus are the only other planetary bodies where life as we know it could plausibly be discovered by direct sampling in the foreseeable future. Thus, missions to Mars should remain a priority as they are currently with NASA and ESA, particularly lander missions (e.g. Viking 1 and 2, Pathfinder, Spirit, Opportunity, Phoenix, Mars Science Laboratory, and ExoMars). In addition, the ease of reaching Venus and the possibility of an atmospheric habitat suitable for life there argue for an atmospheric sampling mission to Venus (Schulze-Makuch and Irwin 2002b; Schulze-Makuch et al. 2005). In the meantime and for the coming decades, search for habitats suitable for life beyond the terrestrial inner planets of our Solar System should focus on geoindicators such as those listed above. The current emphasis on visualization of surface features by the Mars Global Surveyor, Mars Odyssey, Mars Express, Mars Reconnaissance Orbiter, and the visual data collected from the Jovian system by the Galileo orbiter, and still being returned from the Saturnian system by the Cassini orbiter, are compatible with this strategy. These missions have the ability to detect energy gradients, organic chemicals, and near-subsurface as well as surface water.

The Huygens probe, which landed on Titan in January, 2005, added detailed knowledge of that body's atmosphere, weather, and surface chemistry. Because of

Table 11.3 Geoindicators for the possibility of life on the planets and major satellites of our Solar System based on current knowledge (modified from Schulze-Makuch et al. (2002))

Major planetary body	Atmosphere	Thermal gradients/ chemical disequilib	Internal differentiation	Polymeric chemistry	Energy source	Liquid solvent
Mercury	No	Yes	Yes	No	LH	None
Venus	Yes	Yes	Yes	Yes?	LCHP	H_2O, H_2SO_4
Earth	Yes	Yes	Yes	Yes	LCHKGPM	H_2O
Moon	No	No	Yes	No	LG	None
Mars	Yes	Yes	Yes	Yes?	LCH	H_2O
Jupiter	Yes	Yes	Yes	Yes	LCHKPM	?
Io	No	Yes?	Yes	Yes	CLHMG	H_2S?
Europa	Yes*	Unknown	Yes	Yes	CHKGOM	H_2O
Ganymede	Yes*	Unknown	Yes	Yes	CHKGOM	H_2O
Callisto	Yes*?	Unknown	Yes	Yes?	CHKGOM	H_2O
Saturn	Yes	Yes	Yes	Yes	CHKPM	None
Tethys	No	Unknown	No	Yes?	M	H_2O?
Dione	No	No	No	Yes?	M	H_2O?
Rhea	No	Unknown	No	Yes?	M	H_2O?
Enceladus	No	Yes	No?	Yes	CHKM	H_2O
Iapetus	No	Yes?	No	Yes	CM	H_2O?
Titan	Yes	Yes?	Yes	Yes	CHM	C_2H_6, CH_4, NH_3-H_2O?
Uranus	Yes	Yes?	Yes	Yes?	CHKPM	None
Titania	No	Yes?	Yes?	Yes?	CHG	H_2O?
Ariel	No	No?	No	No?	C?H?	None?
Miranda	No	No?	No	No?	C?H?	None?
Umbriel	No	No?	No	No?	C?H?	None?
Oberon	No	No?	No	No?	C?H?	None?
Neptune	Yes	Yes?	Yes	Yes?	CHKPM	None?
Triton	Yes*	Unknown	Yes?	Yes	CHGO	H_2O/ NH_3/N_2?
Pluto/Charon	No*?	Unknown	Yes?	Yes?	CG	H_2O/ NH_3/N_2?
Comets and Asteroids	No	No	Some	Some	L for some	None

Legend: L = light energy, C = chemical cycling, H = heat energy, K = kinetic energy (motion), G = gravitational energy (tides), P = pressure energy, O = osmotic gradients (in a possible high-salinity subsurface ocean), M = electromagnetic energy. Asterisks indicate a protective ice shield and trace atmosphere. Question marks indicate uncertainty, but with our estimate of probability in the indicated direction.

the apparent similarity of its atmosphere to that of the early Earth, and its abundance of organic constituents, Titan should remain a high-priority target for exploration. In fact, geoindicators discussed here point to Titan as a suitable environment for life (Table 11.3), thus Titan should be considered a priority target of astrobiological significance (Shapiro and Schulze-Makuch 2008). We previously proposed a plausibility of life index based on criteria for the existence of life such as the presence of (1) a fluid medium, (2) a source of energy, and (3) constituents and conditions compatible with polymeric chemistry under the key assumptions that (a) life arises quickly under appropriate formative conditions and (b) remains static in stable environments or adapts to changing environments (Irwin and Schulze-Makuch 2001). We assigned a plausibility of life (POL) rating for each major planetary body in our Solar System, while pointing out that the rating must be regarded as a dynamic value consistent with the information currently available. An updated definition of the plausibility of life (POL) categories with some examples are given in Table 11.4. An updated POL rating for all planets and major satellites in our Solar System consistent with knowledge at the time of this writing is provided in Table 11.5.

Attention should also be given to some of the less known satellites. Organic constituents appear to be present on Triton and possibly Iapetus. Triton and Titania show evidence of resurfacing that would indicate the generation of internal energy. The Cassini orbiter has detected water plumes on Enceladus (Porco et al. 2006), indicating geothermal activity on this moon of Saturn. The plume also contained significant amount of carbon dioxide, methane, either carbon monoxide or molecular nitrogen, and apparently trace quantities of acetylene, propane, and ammonia

Table 11.4 Astrobiology plausibility categories (modified from Irwin and Schulze-Makuch (2001))

Category	Defintion	Examples
I	Presence of liquid water, available energy, organic compounds, atmospheric or surface shielding, and evidence of biogenic processes.	Earth
II	Evidence for past or present liquid water, availability of energy, inference of organic compounds, and planetary history favorable for genesis of life.	Mars
III	Physically extreme conditions, but with evidence of energy sources and complex chemistry possibly suitable for life forms unknown on Earth	Titan, Europa, Venus
IV	Persistence of life very different from on Earth conceivable in isolated habitats, or reasonable inference of past conditions suitable for the origin of life prior to the development of conditions so harsh as to make its perseverance at present unlikely but conceivable in isolated habitats	Io, Triton, Enceladus, Gliese 581d
V	Conditions so unfavorable for life by any reasonable definition that its origin or persistence cannot be rated a realistic probability	Jupiter, Neptune, Gliese 581a & b, HD 149026b, Sun, Moon

Table 11.5a Plausibility of Life (POL) index for planets in our Solar System

Body	POL index	Reasoning for rating
Mercury	IV	Intense solar radiation; little if any geological cycling and no atmosphere, but thermal gradients at terminator and water ice at poles,
Venus	III	Extreme heat at surface and highly caustic atmosphere; but primordial ocean likely, water vapor in atmosphere, minute amounts of organic compounds, active geology with chemical recycling likely, and moderate temperatures in lower atmosphere
Earth	I	Salt water oceans, fresh water on surface, plate tectonics provide geological recycling, and oxygen-rich atmosphere with protective ozone layer. Life is present.
Mars	II	Oxidized surface, thin atmosphere, and some geological cycling in recent planetary history, but ample evidence for liquid water on surface in the past and subsurface water now; surface temperatures sometimes above freezing point of water, polar ice caps with some water ice, presence of organic compounds inferred from Martian meteorites.
Jupiter	V	Gas giants with indistinct physical transitions; temperature and pressure extremes; abundant energy and presence of organic and nitrogen compounds, but lack of solid substrates except at core.
Saturn	V	
Uranus	V	
Neptune	V	
Pluto/Charon	V	Extreme cold, density ∼2.1 implies rock/ice composition; mix of light and dark features implies complex chemistry, and tidal flexing could provide energy, but likely origin as asteroids makes genesis of life improbable.

Table 11.5b Plausibility of Life (POL) index for major satellites in our Solar System

Body	POL index	Reasoning for rating
Moon	V	Extremely dry, no protective atmosphere, water ice at poles but no geological cycling.
Io	IV	Sharp thermal gradients and geochemical cycling; volcanic activity generates thin atmosphere and liquid sulfur compounds near surface for some time periods; coloration implies complex chemistry; but temperature fluctuations and radiation doses are extreme.
Europa	III	High radiation and extremely low temperature at surface, but planetary ocean likely beneath ice shell. Surface coloration implies complex chemistry and frequent resurfacing implies geological activity.
Ganymede	III	
Callisto	IV	High radiation and extremely low surface temperature; possible subsurface liquid water, but little energy flux.
Tethys	IV	Little evidence for liquid water at present; very low density and high albedo imply mostly water-ice composition; high radiation environment; extremely cold.
Dione	IV	
Rhea	IV	
Enceladus	IV	High radiation environment, extremely cold, and too small for significant radiogenic heating; but extensive resurfacing with evidence of ice geysers suggest geological activity, subsurface liquid water, and energy from tidal flexing

Table 11.5b (continued)

Body	POL index	Reasoning for rating
Iapetus	IV	High radiation environment, extremely cold, with no evidence for liquid water at present; low density and moderate albedo imply mostly ice composition; but dark leading edge suggests possible hydrocarbon chemistry.
Titan	III	Dense, colored atmosphere implies complex organic (reducing) chemistry; liquid hydrocarbons present on surface with possible water-ammonia liquid beneath surface; density of $\sim$1.8 implies organic liquids and/or water-ice with solid core
Titania	IV	Possible subsurface or recent surface liquid with evidence of liquid flow in canyons; relatively small for radiogenic heating, but tidal flexing could provide energy; extremely cold at surface.
Ariel	IV	Small size and insufficient evidence of energy gradients; high albedo and density of $\sim$ 1.5–1.7 imply rock/ice composition; extremely cold.
Miranda	IV	
Umbriel	IV	
Oberon	IV	
Triton	IV	Coloration implies complex chemistry; tidal flexing, radiogenic heating, or chemistry could provide energy; possible subsurface liquid water or water-ammonia mixes; density of $\sim$2 implies rocky core with water/ice surface; but has coldest surface recorded in Solar System.
Comets and Asteroids	V	Extreme cold, no atmosphere, no persistent internal energy source, rock/ice mixtures in composition, abundant water ice with possible hydrothermal alteration in parent bodies

(Waite et al. 2006). Triton and Io may also be geothermally active (higher resolution images and infrared data from Io would provide a more detailed picture of the complex thermal gradients on that body). Io may have also provided a suitable habitat for life early in the Solar System history, when it may have contained water on its surface. All these examples merit increased attention as future robotic exploration of the outer Solar System is planned.

11.4 Extrasolar Planetary Detection

The strategy for detecting planets around stars, based on perturbations in the star's motion (wobble) or appearance (from periodic occlusion) due to interaction with one or more sizeable, nearby planets has been pursued with vigor since the 1960s (Marcy and Butler 1998), but unambiguous evidence for an extrasolar planet did not come until the mid 1990s. Alexander Wolszczan (1994), a radio astronomer at Pennsylvania State University, discovered two or three planet-sized objects orbiting a pulsar in the Virgo constellation in 1994, and Michel Mayor and Didier Queloz in Geneva announced in 1995 that they had found a planet at least half the size of Jupiter rapidly orbiting the star 51 Pegasi (Mayor and Queloz 1995). This finding was soon confirmed by Geoff Marcy and his colleagues at the University of California, Berkeley (Marcy and Butler 1996; Marcy and Butler 1998), who have gone on to discover over 100 additional extrasolar planets. Since these initial findings, a flood of discoveries had brought the number of confirmed extra-solar planets to over 300 as of this writing.

