Advances in Astrobiology and Biogeophysics

Barbara Cavalazzi · Frances Westall
Editors

Biosignatures for Astrobiology

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Foreword

As a scientific discipline, astrobiology includes the study of life's origin, distribution, and fate in the Universe. By embodying the search for life, astrobiology includes research focused on the study of life's signatures within our Solar System and beyond. Recent discoveries suggest that the Universe is more amenable to life than previously recognized. Hence, the timeliness of *Biosignatures for Astrobiology*, a book edited by B. Cavalazzi and F. Westall, eloquently examines biosignatures in the context of the Earth and Solar System planetary bodies. Earth-like exoplanets are now being detected at a remarkable pace, which is likely to escalate as the Transiting Exoplanet Survey Satellite (TESS) comes online this year and the James Webb telescope to be launched next decade.

The number of interesting planetary targets for astrobiological exploration of extinct and extant life within our own Solar System has also increased as their geologically active nature has been revealed. While it has been known that Mars was potentially habitable early in its lifetime, with large oceans and lakes in abundance, the recent in situ discovery of complex organic molecules preserved in ancient sediments is consistent with the hypothesis that carbonaceous biosignatures could be preserved for long periods of time on the red planet. The recent finding that Mars releases methane seasonally is certainly indicative of the planet's dynamic nature on local scales, regardless of whether it was produced by microorganisms, which portends modern subsurface geochemical activity that could support life.

Evidence of the dynamic nature and habitability potential of other planetary moons in our Solar System has been captured in flyby mission images of geysers on the surfaces of Enceladus and Europa, young icy moons of Saturn and Jupiter, respectively. The incredible images captured by the Cassini–Huygens space probe of liquid methane lakes dotting the surface of Titan reminds us of how little we know about the inventory and distribution of organics in our Universe, a certainty substantiated by the incredible Hubble Space Telescope images of massive star-forming nurseries of the galaxy, regions of space replete with complex organic molecules.

Key to astrobiological exploration for extinct and extant life, whether beyond or within our Solar System, is the search for biosignatures. On Earth, astrobiologists conduct field and laboratory investigations, perform planetary simulations, and generate theoretical models in an attempt to understand how life originated and evolved on Earth. Given the uniqueness of Earth as the only known abode for life, along with the current trajectory of the future of our planet's climate, any improvements in understanding the early evolution of life and the potential for it to adapt to future terrestrial, low-Earth orbit, and eventually extraterrestrial environmental challenges may be essential for our survival as a species.

How life interacts with, and responds to, its environment to produce biosignatures that will be preserved on other worlds is an important thrust of astrobiology. Extremophiles are studied with evermore sophisticated technologies in microbially dominated habitats, in planetary conditions simulated in the laboratory, and in terrestrial samples of their fossilized habitats. These opportunities provide a baseline for testing hypotheses related to understanding what fraction of biosignatures become preserved in the geological record and how best to find, detect, and interpret them. Whether biosignatures of extinct or extant life can be distinguished from abiotic mimics is especially challenging, given the continuous rain of abiotically produced organic matter to planetary bodies throughout the Universe.

The search for biosignatures is compounded by the fact that they range in size from the atomic to planetary scales, and their age could virtually be any age during which life could have inhabited a planet and its biosignatures could have been preserved. On Earth, biosignatures of life were preserved in a variety of geological deposits throughout most of the planet's history. Hence, the amount of alteration that ancient biosignatures on Earth have received may not be directly comparable to that experienced by a similar type of biosignature preserved on another rocky planet like Mars, for example. The correct interpretation of any possible biosignature preserved in the geological record of a planet also requires an understanding of the processes that have altered it since its time of formation.

The book *Biosignatures for Astrobiology* brings together our current understanding of biosignatures with some of the most useful methodologies and technologies used in astrobiology search strategies in an easily readable and comprehensive manner. The book is suitable for the scientifically inclined layperson, the student of astrobiology, and the professional astrobiologist as well. All of the authors contributed background sections to help nascent readers of astrobiology literature grasp the main concepts. In its entirety, the book illustrates why the search for biosignatures beyond Earth is complicated, risky, and a compelling challenge for current and future generations of scientists worldwide. The book is laid out such that it lends itself to be read from cover to cover in sequence or one chapter at a time out of sequence. *Biosignatures for Astrobiology* will be useful for teaching an advanced course in the field or as a reference for practitioners.

