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Astrobiology and the Possibility of Life on Earth and Elsewhere...

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Abstract Astrobiology is an interdisciplinary scientific field not only focused on the search of extraterrestrial life, but also on deciphering the key environmental parameters that have enabled the emergence of life on Earth. Understanding these physical and chemical parameters is fundamental knowledge necessary not only for discovering life or signs of life on other planets, but also for understanding our own terrestrial environment. Therefore, astrobiology pushes us to combine different perspectives such as the conditions on the primitive Earth, the

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physicochemical limits of life, exploration of habitable environments in the Solar System, and the search for signatures of life in exoplanets. Chemists, biologists, geologists, planetologists and astrophysicists are contributing extensively to this interdisciplinary research field. From 2011 to 2014, the European Space Agency (ESA) had the initiative to gather a Topical Team of interdisciplinary scientists focused on astrobiology to review the profound transformations in the field that have occurred since the beginning of the new century. The present paper is an interdisciplinary review of current research in astrobiology, covering the major advances and main outlooks in the field. The following subjects will be reviewed and most recent discoveries will be highlighted: the new understanding of planetary system formation including the specificity of the Earth among the diversity of planets, the origin of water on Earth and its unique combined properties among solvents for the emergence of life, the idea that the Earth could have been habitable during the Hadean Era, the inventory of endogenous and exogenous sources of organic matter and new concepts about how chemistry could evolve towards biological molecules and biological systems. In addition, many new findings show the remarkable potential life has for adaptation and survival in extreme environments. All those results from different fields of science are guiding our perspectives and strategies to look for life in other Solar System objects as well as beyond, in extrasolar worlds.

Keywords Astrobiology · Exobiology · Origin of life · Search for extraterrestrial life · Limits of life · Prebiotic chemistry · Water

1 Introduction

Astrobiology includes "the search for extraterrestrial life", but this interdisciplinary field is much more than this. Indeed, before we can build the most comprehensive and coherent scientific strategy to seek (and perhaps find) life beyond Earth, it is interesting to identify the steps, conditions, and detailed mechanisms that allowed life to emerge on our planet. The questions of how and when life originated on Earth are therefore linked to any astrobiological reasoning.

In 1960, J. Lederberg introduced the word exobiology and acknowledged the legitimacy of the search for extraterrestrial life as a scientific subject (Lederberg 1960). Different names have been attributed to this research field over the years such as bioastronomy, astrobiology, cosmobiology (Brack 2012). This research field also covers the evolution of organic matter into complex structures as well as the distribution and evolution of life on Earth and possibly beyond. As shown in Fig. 1, exobiology and astrobiology are the most widespread titles of this interdisciplinary research field. Today, 55 years after the Lederberg paper, the word astrobiology is the most often used worldwide to describe the discipline, and its rise in use to differentiate the field is due to the eponymous NASA Astrobiology program started in 1997.

To date, it is strictly impossible to say conclusively that terrestrial life is unique (and thus that we are alone in the universe), or that there is an almost infinite number of inhabited worlds hosting multiple life forms throughout the universe. Astrobiology research has however now entered an exciting, promising, and challenging phase since the late nineties, as new tools, new discoveries, and new concepts have profoundly changed the face of the discipline. A continuously increasing number of exoplanets is being discovered, with each

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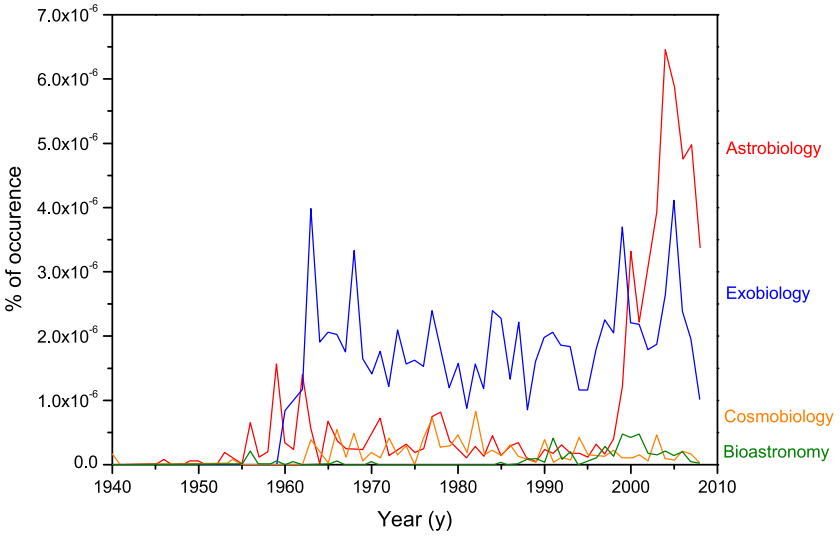


Fig. 1 Comparative use (% of use in the corpus of texts digitalized by Google) of the words astrobiology, exobiology, bioastronomy and cosmobiology from 1940 to 2008. The graph shows that "exobiology" is the first word to appear before being overtaken by "astrobiology" in the late 1990s after the launch of the NASA Astrobiology program in 1997. The use of terms bioastronomy and cosmobiology remains marginal (data from Michel et al. 2011)

new discovery changing our perceptions of the diversity of possible planetary and solar system configurations (Mayor and Queloz 1995, 2012). This is leading scientists to reconsider how unusual both the Earth and our Solar System may be, and indeed whether *every* solar system has its own particularities. The recent theory of the migration of the giant planets has resulted from the discovery of giant exoplanets orbiting close to their host stars, and from this theory a new complex history of the first several hundred million years of the Solar System, the early period during which life appeared on Earth, is being deciphered (Morbidelli et al. 2012a).

Life however prevailed on Earth. After more than a decade of controversial announcements (Brasier et al. 2002; Schopf 1993) it now seems well established that life was fully established on Earth by 3.5 billion years ago. The nature of the early planet on which Life originated, flourished and diversified, is being reconstructed by scientists piece by piece using geological and other evidence.

The consensus in the astrobiological community is that the origin of life (and most probably its sustainability) requires liquid water, most of which was likely imported from space after the Earth formed, and organic matter, either from endogenous sources (atmospheric and/or geochemical synthesis) and/or exogenous sources (*e.g.* comets, carbonaceous asteroids and micrometeorites). After the demonstration of the facility of geochemically plausible organic synthesis by Miller and Urey (Miller 1953), the first goals of prebiotic chemistry during the sixties and seventies were to account for the formation of basic bioorganic molecules such as amino acids, nucleobases, and sugars under prebiotic conditions. Prebiotic chemistry later ran into serious stumbling blocks in attempting to explain the spontaneous origin of more complex biomonomers such as ribonucleotides and biopolymers such as proteins and nucleic acids. More recently researchers have begun to re-examine traditional approaches to some of these problems. A milestone in prebiotic chemistry has been achieved with a quite

convincing pathway for the synthesis of an activated nucleotide bypassing the traditional approaches of adding building blocks one to another (Powner et al. 2009). New concepts such as Systems Chemistry (Ludlow and Otto 2008) and Dynamic Kinetic Stability (Pross 2009) have breathed new life into thinking on prebiotic chemistry, and may lead to significant progress in the not too distant future.

While one group of scientists struggle to understand the origin of life, another has revealed the astounding ability of living systems to adapt to the most extreme and improbable environments on Earth. It seems that almost all terrestrial environments, hot or cold, dry or wet, neutral, basic, or acidic *are* inhabited. Although it remains unclear whether life has the capability to *emerge* in extreme conditions, its tremendous capacity to at least adapt to these conditions opens a perspective for the search for life elsewhere in the Solar System. Whether on Mars, or in the oceans of the satellites of the outer planets (such as Europa, Ganymede, Callisto, Titan or Enceladus), the Solar System may harbor niches that were favorable for the emergence of life. Moreover, future analyses of the composition of the atmospheres of exoplanets could provide clues to the presence of extraterrestrial life far beyond the reach of *in situ* exploration. Which clues could provide evidence and how? These are questions which will probably be highly debated in the next decades.

In 2011, ESA had the initiative to gather a topical team on astrobiology. Chaired by Dr. Julia Michelle Kotler and Prof. Hervé Cottin, the team was asked to produce an update more than 10 years after the previous topical team focusing on exobiology (note ESA's switch between the use of the terms exobiology and astrobiology) which produced the ESA Special Report entitled Exobiology in the Solar System & the Search for Life on Mars (Brack et al. 1999). The ExoMars exploration program was actually inherited from concepts contained in the 1999 report. The goal of the new team was to address the profound transformations in the field of astrobiology that have occurred since the 1999 exobiology topical team report, and, using new scientific questions and discoveries, to focus specifically on experimental studies either in the field (*i.e.* using Earth as a tool for astrobiology) or in space, (*i.e.* using space as a tool for astrobiology). The present paper is an interdisciplinary review of current research in astrobiology, covering the major advances in the field since the beginning of the new millennium. Two additional papers (Cottin et al. 2015; Martins et al. 2015) discuss the two main focuses of the topical team: field campaigns and experiments conducted in Earth orbit.

2 What Were Conditions on the Primitive Earth Like?

2.1 A Common Planet in a Common Planetary System?

The discovery of exoplanets since 1995 (Mayor and Queloz 1995) has radically changed prospects for detecting life beyond Earth. We are no longer limited to a few Solar System objects which can potentially be explored by spacecraft, but rather to hundreds or even thousands of exoplanets which could potentially offer spectroscopic evidence for life. Sophisticated new technologies are under development to detect biosignatures in the spectra of exoplanetary atmospheres (for instance with the Darwin project (Cockell et al. 2009), or the James Webb Space Telescope (Loeb and Maoz 2013)). The diversity of newly observed planetary objects, including giant exoplanets detected orbiting within less than a tenth of an astronomical unit from their stars, has also considerably changed our understanding of how planets form, and consequently our understanding of the history of the formation of our own Solar System and the extent to which our planet may have had an uncommon evolutionary history (Morbidelli 2010).