Because they are easier to detect, most of these planets have been large like the gas giants of our outer Solar System. The smallest planets, which have been discovered as of this writing, are between 5 and 6 Earth masses in size. One of the two, 5.5 Earth masses in size and orbiting around an M star (preliminarily named OGLE-2005-BLG-390Lb) has been discovered by the method of gravitational microlensing (Beaulieu et al. 2006). These very rare microlensing events involve two stars in line of sight in which the front star acts as a magnifying lens. While the gravitational microlensing method works best for distantly orbiting planets, measurements through perturbations in the star's motion (radial velocity measurements) are most sensitive to large planets close to their star. The other planet, Gliese 581c, is 5.03 Earth masses at a distance of 0.073AU from its host star (an M star as well) in a 12.9-day period orbit (Udry et al. 2007). It was suggested to be possibly habitable, but it appears that its companion Gliese 581d, 7.7 times the mass of Earth and in an 83.6-day period orbit is more likely to be habitable based on recent modeling (von Bloh et al. 2007).

Technologies currently operational or under development are hastening the discovery of exoplanets. The Large Binocular Telescope Interferometer is currently under construction in Arizona. It will combine the infrared light from two 8-meter class telescopes to provide interferometry capable of imaging distant galaxies and other faint objects over a wide field-of-view. The Keck Interferometer will combine light from the world's largest optical telescopes to enable the visualization of gas clouds, including large planets within them, around distant stars.

The proportion of planets that may be smaller and more terrestrial like is unknown, but should be answered, at least for neighboring systems in our own galaxy, within the coming decade. On 27 December 2006 the European COROT mission launched, which will investigate transits of planets in front of their star. This method seems to be promising as oxygen and carbon have already been detected in the hydrodynamically escaping atmosphere of the extrasolar planet HD 209458b during four transits with the Hubble Space Telescope (Vidal-Madjar et al. 2004). The COROT mission will allow the determination of the radius of a planet in addition to its mass thus contributing to knowledge of how common large, rocky planets are. The NASA Kepler mission due to launch in 2008 will use the same methodology as COROT, but will have more time for observations to pinpoint planets further away from their star. Unfortunately, all other planned exoplanet missions such as the Space Interferometry Mission (SIM), ESA's Darwin mission and NASA's Terrestrial Planet Finder mission are delayed or cancelled. The SIM Mission aims to measure distances with hundreds of times more precision than by present technologies, and the goal of the Terrestrial Planet Finder is to detect directly gases consistent with life such as carbon dioxide, ozone, and methane, in terrestrial-like atmospheres on planets around stars up to 45 light years away. The possibility of Earth-type habitable planets in other Solar Systems has been modeled and results indicate that this is a plausible scenario (e.g. planetary system of 47 Ursa Majoris (Cuntz et al. 2006)).

One of the most significant variables in the science of astrobiology is the unknown proportion of stars that contain planets, and the proportion of those that contain planets capable of harboring life. While it can no longer be doubted that planetary systems around other stars are relatively common, the frequency of terrestrial planets in those planetary systems remains unknown at the present time. If we assume that our Solar System is not extraordinary, the frequency will likely be high, with a correspondingly high probability that life as we know it could have evolved and may be flourishing throughout the universe. Until that assumption is confirmed, however, the more conservative view that terrestrial planets are rare (Ward and Brownlee 2000) must be considered as a serious possibility. In the latter case, the chances for life as we know it are diminished in frequency, but not rendered implausible. Unlike a number of areas of astrobiology, this is a question that data acquired within the coming decade will likely be able to answer.

11.5 Chapter Summary

The search for extraterrestrial life everywhere but on our closest planetary neighbors (Mars and Venus) is limited for the foreseeable future by our inability to obtain physical samples. Therefore, information that can only be obtained by remote sensing and robotic probes will for now provide the only clues concerning the existence of life elsewhere. The search parameters we have proposed emphasize the importance of detecting the presence of physical and chemical gradients of all kinds, because of their potential for generating free energy. Other geoindicators that would enhance the prospects for life include evidence for polymeric chemistry in association with chemical cycling, the presence of an atmosphere or ice shield, sufficient mass for endogenic heating, and the availability of a liquid that may act as a solvent to enhance chemical reactions. Also, any unusual topographical features or surface patterns that cannot be easily explained by well understood geological and geochemical processes should be regarded as evidence for the possibility of environmental changes induced by living systems.

Chapter 12
Life Detection – Past and Present

Here we review the results and interpretations of the Viking mission – the only life detection experiment ever conducted on another planetary body. We also examine the claim of fossilized life in the Martian meteorite ALH84001, which sparked renewed attention to the analysis of other meteorites from Mars. Finally, we will provide a brief overview on the development of current life detection methods.

12.1 The Viking Mission

The Viking program, consisting of two orbiters with landers, Viking 1 and Viking 2, was the most ambitious mission ever sent to Mars. It was a major milestone in the exploration of our Solar System, following the human landings on the Moon, and is the best example to date of human attempts "to boldly go" in search for life on another world. Despite the unresolved controversy about the Viking life detection experiments, the mission was highly successful in providing an enormous amount of information about the environmental conditions on Mars.

12.1.1 The Viking Landers

Viking 1 was launched on 20 August 1975 atop a Titan III-E rocket with Centaur upper stages, followed two and a half weeks later by the launch of Viking 2. Inserting into orbit around Mars about ten months later, the Viking orbiters functioned flawlessly to transport the landers, performed reconnaissance to locate and certify landing sites, and conducted scientific investigations including imaging the surface, measuring atmospheric water vapor, and obtaining radio science data. About a month after arrival, on 20 July 1976, the Viking 1 lander disattached from its orbiter and touched down at 11:56:06 UT in the western Chryse Planitia region. Transmission of the first surface image began 25 seconds after landing. The Viking 2 lander followed a month and a half later, touching down about 200 kilometers west of the crater Mie in Utopia Panitia on 3 September 1976. The landers carried instruments

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

to study the presumed biology, chemical compositions, meteorology, seismology, magnetic properties, and physical properties of the Martian surface and atmosphere. The team of scientists, selected by NASA in 1969 to plan and conduct investigations on the Viking spacecraft, included Wolf Vishniac, Harold ("Chuck") Klein, Joshua Lederberg, Alexander Rich, Norman Horowitz, Vance Oyama, and Gilbert Levin. The NASA team was aware that the Viking biology experiments could only detect certain types of life. However, the media heralded the Viking biology tests as experiments designed to prove whether life exists on Mars or not. Although the biology experiments were undoubtedly the crown jewel of the mission, the biology payload weighed only 15.5 kg, consisting of three separate experiments, with a Gas Chromatograph Mass Spectrometer (GC-MS) to detect organic molecules.

In the *Gas Exchange Experiment* Martian soil samples were carefully cleansed with helium, and then incubated with carbon dioxide, inert gases, and water. The instrument sampled the atmosphere of the incubation chamber periodically for concentration of several gases including carbon dioxide, oxygen, nitrogen, hydrogen, and methane. The mission scientists believed that metabolizing organisms would either consume or release at least one of the measured gases. The Gas Exchange Experiment was designed to be conducted in two different modes using the same equipment. In the humid mode, Martian surface samples were incubated in the presence of carbon dioxide and water vapor, based on the assumption that substrates might not be limiting on Mars, but that biological activity is dormant in these samples until enough water becomes available in the environment. The second (dry) mode assumed the presence of heterotrophic microbes on Mars that feed on organic molecules under dry conditions.

In the *Labeled Release Experiment* a sample of the Martian soil was inoculated with water and nutrient solution containing glucose with ^{14}C, a heavy, radioactive isotope of carbon. If any heterotrophic organisms feeding on simple organic compounds would be present, they would consume the nutrients and release ^{14}C containing carbon dioxide, which would easily be detected by a radioactivity counter. The ambient environment from which the soil was taken was anaerobic (oxygen-poor) and devoid of liquid water.

The *Pyrolytic Release Experiment* looked for evidence of photosynthesis by incubating Martian soil with light, water, and a carbon-containing atmosphere of either carbon monoxide or carbon dioxide. The gases were enriched with radioactive ^{14}C. If photosynthetic organisms were present on Mars resembling plants or cyanobacteria on Earth, then these organisms would incorporate some of the carbon as biomass by carbon fixation. After several days of incubation, the experiment removed the gases, heated the remaining soil to a sterilizing temperature of 650°C, and collected the product to count radioactivity. If gaseous ^{14}C had been converted to biomass by carbon fixation, it would be vaporized during heating, and the radioactive counter would detect it.

The GC-MS in the Viking instrument load was designed to separate vapor components and to measure the molecular weights of chemicals. Thus, it could separate, identify, and quantify a large number of different chemicals, including organic compounds.

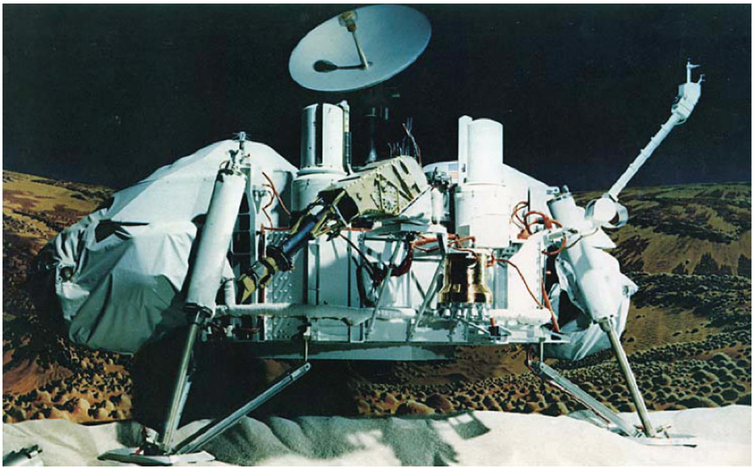

Fig. 12.1 Viking lander (image from NASA)

The operational life time of the Viking 1 lander was more than 6 years, from July 1976 to November 1982, while the Viking 2 lander operated for about 3 1/2 years. The Viking lander is shown in Fig. 12.1.

12.1.2 Mission Preparation

Counter to some arguments or perceptions, the Viking mission was well prepared even though budget cuts reduced its capabilities. A 4th planned biology experiment, the so-called "Wolf Trap", which was designed to monitor a vial of water for increasing turbidity after a soil sample was placed in it, was cancelled, mainly due to payload constraints.