The presence of life forms on Earth that have the capability to withstand the harshest of conditions, even those on nearby planets, underscores the hypothesis that life exists elsewhere in the Universe. As stated in the book's final chapter by Dunér, "So far, we have no conclusive evidence of the existence of extraterrestrial life. But could we ever be 100% sure that we are alone?" To be unequivocally sure that no life exists anywhere but on Earth is something we may never know. Yet we are confident that the innate curiosity of humans to know life's origins, and whether it will or does exist beyond Earth, is certain to drive astrobiological exploration far into the future so long as these questions remain unanswered. Even when answers are forthcoming, the field of astrobiology will endure. Surely, if life exists in at least one other place in the Universe, the possibility that it occurs in a third locality is almost a certainty.

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Preface

This book on *Biosignatures for Astrobiology* has had a long germination. It started with an article that we wrote on *Biosignatures in Rocks* for the *Encyclopedia of Geobiology* published by Springer in 2009, and early suggestions from Ramon Khanna at the 13th meeting of European Astrobiology Network Association (EANA) in 2013 hosted in Edinburgh.

With the ongoing Mars Science Laboratory Mission to Gale Crater and the ExoMars Trace Gas Orbiter (2016) and lander/rover (2020), as well as the future JUICE and Europa Clipper Mission to Jupiter and its satellites and the various telescopes (HUBBLE, Spitzer, Kepler, TESS, JWST, WFIRST) searching for exoplanets, the time is appropriate to review biosignatures of relevance for astrobiology, addressing all aspects of the discipline. Our book thus aims at capitalising on the latest advances to provide overviews in all the domains of astrobiology.

Since the paradigm-changing discovery of the first exoplanet orbiting a main-sequence star and the finding of highly controversial biosignatures in the Martian meteorite ALH84001 by David McKay and his colleagues in 1996, biosignature research across the board in astrobiology has made enormous advances. Whether or not ALH84001 or other Martian meteorites harbour traces of life, the very idea that microbial fossils could be preserved in a meteorite from Mars sparked a huge interest in biosignature research covering the minimum size of microorganisms, extremophiles, through to the fossilised traces of life, and astrobiology missions to Mars.

We address the signatures of life with respect to life on Earth as well as life elsewhere in the Solar System (i.e. Mars) and exoplanets. For our purposes, we are assuming that the extraterrestrial life forms, hopefully encountered in the future (even if in fossil form), are based on carbon molecules and water as a solvent. Therefore, in order to place the topic of the biosignatures in context, we start with a couple of chapters that "set the scene". André Brack starts Chap. 1 with an overview of the chemical signatures at the origin of life in which he underlines the basic precepts of carbon and life and the carbonaceous signatures of life, namely an overrepresentation of organics and long strands of homochiral sequences. Since it is widely believed that the majority of the carbon required for the emergence of life on Earth came from extraterrestrial sources, and that the flux of this kind of carbon continues to this day, albeit at a much lower rate than on the early Earth or the early planets and satellites, André Brack's chapter is followed by a contribution from Eric Quirico and Lydie Bonal who, in Chap. 2, review the present state of knowledge on the composition, structure, and formation and evolution of the exogenous organics accreted by the Earth on their original asteroidal or cometary parent bodies. The importance of this knowledge is put into perspective when one considers the fact that, despite the harsh radiation and oxidising environment reigning at the surface of Mars for more than 3 billion years that effectively destroys the more volatile fraction of any organic matter, abiotic (meteoritic) or potentially biogenic, recent, hard-won results from the SAM instrument on the Curiosity rover on Mars do, indeed, show that organic molecules are present in the Martian surface.

Both the MSL and the ExoMars missions hope to find traces of life on Mars, more likely fossil life than extant life. The molecular compounds detected in Gale Crater are important in their own right since it is to be expected that, at a minimum, extraterrestrial carbon should be present at the surface. The continued hope is to find signatures of life. David J. Des Marais and Linda L. Jahnke address biosignatures of cellular components and metabolic activity in Chap. 3. They review life's basic capabilities of energy harvesting, metabolism, and self-replication, which can create objects, substances, and patterns—biosignatures—that indicate their biological origins. They conclude that the simultaneous presence of multiple biosignature objects, substances, and patterns in a demonstrably habitable earlier environment constitutes the most compelling evidence of past life.