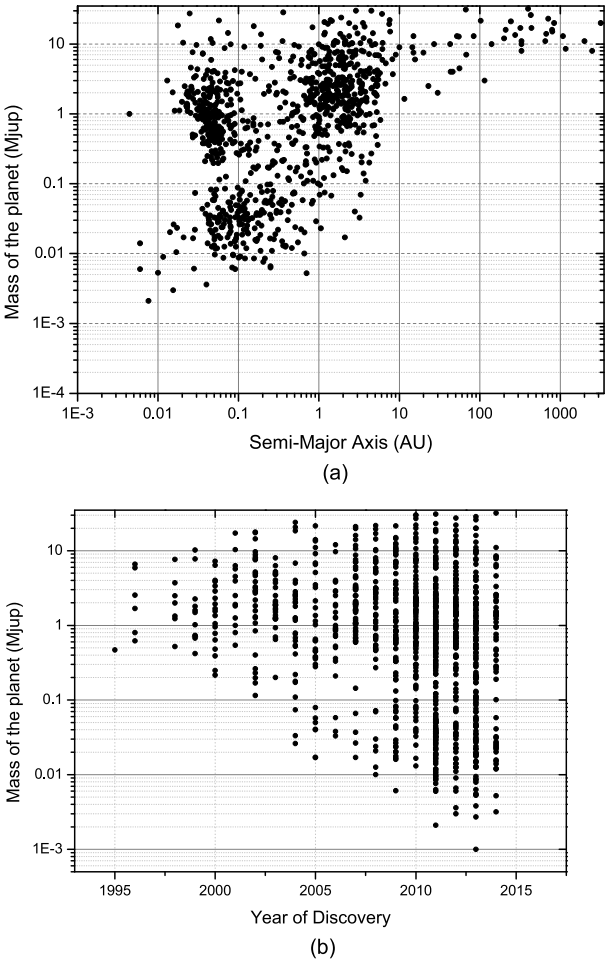


Fig. 2 Exoplanets discovered around other stars (as of July 2014). Planetary mass as a function of (**a**) the distance to the host star (semi-major axis in astronomical units) and (**b**) year of discovery. Most of them, especially those discovered until the end of the first decade of the 21st century, were giant planets, orbiting close to their host star (source exoplanet.eu). For reference, the mass of the Earth is 3.15×10^{-3} M_{jup}

2.1.1 Other Planetary Systems, the Migration of Giant Planets

To date, almost two thousands exoplanets have been discovered around other stars (Fig. 2), mostly thanks to indirect methods such as transit detection and radial velocity measurement. As these methods are most sensitive to giant planets orbiting close to their host stars, many peculiar planetary systems have been discovered, giving the probably false notion that the architecture of our Solar System, with telluric planets in the inner system and giant planets in the outer system, is uncommon. However, new instruments have shown that this idea has been biased by instrumental limitations, and detecting telluric planets in the Earth mass range has become increasingly common, and will probably increase in frequency in the next few years (Mayor and Queloz 2012). Noteworthy is the recent detection of the first Earth sized planet within the habitable zone of its star (M class) thanks to observations of the Kepler telescope (Quintana et al. 2014). Nevertheless, "classical" models of planetary formation have required considerable modification to be consistent with observations of giant exoplanets close to their stars, including the introduction of the concept of giant planet migration from the outer reaches of a planetary system inwards toward their host star (Alibert

et al. 2005; Trilling et al. 1998). Thus, an unexpected and important lesson learned from the discovery of exoplanets is that planets do not always stay in the orbit in which they formed.

2.1.2 Formation of the Solar System and Earth Accretion

Recent improvements in our understanding of the physical processes governing the formation of planetary systems, based on exoplanet discoveries, have also changed our view of the history of our Solar System. Impressive results have been obtained in the modeling of the accretion of the telluric planets from planetesimals, ranging from "simple" modeling of Earth like planets formed from lunar-sized embryos (Chambers 2001), to more refined high resolution calculations showing that hydrated planetesimals may have been incorporated into the growing Earth during the latest stages of its accretion (Raymond et al. 2006), and finally the "Grand Tack" scenario where the formation of the terrestrial planets and distribution of dry and hydrated small bodies in the Solar System are influenced by the inward and outward migration of Jupiter and Saturn after their formation (Walsh et al. 2011). Although many questions remain, our understanding of the history of the formation of telluric planets and, subsequently, habitable worlds, has improved significantly since the beginning of the 21st century.

The early history of the Earth has also been reconsidered. It has long been taken for granted that the impact rate of comets and meteorites on the early Earth slowly decreased from the initial accretion stage of the telluric planets to a relatively slow rate about 3.8 Ga ago. This resulted in the commonly held idea that life could not have arisen on Earth before this harsh bombardment period ended, or life would have been wiped out by sterilizing impacts (Maher and Stevenson 1988; Zahnle and Sleep 2006). However, lunar cratering records suggest that a spike in the cratering rate occurred ∼700 million years after the planets formed, the so-called "Late Heavy Bombardment" (Tera et al. 1974). This observation is consistent with modelling results (the "Nice Model" Gomes et al. 2005; Morbidelli et al. 2005; Tsiganis et al. 2005) showing that a major migration event within the orbits of the giant planets (with an inversion of the positions of Neptune and Uranus with respect to the Sun) may have occurred at this time, destabilizing the asteroid belt and ejecting a large number of outer solar system planetesimals toward the inner Solar System. This inversion resulted in a "Late Heavy Bombardment" on Earth and all the inner Solar System objects (Gomes et al. 2005) (Fig. 3). The size of the impactors on the Earth during and even before this event may not have been large enough to sterilize the planet (Abramov and Mojzsis 2009; Morbidelli et al. 2012b) and therefore Earth may have been a habitable planet since 4.4 Ga. However, a recent re-evaluation of the ages of lunar rocks upon which the LHB theory was founded has cast doubt on this scenario (Spudis et al. 2011) and indeed there is still some debate as to whether the LHB ever occurred at all.

Whether the history of our planet is typical is still unknown, but its structure and global geophysical properties are the result of the whole architecture of the Solar System and its sequence of formation. However, detecting exoplanets in the "habitable zone" around a star—the "holy grail" of exoplanet hunters from 2000 to 2010, is now quite common (see for instance Borucki et al. 2013 and Gaidos 2013).

2.2 Water: Its Origin and Importance for Life

Hydrogen and oxygen are among the most abundant elements in the universe (ranks 1 and 3), and consequently it should not be surprising that water is the second most abundant molecule in space after molecular hydrogen. Water ice is widely distributed in space and is by far the

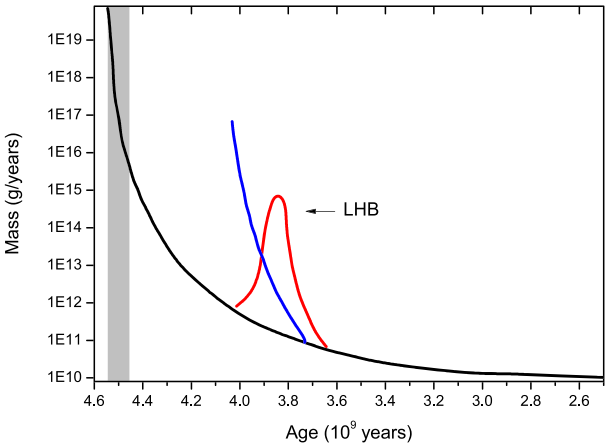


Fig. 3 Estimations of the accretion rate from impacts at the surface of the Moon (adapted from Koeberl 2006). The *black line* is an extrapolation of the current background flux constrained with lunar impact data, back to the formation of the Solar System. The *red bell shaped curve* shows the Late Heavy Bombardment event as suggested from the dating of the most important lunar impact basins and modeling of the dynamics of the early Solar System. The *blue line* shows a very unlikely accretion curve that includes the masses of the basin-forming projectiles in the extrapolation; this leads to the accretion of the Moon at 4.1 Ga instead of 4.5–4.4 Ga (indicated by the *grey area*)

most abundant condensed-phase species in the universe (Hanselmeier 2011). Water has been observed in the interstellar medium by numerous ground- and space-based telescopes. The Atacama Large Millimeter/submillimeter Array (ALMA) has provided evidence for water in the most distant galaxies indicating that water was already present in the early universe (Vieira et al. 2013). Ultrathin, water-rich icy layers cover dust particles in the cold regions of the interstellar medium. Water ice is also widespread in the solar system. It covers the poles of terrestrial planets (*e.g.* the Earth and Mars) and most of the outer-solar-system satellites. Smaller solar system bodies, such as comets and Kuiper Belt Objects (KBOs), contain a significant fraction of water ice. Icy particles are also present in planetary atmospheres and play an important role in determining the climate and the environmental conditions on Earth. Moreover, liquid water oceans may exist beneath the ice crust of several moons of Jupiter and Saturn (Hussmann et al. 2006).

Water is the most abundant compound in icy interstellar grain mantles as evidenced by infrared observations of cold dense clouds. However, the mechanism of formation of water-ice-dominated mantles is not yet fully understood (Cuppen and Herbst 2007) and routes of plausible hydrogenation reactions are currently being explored with the help of laboratory experiments (Ioppolo et al. 2008). Recently the Herschel Space Observatory identified emission lines of cold water vapor from the disk around the young star TW Hydrae. The water lines seem to originate from icy dust particles close to the disk surface and represent a large reservoir (Hogerheijde et al. 2011).

H_2O can act both as a hydrogen donor and acceptor and can take part in multiple hydrogen bonds, giving it numerous unusual physical properties. It has a complex phase diagram, and it can form an extensive range of crystalline solid phases, mostly under high-pressure conditions. The physical properties of water ice, such as density, conductivity, vapor pressure and sublimation rate, depend on its crystalline structure. The phases are determined and can be distinguished from each other by the arrangement of H_2O molecules in the solid lattice. In all crystalline H_2O ices, the H_2O molecules have 4-fold coordination, donating

two hydrogen bonds, and accepting two others, even if the bonds are distorted. Most phases are thermodynamically stable under a limited range of pressure and temperature conditions, and some phases are metastable. The prevailing temperature and pressure conditions in our galaxy under which icy particles form result in the formation of hexagonal, cubic crystalline, or amorphous phases of H_2O-ice (Ehrenfreund et al. 2003).