Countless samples were tested before flight by the Viking instruments using a variety of microbial cultures, testing out the widest array of microbial populations that were available. Also, soil samples from widely differing geographic regions were obtained and tested, including samples from the Antarctic, the Gobi Desert, and Alaska. Large amounts of data were collected, analyzed, and interpreted. The principal investigators of the biology experiments agreed in advance how they would decide on a positive and negative outcome of the life detection experiments. Detectors, chromatograph columns, and other actual flight components were extensively tested for their scientific as well as their engineering characteristics. Both the Gas Exchange and Labeled Release Experiments were tested against a wide variety of terrestrial soils. The Viking team detected the presence of microbes in most samples when they were incubated under terrestrial conditions. When the soil samples were incubated under Martian environmental conditions similar responses were seen but with a prolonged lag period. The lag period, however, was not necessarily representative of possible Martian organisms, since it reflected the response of Earth organisms to the very different conditions on Mars. The Gas Exchange Experiment of the Viking mission was tested using sixteen different terrestrial soils (Oyama 1972). Fourteen of the sixteen soils showed positive gas exchanges related to microbial metabolisms, both under aerobic (oxygen-rich) and anaerobic (oxygen-poor) conditions. However, in retrospect, the two negative samples from extreme environments, including one from Antarctica, almost certainly contained organisms, but the Viking Gas Exchange Experiment was not able to detect it. There was another intriguing result from the test series as well. The team realized that false positives could occur when nutrient medium made contact with Martian soil. This was particularly evident if the elements calcium, cadmium, iron, lithium, magnesium, and zink were involved – some of which were expected to be common in Martian soil. Oyama (1972) concluded that these reactions would occur only early during the first cycle of the experiment and dissipate quickly during repeated rechargings. Especially, the production of, hydrogen and methane gas accompanied by a relatively fast rate of carbon dioxide disappearance could be a nonbiological consequence of initial contact between Martian soil and the aqueous nutrient medium. This left open the possibility of other chemical and physical phenomena that could affect gas release rates. Thus, signs of potential trouble for the interpretation of the anticipated life detection results were present from the beginning.

12.1.3 Mission Results

The initial results from both landers were very exciting, but also very confusing. All three experiments observed changes that indicated the possible presence of life, although the expected signals were not always as large as expected, and often tapered off over time, casting doubt on a biological explanation:

First, the *Gas Exchange Experiment* was conducted in the humid mode. Results indicated that some carbon dioxide and nitrogen gas (N_2) was desorbed from the soil, and there was a surprising and rapid accumulation of oxygen after humidification. Oxygen release upon humidification had not been observed before with samples either from Earth or the Moon, and is still puzzling today. After the initial rapid gas release, later addition of water to the soil caused no further release of oxygen. In another experiment that was conducted in the humid mode at a sterilizing temperature of 145°C, oxygen was again released from the sample, suggesting a chemical explanation for the observed phenomenon. The source of the N_2 is unclear. No nitrogen gas was added to the soil, but the nutrient contained nitrogen-containing compounds such as amino acids and nitrates.

In *the Labeled Release Experiment* the addition of an aqueous solution of dilute radioactive organic compounds to Martian samples resulted in a rapid release of labeled gas (Fig. 12.2). The process was virtually eliminated by prior heating of the samples at a sterilizing temperature of about 160°C for three hours, and was substantially reduced by heating to only 45 to 50°C. As in the case of the Gas Exchange

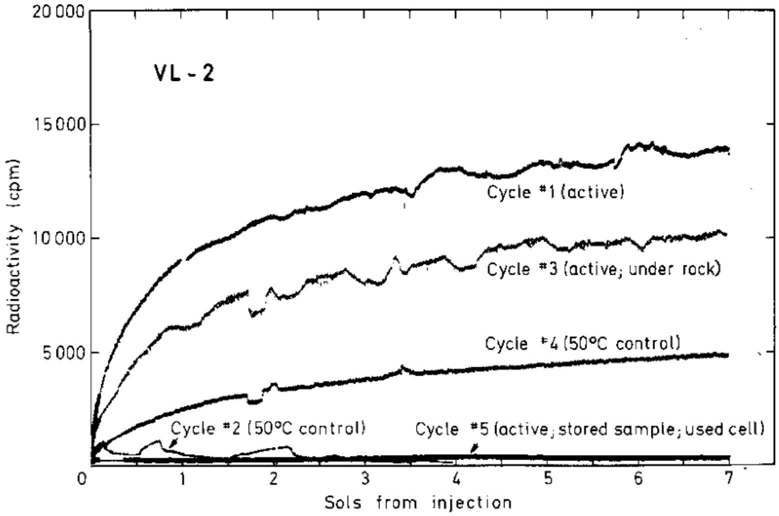

Fig. 12.2 Radioactivity evolved in the Labeled Release Experiment following the first injection of radioactive nutrient to each analysis cycle in the Viking 2 lander. A fresh sample was used for each cycle except cycle 5 which used a sample stored approximately 84 Sols (Martian days) at 7°C prior to injection. The sample used in cycle 3 was obtained from under a rock. Cycles 1, 3, and 5 were active sequences, whereas cycles 2 and 4 were control sequences in which the samples were heated for 3 h at approximately 51.5°C and 46°C, respectively, prior to nutrient injection. All data have been corrected for background counts observed prior to injection (figure courtesy of Gilbert Levin, Spherix, Inc.)

Experiment, upon prolonged incubations, there was a slow continued release of labeled gas after the initial rapid reaction was over. Also, each time additional liquid was added, about 30% of the labeled gas in the test cell went into solution. In contrast to the results obtained in the Gas Exchange Experiment, storage of the samples for 2 to 4 months essentially eliminated the agent responsible for the rapid decomposition of the nutrient in the Labeled Release Experiment.

In the *Pyrolytic Release Experiment* significant positive reactions were found at both Viking landing sites (Table 12.1). Prior heating of a sample at a sterilizing temperature of 175°C for three hours drastically cut down the reaction, while heating at 90°C had no deleterious effects. The data also suggested that the observed reaction was proceeding better in light, but this conclusion was based on comparing reactions under "light" conditions on one lander site with "dark" conditions on the other. Storage did not reduce the capacity of the Martian samples to yield statistically positive results. In one experiment the soil sample was first humidified for several hours, after which the test cell was heated and vented to dry out the sample. This treatment was intended to remove, or at least greatly decrease any major postulated oxidants such as superoxides and hydrogen peroxide. However, even after this treatment the Martian samples still yielded a positive result.

The GC-MS instrument on board the Viking landers did not detect conclusively any indigenous organics in any of the samples tested, at the levels down to what was

Table 12.1 Data from the Pyrolytic Release Experiment (Horowitz et al. 1977). The Conditions Column indicates whether the lamp was on or off, whether or not water vapor was injected, and whether the soil sample was heat-sterilized (control is 175°C for 3 hours). The radioactivity of Peak 2 column represents organic matter synthesized from the labeled gases

Experiment	Conditions	Peak 2 (count/min)
Chryse 1	Light, dry, active	96 ± 1.15
Chryse 2	Light, dry, control	15 ± 1.29
Chryse 3	Light, dry, active	27 ± 0.98
Chryse 4	Light, dry, active	35 ± 1.6
Utopia 1	Dark, dry, active	23 ± 1.7
Utopia 2	Light, wet, active	2.8 ± 0.92
Utopia 3	Dark, dry, active	7.5 ± 2.5

thought parts per billion. A much later analysis indicated that the Viking GC-MS was much less sensitive than originally thought (Navarro-González et al. 2006).

As pointed out by Harold Klein, the lead scientist of the biology payload in 1977, the Viking experiments were predicated on the assumption of a widespread distribution of Martian biota that was reliably sampled at the two Viking landing sites. If, however, life were to exist on Mars in highly localized habitats, and perhaps constrained by unfamiliar metabolic limitations, the ambiguous results of the Viking experiments could well have been obtained, with inconclusive evidence for the presence of life on Mars.

12.1.4 Interpretation of Mission Results

After several months of receiving data from the Viking landers, controversy erupted within the Viking Program team. Harold Klein and most other participating scientists believed that the results from the experiments, taken all together, could best be explained by non-biological chemical reactions. Gilbert Levin, principal investigator of the Labeled Release Experiment, deviated from this opinion, arguing that the Labeled Release results were entirely consistent with a possible biological interpretation (Levin and Straat 1977) based on

1. the uniform production of gas from the Labeled Release nutrient when it was added to Martian soil at both lander sites;
2. a net loss of radioactive gas following the addition of more nutrient after the reactions had approached completion;
3. the lack of labeled release following direct exposure of the sample to visible or ultraviolet light on the Martian surface prior to placing it in the test cell (which would have been the case if oxidants produced by light were the reacting agent rather than a biological process); and
4. the reactant in the Martian soil being completely unreactive at the sterilizing temperature of 460°C, whereas, in contrast, exposure to 18°C for two Martian days did not inhibit the reaction.

Gilbert Levin also pointed out that the Labeled Release Experiment was the most sensitive test for the detection of life, and that by prior consensus only one experiment with a positive outcome would be needed to count as a positive sign of life. Nonetheless, scientific consensus shifted toward a non-biological explanation. The inability of the GC-MS to detect significant amounts of organic molecules in the Martian soil was particularly difficult to explain if Martian microbial metabolism was responsible for the positive results seen by the Labeled Release, Pyrolytic Release, and Gas Exchange Experiments. Harold Klein, the lead scientist of the biology payload, acknowledged humbly that all of the Viking biology experiments deviated to some extent from ambient Martian conditions and stated that "while we have obtained significant and fascinating data in the Martian experiments, we may not have hit upon the proper conditions to elicit evidence of Martian metabolism" (Klein 1977). Various interpretations continued to be offered nonetheless. Klein (1978) compared the merits of various chemical and biological explanations for the detailed results of each experiment. He concluded that, while some of the results were consistent with a biological interpretation, most were not. Interestingly, the experiment that he deemed to be closest to a biological explanation was the Pyrolytic Release Experiment (Table 12.1). Most scientists, however, focused on the Gas Exchange Experiment and ignored somewhat the more challenging results from the Labeled Release and Pyrolytic Release Experiments.

A number of scientists proceeded to advance the idea that inorganic compounds were responsible for the observed behavior (Benner et al. 2000; Klein 1999; Mancinelli 1989; Quinn and Zent 1999; Yen et al. 2000), most of them championing some kind of very strong oxidant that would react with the added water to produce oxygen and hydrogen, and with the nutrients to produce carbon dioxide (Ballou et al. 1978; Klein 1978; Oyama et al. 1977). However, the oxidant would have to be a chemical unfamiliar on Earth, because the presence of humidity in Earth's atmosphere would immediately destroy any oxidant strong enough to react with water. Unfortunately, none of the successful follow-on missions after Viking was equipped with a suitable sensor for the detection of oxidants. Another interesting suggestion was advanced by Nussinov et al. (1978) who argued that oxygen gas might physically be trapped in soil micropores. The trapped gas would have to be created by the direct interaction of solar UV radiation with the soil matrix, however, and the positive response in the Labeled Release Experiment on the sample from underneath a rock at the Viking 2 landing site is a problem for this hypothesis and similar ones (Cycle 3 in Fig. 12.2).