Although it is widely believed that the likelihood of extant life forms at the surface of Mars is very low, the idea that life could subsist in the Martian subsurface is gaining credence. In this perspective, Frédéric Gaboyer, Gaëtan Burgaud, and Virginia Edgcomb in Chap. 4 describe very slow living extremophiles found up to several kilometres deep in subsea sediments and emphasise their relevance for the search of biosignatures in the Martian subsurface. The search for life in situ on another planet requires an approach that incorporates systematic preparation in terms of ground- and space-based studies before a mission. Jean-Pierre de Vera and colleagues from the BIOMEX and BIOSIGN experiments provide an overview of the necessary steps in order to search for life in situ on another planet or moon in Chap. 5 and show results obtained from research performed in the field, in the lab, and in space to help enhance knowledge of the traces and signatures of life, and how to recognise life itself. The different kinds of mineralogical traces that can be produced by microbial life forms are described in Chap. 6 by Karim Benzerara, Sylvain Bernard, and Jennyfer Miot. They review the manner in which many organisms impact mineral nucleation and growth, thus producing biominerals with specific chemical, structural, and textural properties that can provide clues to their biogenicity. Taking the concept of mineralisation and the preservation of microorganisms further, Fances Westall, Keyron Hickman-Lewis, and Barbara Cavalazzi make an overview of biosignatures in deep time, concentrating specifically on the oldest preserved biosignatures in well-preserved, although moderately metamorphosed, rocks up to 3.5 billion years old from the greenstone belts of Barberton in South Africa and the Pilbara in Australia. They show that the earliest preserved traces of life record an already thriving and, for an anaerobic world, evolved microbial ecosystem that included anoxygenic photosynthesis.

Indeed, carbonates as biominerals were described by David McKay and co-authors (1996) in the ALH84001 meteorite from Mars as one of the criteria in their interpretation of fossil life in the meteorite. Fractures within the meteorite contain rosette-shaped, aqueously deposited carbonate containing small ovoid to filamentous-shaped objects that the McKay team believed to be microbial nanofossils. Associated with the carbonates are minute magnetite crystals that were interpreted as biominerals produced by magnetotactic bacteria. Harry Y. McSween in Chap. 8 makes a critical appraisal of the original claims and the mountain of experimental data that ensued the 1996 publication, concluding that the evidence for biogenicity is weak.

Continuing on the theme of minerals, John Robert Brucato and Teresa Fornaro look at the role of mineral surfaces in prebiotic processes and life detection investigations focusing mainly on Mars exploration in Chap. 9. They show how molecule–mineral interactions provide important support for space missions aimed at searching for past or present signs of life in the form of molecular biomarkers within rocks.

One way of studying organic molecules as prebiotic or biosignatures in rocks is to look at the effects of photochemistry in space on astrobiologically relevant substrates. These molecules formed part of the organic inventory that was used for the prebiotic processes leading to the emergence of life. In Chap. 10, Avinash Dass, Hervé Cottin, and André Brack review the history of experiments to expose organic molecules to space radiation, observing the kinds of changes that occur in them.

The search for extraterrestrial life concerns not only our nearest planetary neighbour, Mars, but also rocky, Earth-like (or other habitable but not so Earth-like) planets in general. John Lee Grenfell in Chap. 11 provides a brief overview of potential biosignatures of relevance to remote observation and reviews knowledge of the main processes which influence biosignatures in an exoplanetary context, looking specifically at atmospheric model studies for Earth-like planets which predict climate, photochemistry, and potential spectral signals of biosignature species.

Just such a potential atmospheric signature for life has been found on Mars over the last couple of decades. Methane has been measured in the Martian atmosphere from ground-based telescopes, from Martian orbiters, and now in situ by the Curiosity rover. Franck Lefèvre reviews the history of the observations and evaluates their implications for the origin of methane as a possible biogas in Chap. 12.

One of the instruments in the Pasteur payload of the ExoMars 2020 rover is a Raman spectrometer, and another Raman spectrometer will fly on the Mars 2020 caching mission. Frédéric Foucher in Chap. 13 presents an overview of the different types of biosignatures that can be detected and/or characterised using Raman spectroscopy, including organic molecules, microfossils, biominerals, or even living cells.