2.2.1 The Origin of Water on Earth

The origin of water on terrestrial planets is a dynamic research topic focused on determining how much water was accreted during planet formation or delivered later via asteroid and comet impacts early in the history of our solar system (Elkins-Tanton 2013; Morbidelli et al. 2012a). Unfortunately, contradictory data and arguments in the literature do not presently exclusively support either of these scenarios. In the late 1990s, the cometary origin of Earth's water was dismissed since the D/H ratio measured in comets until 2011 ($\sim 3 \times 10^{-4}$) was approximately twice the Standard Mean Ocean Water (SMOW) value (1.56×10^{-4}) (Mumma and Charnley 2011). However, all these observations had been of comets originating from the Oort Cloud. After a measurement of the D/H ratio in the Kuiper Belt comet 103P/Hartley 2 consistent with the SMOW value (Hartogh et al. 2011), it was expected that comets originating from the same reservoir would have the same D/H value. This extrapolation was however contradicted by a recent measurement in comet 67P/Churyumov-Gerasimenko (thought to originate from the Kuiper Belt) by the Rosetta spacecraft D/H $= 5.3 \pm 0.7 \times 10^{-4}$, *i.e.* 3 to 4 times the SMOW value (Altwegg et al. 2015). Bulk hydrogen isotopic composition of CI chondrites suggests that meteorites were the principal source of Earth's volatiles (Alexander et al. 2012) with an additional $\sim$10 % contribution of water ice from comets. However, during the last decade the boundary between comets and asteroids has been blurring. For instance, it has been claimed that the Orgueil CI type chondritic meteorite could be a comet (Gounelle et al. 2006), while comet-like activity (*i.e.* water outgassing) is observed for some objects of the asteroid belt (so called "main belt comets" or "active asteroids") (Bertini 2011; Jewitt 2012). To add confusion to the discussion of the origin of Earth's water, some authors claim that the Earth was formed from relatively dry material and that our planet's volatile components (including water) were brought in later (Albarède 2009; Albarède et al. 2013), while other scenarios indicate that rocky planets were all built of material that contained enough water to form the oceans and atmospheres, and that later impact sources were relatively insignificant (Elkins-Tanton 2013; Hamano et al. 2013; Wood et al. 2010).

2.2.2 The Importance of Water for the Origin of Life

Today the presence of life on Earth depends on the availability of *liquid* water. In living systems water is pervasive and ubiquitous and cannot be considered as a simple diluting fluid. It performs many functions: it transports, structures, stabilizes, lubricates, reacts and partitions. Because of its unique characteristics described below, it is not unwarranted to suggest that water has allowed the progressive transition of non-living to living matter (Bruylants et al. 2011a, 2011b). No other molecule, abundant on the primitive Earth and abundant in the Solar System, could have played this role. It may even be highly probable that if any other form of life exists in the Universe, it is also based on liquid water.

Liquid water is highly structured and can be described as a fluctuating lattice of molecules linked to each other by H-bonds. This explains the unusual properties of liquid water, such as its high dielectric constant, high cohesion energy density and high surface tension and

also its capacity to facilitate the organization of matter necessary to achieve a living and functioning cell.

Several authors (Berti et al. 1998; Bloechliger et al. 1998; Luisi et al. 1999; Ourisson and Nakatani 1996; Pozzi et al. 1996; Takajo et al. 2001) consider that the spontaneous formation of membranes is one of the primordial steps in prebiotic evolution. One plausible model for the prebiotic formation of proto-cellular compartments, the spontaneous formation of stable vesicles, characterized by an inner and an outer space separated by a semi-permeable membrane, is a well-known and reproducible process in water. The formation is governed by the hydrophobic effect *i.e.* an increase in the entropy of water as a consequence of the desolvation of the hydrophobic surfaces of the amphiphilic molecules that constitute the vesicles (Ben-Naim 1980; Blokzijl and Engberts 1993; Chandler 2005; Lynden-Bell and Head-Gordon 2006; Pratt and Chandler 1977).

Water molecules also play an invaluable role in governing the structure stability and dynamics of life's major macromolecules, such as proteins and nucleic acid (Ball 2008; Orgel 2004). They are furthermore extremely important in binding and recognition processes and in the formation of molecular complexes which are essential for living systems (Ben-Naim 2002). As the water molecule can form multiple H-bonds, it can link functional groups within a macromolecule or between molecules. Due to its small size, it is furthermore a highly versatile component at the interface of (bio)molecular complexes and confers a high level of adaptability to a surface. It provides specificity and increased affinity to an interaction. The water molecules involved in (bio)molecular interactions can be seen as extensions of the molecular structure allowing optimization of the fit at the interface. For these water molecules, the energetic gain from water-mediated contacts is greater than the entropic cost resulting from their immobilization. It is now generally accepted that water molecules are part of association complexes and must be explicitly considered when attempting to understand the factors that govern molecular recognition processes in water.

Liquid water is also a unique solvent as it can efficiently solubilize both cations and anions. Currently no living systems are known that do not require the presence of ionic species and ionic gradients between the intra- and extra-cellular media. The solubilizing properties of water are due to the fact that water molecules interact efficiently with anions via H-bonds and with many cations via coordination between the lone pairs on the oxygen atom and the empty orbitals of the cations. Water's large dielectric constant also favors the solubilization of ion pairs.

From the above considerations, it seems reasonable to suppose that liquid water may be universally required for the origin and evolution of life, and thus one of the key criteria in the search for habitable environments where life could have emerged. Some other liquids, such as liquid ammonia or formamide, have some properties comparable to those of water but they do not possess all of its properties and often not under the pressure and temperature conditions under which biological activity (as we know it) could have been optimized. The spontaneous formation of vesicles has, for example, been reported to occur in formamide (Lattes et al. 2009) but formamide does not have the capacity to play, as water can, a role in the structure and dynamics of (bio)molecular complexes.

2.3 Hadean and Archean Earth

2.3.1 Was the Hadean Earth Hell-Like? The End of the Heavily Bombarded Planet Paradigm

The formation of Earth occurred about 4.55 Ga with this approximate age being accepted by the scientific community for nearly 50 years (Allegre et al. 1995). The first geologic

eon, which includes the formation of the Earth, is commonly referred to as the Hadean, although formal classification and recognition of the terminology varies. The Hadean has been loosely described as a hell-like environment with immense magma oceans and variable degrees of non-stop chaos induced by the formation and differentiation of the planet into the core, mantle and crust (Goldblatt et al. 2009). However, the lack of a well-preserved rock record from this time period makes speculation about the length that this hellish environment persisted highly contested, and alternate theories about the extent and types of crustal formation which occurred have been presented. Geologists extensively use the mineral zircon ($ZrSiO_4$) and particularly detrital zircons (grains that have been eroded from parent crustal/sedimentary rocks) to reconstruct the ancient history of "continental" crust and its detrital derivative, sediments, in the rock record (for an extensive review of detrital zircon analysis in sedimentary rocks see Fedo et al. 2003). Zircons are important because they are formed by crustal fractionation in the presence of water (note, though that they can also form through fractionation in a magma chamber). Fractionation of the crust can therefore be correlated with formation of initially proto-continental crust (granitoids) then true continental crust (granite). Zircon crystals are extremely resistant and are redeposited in sediments after erosion of these continental rock types. Thus, evidence from Hadean detrital zircons suggests that crust-forming processes may have begun much earlier than previously assumed and that the Hadean may have been more habitable than traditional hellish barren early Earth models predict (Harrison 2009; Wilde et al. 2001). Interestingly, oxygen isotope values measured in zircons >4.3 Ga-old indicate alteration of the crust in the presence of low temperature hydrothermal fluids (Wilde et al. 2001).

The division between the Hadean and the next geologic eon, the Archean, largely remains undefined, however, the latest geologic timescales place the boundary between the two eons at ~4.0 Ga limiting the duration of the Hadean to approximately 0.5 Ga (Walker et al. 2013). Many authors suggest that this division should be based on the age of the oldest known terrestrial rocks, the Acasta Gneiss a rock outcrop of Hadean tonalite gneiss in the Slave craton in Northwest Territories, Canada dated at 4.03 Ga (Eriksson et al. 2012; Van Kranendonk et al. 2012). In terms of astrobiology and the origin of life, many scientists find this convention awkward and prefer to place late heavy bombardment (LHB) within the Hadean (Sleep 2010). This is likely due to the earliest evidence of life and microbial habitability that are dated near the end of the LHB and the implied lithospheric stability necessary for habitable regions on the surface of the Earth (Abramov and Mojzsis 2009), although note that the oldest traces of life do not record the earliest forms of life (Westall 2011). The LHB, if it occurred (Spudis et al. 2011), is thought to have ceased between 3.8–3.85 Ga, however, recent evidence suggests that the LHB may have extended further into the Archean Eon (Bottke et al. 2012). The oldest evidence of life in the rock record correlates to the end of this period and is of particular interest to the astrobiology community for the emergence of life in the Archean Eon (Court and Sephton 2012). A recent paper by (Marchi et al. 2014) provides evidence for widespread mixing and burial of Earth's Hadean crust by asteroid impacts. The authors discuss that the peak of Hadean zircon ages at 4.1–4.2 Gyr reflects the onset of the LHB.

2.3.2 The Oldest Traces of Life on Earth

There is no continuous record of life on Earth from its appearance to the present day mainly because of the lack of well-preserved crustal rocks from the first billion years of Earth's history. Nevertheless, there is tantalizing evidence in the rock record starting with the oldest sediments from Greenland dating back to 3.8 Ga (the Early Archaean era, 4–3.3 Ga) in which carbon isotope ratios have been used to suggest the

presence of microbial metabolism at that period (Rosing 1999; Rosing and Frei 2004; Schidlowski 1988). Unfortunately these rocks have been severely metamorphosed and cannot tell us much about the kinds of life forms that might have inhabited the early Earth. On the other hand, there is a good record of well-preserved sediments dating from 3.5–3.3 Ga occurring in the ancient terranes of South Africa and the Pilbara in Australia. These rocks record evidence of simple chemotrophic microorganisms (*e.g.* chemolithotrophs deriving their energy from the oxidation of inorganic compounds) that lived in hydrothermal environments on the early Earth. Their energy sources would have included molecular hydrogen produced by redox alteration of volcanic rocks and hydrothermal activity while their carbon source may have been CO_2 dissolved in seawater. Dissolution features in the surfaces of the volcanic rocks attest to microbial attack on these substrates in search of nutrients (Furnes et al. 2004; Westall et al. 2011a, 2011b). Physical traces of the existence of these chemotrophs occur in volcanic sediments deposited in the shallow water littoral environment (Westall et al. 2006, 2011a, 2011b) and on the vitreous surfaces of pillow lavas erupted under water (Furnes et al. 2004). Apart from the afore-mentioned corrosion tunnels, multi-species colonies of small (generally <1 μm diameter), mainly coccoidal fossilized microorganisms coat the surfaces of volcanic grains (Fig. 4) and are present in the interstitial pore spaces between the volcanic grains (Westall et al. 2006, 2011a, 2011b). The carbonaceous cells were preserved by silica that was precipitated at a very early stage and the carbon isotope ratios of the carbon in the rock are consistent with microbial fractionation. The direct association of the microfossils with the volcanic detrital grains suggests their chemolithotrophic nature.