Zent and McKay (1994) pointed out the problems with oxidant reaction explanations under the environmental conditions on Mars. They concluded that none of the hypotheses in the literature is free of serious objections, many having to do with the instability of putative oxidants in the presence of heat, light, or atmospheric carbon dioxide. Or, the suggested hypotheses would require elaborate formation mechanisms for which there is no evidence. However, Zent and McKay (1994) also rejected the biological explanation, believing rather that the results obtained by Viking can best be explained by some kind of heterogeneous surface chemistry, yielding one or more types of oxidizing surfaces on the Martian regolith particles.

Unfortunately, the Mars Oxidant Experiment on board the Russian Mars ’96 mission, which was to have tested the supposition of a reactive, oxidizing surface on Mars, was lost when the mission failed soon after launch in 1996.

In 2007 a new biological explanation for the Viking results was advanced by Houtkooper and Schulze-Makuch (2007). They suggested that Martian organisms, if they exist, might utilize a water-hydrogen peroxide (H_2O-H_2O_2) mixture rather than water as an intracellular liquid. This adaptation would have the particular advantages in the Martian environment of providing a low freezing point, a source of oxygen, and hygroscopicity, and would provide a logically consistent explanation to the Viking results (Table 12.2). Hygroscopicity would be an especially useful trait since it might allow the suggested organisms to scavenge water molecules directly from the Martian atmosphere. However, at the same time it would make them extremely vulnerable to abundant liquid water (as used in some of the Viking experiments).

H_2O_2-H_2O solutions are mostly known as disinfectants and sterilizing agents on Earth, but some microbial organisms (e.g., certain *Streptococcus* and *Lactobacillus sp.* (Eschenbach 1989) and even human cells (e.g., macrophages, endothelial cells) produce hydrogen peroxide, while other microbes utilize H_2O_2 (e.g., *Neisseria sicca*, *Haemophilus segnis*; Ryan and Kleinberg 1995), and some others such as the microbe *Acetobacter peroxidans* use H_2O_2 in their metabolism (overall reaction $H_2O_2(aq) + H_2(aq) \leftrightarrow 2H_2O$; Tanenbaum 1956). Hydrogen peroxide is in fact widely used by organisms. H_2O_2 is included in many cells in nanomolar amounts and has an ancient relationship to metabolism, because many cells contain the enzyme hydrogen peroxide catalase.

Schulze-Makuch et al. (2008) have simulated the experiments to be conducted by the TEGA instrument of the Phoenix lander to test the hydrogen peroxide-water hypothesis. They used differential scanning calorimetry to analyze phase transitions and thermodynamic properties of various compounds including pure water, various concentrations of hydrogen peroxide solution, Fe_2O_3, TiO_2, tetrasodium pyrophosphate ($Na_4P_2O_7$), phenacetin ($C_{10}H_{13}NO_2$), quartz sand, Martian regolith simulant soil, and combinations thereof. $Na_4P_2O_7$ and phenacetin are stabilizers of H_2O_2 and were included in the test set, because if the Martian H_2O_2 would be mostly of biogenic nature, a chemical stabilizer would have to be invoked to control the reactivity of the hydrogen peroxide. The addition of a chemical stabilizer in the tested H_2O_2 solutions was identified in the experimental thermograms and may serve as a biomarker for hydrogen peroxide-water supported life for the Phoenix and other future missions (Schulze-Makuch et al. 2008).

Though widely perceived as a disappointment and the cause of a 20 year hiatus in the continued exploration of Mars, the Viking Mission in retrospect stands as a valiant testimony to the creativity and resourcefulness of the first human attempt to detect life on another world. Given the limitations of technology, distance, and lack of knowledge about the Martian environment at the time, the ambiguous results from the Viking landers are hardly surprising. Even today, the view that Viking may have provided the first evidence for life on Mars cannot be discounted.

Table 12.2 Comparison of chemical hypothese and the biological H_2O_2-H_2O hypothesis based on Viking observations (modified from Houtkooper and Schulze-Makuch 2007)

Observation	Chemical explanation	H_2O_2-H_2O hypothesis
Lack of identified organic molecules	Organics were oxidized to nonvolatile salts of benzenecarboxylic acids, and perhaps oxalic and acetic acid (Benner et al. 2000).	Upon death of organisms, organics were spontaneously oxidized by intracellularly bound H_2O_2 with little or no organic residue – a notion also supported by the release of 50-700 ppm of CO_2 as measured by the Viking GC-MS.
Lack of identified oxidant	An as yet unidentified mechanism on Mars produces H_2O_2 or other oxidants with no analog on Earth.	H_2O_2 in the H_2O_2-H_2O mixture is part of the biochemistry of putative Martian organisms.
Release and partial resorption of O_2, CO_2, and N_2 in Gas Exchange Experiment	Evolution of O_2 on humidification involved one or more reactive species such as ozonides, superoxides, and peroxides (Oyama and Berdahl 1977). CO_2 production in the wet mode could have been related to the oxidation of organic nutrients, with N_2 release related to initial N_2 desorption from soil by water vapor and subsequent resorption in liquid water (Oyama et al. 1977).	Release of O_2 (and possibly CO_2 to lesser degree) resulted from energy-producing metabolism. Also possibly produced by decomposition of dying Martian biota upon humidification. N_2 decrease could have been due to biological fixation exceeding the amount due to physical sorption.
Synthesis of organic material in Pyrolytic Release Experiment	Instrument malfunction, incorporation of ^{14}CO into carbon suboxide polymer preformed on the Martian surface, and reduction of ^{14}CO by H_2O_2 in the surface material (Horowitz et al. 1977).	Putative organisms were able to metabolize and synthesize organic compounds before they died from hyperhydration.
Results of Labeled Release Experiment	Inorganic process simulated by laboratory tests on Earth using inorganic oxidants and clay minerals, except for decrease of responses after storage at elevated temperatures (Klein 1999).	Limited metabolism (Levin and Straat 1977, 1981) before the organisms died due to hyperhydration, osmotic pressure, and/or heat shock.

12.2 Martian Meteorites and Evidence for Ancient Life

On an early August day in 1996 television lights illuminated the South Lawn of the White House. President Clinton, with NASA administrator Dan Goldin at his side, read a carefully crafted statement on the significance of the announcement to be made. An historic press conference had started, in which David McKay from the

NASA Johnson Space Center and his colleagues announced to the world that they believed they had found evidence of ancient life in a Martian meteorite. The claim for ancient life on Mars from this potato sized meteorite, ALH84001, changed the field of astrobiology, and brought the discussion of possible extraterrestrial life back to the front burner of the public's mind and the agenda for space science.

12.2.1 The Claim of Fossilized Life in Martian Meteorite ALH84001

The meteorite on which the claim of evidence for ancient life was based had been found in the Allen Hills of Antarctica in 1984 during a National Science Foundation search for meteorites in the Antarctic, hence the name, ALH (Allen Hills) 84 (1984) 001 (number 001). Visually the most unusual rock collected during the 1984-1985 field season, it was at first incorrectly classified as a rare achondritic meteorite and filed away. It took another nine years before it was correctly identified as a member of the SNC (shergottite, nakhlite, chassignite) group of meteorites (Mittlefehldt 1994; Miura et al. 1995). The following picture appeared: ALH84001 is one of the oldest meteorites of the Solar System. It had formed a few kilometers deep within the congealing crust about 4.5 billion years ago, shortly after Mars itself had formed. Later, it was broken by the shock of one or more asteroid impacts on the surface about 3.6 billion years ago when Mars was warmer and wetter. Groundwater likely seeped through the fissures and fractures and filled them with carbonate material. Another huge asteroid must have struck Mars about 16 million years ago with such a tremendous force that it ejected parts of the Martian surface into space free of the gravitational pull of the planet. One of those pieces was ALH 84001. It remained in space until about 13,000 years ago when it was pulled in by Earth's gravity and fell onto Antarctica, where it was found in 1984. The dates are confirmed by a variety of radioactive isotope dating techniques. Although many thousands of meteorites have been recovered, only very few of them have been identified as Martian in origin (close to thirty at the time of this writing). The link to Mars is made by mineral geochemistry of the meteorites, and particularly by the gas content trapped in tiny pockets (Mittlefehldt 1994; Miura et al. 1995). The Viking and later rover missions revealed a very distinct gas mix on Mars that differs from any known atmosphere elsewhere.

McKay et al. (1996) made their case for biology in ALH84001 based on (1) carbonate globules and features within the meteorite that resembled terrestrial biogenic carbonate structures, (2) magnetite and iron sulfide particles that could have resulted from oxidation and reduction reactions known to be important for microbial organisms on Earth, (3) the presence of complex organic compounds, specifically polycyclic aromatic hydrocarbons (PAHs), that were associated with the carbonate globules, and conceivably could represent breakdown products of organisms, and (4) ovoid and bean shaped structures that resemble fossilized ancient microbes (Fig. 12.3). They acknowledged that no single one of their observations was itself

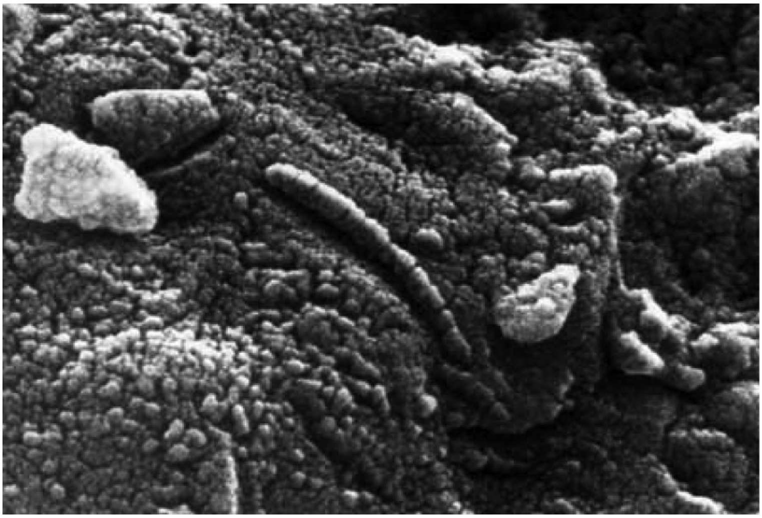

Fig. 12.3 The image that went around the world in 1996. Putative Martian microbe (segmented worm-like center structure) in meteorite ALH 84001. Image from NASA

conclusive for the existence of past life on Mars, due to alternative possible explanations for each of the phenomena. However, they argued that the totality of their observations considered collectively, particularly in view of their spatial associations, constituted evidence for primitive life on early Mars.

There were several important implications regarding the organic material within ALH84001. First, the organic compounds provided proof that in fact organic material existed on Mars – one of the main arguments against a biological explanation for the Viking experiments. Second, the organic material was in the parts per million range, which is low, but much higher than the one part per billion range or lower for organic carbon detected in other meteorites found in Antarctica, or the parts per trillion range expected from contamination. Also, the fact that the organic carbon content increased towards the center of the meteorite was consistent with a fusion crust caused by an Earth atmospheric entry. Organic matter derived from contamination would have been more common near the outside than inside the meteorite. Thus, the organic compounds were presumed to be indigenous and therefore from Mars.