The search for life on Mars is not new. The two 1976 Viking landers on Mars were the first dedicated astrobiology missions to the red planet. Jorge L. Vago, Frances Westall, and Barbara Cavalazzi in Chap. 14 review the ambiguous results from this mission and introduce the objectives of the ExoMars 2020 rover and its approach to the search for past or present life on the planet.

The final part consists of a philosophical appraisal of the notion of biosignatures by David Dunér in Chap. 15 examines the human search, understanding, interpretation of biosignature natures, the concepts of conceptualisation, analogy, perception, and the semiotics of biosignatures.

Bologna, Italy — Barbara Cavalazzi
Orléans, France — Frances Westall

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During a long career studying biosignatures and astrobiology, FW has benefitted from interactions with many colleagues in many disciplines. In particular, she acknowledges the contributions of the first two presidents of EANA, André Brack and Gerda Horneck, to the field.

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We covered many of the fundamentals in our *Biosignatures for Astrobiology*; however, we would like to emphasise that if we are far away from being complete—always there are questions left without response—we would like to stimulate further discussions and open new perspectives in the research for life.

Bologna, Italy
Orléans, France
May 2018

Barbara Cavalazzi
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Part I
Biosignatures on Earth

Chapter 1
Chemical Biosignatures at the Origins

André Brack

Abstract Chemists searching for chemical biosignatures begin to define the chemical prerequisites for the emergence of life, a process based on organized molecules capable of self-reproduction and also with the capability of evolution. It is generally accepted that these prerequisites are liquid water and organic molecules, i.e. molecules that contained carbon and hydrogen atoms associated with atoms of oxygen, nitrogen and sulphur. This is not just an anthropocentric point of view, since water and carbon chemistry have very specific peculiarities. Two different kinds of chemical biosignatures are considered: an overrepresentation of organics and a long strand of homochiral sequences.

1.1 Introduction

From a chemical point of view, it is difficult to define life (Luisi 1998). Perhaps the most general working definition is that adopted in October 1992 by the NASA Exobiology Programme: "Life is a self-sustained chemical system capable of undergoing Darwinian evolution" (Joyce 1995). The concept of evolution implies that the chemical system transfers its information fairly faithfully but, in so doing, makes a few random errors. These may potentially lead to a higher complexity or efficiency, and possibly to a better adaptation to changes under existing environmental constraints. Life is expected to appear as an open chemical system capable of self-reproduction, i.e. making more of itself by itself, and to be capable of evolving, and can thus be defined as a sort of chemical automaton (Brack and Troublé 2010).

Chemists tackle three different aspects of the origins of life: the origin of terrestrial life, the possibility of an alien life on Earth, and the possible emergence of an extraterrestrial form of life. For each of these three fundamental questions, it is necessary to define the biological prerequisites before searching for any chemical biosignatures.

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1.2 Chemical Prerequisites

It is generally believed that the requisite for the an emergence of life is the simultaneous presence of liquid water and organic molecules, i.e. molecules that contained carbon and hydrogen atoms associated with oxygen, nitrogen and sulphur, as in the case of present life. This is not just an anthropocentric guideline, since water and carbon chemistry have a number of peculiarities when compared, for example, to silicon-based biochemistry in non-aqueous solvents (Bains 2004).

1.2.1 Liquid Water

As parts of an open system, the constituents of a living system must be able to diffuse at a reasonable rate. A solid-state life is generally discarded, the constituents being unable to migrate or to be easily exchanged. A gaseous phase would allow fast diffusion of the parts but the limited inventory of stable volatile organic molecules would constitute a severe restriction. A liquid phase offers the best environment for the diffusion and the exchange of dissolved organic molecules. Besides liquid water, other solvents can be considered such as liquid ammonia, hydrogen sulphide, and sulphur oxide, together with hydrocarbons, organic acids and/or alcohols. Compared to any of these possible solvents, liquid water exhibits many promising specificities. Liquid water is a fleeting substance that can persist only above 0 °C and under a pressure higher than 6 mbars. The freezing point of water can be depressed by adding salts (brines). For instance, the 5.5% by weight salinity of the Dead Sea depresses the freezing point of seawater by about 3 °C. Large freezing point depressions are observed for 15% LiCl (23.4 °C) and for 22% NaCl (19.2 °C). Monovalent and divalent salts are essential for terrestrial life because they are required as co-catalysts in many enzymatic activities. Usually, the tolerated salt concentrations are quite low (<0.5%) because high salt concentrations disturb the networks of ionic interactions that shape biopolymers and hold them together. However, both eukaryotic and prokaryotic salt-loving microorganisms—known as extreme halophiles—tolerate a wide range of salt concentrations (1–20%) and some prokaryotes have managed to thrive in hypersaline biotopes (such as sabkhas, salt-lakes) containing up to 25–30% sodium chloride.