Other studies indicate the presence of chemo-organotrophic microorganisms, whose carbon source is organic carbon. They have been found in association with photosynthetic microbial mats/biofilms, as described below, and with microbial biofilms around quartz grains (Wacey et al. 2010). In addition to these chemotrophs, rocks from South Africa and Australia contain a variety of evidence in support of photosynthetic organisms. On the microbial scale, Westall and colleagues (Westall et al. 2006, 2011a, 2011b), have documented the physical and geochemical characteristics of an individual, well-preserved mat that formed on a beach surface, probably in the outflow channel of a hydrothermal spring. The mat was composed of small ($\sim$0.3 μm diameter, 10 s of μm in length), parallel-orientated microbial filaments whose decomposing remains beneath the mat surface were degraded by probable sulfate-reducing microorganisms, as indicated by the relatively high concentration of sulfur in the mat subsurface (sulfurisation) and by the *in situ* calcification of the mat. The sulfurisation and *in situ* calcification, on the other hand, attest to the activity of sulfur reducing bacteria (chemoorganotrophic organisms whose carbon source is organic matter itself). Thus, the environment of formation and the physical and mineralogical characteristics of the mat indicate a probable photosynthetic origin, as does its isotopic signature. This particular mat was exquisitely preserved by very early silicification, like the many other mats described from other rock formations in the Barberton Greenstone Belt of South Africa (Walsh 1992, 2004; Tice and Lowe 2004). The lithified expression of photosynthetic microbial mats often results in macroscopic-scale tabular and domical or columnar features called stromatolites. The oldest known examples are small, finely layered domical structures formed on a shallow carbonate platform (Allwood et al. 2006, 2009; Hofmann et al. 1999).

Photosynthesis whereby sunlight is used as an energy source is a relatively sophisticated metabolism that is believed to have developed after chemotrophy (use of organic or inorganic sources of energy).

The general equation for photosynthesis is:

$$2nCO_2 + 2nDH_2 + \text{photons} \rightarrow 2(CH_2O)_n + 2nDO$$

$$\{\text{Carbon dioxide} + \text{electron donor} + \text{light energy} \rightarrow \text{carbohydrate} + \text{oxidized electron donor}\}$$

In anoxygenic photosynthesis chemical compounds, *e.g.* H_2, serve as electron donor and become oxidised, here to H_2O.

In oxygenic photosynthesis water is the electron donor and, since its hydrolysis releases oxygen, the equation for this process is:

$$2nCO_2 + 4nH_2O + \text{photons} \rightarrow 2(CH_2O)_n + 2nO_2 + 2nH_2O$$

$$\{\text{carbon dioxide} + \text{water} + \text{light energy} \rightarrow \text{carbohydrate} + \text{oxygen} + \text{water}\}$$

It is widely believed that anoxygenic photosynthesis preceded the more complicated, two-step oxygenic photosynthesis, which produces far more energy than the former. The fossil record shows that by 3.46 Ga there are several lines of evidence for photosynthesis but was it anoxygenic or oxygenic photosynthesis? The contextual geochemical data suggest that the environment in which the mats formed was probably anoxic (Westall et al. 2011a, 2011b). Oxygenic photosynthesis had to have arisen by some kind of mutation at the level of individual microbial mats and it is generally believed that it appeared only once and then rapidly spread elsewhere (Olson 2006). Olson (2006) suggests a possible transition from use of strong reductants, such as H_2 or H_2S, for anoxygenic photosynthesis to an intermediate reductant, such as ferrous iron used by proteobacteria and protocyanobacteria, before the full scale ability to oxidize H_2O was developed by the newly evolved cyanobacteria. There is still uncertainty about the earliest evidence for oxygenic photosynthesis but it must have appeared well before the measurable rise of oxygen in the atmosphere, dated at about 2.4 Ga. Large stromatolites from the 2.8–2.6 Ga time frame are found in Canada (Steeprock formation, 2.8 Ga), South Africa (Transvaal Group, ~2.6 Ga) and Australia (Fortescue Group, 2.7 Ga). There are other occurrences of photosynthetic microbial mats and stromatolites from the intervening time period, for example from the 3.2 Ga-old Moodies Group (Noffke et al. 2006) or the 2.9 Ga Pongola stromatolites, both in South Africa (Beukes and Lowe 1989), for which the respective authors suggest an oxygenic nature but this is by no means certain.

The above descriptions record the evidence for early microbial life that is directly surface-related. There have been recent descriptions of rare enigmatic microbial structures from rocks dating between 3.4 and 3.0 Ga that are significantly larger (by one to two or more orders of magnitude) than the small chemotrophs and photosynthetic filaments of the 3.5–3.3 Ga described above (Fig. 5) (Javaux et al. 2010; Sugitani et al. 2009). The nature and origin of these structures is not yet fully understood. Their large size suggests that they may be planktonic.

It is clear that these oldest traces of life record an evolutionary stage that is far beyond the origin of life or even very primitive cells. It may be difficult to find evidence of such earlier, intermediate life forms due to the lack of older, well-preserved rocks. The oldest rocks known represent a crustal sequence possibly dating back to >4.2 Ga (O'Neil et al. 2012) and occur in Canada. However, they and other rocks older than 3.5 Ga are so severely metamorphosed that any potential prior trace of life has been completely eliminated.

Thus, the most important stage in the history of life on Earth is missing. One can hope that, if life ever existed on Mars, rocks containing traces of life's earliest steps there will be discovered.

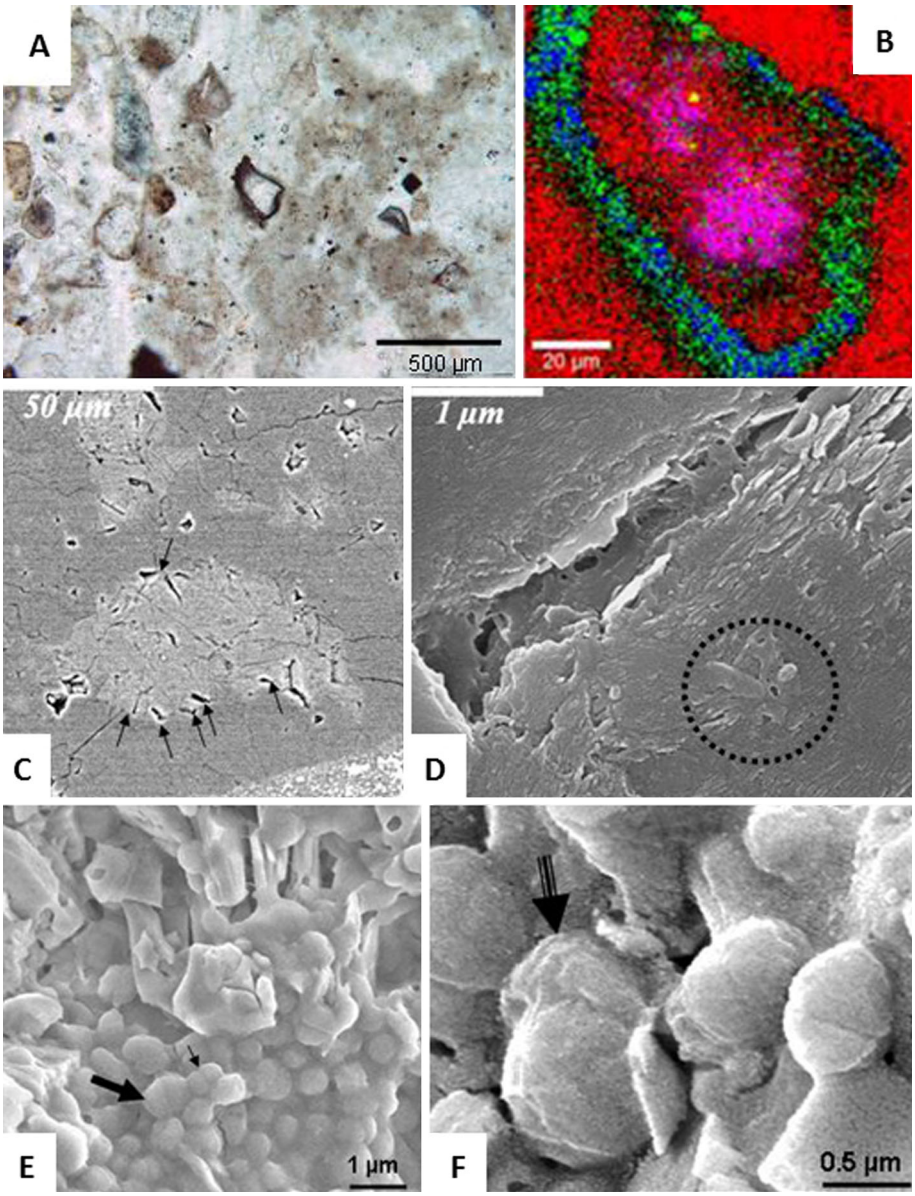


Fig. 4 Traces of chemolithotrophic life forms from the Early Archaean (3.45 Ga) Kitty's Gap Chert, Pilbara, N.W. Australia. (**A**) Thin section micrograph of a volcanic sediment showing the volcanic clasts. (**B**) Raman map of the clast in the center of (**A**) showing the presence of carbon (*blue*) around its edge. The other colours represent the quartz cement and replacement (*red*), anatase (*green*) alteration of the volcanic particle, muscovite (*pink*) replacement of the volcanic grain (originally smectite). (**C**) Scanning electron microscope (SEM) view of a thin section surface in backscatter mode showing a volcanic clast (*light grey*) characterised by tunnels in its surface (*arrows*). *Mid-grey* colour represents the quartz cement. (**D**) SEM view of one of the tunnels showing a mucus-like infilling. The *circle* represents carbonaceous matter in the phyllosilicate-altered volcanic particle. (**E**) SEM view of a silicified colony of coccoidal microorganisms attached to the surface of a volcanic particle. The *arrows* represent two species of different sizes (0.8 and 0.4 µm). (**F**) Close up details of the silicified coccoidal microorganisms. Figure adapted from Westall et al. (2011a, 2011b)

3 What Was the Prebiotic Soup?

3.1 The Earth Early Atmosphere

It is widely believed that life began on Earth sometime between the time that the Earth's surface cooled enough to support liquid water ~4.3 Ga, and the time which generally agreed-upon microfossils appear in the geological record ~3.5 Ga, as discussed in the previous section. It is further generally agreed that the first organisms were likely composed of and self-assembled from environmentally supplied organic compounds (Cleaves and Lazcano 2009; Miller and Orgel 1974). The source and nature of these organic precursors is a central issue in the effort to understand the origin of life on Earth (Des Marais et al. 2003). Besides extraterrestrial sources for these organic compounds, which will be described below, two important terrestrial sources merit discussion: atmospheric and deep geochemical syntheses.