Details are important for this type of investigation. McKay et al. (1996) noted that the carbonate globules tended to be disc-shaped rather than spherical and were flattened parallel to the fracture surface indicating that the carbonates formed in the restricted width of a thin fracture by aqueous processes. The authors claimed that stable oxygen isotope data suggested that the carbonates formed at temperatures between 0° and 80°C, compatible with a biogenic formation. They noted that the larger globules had calcium and manganese-rich cores, which were surrounded by alternating iron and magnesium-rich bands possibly containing iron sulfide – another observation consistent with biological processes. More importantly, they detected single-domain magnetite crystals in ALH84001 with no structural defects and without any detectable amounts of other elements. McKay et al. (1996) explained the co-existence of magnetite and iron sulfides within partially dissolved carbonate by biological processes, which are known to operate under extreme disequilibrium conditions. The importance here is that precipitation of iron sulfides and magnetite within individual bacterial cells is known to occur and that the magnetite particles in ALH84001 are chemically, structurally, and morphologically very similar to magnetite particles known to occur in some Earth organisms. This type of magnetite had also been found in ancient limestones on Earth, where it has been interpreted as biogenic in origin. Finally, and most controversially, was the claim that the jelly-bean shaped and threadlike structures in the images represent fossilized microbial organisms (Fig. 12.3). The researchers acknowledged that these structures were much smaller than typical microbes on Earth, and pointed to the more recent discovery of very small microbial organisms on Earth, named nanobacteria, by Bob Folk from the University of Texas and others, which have about the same size as the structures in the meteorite. They pointed out that these objects were about 380 nanometers long and thus big enough to pack in all the cellular components needed for a typical terran microbe to function. Some of the other structures claimed to be of biological nature were much smaller, 20 to 170 nanometer inside, and interpreted to represent fragments or appendages, similar to the ones found in deep basalt samples near the Columbia River in Washington State (USA).

12.2.2 A Cold Reception by the Scientific Community

McKay et al. (1996) admitted that none of the lines of evidence provided a conclusive case for Martian life. Not surprisingly, therefore, each claim was soon met by a host of scientific critiques and counterclaims, ranging from disputes over the formation temperature of the meteorite, to the evidence for fossilized microbes and biogenically generated magnetite.

12.2.2.1 Formation Temperatures of ALH84001

The question of formation temperature is critical, because if the carbonate globules within ALH84001 formed above sterilization temperatures, the claim of ancient life in the Martian meteorite would be off the table. Several arguments were advanced in favor of a sterilizing formation temperature. These included the absence of water-rich minerals in the carbonates, an elemental composition indicating formation reactions most likely between hot (>650°C) CO_2-rich fluid and host rock during an asteroid impact (Harvey and McSween 1996), the presence of whiskers and platelets consistent with vapor phase growth and a formation temperature of 500 – 800°C (Bradley et al. 1996), and a formation model by Leshin et al. (1998), which indicated that the carbonates in ALH840001 formed either at temperatures of 125° to above 250°C, or above 500°C, both inconsistent with a biological explanation.

Their claims, however, were countered by other studies. Kirschvink et al. (1997) noted that heating can re-magnetize or erase previous magnetization, but mineral grains from the crushed zone of ALH84001 revealed a stable natural remnant magnetization indicating that the minerals had not been heated significantly since the formation of the internal crushed zone about 4 billion years ago. Since the carbonate globules formed later, they concluded that they must have formed at low temperatures. Valley et al. (1997) reported that the isotopic variations and mineral compositions of ALH84001 offered no evidence for high temperature (>650°C) carbonate precipitation. Instead, they suggested non-equilibrium processes at low temperatures. Warren (1998) argued that the high-temperature models for the origin of carbonates in ALH84001 are implausible due to the absence of alterations in the mineral grains. He also dismissed the hydrothermal model, pointing to the lack of secondarily formed water-rich silicates in ALH84001. Instead, he suggested that the carbonates formed either as evaporate deposits from floodwaters that percolated through the fractures of the meteorite, or as a Martian form of calcrete, which forms as calcite is dissolved in groundwater and, under drying conditions, are precipitated when the water evaporates at the surface. Kent et al. (2001) used chemical diffusion rates of magnesium and calcium to suggest formation of carbonates in ALH84001 at low temperatures, most probably less than 200°C. They also pointed out that carbonate zoning at formation temperatures in excess of 600°C could only occur within the uppermost melt-rich portions of an impact structure.

The question appeared to be resolved when Eiler et al. (2002) reported that there were at least two distinct carbonate populations within ALH84001: one consisting of low-temperature water precipitates and the second produced by shock melting of the first due to asteroid impact. Romanek et al. (2002) confirmed the presence of at least two chemically distinct carbonates and claimed that the oxygen isotope composition of the carbonates indicated that they were precipitated from a low-temperature fluid in the Martian crust. In summary, none of the arguments either for or against a formation temperature consistent with the biogenic origin of carbonates is conclusive.

12.2.2.2 Fossil-like Structures in ALH84001

The argument for a fossil microbe in ALH84001 (Fig. 12.3) has always been tenuous. Recognizing fossil evidence is even an extremely contentious issue for early life on Earth (Brasier et al. 2002; Schopf 1993). The rod-like structure in ALH84001 clearly resembles a microorganism of some sort; but Bradley et al. (1997) claimed that these structures were just as likely to be laboratory artifacts from the deposition of conductive heavy-metal coating, a charge heavily disputed by the McKay group. One of the strongest initial arguments against the biological origin of these structures was their much smaller size than typical Earth organisms. However, as pointed out by McKay et al. (1996), recent discoveries have in fact revealed the existence of such very small organisms on Earth.

The term nanobacteria was first used by Folk (1993) to describe 10-200 nm sized objects observed in geological materials. Mineral forming nanobacteria have been isolated from human kidney stones, blood and blood products, among various other media (Ciftςioglu et al. 1999; Folk 1999; Kajander et al. 1997; Kajander and Ciftςioglu 1998; Kirkland et al. 1999; Schieber and Arnott 2003). Kajander et al. (1997) described coccoid cell-walled organisms with a size of 80 to 500 nm occurring in clusters and producing a biofilm containing carbonate and hydroxyl apatite. They found that the growth rate of the observed nanobacteria was about one hundredth of ordinary bacteria, that they contain DNA, and noted their high resistance to heat, gamma-radiation, and antibiotics. Their claim is highly controversial though, because most scientific groups were not able to reproduce their results, particularly of finding DNA associated with the nanobacteria. Since it is not clear what these nanobacteria represent, they are often referred to as calcifying nanoparticles. However, a more definite detection has recently been made of an acidophilic Archaea, which has a cell volume of less than 0.006 cubic micrometer (Baker et al. 2006) and is smaller than the minimum size expected on the basis of theoretical considerations for free-living cells. The organisms were discovered by community genomic analysis from acid mine drainage. Starvation of laboratory-cultured bacteria commonly leads to reduction in cell size. Thus small cells may be starved, miniaturized versions of culturable bacteria. Torrella and Morita (1981) reported that some microbes of small size respond to nutrient addition by increasing in cell number and size while others multiply but retain their small size. Thus, the counter argument based on size has weakened over time, but the possibility that the observed structures might be artifactual still cannot be discounted.

12.2.2.3 A Magnetite Biosignature?

Perhaps the most contentious discussions erupted around the magnetite grains in ALH84001, which were claimed by McKay et al. (1996) to represent a biomarker for life on Mars, due to their single-domain crystals, purity, and lack of structural defects. Bradley et al. (1996) disputed that point by reporting that their analysis of magnetite crystals in ALH84001 indicated the presence of whiskers and platelets that most likely formed in the temperature range of 500 – 800°C by direct condensation from a vapor or precipitation from a supercritical fluid. In 2000 the McKay group, led on the magnetite issue by Kathie Thomas-Keprta, responded to clarify their argument. Thomas-Keprta et al. (2000) studied 594 magnetites from ALH84001 and grouped them into three populations based on morphology, and asserted six properties of biogenicity, which included narrow size range, restricted width to length ratios, chemical purity, few crystallographic defects, crystal morphology, and elongation along only one of the possible rotation axes of a regular octahedron. They emphasized that a potential seventh property, the presence of magnetite crystals aligned in chains would be even more revealing. Thomas-Keprta et al. (2000) claimed that about 25% of the magnetite crystals in ALH84001

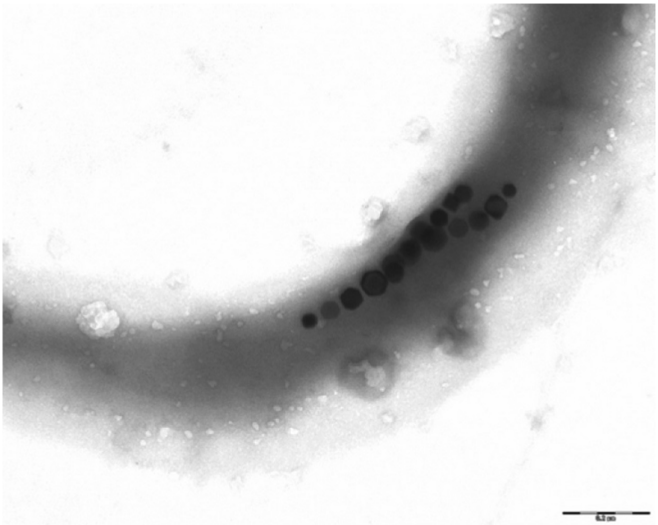

Fig. 12.4 Magnetite chain in a terran magnetotactic bacteria from Kelly Lake, Canada. Image is courtesy of Alfonso Davila from the NASA Ames Research Center

conformed to these 6 properties. The elongated prisms were very similar to those of magnetotactic bacteria on Earth, particularly those from bacterial strain MV-1. Magnetotactic bacteria align to Earth's magnetic field and produce a single intracellular chain of about 12 well-ordered magnetite crystals, each encapsulated within a coating or membrane (Fig. 12.4). The chain of magnetite crystals acts very much like a compass needle to enable the passive alignment of the bacterium along the Earth's geomagnetic field lines. Thus, bacterial cells appear to exert strict physical and chemical controls on the formation of magnetite and this, the argument was, would produce a suitable biomarker for life within rocks. The association of biogenically produced magnetites with inorganically produced ones was not considered as surprising, because magnetites formed by bacteria from Earth are usually found in environments where inorganic magnetites are common. Shortly thereafter, Thomas-Keprta et al. (2001) extended their argument to a bolder claim that the magnetite crystals are in fact Martian "magnetofossils" and that these magnetites constitute evidence of the oldest life yet found. Independently, Friedmann et al. (2001) found magnetites aligned in chains in ALH84001 and argued that they would be nearly impossible to produce inorganically and were consistent with a biological origin.