Water is a good solvent thanks to its hydrogen bonds. According to its molecular weight, water should be a gas under standard terrestrial conditions by comparison with CO_2, SO_2 or H_2S. Its liquid state is due to its ability to form hydrogen bonds. This is not restricted to water molecules since alcohols exhibit a similar behaviour, however, the polymeric network of water molecules *via* H-bonds is so tight that the boiling point of water is raised from 40 °C, a temperature inferred from the boiling point of the smallest alcohols, to 100 °C. Biopolymers, such as nucleic acids, proteins and membranes, contain C_xH_yO, N, S-groups and C_xH_y-groups (hydrocarbon groups). Groups like C_xH_yO, N, S, especially those bearing ionisable groups such as –COOH or –NH_2, form hydrogen bonds with water molecules and therefore display an affinity for water. They are soluble in water and hydrophilic. The large dipole moment of water (1.85 debye) favours the dissociation of the ionisable groups while the high dielectric constant ($\varepsilon = 80$) prevents recombination of the ions, the attraction forces for ion re-association being proportional to l/ε. This is also true for metallic ions, which are associated with the biopolymers. C_xH_y-groups cannot form hydrogen bonds with water molecules and thus water molecules tend to escape. They are insoluble in water and hydrophobic. These two groups co-exist in biopolymers and this co-existence drives the conformation (geometry) of the biopolymers in water, i.e. into forms such as helices, β-sheets, micelles, vesicles or liposomes. Water participates in the production of clays, which probably played an important role in the emergence of life. It stabilises the biopolymer conformation by hydrophobic clustering and is also a good heatsink.

Liquid water was almost permanently present at the surface of the Earth thanks to both the size of the planet and its distance to the Sun (Pinti 2005). If the planet were happened to be much smaller, like Mercury or the Moon, it would not have been able to retain any atmosphere and, therefore, no ocean of liquid water. If the planet were too close to the star, the mean temperature would have risen due to starlight intensity. Any seawater present would evaporate delivering large amounts of water vapour to the atmosphere thus contributing to the greenhouse effect. Such a positive feedback loop could lead to a runaway greenhouse: all of the surface water would be transferred to the upper atmosphere where photo-dissociation by ultraviolet light would break the molecules into hydrogen, which escapes into space, and oxygen, which would be recombined into the crust. The Earth hosted permanent liquid water thanks to its constant greenhouse atmosphere, however, water risked provoking its own disappearance. The atmospheric greenhouse gas CO_2 normally dissolves in the oceans and is eventually trapped as insoluble carbonates through rock weathering. This negative feedback is expected to lower the surface pressure and temperature to an extent that water would be largely frozen. On Earth, active plate tectonics and volcanism recycled the carbon dioxide by breaking down subducted carbonates.

1.2.2 Organic Molecules

Life is autocatalytic in essence and must be able to evolve. To evolve, i.e. improving its efficiency of self-reproduction and increasing its diversity, the molecules bearing hereditary memory must reach a certain level of complexity. This can be best achieved with a scaffolding of polyvalent atoms. In chemists' hands, carbon chemistry is very productive in this respect. Another clue in favour of carbon is provided by radio astronomers: about 110 carbon-containing molecules, up to $HC_{10}CN$, have been identified in the interstellar medium, whereas while only 11 silicon-based molecules, up to SiH_4, have been detected (Wikipedia).