The current atmosphere is composed of ~78 % N_2, ~21 % O_2, ~1 % Ar and the remainder trace gases such as CO_2, CH_4 and H_2O. It is generally agreed that the source of contemporary atmospheric O_2 is biological photosynthesis, and thus that the prebiological atmosphere would have contained relatively little free O_2 (Zahnle et al. 2010). Besides this, little else can conclusively be said about the prebiotic atmosphere. For example, while it is generally considered that the inventory of atmospheric N_2 has remained constant due to N_2's chemical inertness, there is now some speculation that the abundance of atmospheric N_2 may have changed significantly over time (Goldblatt et al. 2009).

Of crucial importance with respect to atmospheric abiotic organic synthesis are the abundances and oxidation states of C containing gases, the most important being CO_2, CO and CH_4 (Zahnle et al. 2010), and for deep geochemical synthesis, the oxidation state of the upper mantle and the abundance of C species in such reservoirs. These considerations would have been largely determined by events occurring during and shortly after the accretion of the Earth.

The Earth is believed to have formed via the accretion of asteroid-like bodies, which released their volatile components during the growth of the planet (Marty 2012). As this process continued, a primitive carbon cycle likely began, in which gaseous, dissolved and solid carbon species were cycled between various reservoirs, including the atmosphere and oceans, and the nascent crust, mantle and core (Dasgupta 2013). Iron and nickel are of central importance in this discussion, being abundant non-volatile pre-solar elements in the materials from which the Earth is thought to have formed. Since Ni and Fe can easily change their redox state, they likely governed the oxidation state of carbon in the upper mantle and in the gases entering the atmosphere from it (Kasting et al. 1993). Equilibration of carbon with chondritic materials may have produced a relatively reducing primordial atmosphere (Schaefer and Fegley 2010), however, there is evidence that the upper mantle was at or near the present redox state very early in the Earth's history (Trail et al. 2011), which would have led to a relatively non-reducing primitive atmosphere, except perhaps in localized environments (Johnson et al. 2008). More recently, reinterpretation of Trail et al.'s (2011) data suggests that the early crust and upper mantle may indeed have been more reducing than previously believed (Yang et al. 2014). The actual redox states of the early Earth upper mantle and crust, and resulting outgassed atmosphere are therefore not sufficiently constrained to reach a final conclusion about its composition.

The importance of a reducing atmosphere is that the action of various energy sources on reduced C gas mixtures, including CO and CH_4, results in the formation of a variety of more complex organic compounds, whereas using CO_2 this chemistry is less productive (Miller

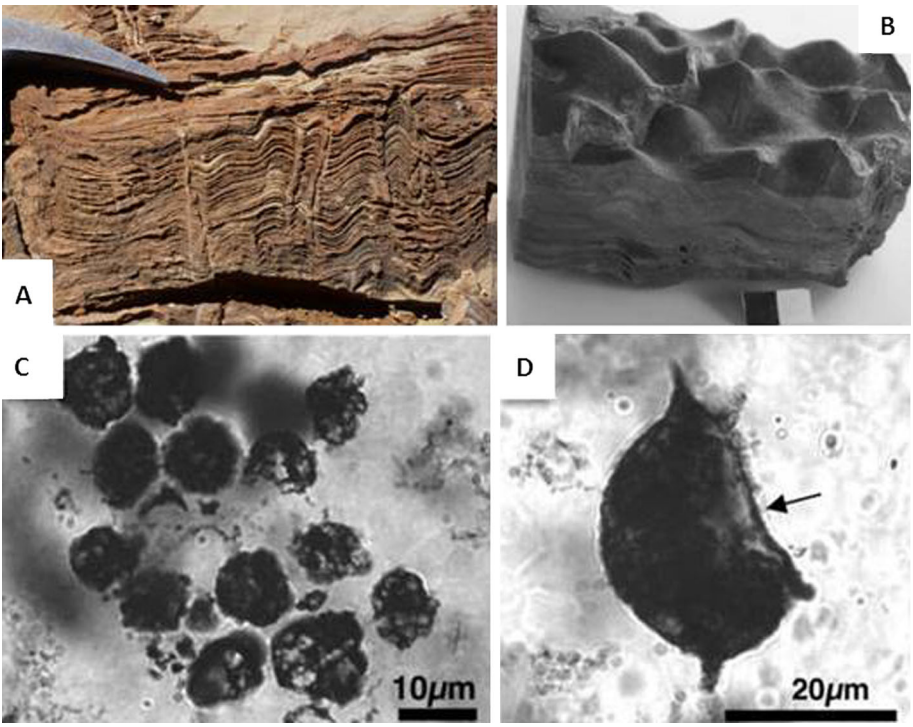


Fig. 5 Larger, more complex fossils from the Early Archaean Strelley PoolChert, Pilbara, N.W. Australia. (**A**) Outcrop showing vertical section through small stromatolites photographed in the field (F. Westall). (**B**) Hand specimen of "egg carton" stromatolites (figure from Allwood et al. 2009). (**C**, **D**) Larger carbonaceous microfossils (possibly planktonic?) embedded in chert (figure from Sugitani et al. 2010)

and Schlesinger 1984; Schlesinger and Miller 1983a, 1983b). In the presence of nitrogen, in the form of N_2 or NH_3, important biological compounds including amino acids, purines and pyrimidines can be formed (Cleaves and Lazcano 2009).

More recently, it has been demonstrated that organic aerosols can be produced in atmospheres composed predominantly of CO_2 with minor admixtures of CH_4 (DeWitt et al. 2009), and that these aerosols may liberate prebiotic compounds directly upon hydrolysis (Trainer 2012), potentially easing the requirement for reducing conditions to produce abundant atmospheric organic synthesis.

3.1.1 The Miller/Urey Experiment

In 1953, the results of the now classic Miller-Urey experiment were published (Miller 1953), showing that organic compounds among which several amino acids can be produced from the action of an electric discharge acting on a reduced gas mixture composed of H_2, CH_4, NH_3 and H_2O. The experiment was designed to mimic the primitive Earth's geochemical cycling (Fig. 6). A gas reservoir approximating the primitive atmosphere was placed in contact with an aqueous reservoir simulating the primitive oceans, and the two were coupled via heating, evaporation and condensation representing the hydrologic cycle. An electric arc, simulating lightning, was discharged into the gas-water vapor mixture.

Besides the various unknowns regarding the actual composition of the primitive atmosphere, discussed in the section above, the experiment's simulation of the Earth system was simplistic with regard to the time scales of entry and removal of species from the various reservoirs, which were highly accelerated relative to natural rates, and the energy flux, which was highly simplified and intensified.

The question of the flux of products from the primitive atmosphere is especially significant. At low fluxes, compounds such as HCN may hydrolyze to less complex species faster than they undergo reactions that produce biologically interesting molecules (Miyakawa et al. 2002a, 2002b, 2002c), with the specific rates depending on aqueous temperature and pH conditions. Thus, terrestrial surface conditions may also have been important factors when considering the efficiency of atmospherically-mediated organic synthesis on the primitive Earth. The pH of primitive surface waters (*e.g.* Kempe and Degens 1985), their ammonia content, the abundance of sub-aerial landmasses, which might allow for evaporative concentration, and the nature and flux of energy sources (*e.g.* γ rays, radioactive decay, electric discharges and UV light) (Miller and Orgel 1974) are important variables which remain poorly constrained.

3.1.2 Variations of the Miller/Urey Experiment with Respect to the Initial Redox State of the Early Atmosphere

Since Miller's initial publication, many laboratories have replicated and extended his results, exploring variations on the synthesis using other types of apparatus designs, gas mixtures and energy sources (Groth and Weyssenhoff 1957; Menor-Salvan et al. 2009; Miller 1957a, 1957b; Miyakawa et al. 2002a, 2002b, 2002c; Parker et al. 2010, 2011; Ring et al. 1972; Schlesinger and Miller 1983a, 1983b), demonstrating the synthesis of a much wider variety of organic compounds. There is a consensus of the types of products obtained using similar gases, though there are important differences in the C and energy yields of various intermediate species such as HCHO and HCN (Miller and Schlesinger 1984) depending on the energy source and gas mixture used (Heinrich et al. 2007), factors independent of surface conditions.

Urey postulated that Earth's primordial atmosphere was highly reducing based on the preponderance of hydrogen in the universe and solar system (Urey 1952), though the idea of a primitive terrestrial, highly reducing atmosphere had already been contested by that time (Rubey 1951). A primordial reducing atmosphere subsequently fell out of favor for a variety of reasons, including the perceived need for greenhouse warming, possibly provided by a high CO_2 pressure in the atmosphere, to compensate for a presumably less luminous young sun (Sagan and Chyba 1997). More recently, the idea of a highly reducing atmosphere has been resurrected based on reduced hydrogen escape rates (Tian et al. 2005), and it has been postulated that, even if a reducing atmosphere were not long-lived, such an atmosphere could have occurred transiently and repeatedly in Earth's early history (Zahnle et al. 2010). There is evidence that even non-reducing atmospheres can produce organics, albeit in lower yield and providing specific conditions (pH buffering, availability of oxidation inhibitors, etc.) (Cleaves et al. 2008; Plankensteiner et al. 2004; Schlesinger and Miller 1983a, 1983b). In any event, it is generally conceded that very similar compounds can be derived from the infall of extraterrestrial materials (Chyba and Sagan 1992; Wolman et al. 1972) (see below).

Hence, for about a decade, it has been shown that the argument that a reducing atmosphere was required to produce organic compounds may not be strictly true, and various oxidation state atmospheres could have provided similar types of organic molecules, albeit in yields varying over many orders of magnitude. The global yield of organic compounds

may not have been limiting, rather the ability of small amounts of organic molecules to be concentrated in localized environments may have been crucial. In this case, the extent of subaerial landmasses and seasonal and daily temperature fluctuations may have been more important (Lathe 2004). However, both models and evidence from rocks dating back to the Archaean epoch indicate that, until about 2.5 Ga ago, much of the Earth's crust, including the continental crust was submerged and that perhaps only 2–3 % of the crust was above water (Flament et al. 2008).

3.2 Black/White Smokers Syntheses

Currently large amounts of energy are commercially extracted from the Earth in the form of various hydrocarbons (*e.g.* coal, petroleum and natural gas). Despite some claims to the contrary (Gold 1992; Kenney et al. 2002), there is little doubt that the majority of this material is derived from biological sources. However there is evidence that some abiotic production of simple hydrocarbons does occur in submarine hydrothermal systems (Proskurowski et al. 2008) and other deep Earth environments (Lollar et al. 2002). The degree to which such synthesis could have competed in quantity and quality with atmospheric organic synthesis and extraterrestrial input on global and local scales on the primitive Earth is open to debate.