These claims were vigorously disputed by arguments that an inorganic pathway could produce the carbonate globules that hosted the magnetites (Golden et al. 2001), or that magnetite alignment could be produced by solid-state diffusion as a result of carbonate decomposition during impact heating (Barber and Scott 2002). Thomas-Keprta et al. (2002) responded by arguing that the heat necessary to decompose iron carbonates and form magnetite was simply not present and would require homogenization of all magnetic dipoles. Instead, considerable heterogeneity was observed in the ALH84001 carbonates inconsistent with significant heating. A somewhat neutral perspective was provided by Weiss et al. (2004), who argued that magnetite crystals in the carbonate from ALH84001 have a composition and morphology indistinguishable from that of magnetotactic bacteria. They noted that the alignment of magnetites in chains was the strongest argument for a biogenic origin of the magnetite, even though no more than 10% of the magnetite in ALH84001 occurs in chains. They also pointed out that the magnetite is unusually pure and fine-grained, similar to terran magnetofossils, but that it would be difficult to conclusively prove the biogenic origin of the magnetites due to the low abundance of chains. Even in sediment deposits from Earth that have undergone diagenesis, typically more than half of the chain structures have been disrupted. Thus, like other aspects of the argument for biosignatures in ALH84001, the evidence from magnetite remains plausible but inconclusive.

12.2.3 Signs of Ancient Life in another Martian Meteorite?

A new twist appeared in the discussions about life in the Martian meteorite ALH84001 when McKay et al. (2006) showed microscopic slides that revealed complex organic matter within microscopic veins in another Martian meteorite called Nakhla. These veins were similar to those observed in ALH 84001. At about the same time, Fisk et al. (2006) reported tunnel and borehole-like structures in basalts from Earth, the meteorite Nakhla, and one other meteorite (called Lafayette) related in origin to Nakhla. They pointed out that these tunnel structures tested positive for the presence of cellular material in the samples from Earth, and that the tunnel structures in the Martian meteorite Nakhla were indistinguishable in size, shape, and distribution from the Earth samples. Tunnel structures had previously been discovered in 3.5 billion year old rocks in the Barberton Greenstone Belt in South Africa (Furnes et al. 2004), providing evidence of submarine microbial activity during the very early history of Earth. Gibson et al. (2006) reported possible biogenic features in two additional Martian meteorites, Nakhla and Shergotty, which bore a strong resemblance to very similar structures discovered in Earth rocks that were almost surely biogenic in origin. The evidence remains in dispute, however. Fisk et al. (2006) pointed out that the biogenic-like features in Nakhla appear to be contemporary with hydrous alteration on Mars less than 1,300 million years ago, which was a time when Mars was not wet and warm anymore, but likely experienced only intermittent events of liquid water. Further, meteorite Nakhla fell to Earth in Egypt in 1911 killing a dog and leaving plenty of time for Earth organisms to contaminate the meteorite in an environment more conducive than Antarctica. Furthermore, organic ingredients were used in the preparation and preservation of samples from Nakhla. In short, the evidence for biomarkers in other Martian meteorites remains equivocal as well.

12.2.4 Conclusions Concerning Biomarkers in Martian Meteorites

McKay et al. (1996) argued from the beginning that the evidence for life on Mars deduced from ALH84001 consisted of a group of facts and observations, any one of which in isolation was not conclusive, but considered collectively added to a plausible argument for evidence of biogenic activity. The weakness of individual chains in the argument has elicited numerous and legitimate counter arguments, but the logic of the collective evidence remains persuasive. At a minimum, ALH84001, and to a lesser extent, the other Martian meteorites studied to date, provide circumstantial evidence justifying the continuation of a vigorous search for additional signs of past or present life on Mars.

12.3 Current Life Detection Instrumentation

It has been a long time, more than 30 years, since the only Life Detection Experiments ever attempted were conducted by the Viking landers. Improvements in technology, especially by making instruments smaller and lighter, have enhanced the prospects for success on new robotic space missions. The basic problem, however, still remains. What evidence is sufficient to provide an unequivocal case for life? The strategy of the Viking landers was largely based on presumed metabolic activities. Since the metabolic approach gave equivocal results, it has largely fallen out of favor with the scientific community. Instead, the focus has been to increase the capability and sensitivity of instruments to detect biosignatures, especially the so-called biomarkers of life.

Biomarkers are complex molecular fossils derived from biochemicals in once-living organisms (Peters et al. 2004). Examples include visible and near infrared spectrometric searches for chlorophyll (Wettergreen et al. 2005), the single molecule detector (SMD) approach as suggested by Ishii and Yanagida (2000) to screen for DNA, enzymes and proteins, and fluorescence imagers that use a dye, which only fluoresces if it binds to a target molecule such as a specific protein, nucleic acid or other biomolecule. Various instruments are sensitive to different biomarkers. While some research groups target relatively simple organic macromolecules such as amino acids (Glavin et al. 2001), others (e.g., Steele et al. 2001) focus on detecting more complex molecules. For example, the Micro-Capillary Electrophoresis Chip designed by Glavin et al. (2001) is an example of the targeted detection of amino acids with a sensitivity of about 10^{-18} mole! The Mars Organic Detector (MOD) has been developed for detecting amino acids, amines and polycyclic aromatic hydrocarbons (PAHs) on the Martian surface (Bada 2001). While PAHs have no known role in terran biochemistry, they can be a product of long-term degradation of biologically derived organic compounds (MacKenzie et al. 1982). Amino acids are readily destroyed on the Martian surface by UV irradiation (Stoker and Bullock 1997). However, amino acids can be preserved in the subsurface for billions of years, but a space probe has to drill deep enough to overcome the detrimental effects of gamma radiation in the near subsurface (1.5 to 2 m) to detect any amino acids from ancient life that may have been present 3 billion years ago (Kminek and Bada 2006). The upgraded Mars Organic Detector III is more versatile and is capable of detecting nucleobases, sugars, and organic acids and bases. Even more ambitious is the Mars Immunoassay Life Detection Instrument (MILDI), which has the ability to look for three classes of biomarkers including biomarkers from extant life such as RNA, from extinct life such as hopanes, and from organic compounds not necessarily associated with life such as PAHs (Steele et al. 2001). The list of possible detections also includes lipopolysaccharides, exopolymeric substances, porphyrins including chlorophyll, specific amino acid and peptide sequences, RUBISCO, and flavin adenine dinucleotide (FAD) and nicotinamide adenine dinucleotide (NAD). The Life Marker Chip, which also utilizes an immunoassay approach to detect specific organic molecules or classes of molecules is currently considered for the ExoMars mission of the European Space Agency (Parnell et al. 2007). While the list of possible organic molecules that can be detected with immunological approaches is impressive (Tang 2007), it warrants some concern for being overly focused on biochemistry as we know it on Earth. For example, the National Research Council elaborated on its concern that molecular methods would not likely find any life that is not related by common ancestry to the life we already know. A universal feature of chemical characteristics of living systems is believed to be chirality (Baross et al. 2007), the predominance of one enantiomer over the others. This approach was also proposed by Levin (1998) as a modification to the Labeled Release experiment of the Viking mission.

Life detection methods are not based only on chemical or biochemical reactions, but also on spectroscopic approaches. An example is the Scanning for Extinct Astrobiological Residues and Current Habitats (SEARCH) method. SEARCH utilizes integrated spectroscopic sensing with a laser-diode array and photodetectors processed by a hyperspace data analysis algorithm (Dieter et al. 2005). Its spectrum includes UV, visible and near-IR wavelengths. The instrument can be mounted on a rover to scan ranges of up to 10 m. The reflectance data is processed for each illuminated point such that amino acids, carbohydrates, PAHs, and even organisms or fossils can be identified (Dieter et al. 2005). Also, Raman spectroscopy, a non-invasive method that provides a unique spectral "fingerprint" for any molecule depending on its vibrational state (Edwards and Newton 1999; Chen et al. 2008; Bowden et al. 2008) has a great potential as a tool for life detection, especially if Raman spectrometers can be sufficiently miniaturized. The shift in wave number of the exciting radiation can be related to the structure, composition, and identification of the scattering molecules (Long 2002). Spectral methods, of course, are also used to scan planetary atmospheres for biomarkers such as the simultaneous detection of ozone or oxygen and methane. An example of improving technology in this area is the Multiple Instrument Distributed Aperture Sensor (MIDAS), which provides a large-aperture, wide-field, diffraction-limited telescope by integrating optical interferometry technologies into a mature multiple aperture array concept (Pitman et al. 2004). However, to succeed with an unequivocal detection of life, multiple approaches have to be pursued. A proper search strategy for life requires detailed orbital imaging and spectrometry to home in on potential habitable sites, and collection of surface data by spectrometric, biochemical, and microscopic instruments (Lipps et al. 2004).

12.4 Planetary Protection Considerations

Planetary protection is a serious consideration for both robotic and human missions. Protective measures are needed to preserve Solar System bodies from contamination by terran life, and to protect life on Earth from possible forms of life that may be returned from other Solar System bodies. The rationale is to preserve our ability to study other worlds as they exist in their natural states and to avoid contamination that would obscure our ability to find life elsewhere. Also, if we find life on other planetary bodies, we need to ensure that prudent precautions are taken to protect Earth's biosphere. In order to achieve this, spacecrafts and their components need to meet stringent cleanliness requirements. Specific planetary protection requirements for each mission and target body are based on the scientific advice of the Space Studies Board and on NASA or international policy guidelines. For example, a spacecraft destined for Mars with the objective of detecting life would have to meet the highest possible level of cleanliness, and some specific operating restrictions would be imposed.

The Committee on Space Research (COSPAR) implements planetary protection policy for the reference of spacefaring nations, both as an international standard on procedures to avoid spreading organic constituents and biological contamination through space exploration, and to provide accepted guidelines for complying with the wording of the UN Space Treaty and other relevant international agreements. For example, so-called Special Regions have recently been defined for Mars in which Earth organisms could potentially survive and thus pose a risk to the forward contamination of Mars (Special Regions Science Analysis Group 2006, 2007). These special regions would not be off limit for future space exploration, but any spacecraft intended to land there would have to undergo state-of-the-art sterilization procedures.

12.5 Chapter Summary

The Viking Mission was a great success story, but it failed to provide a clear answer to the question of whether there is life on Mars. The claim for fossilized remnants of life in the Martian meteorite ALH84001 is a relatively persuasive collection of facts and observations consistent with biogenic origins, but individual links in the collective chain of evidence remain weak and controversial. Recent evidence for contemporary liquid water on Mars, and the detection of methane in the Martian atmosphere appears further to enhance the case for life on Mars, but what is needed is a new mission devoted to the detection of life. Thus, work should continue on in-situ life detection methods that can be tested on Mars and our other neighboring planets and moons in the near future. Screening methods and experiments should be designed with an open mind to allow the detection of life that may not utilize many, or any, of the biomolecules that are used by life on Earth.

Chapter 13
Optimizing Space Exploration

Both robotic and human missions into space are necessary for an effective program of space exploration. For the nations that have sent humans into space (Russia, China, and the United States) the competition for limited budgets between human and robotic exploratory strategies is inevitable. Yet, the two strategies are complimentary and mutually supportive. Robotic missions are much cheaper than human missions and will remain the best if not only way to investigate difficult to reach planetary bodies and to explore hostile environments such as the radiation-intense surfaces of the Jovian moons. Also, any initial mission to a planetary body will have to be robotic to understand the planetary environments, avoid unnecessary risks, and conduct space exploration in a cost-efficient way. However, eventually human missions are warranted on philosophical grounds and necessary on practical grounds.