Charles Darwin was the first to envision an organic approach to the origin of life. In February 1871, he wrote in a private letter to Joseph Hooker: "If (and oh, what a big if) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present that a protein compound was chemically formed, ready to undergo still more complex changes, at the present day such matter would be instantly devoured or adsorbed, which would not have been the case before living creatures were formed".

1.2.2.1 Production of Organics in the Atmosphere

The simplest sources of carbon susceptible to building up the prebiotic organic molecules are gaseous, i.e. carbon dioxide (CO_2) and monoxide (CO) for the oxidised forms and methane (CH_4) for the reduced forms. Oparin (1924) suggested that the reduced small organic molecules needed for primitive life were formed in a primitive atmosphere dominated by methane. His idea was tested in the laboratory by Miller who exposed a mixture of methane, ammonia, hydrogen, and water to spark and silent electric discharge (Miller 1953). In this initial experiment, Miller obtained three amino acids (glycine, alanine and β-alanine) *via* the intermediary formation of hydrogen cyanide and aldehydes. More generally, simple gaseous molecules, like CH_4, H_2, NH_3, and H_2O, require a supply of energy (UV, heat, electric discharges, cosmic rays, shock waves) to react with each other. They generate compounds like formaldehyde and hydrogen cyanide, which store chemical energy in their double and triple chemical bonds, respectively. Chang (1993) reviewed the possible sources of atmospheric synthesis including electric effects, solar UV and impact shocks.

Miller's laboratory synthesis of amino acids occurs efficiently when a reducing gas mixture containing significant amounts of hydrogen is used. However, the true composition of the primitive Earth's atmosphere is not known. The dominant view is that the primitive atmosphere consisted mainly of CO_2, N_2, and H_2O, along with small amounts of CO and H_2 (Kasting and Brown 1998; Catling and Kasting 2007). Only small yields of amino acids are formed in such a mixture (Schlesinger and Miller 1983; Miller 1998). More recent studies show that the low yields previously reported appear to be the outcome of the oxidation of organic compounds during hydrolytic workup by nitrite and nitrate produced in the reactions. The yield of amino acids is greatly increased when oxidation inhibitors, such as ferrous iron, are added prior to hydrolysis, suggesting that endogenous synthesis from neutral atmospheres may be more important than previously thought (Cleaves et al. 2008). Additionally, twenty-two amino acids and five amines were obtained when re-analysing archived Miller's archived samples obtained by lightning applied to volcanic gases. The volcanic apparatus experiment suggests that, even if the overall atmosphere was not reducing, localized prebiotic synthesis could have occurred in volcanic plumes (Johnson et al. 2008). Stanley Miller also sparked a gaseous mixture of CH_4, NH_3, and H_2O, while intermittently adding the plausible prebiotic condensing reagent cyanamide. For unknown reasons, an analysis of the samples was not reported. After his death, the archived samples were analysed for amino acids, dipeptides, and diketopiperazines by liquid chromatography, ion mobility spectrometry, and mass spectrometry. A dozen amino acids, ten glycine-containing dipeptides, and three glycine-containing diketopiperazines were detected. Miller's experiment was repeated and aqueous heating experiments indicate that Strecker synthesis intermediates play a key role in facilitating polymerization (Parker et al. 2014).

The escape of hydrogen from the early Earth's atmosphere has recently been re-evaluated (Tian et al. 2005). It likely occurred at rates two orders of magnitude more slowly than previously thought. The balance between slow hydrogen escape and volcanic outgassing could have maintained a hydrogen mixing ratio of more than 30%, thus producing more amino acids than previously thought.

Intense bombardment probably caused some chemical reprocessing of the Earth's primitive atmosphere by impact shock chemistry (Brack 2009). An indication of the number and timing of the impacts onto the early Earth can be obtained by comparison with the crater record of the Moon, which records impacts from the earliest history of the Solar System (Ryder 2003). Because of the larger size of the Earth and its greater gravitational pull, about 20 times as many impacts would have occurred on the early Earth as on the Moon. Computer modelling of the resulting impact shock chemistry shows that the nature of the atmosphere strongly influences the shock products (Fegley et al. 1986). A neutral CO_2-rich atmosphere produces CO, O_2, H_2 and NO, whereas a reducing CO-rich atmosphere yields primarily CO_2, H_2, CH_4, HCN, NH_3, and H_2CO. The last three compounds are particularly interesting for prebiotic chemistry since they can lead to amino acids *via* Strecker synthesis. However, a CO-rich primitive atmosphere probably has no counterpart in prebiotic reality. In laboratory experiments, a gas mixture of methane, ammonia and water subjected to shock heating followed by rapid thermal quenching yielded the amino acids glycine, alanine, valine and leucine (Bar-Nun et al. 1970). Here again, the gas mixture used does not represent a realistic primitive atmosphere, which was dominated by CO_2. Laboratory simulations of shocks were also run with a high-energy laser. CH_4-containing mixtures generated hydrogen cyanide and acetylene but no organics could be obtained with CO_2-rich mixtures (McKay and Borucki 1997).