Debate regarding the oxidation state of the primitive atmosphere (Rubey 1951) originally raised doubt about the fecundity of abiotic atmospheric organic synthesis. Before widespread recognition of the potential importance of extraterrestrial input, the transference of the heterotrophic hypothesis to a dependence on geochemical synthesis occurred by a roundabout pathway. Deep-sea habitats that appeared to be dependent on geochemical energy and carbon sources were discovered using robotic submersibles (Corliss et al. 1981). The tree of life was also redrawn using rRNA sequence data to delineate the Archaeal domain (Woese and Fox 1977), which includes several hyperthermophilic species that cluster near the root of the universal tree of life built on 16S ribosomal RNA (Di Giulio 2001). It should be noted, however, that it remains unknown whether such hyperthermophilic microorganisms are representative of the first organisms or even the Last Universal Common Ancestor (LUCA) of all extant life, or merely survivors of some bottleneck event in evolution (Arrhenius et al. 1999). Moreover, recent work suggests that if the ancestor of all existing bacteria and archaea was living at high temperature, it also suggests, surprisingly, that LUCA (*i.e.* the ancestor of bacteria, archea *and* eucarya), lived at a moderate temperature (Groussin and Gouy 2011). Even if these notions do not require reassessment of the importance of atmospheric organic synthesis, the idea of geothermal organic synthesis merits consideration in its own right.

There are a variety of deep rocky planetary environments in which organic synthesis could occur. Besides deep, relatively dry environments, which will not be considered here, but are interesting in their own right (*e.g.* Steele et al. 2012), presently two main types of submarine hydrothermal systems are recognized: those that are near the central axis of seafloor spreading centers, characterized by high-temperature acidic fluids with high fluxes, and those that occur off-axis, typically associated with slower, diffuse flow, reduced effluent and lower temperatures (Schrenk et al. 2013). However, it must be noted that plate tectonics, as we know them today, probably did not exist on the early Earth and there is considerable debate as to when and how such tectonic cycling began. Condie and Kröner (2008) suggest that the phenomenon was not widespread until after 3 Ga, but may have occurred earlier episodically (Moyen and van Hunen 2012).

The prevalence of biology in hydrothermal environments, as well as the introduction of ubiquitous biologically-derived materials from sediments, often makes it difficult to determine the abiogenicity of the organic compounds detected in them (Bassez et al. 2009).

Paired isotopic systematics have been used to infer the abiotic origin of some organic materials in hydrothermal environments, and it is now generally accepted that simple abiogenic hydrocarbons are present and likely generated in such environments (Sephton and Hazen 2013). Whether more complex organics are endogenously produced remains an open question, and whether early Earth hydrothermal systems allowed for complex abiotic synthesis yet another. The abundance of nitrogen species in such systems, which would be important for the generation of bioorganic compounds such as amino acids and nucleobases, may be more problematic (Aubrey et al. 2009; Li et al. 2012).

Though assessment of complex organic synthesis in natural deep Earth environments is complicated, many research groups have expended a good deal of effort on modeling them under more controlled conditions in the laboratory. To date, a large number of compounds including amino acids, peptides, fatty acids and even sugars have been produced under conditions that are arguably similar to natural ones with respect to speciation (Aubrey et al. 2009; Imai et al. 1999; Kopetzki and Antonietti 2011; McCollom et al. 1999). Laboratory simulations modeling more realistic conditions typically produce products more reminiscent of natural systems, namely, methane, CO and some light hydrocarbons (Seewald et al. 2006). Whether C and N cycling through such hydrothermal environments prior to the origin of life was significantly different than at the present time remains an open question.

3.3 Exogenous Sources

The origin of life on Earth is widely thought to have required the presence of water and organic compounds. In addition to the endogenous abiotic formation of these compounds discussed in the previous section, exogenously delivered organic matter could also have contributed to the early Earth's inventory, providing the first building blocks of life. The primitive Earth was almost certainly bombarded by comets, asteroids and their fragments (*i.e.* meteorites and interplanetary dust particles (IDPs)). Even though the intensity of this bombardment as a function of time is still debated, it is likely that the Earth collected a significant amount of extraterrestrial material between 4.55 to 3.8 billion years ago (Chyba and Sagan 1992), the period which is thought to be predating the appearance of the first living organism on Earth.

More than a century ago comets were proposed to have delivered organic molecules to the early Earth (Chamberlin and Chamberlin 1908), and indeed several organic compounds have been detected in comets (Bockelée-Morvan et al. 2004; Mumma and Charnley 2011), or are expected to be present (Cottin et al. 1999). Among these, several amino acid precursors have been detected, including ammonia, HCN, formaldehyde, cyanoacetylene, and a very limited number of carbonyl compounds (Crovisier et al. 2009). Analyses of the dust from the coma of the Wild-2 comet showed the presence of glycine (Elsila et al. 2009), and a series of shock experiments of aqueous amino acid solutions demonstrated that a large fraction of amino acids could survive the impact, showing the feasibility of the delivery of organic compounds to the Earth via comets (Blank et al. 2001). Furthermore, *ab initio* molecular dynamics simulations indicated that the impact-shock of analogue comet ice mixtures might produce complex organic molecules (Goldman et al. 2010; Pierazzo and Chyba 2006). In fact, laboratory experiments showed that the hypervelocity impact-shock of ice mixtures analogous to those found in a comet produced several amino acids (Martins et al. 2013). In addition, shock experiments simulating comet impacts show that glycine oligomerization up to trimers could be achieved, and that linear peptides were preferentially synthesized relative to cyclic peptides (Sugahara and Mimura 2014).

Micrometeorites (MMs) and IDPs are extra-terrestrial dust particles that may have brought organic molecules intact to the Earth. The current terrestrial mass accretion rate

through MMs and IPDs is $(\sim 40 \pm 20) \times 10^6$ kilograms per year (Love and Brownlee 1993; Brownlee 1985). MMs typically range in diameter from 50 to 500 μm, and some of them contain organic carbon (Love and Brownlee 1993; Maurette et al. 2000), while IDPs range in diameter from 5 to 40 μm and are ∼10 % organic carbon by mass (Brownlee 1985; Messenger 2002; Sandford 1987; Schramm et al. 1989). Molecules such as ketones, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and their alkylated derivatives have been detected, and amino acids were tentatively identified or identified at very low abundances in MMs and IDPs (Brinton et al. 1998; Clemett et al. 1993, 1998; Flynn et al. 2003, 2004; Glavin et al. 2004; Keller et al. 2004; Matrajt et al. 2004, 2005). Recently, a new family of extraterrestrial particles with an origin from the cold regions of the protoplanetary disk has been recovered from the snow of Antarctica (Duprat et al. 2010). These ultracarbonaceous Antarctic micrometeorites (UCAMMs) contain 50 to 80 % of carbonaceous material, and this high organic matter content has no equivalent in other available extraterrestrial material (Duprat et al. 2010). UCAMMs are unusually enriched in nitrogenated and deuterated organic matter compared to the classical insoluble organic matter (IOM) found in carbonaceous (micro)-meteorites and IDPs, and they are characterized by nitrogen concentration with bulk atomic N/C ratios of 0.05 to 0.12 (locally exceeding 0.15) (Dartois et al. 2013).

Meteorites can be divided into iron, stony-iron, and stony types, and further divided into classes according to their chemical, mineralogical, and isotopic composition (McSween 1999; Weisberg et al. 2006). Carbonaceous chondrites are a very primitive class of stony meteorites, with a high carbon content of up to up to 3 weight% organic carbon (Alexander et al. 2013; Botta and Bada 2002; Sephton 2002). More than 70 % of this carbon is in the form of insoluble organic matter (IOM), a solvent-insoluble macromolecular material consisting mainly of aromatic hydrocarbons (Cody et al. 2002; Cody and Alexander 2005; Gardinier et al. 2000; Pendleton and Allamandola 2002). Less than 30 % of the total organic content is a mixture of soluble organic molecules, including organic compounds that are important in terrestrial biochemistry. These include amino acids, carboxylic acids, nucleobases, polyols, diamino acids, dicarboxylic acids, sulfonic acids, hydrocarbons, alcohols, amines and amides, aldehydes and ketones (for reviews see Cronin and Chang 1993; Martins and Sephton 2009; Pizzarello et al. 2006; Sephton 2002; Sephton and Botta 2005). The soluble organic content of the Murchison meteorite has been extensively analysed, thus serving as a reference for the analysis of soluble organic compounds in other carbonaceous chondrites (Table 1).

Chirality is a useful tool for determining the origin of the organic molecules present in meteorites. Chiral molecules exist as the mirror image of each other (called enantiomers) but cannot be superimposable. For example, amino acids may exist as left-handed (L-amino acids) or right-handed (D-amino acids). On Earth most living organisms use only the L-enantiomer of chiral amino acids. Carbonaceous meteorites contain more than 80 different amino acids with racemic mixtures (D/L = 1) for most of them (for reviews see Cronin and Chang 1993; Martins and Sephton 2009). However, L-enantiomeric excesses (Lee) have been detected for some non-protein amino acids, such as α-methyl-α-amino acids, which have Lee of up to 18.5 % in Murchison, 6.0 % in Murray and 15.3 % in Orgueil (Glavin and Dworkin 2009; Pizzarello et al. 2003). Possible reasons for this excess include UV circularly polarized light (UV-CPL) in the presolar cloud (Bailey et al. 1998; Bonner and Rubenstein 1987; Lucas et al. 2005), a mechanism supported by laboratory simulations (de Marcellus et al. 2011; Modica et al. 2014), and/or solid-solution phase behaviour leading to the formation of conglomerate enantiopure solids during crystallization (Glavin et al. 2012).