The urge to explore is a fundamental drive in human nature, and history shows that new worlds present an irresistible attraction to this urge. "When ships to sail the void between the stars have been invented," wrote Johannes Keppler centuries ago, "there will also be men who come forward to sail them." The first steps have already been taken with human visits to the Moon. Mars is the next inevitable destination, and humans will go there for a variety of reasons, not the least of which is simply that it is there. A more sophisticated treatment of the philosophical basis for human exploration of space is beyond the scope of this book, but we would note that the human condition on Earth, especially in the face of rapid climate change, continued population growth, and strife from many sources, will likely affect the urgency with which humans spread onto neighboring worlds in our Solar System within the coming century.

As a practical matter, human exploration has the advantage over machines at our current state of robotic technology of being much more maneuverable, with a much greater capacity to analyze complex information and make decisions locally and in real time. Collection of productive and appropriate samples, problem troubleshooting, astute evaluation of immediate and long-term environmental challenges, anticipation of pitfalls, and complicated physical manipulations are among the many advantages that a human explorer has over a robot. While a rover can cover square meters in a day with the risk of becoming stuck in a trivial depression for days at a time, a human can cover square kilometers in a day and avoid getting stuck in the

D. Schulze-Makuch, L.N. Irwin, *Life in the Universe*. Advances in Astrobiology and Biogeophysics,

first place. Thus, while human exploration is vastly more expensive, the payback is vastly greater.

The Lunar Apollo program carried humans to the Moon on six occasions, then suspended the effort. Such a program of human exploration which only visits a certain planetary body and then abandons it is neither cost-effective nor scientifically very valuable. With NASA now committed to a human return to the Moon and eventually to Mars, and with China and possibly Russia and other nations joining the effort to transport humans beyond the Earth, the time to start planning a more extensive and systematic exploration of our nearest planetary neighbors is at hand. Humans and machines will increasingly be used in tandem to explore and ultimately colonize some of those worlds. Below, we enumerate a general strategy for the near-term exploration of our Solar System and beyond.

13.1 Mars

Mars is our second closest planetary neighbor (after Venus) and is a dynamic water-rich planet similar in many respects to Earth. It is the only planet in the Solar System similar enough to Earth to provide limited habitability to terrestrial organisms including humans. However, surface conditions on Mars are challenging due to cold temperatures averaging about $-65°$C and ranging from $-115°$C to $+20°$C, the lack of an ozone layer and magnetospheric shielding, and the absence of liquid water on the surface. Mars has a thin but substantial atmosphere mostly consisting of carbon dioxide (95%). A trip to Mars at the most favorable launch option takes about six months with present chemical rocket technology. Although Mars is currently cold, it once was apparently warmer and more humid, with running water producing floodplains and carving canyons and valleys. It probably harbored a large ocean in its northern hemisphere long ago (Fairén et al. 2004). Although at most locations on Mars today, liquid water is not stable and would turn to vapor within a very short time, there is substantial evidence suggesting the presence of water beneath the surface and possibly in caves (Boston 2003; Boynton et al. 2002; Feldman et al. 2002; Malin et al. 2006; Mitrofanov et al. 2002).

13.1.1 Robotic Missions to Mars

Prior robotic missions to planetary bodies such as Mars have focused either on exploration of a single site with a single lander or rover, or on global mapping from an orbiter. Several of these missions are still active on or at Mars. The lander/rover missions analyze a confined, readily accessible site in detail, but lack the capacity to achieve a regional overview, while orbiter missions return immense data sets that are global in scope but provide limited local detail. Thus, it has been suggested that a hierarchical mission design be employed that includes spaceborne (orbital), atmospheric (airborne), surface (mobile such as rover, and stationary such as lander or sensor), and subsurface (ground-penetrating radar, drilling, etc.) agents working in concert to allow for sufficient mission safety and redundancy, to perform extensive and challenging reconnaissance, and to lead to a thorough search for evidence of life and habitability (Fink et al. 2005; Schulze-Makuch et al. 2005). This is especially warranted for sites of astrobiological interest such as (1) canyons (e.g., Valles Marineris on Mars and chasms on Venus), (2) mountain ranges (e.g., Thaumasia highlands on Mars and Isthar Terra on Venus), (3) sites of suspected magmatic-driven uplift and associated tectonism and possible hydrothermal activity (e.g. the Warrego Valles rise on Mars and Maxwell Montes on Venus), (4) polar ice caps on Mars, (5) ice deposits within impact basins (Mercury and Mars), (6) volcanoes of diverse sizes and shapes (e.g., Apollinaris Patera on Mars and Beta Regio on Venus), (7) putative ancient accreted terrains and associated volcanism on Mars, (8) regions indicating potential recent hydrologic activity such as spring-fed seeps on Mars, and (9) chaotic terrain, such as the source areas of the circum-Chryse outflow channel system on Mars (Schulze-Makuch et al. 2005).

A sample return mission would be the next logical step in the robotic exploration of Mars. A region of high astrobiological interest for a sample return mission would be a site where water may be present at or near the surface. A priority of putative hydrothermal target areas has been proposed by Schulze-Makuch et al. (2007), which could serve as a baseline for further site selection efforts. After the sample return mission, a permanent robotic station would be the next step in robotic exploration and an intermediate goal in a combined robotic-human exploration effort for Mars. A more thorough investigation of specific localities of interest (such as those described above) would be aided by a permanent robotic base. For example, any drilling investigation to probe the Martian deep subsurface for microbial life beneath the permafrost would mean energy requirements and an infrastructure that could only be met with permanent equipment on Mars. A permanent robotic base would not have to be very elaborate, but could simply consist of a communication relay and a power generator, perhaps together with a remotely operated telescope. The power generator could produce energy using solar panels that are laid out in a suitable location protected from wind-blown dust with wipers to remove any dust if needed. Alternatively, nuclear fuel (e.g., a plutonium rod) could be considered as well, especially if the robotic spacecraft that brought the equipment used one in the first place. The most straightforward strategy might be to land a spacecraft designed to be used as a permanent station, and have later equipment brought by other robotic missions with the capability to hook up to the base station. Even now such a limited base would be useful if it were located close to one of the MER rovers. The battery of the rover could be recharged and minor mechanical repairs could be made.

13.1.2 Human Missions to Mars

No destination in our Solar System offers a more enticing target for human mission exploration than Mars. The recent detection of methane (Formisano et al. 2004; Krasnopolski et al. 2004; Mumma et al. 2004) and abundant water ice (Boynton et al. 2002; Feldman et al. 2002; Mitrofanov et al. 2002) on the Red Planet elevates it to one of the highest priority targets for both robotic and human exploration. Mars is also the most Earth-like planet in our Solar System and offers various resources, including shelter, minerals, water, limited oxygen, and a tenuous atmosphere, that make its colonization a possibility, in principle. Observations from Earth-based telescopes and various robotic missions have provided some initial understanding about Mars and its current and past environments. NASA's immediate goal is set on a human mission to the Moon and Mars, apparently modeled after the Apollo missions to the Moon. However, such a mission may be of limited scientific value unless a meaningful objective and more comprehensive vision are put forward. The initial establishment of a permanent robotic station, eventually followed by a permanent human station, could provide much greater scientific and public benefit over the long run than episodic visits of the Apollo type to Mars.

Many extensive robotic missions would be needed to prepare a human mission to Mars, and we consider a robotic base station as described above as a minimum requirement for a successful human mission. However, the mission should entail more than just a walk on Mars and the return of some environmental samples. Otherwise, the science objective could be as easily achieved with a robotic mission at a much lower cost. The goal rather should be to have the crew stay for an extended period of time, to explore interesting sites and conduct research on various aspects of habitability on Mars.

Resources on Mars itself could aid an extended stay. Instead of building radiation-protected shelters, astronauts could simply use natural shelters such as caves that would provide shelter from the intense ionizing radiation and strong ultraviolet light. Most of the natural caves appear to be lava tubes, and some of them are located at a low elevation in close proximity to the former northern ocean (Fairén et al. 2004), which means that they could harbor ice deposits similar to many ice caves on Earth (Boston 2000). If ice caves are found, they would also partially meet the needs of a human mission or future settlement for water and oxygen. Caves on Mars are likely to be much larger than on Earth due to the lower gravity on Mars ($0.38g$), which allows larger spans of unsupported rock to exist. Mars with its thin atmosphere has no ozone layer and no magnetospheric shielding; thus some natural or artificial shielding from ionizing and ultraviolet radiation will be required. The damage to DNA on the surface of Mars may be as much as a thousand times higher than on Earth under the worst case scenario, such as dust free skies (Cockell et al. 2000; Patel et al. 2003). However, a layer of 1 mm or less of Martian analog soil was shown to protect microorganisms sufficiently to prevent loss of viability (Cockell et al. 2005; Mancinelli and Klovstad 2000; Schuerger et al. 2003), thus a protective spacesuit or a cave could certainly provide sufficient protection for humans. Some of the caves may even hold water in the frozen form, but even if no ice caves are found, evidence is accumulating that water is present in the subsurface. Although at most surface locations on Mars today, liquid water is not stable and would sublimate within short time frames into the atmosphere, evidence indicates that there is water beneath the surface (Boynton et al. 2002; Feldman et al. 2002; Malin and Edgett 2000a; Malin et al. 2006; Mitrofanov et al. 2002) and possibly in caves (Boston et al. 1992; Zubrin and Wagner 1996), but definitely present in the highly visible polar areas. Since temperatures on Mars can be extremely low, sometimes dipping below $-100°C$, the use of natural caves would be a further asset by providing more temperate environments. Mars was and possibly still is a site of substantial volcanic activity with the episodically active Tharsis magmatic complex being the dominant release point for the internal heat energy of the planet (Dohm et al. 2001). Thus the presence of liquid water in caves associated with Tharsis is not unthinkable. Numerous igneous flow features, including lava tubes (Fig. 8.1), have been identified on Mars (Boston 2003).

13.1.3 A Vision for Mars Exploration

A far-reaching vision would be to establish human settlements on Mars. Natural caves could again be the focal point of those settlements with greenhouses extending out of them. In principle, plants could be grown in the greenhouses outside of the caves while affording some UV protection and enrichment of soil, thus providing the inhabitants of the cave with food and an additional supply of oxygen. Microbes could be used to break down and recycle wastes; thus each cave settlement would constitute its own independent biosphere with some additional resources provided by the Martian environment. Several of these cave-centered biospheres could be created, each being in constant communication with the others to share experiences on which technological approaches are working best. It would take a tremendous effort to establish such substantial settlements on Mars, but they are technologically achievable, in principle. Mars can provide some essential resources such as water and shelter, which would not need to be brought in from Earth or be constantly recycled, making such an endeavor more likely to succeed. While some robotic missions would need to re-supply the human outpost periodically, becoming as self-sufficient as possible would obviously be desirable. The ultimate goal of Martian exploration efforts should be a scientific station for maximum scientific return, including the in-situ analysis of Martian environmental samples. The logistics of implanting a persistent human presence on Mars are challenging, hence a substantial amount of further research on the feasibility of enclosed self-sustaining habitats needs to be carried out and successfully demonstrated under harsh conditions as analogous to those on Mars as possible, such as in Antarctica, prior to the attempt to establish such bases on Mars. Also, planetary protection issues are a major concern for any human mission, especially if indigenous life exists on Mars, so a great deal of care would have to be exercised in the establishment of the first scientific field stations on Mars. Whether a permanent station can ever be taken off Earth's "life support" is an open question, but the establishment of such a station provides a suitable vision for future exploration of the Red Planet. Without such a vision, humans will likely visit Mars, but with no further goals or lasting achievements.