Hydrogen cyanide was produced in the laboratory by the impact of a polycarbonate projectile and graphite through N_2-rich atmosphere. A significant fraction ($>$0.1 mol%) of the vaporized carbon was converted into HCN and cyanide condensates, even when the ambient gas contains as much as a few hundred mbar of CO_2 (Kurosawa et al. 2013).

1.2.2.2 Submarine Hydrothermal Systems

The reducing conditions in hydrothermal systems may have been an important source of biomolecules on the primitive Earth (Baross and Hoffman 1985; Holm 1992; Holm and Andersson 1998, 2005). The reducing environment results from the flow of substances dissolved in seawater through inorganic compounds present in very hot crustal material that reduces compounds in seawater. These reduced compounds flow out of the hydrothermal system and the resulting inorganic sulphides formed precipitate when they mix with the cold (4 °C) ocean water. For example, hydrocarbons containing 16–29 carbon atoms have been detected in the Rainbow ultramafic hydrothermal system, Mid-Atlantic Ridge (Holm and Charlou 2001). Hydrothermal vents are often disqualified as efficient reactors for the synthesis of bioorganic molecules due to their high temperature. Experiments exploring the potential for amino acid synthesis at high temperature from synthetic seawater solutions of varying composition have been conducted (Aubrey et al. 2009). The synthesis of amino acids was examined as a function of temperature, heating time, starting material composition and concentration. Using very favourable reactant conditions (high concentrations of reactive, reduced species), small amounts of a limited set of amino acids can be generated at moderate temperature conditions (~125–175 °C) over short heating times of only a few days, but even these products are significantly decomposed after exposure times of approximately one week. Therefore, although amino acids can be generated from simple, likely environmentally available precursors under submarine hydrothermal system conditions, their equilibrium at high temperatures favours net amino acid degradation rather than synthesis, and that synthesis at lower temperatures may be more favourable. However, the products that are synthesized in hot vents are rapidly quenched in the surrounding cold water thanks to the good heat conductivity of water and may therefore be preserved (Ogata et al. 2000).

1.2.2.3 Delivery of Extraterrestrial Organic Matter

The Earth has experienced a large range of impactors ranging from the huge Mars-sized impactor that created the Moon to cosmic dust less than 1 μm in size. A great number of organic molecules, including amino acids, have been found in carbonaceous chondrites. Micrometeorite collection and analysis from the Greenland and Antarctic ice sheets suggests that the Earth accreted large amounts of complex organic molecules of extraterrestrial origin. Intense bombardment probably also caused some chemical reprocessing of the Earth's primitive atmosphere.

Comets—Comets are, as is known thus far, the planetary objects richest in organic compounds. Ground-based observations have detected hydrogen cyanide and formaldehyde in the coma of comets. In 1986, on-board analyses performed by the two Russian missions Vega 1 and 2, as well as observations obtained by the European mission Giotto and the two Japanese missions Suisei and Sakigake, demonstrated that Comet Halley shows substantial amounts of organic material. On average, dust particles ejected from the nucleus of Comet Halley contain 14% of organic carbon by mass. About 30% of cometary grains are dominated by the light elements C, H, O, and N, and 35% are close in composition to the carbon-rich meteorites. Many chemical species of interest for astrobiology were detected in Comet Hyakutake in 1996, including ammonia, methane, acetylene, acetonitrile, and hydrogen isocyanide. In addition, the study of Comet Hale-Bopp in 1997 led to the detection of methane, acetylene, formic acid, acetonitrile, hydrogen isocyanide, isocyanic acid, cyanoacetylene, formamide and thioformaldehyde.