Compound-specific stable isotope measurements of hydrogen (D/H), carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) are a useful way to determine the abiological origin of organic

Table 1 Abundances (in part-per-million) of the soluble organic matter found in the Murchison meteorite[1]

Compounds	Abundance (ppm)
Carboxylic acids (monocarboxylic)	332
Sulphonic acids	67
Amino acids	60
Dicarboximides	> 50
Dicarboxylic acids	> 30
Urea	25
Polyols	24
Ammonia	19
Ketones	17
Hydrocarbons (aromatic)	15–28
Hydroxycarboxylic acids	15
Hydrocarbons (aliphatic)	12–35
Alcohols	11
Aldehydes	11
Amines	8
Pyridine carboxylic acid	> 7
Phosphonic acid	1.5
Purines	1.2
Diamino acids	0.4
Benzothiophenes	0.3
Pyrimidines	0.06
Basic N-heterocycles	0.05–0.5

[1] Abundances taken from references (Cooper et al. 1997, 1992, 2001; Cooper and Cronin 1995; Cronin et al. 1988; Hayatsu et al. 1975; Jungclaus et al. 1976a, 1976b; Kvenvold et al. 1970; Lawless et al. 1974; Lawless and Yuen 1979; Meierhenrich et al. 2004; Pering 1971; Pizzarello et al. 1994, 2001; Shimoyama and Katsumata 2001; Stoks and Schwartz 1979, 1981, 1982; Yuen et al. 1984)

molecules present in meteorites. The soluble organic molecules indigenous to meteorites have δD, δ^{13}C and δ^{15}N values distinct from those of terrestrial organic matter (Martins et al. 2008; Sephton and Botta 2005). Terrestrial organic matter has typical values for δD smaller than -30 ‰, δ^{13}C ranging from -5 ‰ to smaller than -30 ‰, and δ^{15}N ranging from -5 ‰ to $+20$ ‰ (Fogel and Cifuentes 1993). The highly enriched δD, δ^{13}C and δ^{15}N values determined for the organic molecules present in meteorites indicate primitive extra-terrestrial organic matter (Kvenvold et al. 1970). The deuterium and ^{15}N enrichment of meteoritic organic matter is thought to be the result of interstellar chemical reactions (*e.g.* gas-phase ion–molecule reactions and reactions on interstellar grain surfaces) occurring at low temperatures in which chemical fractionation is efficient (Aleon and Robert 2004; Millar et al. 1989; Sandford et al. 2001; Terzieva and Herbst 2000; Tielens 1983; Yang and Epstein 1983).

To date, all of the major organic compound classes important in terrestrial biochemistry have been identified as extra-terrestrial components in carbonaceous meteorites, indicating that exogenous delivery of organic compounds may have been important for prebiotic chemistry on the early Earth. Moreover, in addition to highly scrutinized compounds such as amino acids, nucleobases and sugars, bulk analysis using high resolution mass spectrometry of the soluble fraction of the Murchison meteorite has revealed tens of thousands of different molecular formulae, likely representing millions of organic structures (Schmitt-Kopplin et al. 2010). Therefore comets, MMs, IDPs and meteorites may have provided a wealth of building blocks for life just before the first living organism appeared on our planet.

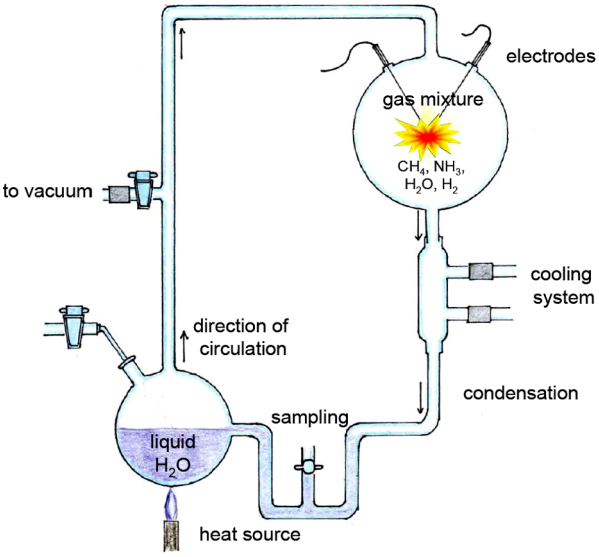


Fig. 6 The Miller/Urey experiment was built to simulate in the laboratory the chemistry in a putative primitive Earth environment, coupling a hypothesized primitive Earth atmosphere (*upper right bulb*) and oceans (*lower left bulb*). For the first results published in 1953, an atmosphere made of CH_4, NH_3, H_2O and H_2 was considered. A spark discharge simulated atmospheric lightning

4 How Did Chemistry Turn into Biology?

4.1 Classical Approach

Since the Miller-Urey experiment, prebiotic chemistry has mostly been devoted to the study of the formation of building blocks of life and how these can sequentially be linked to each other. The possibility of abiotic syntheses of organic mixtures containing compounds of interest has been demonstrated provided that generally oxidizing conditions are avoided.

In the "classical" prebiotic approach, three types of organic compounds are seen as prerequisite for chemical evolution leading to the origin of life (Fig. 7). Those "prebiotic" molecules are amino acids (the building blocks of proteins), the components of nucleotides (the building blocks of DNA and RNA) *e.g.* nucleobases (including adenine, guanine, cytosine, uracil and thymine), sugars (including ribose) and phosphate, and amphiphilic compounds with a water-soluble head and a water-insoluble tail (the building blocks of membranes). The chemistry leading to those families of organic compounds has been extensively studied during the second half of the 20th century. Each of these families of organic compounds could have been synthesized on the primitive Earth, via classical organic reactions such as the Strecker synthesis (to make amino acids) (Miller 1957a, 1957b) or Butlerov reactions (to make sugars) (Butlerow 1861; Reid and Orgel 1967; Shapiro 1988). Alternative chemical pathways toward the formation of amino acids in photolyzed ice mixtures have also been recently proposed (Bossa et al. 2010) with circularly polarized light initiating an enantiomeric excess of amino acids (Modica et al. 2014). Various nucleobases synthesis pathways have been established since the 1960s (see for instance: Ferris and Orgel 1966; Menor-Salván and Marín-Yaseli 2013; Miyakawa et al. 2002a, 2002b, 2002c; Oro 1960; Oro and Kimball 1961; Robertson and Miller 1995) (see also Martins 2012 for a review). It has also been shown that a component of the organic residue synthesized by irradiation of interstellar and cometary ice spontaneously organizes into boundary structures (Dworkin et al. 2001).

However, whether those monomers were synthesized on the primitive Earth, or brought in by meteorites and comets, a critical challenge for prebiotic chemistry is to understand

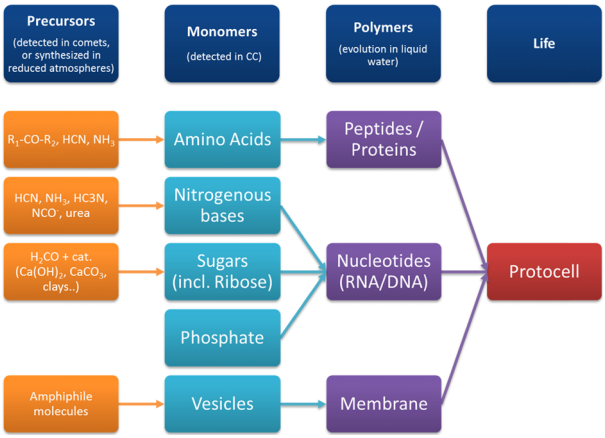


Fig. 7 A classical view of prebiotic chemistry showing the building of a protocell from prebiotic compounds observed in comets, detected in carbonaceous meteorites or produced in reduced or neutral atmospheres. Amino acids are the building blocks of proteins, nucleobases, ribose and phosphate are the building blocks of nucleotides (which are the building blocks of RNA and DNA), and amphiphilic molecules are known to spontaneously self-assemble into vesicles in water (*i.e.* into primitive cell-like structures). This approach has strong limitations in that it fails to propose realistic scenarios for producing polymers from monomers

how monomers can be concentrated and linked under plausible prebiotic conditions. Although some progress has been made using mineral surfaces as templates for adsorbing and oligomerizing activated monomers (Brack and Orgel 1975), the next steps of self-organization towards the emergence of life remain unknown. Jacques Monod and other researchers have considered the formation of a first living organism as a highly improbable contingent event leading to what may be as simple as a single RNA molecule (Monod 1971). But recent breakthroughs and concepts have given a new perspective to investigations in prebiotic chemistry. They are described in the next section of this paper.

4.2 Prebiotic Chemistry New Area

A new approach to studying the origin of life is developing based on the notion of autocatalysis, following the early suggestions by Eigen (1971). This is based on the idea that replication in chemical systems may have preceded autonomous life, *i.e.* the first protocells may have had a degree of autonomy similar to that of present day free-living microorganisms. The idea that replicative systems exhibit a novel and specific form of stability, namely Dynamic Kinetic Stability, has been developed by Addy Pross (Pross 2011, 2012; Pross and Pascal 2013). Stability is understood in this view as persistence in time. However, in contrast to thermodynamic stability, it is not the result of an absence of reactivity. It is, on the contrary, based on the ability of multiplying entities to make more and more of themselves. Chemical evolution and biological evolution may not be separated by an easily defined boundary (Pascal et al. 2013) but rather may constitute a single evolutionary process governed by Dynamic Kinetic Stability (DKS) that encompasses the concept of fitness in biology (Fig. 8). DKS is a new kind of stability specific to entities that are capable of reproducing themselves. It constitutes a driving force that remains unchanged during the transition from the non-living state to life. This new approach is a self-consistent description of the whole self-organization process starting from the development of autocatalysis up to biological evolution without fundamental discontinuity.

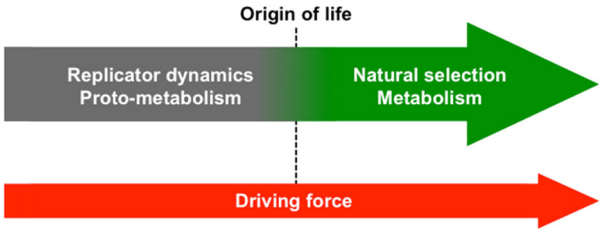


Fig. 8 The origin of life considered as a transition in a single process encompassing chemical replicators and biological species and governed by Dynamic Kinetic Stability (DKS) as a driving force

The self-organization process which gave rise to life can be considered as one aspect of a new scientific field called *Systems Chemistry* in which chemical processes involving a large number of intermediates and reactant steps are studied rather than simply analyzing simple chemical transformations (Kindermann et al. 2005; Ludlow and Otto 2008). Considering potential chemical networks of reactions of this kind leads to the definition of rules governing their existence. Eschenmoser (1994) proposed that they require chemical environments held far from equilibrium by chemical barriers. This idea and the need for an energy flow associated with irreversibility were then analyzed semi-quantitatively (Pascal and Boiteau 2011; Pascal 2012a, 2012b) leading to the identification of a relationship connecting three parameters, temperature, the generation time of the process and the free energy barriers protecting the system. At temperatures over which water is liquid, the need for irreversibility thus leads to the identification of energy sources capable of initiating self-organization, namely photochemistry (UV or visible light), as well as lightning and meteorite and comet impacts. Other forms of energy (chemical gradients in hydrothermal systems for instance) may be useful, though this utility would be limited to driving the formation of organic matter without direct connection with the self-organization process.