How could a permanent human settlement on Mars be achieved? Davies and Schulze-Makuch (2008) suggested a series of one-way missions to initiate the human exploration of Mars. Eliminating the need for returning early settlers to Earth would cut the costs several fold, while ensuring a continuous commitment to the exploration of Mars and space in general. Hardware currently being developed for the Moon program could be adapted for settlements on Mars. The colonists would be resupplied on a constant basis from Earth with elemental necessities, but otherwise would harvest resources available on Mars. Once the outpost was established and mostly self-sufficient, it could serve as a hub for the arrival of more personnel brought in to expand the colonization effort. With time and advancing technology, two-way travel between Mars and Earth would eventually be established, but a series of one-way human missions to Mars would represent a continuing commitment to explore and colonize the planet in the first stages of human progression to another world. Clearly, such a strategy would require a return to the exploratory spirit of the Vikings and the age of Columbus, but the appeal of space and the lure of adventure inherent in the human spirit would almost surely generate an abundance of volunteers.

13.2 The Moon

The Moon is extremely anhydrous. Given the likelihood that no water or other volatiles ever formed an atmosphere or were present on the surface or in the subsurface, the Moon is not a likely candidate for the origin or persistence of life. However, the Moon may hold some evidence of the early evolution of life on Earth, since meteorite impacts on Earth may have delivered biogenic material to the surface of the Moon (Armstrong et al. 2002).

Recently the Moon has drawn renewed attention as a target for space exploration. The objective for further exploration of the Moon should be centered on a permanent human presence. As a large body, the Moon provides a solid surface to meet any structural requirements. The gravitational force is about 1/6 of that of Earth, but humans and other organisms should be able to adapt better to a fractional gravity environment than to the microgravity experienced in space. However, the Moon is devoid of any type of atmosphere. Lacking an atmosphere or other protective shielding, the Moon is susceptible to an enormous amount of irradiation from the solar wind. Thus, any settlement would have to be shielded from radiation either by thick surface structures, by artificial subsurface structures, or by one of the numerous natural lunar lava tube caves that have been recognized since the Apollo era. Long-term survival is difficult on the Moon due to the apparent lack of oxygen and water. Possible water ice may have been detected by the Clementine Mission in 1996 but it was not clearly detected by the Lunar Prospector Mission two years later and remains to be confirmed. If water ice at the South Pole of the Moon is confirmed, it may serve as a relatively accessible reservoir to analyze cometary ice and provide water and oxygen for the possible future human habitation of the Moon. However, the ice would have to be extracted from the subsurface as the surface ice has been altered by radiation. About 2-3 m of lunar soil cover is required to protect surface ice from radiation damage (Schulze-Makuch et al. 2005). A recent study has focused on the possible adaptation of humans to long-time exposure to radiation and limited gravity such as on a lunar station at the South Pole (Horneck et al. 2003).

Temperatures are extreme, either very hot on the side facing the Sun or extremely cold on the side opposite the Sun. The best way to deal with the lack of oxygen, water, and extreme temperatures would be to locate the settlement near the South Pole where water ice deposits may exist and temperatures are somewhat more moderate. A thorough exploration of the Moon would be greatly aided if nuclear fusion becomes a viable alternative for producing energy on Earth. Helium-3, a helium isotope rare on Earth but deposited on the Moon by the solar wind, could then be harvested on the Moon as a fuel for nuclear fusion reactors in the future (although this is controversial). The refocus of NASA on human colonization of the Moon and missions to Mars, and Chinese interest in the same direction, should accelerate the development of technology for sustaining long-term human habitations in hostile environments.

13.3 Venus

As discussed in Section 8.3, microbial life could exist in the lower Venusian atmosphere. Therefore, a sample return mission from the lower cloud layer of Venus should be considered. Schulze-Makuch et al. (2002b) contemplated various mission options and concluded that a sample return mission involving a Parachute Drop – Balloon Floatation Mission, designed to return astrobiologically relevant material for analysis to the International Space Station, would be the most preferable option.

The relative ease of reaching Venus and returning to Earth, and the availability of appropriate existing technology, makes such a mission feasible in the near term. For example, a blimp/balloon could be deployed, which would be able to hover at an altitude of 51 km or descend to lower altitudes, where it could collect samples of cloud particles with aerogels similar to the Stardust and Genesis missions. Knollenberg and Hunten (1980) reported a cloud particle density of 10-100 particles per cm^3 at about 50 km altitude. These cloud particles, once obtained by the blimp/balloon, could be transported into orbit, and from there to the International Space Station or Earth for analysis. Even if the promising mode 3 particles in the Venusian atmosphere turn out not to be biological, a sample return mission would significantly increase our knowledge about the composition and dynamics of the atmosphere of Venus.

13.4 Other Exploration Targets

There are many other potential targets of astrobiological interest in our Solar System and beyond. Titan is of special interest because of its atmosphere uniquely rich in organic compounds and because of its potential to harbor alien life of a separate origin (Baross et al. 2007; Shapiro and Schulze-Makuch 2008). Others, such as Iapetus and Triton, appear to harbor complex chemistry as well. The icy satellites of the giant gas planets (Europa in particular) are prime targets because of their abundance of water, which may be liquid beneath the surface in some cases, and their dynamic gravitational perturbations and/or geothermal activity. As the list and variety of extrasolar planets grows, so does the motivation to develop the technologies necessary for determining their possible suitability for life.

The Cassini-Huygens mission still transmits stunning images from Titan (as of this writing), Saturn's largest Moon and the second largest satellite in the Solar System, displaying a world where methane instead of water acts as the main surface transforming agent. The presence of methane rain inferred from modeling (Toon et al. 1988) appears to be supported by observations from the Cassini-Huygens mission (Griffith et al. 2005). Lakes of liquid ethane/methane have been confirmed (Stofan et al. 2007), and methane aquifers are thought to exist in Titan's subsurface (Mitri et al. 2007). The possibility of life on Titan has been suggested (McKay and Smith 2005; Schulze-Makuch and Grinspoon 2005). But even if life is not present on Titan, its rich organic inventory makes it the closest analog to early Earth conditions that we can study. Thus, a follow-up mission to Titan should be launched, for a more close-up and detailed study of its surface. Titan's dense atmosphere is ideally suited for exploration by balloon-type vehicles. Particularly efficient would be an aerorover that uses a hot air balloon concept and is supported by an orbiter (Sittler et al. 2006).

Another target of great astrobiological importance is Europa. The presence of an ocean beneath its icy crust has been inferred from the observations of (1) magnetic fields induced by eddy currents in a mobile conducting medium within the body of the satellite (Khurana et al. 1998), (2) asynchronous rotation of Europa that implies subsurface generation of friction (Geissler et al. 1998), and (3) surface fracture features consistent with mobile icebergs driven by subsurface liquid (Carr et al. 1998; Hoppa et al. 1999). Doppler tracking by the Galileo spacecraft suggested that Europa has a differentiated internal structure, which includes a dense core of metal or metal sulfides, a rocky mantle, and a low-density ice crust or ice-crusted ocean with a thickness of 80–170 km (Anderson et al. 1998). A metallic core may provide internal heat through radioactive decay, subjecting the ocean floor to volcanic eruptions. Volcanic activity would also be expected since Europa's neighbor Io is volcanically the most active planetary body of the Solar System, and planetary evolution theories assume a roughly similar initial composition of Io and Europa (Consolmagno and Lewis 1976). The deep ocean environment on Europa may thus resemble that on Earth where hydrothermal discharge areas on the aphotic ocean bottom support hydrothermal vent communities (Amend and Shock 1998; Vinogradov et al. 1996). Irwin and Schulze-Makuch (2003) estimated that an ecosystem consisting of reasonably dense populations of macroorganisms could be supported by energy from plausible estimates of methanogenesis in the subsurface liquid ocean of Europa. Using similar modeling techniques, other estimates of potential biomass have been both higher, based on radiolytic generation of O_2 (Chyba 2000), and lower, based on sulfate reduction (Zolotov and Shock 2003).

Because of Jupiter's intense radiation environment, Europa most likely is suitable only for robotic exploration. A robotic mission should be launched that includes an orbiter and probes that sample the surface ice of Europa below the radiation-reworked upper 1 meter or so. Criteria for selecting landing sites of astrobiological interest have been suggested by Figueredo et al. (2003). If samples can be retrieved from suitable locations beneath the uppermost layer of ice, they may contain organisms, since frozen ice would preserve them very well. Other icy satellites of astrobiological interest include Ganymede, the largest satellite in the Solar System, which also shows evidence of surface remodeling and likewise may contain a subsurface liquid ocean, and the Saturnian Moons, Enceladus and Tethys. Recent observations from the Cassini orbiter strongly suggest geothermal activity on those bodies. Titania, the largest Moon of Uranus, also shows abundant evidence of surface resculpturing. Though small, remote, and therefore logistically difficult to explore, these smaller icy satellites should yield sufficiently important clues about the evolutionary history of the Solar System, whether or not they harbor life, to justify efforts to explore them.

Other intriguing targets for space exploration include comets and asteroids, which are important for sampling early Solar System material, and the Sun and its cycles, which directly affect every organism on Earth, as well as the planetary environment at least as far out as Saturn. Efforts to detect Earth-like planets in other Solar Systems, as discussed in Section. 11.4, also need to continue. Further, many fundamental constants necessary for a full understanding of the physical universe and the biology contained within it, can be measured by both space probes and ground-based telescopes. Thus, there is no lack of intriguing and significant targets for space exploration. The challenge will be to fit them into budgets that able governments are willing to appropriate. With intense competition for funds from the cost of persisting human conflicts and compelling social needs, perhaps the greatest hope for sustained space exploration lies within the private sector. The ability to finance relatively uncomplicated robotic missions appears to be within the reach of the world's wealthier individuals and corporations. Harvesting planetary resources, such as Helium-3 on the Moon, may prove financially lucrative in time. And, while still in its infancy, space tourism may make travel at least to our nearest neighbor(s) a more common endeavor in the future. The history of human nature shows little evidence that the urge to go forth to other worlds, both in person and by robotic extension, will be stifled indefinitely.

13.5 Chapter Summary

Robotic and human exploration should proceed together to meet the challenges of discovery on other worlds. The history and characteristics of Mars make it the most suitable target for human exploration. With orbiters and rovers already there, the next goal should be to assemble a permanent robotic station, which would aid in the systematic exploration of Mars. Such a station on Mars, with experimental human colonization on the Moon, can serve as building blocks for an extended human mission and eventual human settlement on Mars. It should be emphasized that this long-range vision should not be implemented by ignoring other goals in space exploration that promise to provide a significant scientific return. Among others, these include the further robotic exploration of the outer Solar System, Venus, our Sun, the detection of extrasolar planets, and measurements of the fundamental constants of the universe.

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