Lastly, considering the origin of life in terms of processes rather than molecules means that the formation of biopolymers (such as peptides and nucleic acids) must not be considered as a two-step process (formation of monomers and then polymerization) but studied as an overall system. These views led in the past years to the synthesis of activated nucleotides (Powner et al. 2009) through pathways starting from activated starting materials and avoiding stable building blocks. Recent results support the role of photochemistry of cyanide complexes of copper (I) in the formation of aldehyde precursors (Ritson and Sutherland 2012, 2013). Similar views were proposed in prebiotic peptide chemistry (Danger et al. 2012, 2013). These recent discoveries lead to a new approach to prebiotic chemistry and are promising after a few decades of stagnation. Identification of abiotically produced self-replicating chemical networks is a goal for scientific research in the coming decades. The generation of artificial living systems also requires a molecular basis for inheritance and evolvability (Vasas et al. 2010, 2012). This essential feature of living systems could most probably be brought about by sequence variations in imperfectly replicable polymers.

5 What Are the Limits of Life?

The quest to understand modern life in extreme environments addresses some of humankind's most profound questions. Some of the questions asked in this context are: what are the physical and chemical limits of life as we know it? It was long believed that life can only thrive in a very narrow range of (mesophilic) conditions, and that every environment outside these conditions could not harbor life. This dogma changed in 1969 with the discovery, isolation and cultivation of *Thermus aquaticus* from a hot spring in Yellowstone

Table 2 Some limiting environmental parameters for life

Extreme	Upper/Lower limit	Organism	Environment	Reference
Temperature	Lower limit: −18 °C	*Halorubrum lacusprofundi*	Deep Lake, Antarctica	(Cavicchioli 2006)
	Upper limit: +122 °C	*Methanopyrus kandleri*	Kairei hydrothermal field	(Takai et al. 2001, 2008)
pH	Upper limit: 12.4	*Alkaliphilus transvaalensis*	Mine water, South Africa	(Takai et al. 2001)
	Lower limit: 0	*Picrophilus oshimae*	Hydrothermal field, Hokkaido, Japan	(Schleper et al. 1996)
Salinity	Upper limit: salt saturation	All halophilic archaea	Solar salterns	(Oren 2002)
Pressure	130 Mpa at 2 °C	Isolate MT41	Deep sea amphipods	(Yayanos 1986)
Radiation	approx. 20 kGy	*Kineococcus radiotolerans; A. pyrophilus; I. hospitalis*	Various environments	(Bagwell et al. 2008; Beblo et al. 2011)
Heavy metals	varies with species	Various	*e.g.* River Tinto	(Nies 1999)
Aridity	aw 0.62	*Xeromyces*	Dry surfaces	(Leong et al. 2011)

National Park (Brock and Freeze 1969). Since then, organisms known as "extremophiles" (a term introduced by Macelroy 1974), continue to be isolated from various environments. The limits of life as we know it are therefore continuously pushed toward new boundaries.

5.1 What Are the Limits?

The limiting environmental factors for terrestrial life include but are not limited to the following: temperature, pH, salinity, pressure, radiation, heavy metals and aridity. However, when discussing about the physical and chemical limits of life a careful differentiation between the biological endpoints, survival, metabolic activity and growth/multiplication, has to be made. Table 2 gives an overview of the limits of life for active cellular processes, the environment where these conditions are found, and an example of an inhabitant of this environment. The resistance of specialized dormant forms some organisms can change into is not considered here. It is usually much greater than the resistance of actively metabolizing organisms.

But why are these parameters limiting for life? Some limits may be defined by damage to macromolecules within the cell. For example, high temperature causes thermal damage to molecules such as proteins and nucleic acids (Rothschild and Mancinelli 2001). Many of the limits are also caused by the detrimental influence of physical and chemical extremes on the capacity for cell metabolism, which may itself entail damage to macromolecules. For example, the lower limit for life may be defined by the temperature at which cytosol vitrification occurs, limiting cell activity (Clarke et al. 2013). Ultimately the extremes of life are defined by the conditions under which the organisms can no longer harvest sufficient energy to repair or overcome the detrimental effects of stress and background mutation (Hoehler et al. 2007).

The situation is similar with controlling the intra-cellular pH in organisms that inhabit alkaline or acidic environments. At the lower end of the pH scale, acidophilic organisms

have to tightly control the influx of protons (Baker-Austin and Dopson 2007), whereas alkaliphilic organisms actively pump protons into their cytoplasm to create a neutral pH (Horikoshi 1999). Salinity lowers the activity of water and lowers the solubility of molecular oxygen. In addition to their water activity-reducing property, solutes may act as chaotropes, which weaken electrostatic interactions and destabilize biological macromolecules, or kosmotropes (*e.g.* most compatible solutes), which strengthen electrostatic interactions and stabilize macromolecules (Hallsworth et al. 2007). Therefore, chaotropicity defines also a window for habitabilty (Williams and Hallsworth 2009). Similarly, under hyper-arid conditions there may be too little water available for organisms to meet their minimal metabolic requirements. Pressure challenges life because it forces volume changes. It compresses lipids resulting in decreased membrane fluidity (Rothschild and Mancinelli 2001). Radiation in general causes substantial damage to both DNA and proteins in the cell, both directly and through the generation of reactive oxygen species created from the radiolysis of water in the cell (Daly 2009). Although heavy metals play an important role in life as trace elements, at higher concentrations they form non-specific complexes with toxic effects (Nies 1999) in the cell. The description of the mechanisms by which different organisms cope with these stresses is beyond the scope of this paper, and has been described in great detail elsewhere (*e.g.* de Carvalho and Caramujo 2012; Ohmae et al. 2013; Reed et al. 2013; van Wolferen et al. 2013). By studying the different defense and adaptational mechanisms of organisms in response to their environments, we expand our knowledge about the physical and chemical limits of life, which will enable a target-oriented search for life on other planets.

In many environments on the Earth extremes are not experienced in isolation. Instead, environments usually combine multiple extremes. For example, the deep oceans combine high pressure and low temperature (~4 °C). Organisms that inhabit these extremes are 'polyextremophiles'. Yet, despite the importance of multiple extremes for astrobiology, little is known about the synergistic effect of multiple extremes on biology (Harrison et al. 2013; Kminek et al. 2010).

Some adaptations are also synergistic. For example, the range of water activity tolerated by some bacteria in habiting sea-ice brines (*Glaciecola* sp.) was reported to expand when these organisms were grown at low temperature (Nichols et al. 1999). The biochemical basis for this is not fully understood. These data suggest that the boundaries for life in some instances can be expanded by the imposition of multiple extremes. However, given that adaptation to extreme conditions requires the expenditure of energy, it might be expected that as multiple environmental conditions become more extreme, in general they would restrict the possible growth of many organisms.

At the current time, the absolute boundary conditions for life cannot be defined. There are gaps in the boundary space of life (for example highly acidic saline environments) (Harrison et al. 2013) that might either be caused by the difficulty in adapting to such conditions, or that might be caused by the lack of sampling of these environments. Two challenges in astrobiology are to determine the energetic and biochemical basis of life's limits and to explore a greater range of natural environments.

5.2 Limits of Life and Astrobiology?

The exploration of new environments and the quest for life elsewhere have inspired humans and driven scientific research over the last few centuries. Other planets have environments that have only a few features in common with the Earth. However, the exploration of extreme environments on Earth may increase our knowledge of the limits of life, and inform the search for extraterrestrial life

Lake Vostok, in Antarctica, is buried under almost 4000 meters of ice and may serve as a model for the hypothetical sub-surface ocean on Europa (Marion et al. 2003; Rothschild and Mancinelli 2001). Recent drilling efforts and subsequent analysis suggest life is present in this environment. Also in Antarctica, the dry valleys are home to some of the toughest fungi known. These fungi are able to withstand extreme desiccation, high UV exposure, extremely low temperatures and a wide range of thermal fluctuations (Javaux 2006; Onofri et al. 2004), extremes likely to occur on other planets. When conditions on the surface of a planet are too extreme for even the hardiest organism, shelter might be found in the deep surface. On Earth subsurface biospheres harbor chemolithotrophic microbes, and analog habitats in which life is protected from harsh surface conditions are probably common on other planets with some geothermal activity (Javaux 2006).

New organisms are constantly discovered, using new methods and strategies to adapt to extreme environments. By expanding our knowledge of the limits of life on Earth, we may be able to inform our search for extraterrestrial life.

Temporal and spatial scales of habitability relevant to microbial ecosystems should also be considered (Westall et al. 2013). These scales differ depending on the situation. For example, relatively large areas and long time scales may be necessary for the origin of life because of the need for stable surface water over periods ranging from perhaps hundreds of thousands to millions of years (over scales of 100 km and more). On the other hand, established life can rapidly colonize environments that are only briefly habitable (stable for only hours or days, and only a few 100 μm in size). Dormant life can survive over longer time scales although the spatial scales would be those of individual colonies. These different habitability scales should inform our understanding of the ability of life to inhabit different environments on other planets and satellites. Last, but not least, it must be stressed that the environments which evolved life can inhabit may be very different from those in which life can originate. The habitability of moons or planets may not only be the consequence of the presence of free energy and liquid water and may be different when considering the origin, the survival or the proliferation of life.

6 Is There Life Beyond Earth?

6.1 Mars?

6.1.1 The Search for Organics and Habitability on Early Mars

Mars is the nearest logical planet on which to search for organic material. Mars experienced a long history of bombardment (Marcus 1968; Werner 2008) by comets, meteorites (an estimated yearly accumulation rate of 5×10^2 to 5×10^5 meteorites greater than 10 g in mass per square kilometre Bland and Smith 2000), and dust particles. The total mass accretion rate by comets, meteorites, and dust particles is estimated between 1.8×10^{-5} and 4×10^{-4} $\mathrm{g\,m^{-2}}$ per year (Flynn and McKay 1990), which corresponds to an annual arrival of organic material at the Martian surface on the order of 10^6 kg (Flynn 1996). Another possible source of organic matter is through production on, or beneath, the Martian surface. Several mechanisms for endogenous production of organic material on early Earth have been suggested, which may have played a role on early Mars as well, such as lightning, coronal discharge, UV radiation, and atmospheric shocks (Chyba et al. 1990).

The first mission searching for organic compounds and life was the Viking mission, which consisted of consisting of two landers equipped with several instruments (Soffen

1977). The gas chromatograph–mass spectrometer analysed four (sub)surface samples from both landing sites, and detected water (0.1–1.0 wt%), carbon dioxide (0.05–0.6 ppm), and some organic molecules, including benzene and toluene. Furthermore, Viking 1 detected traces of chloromethane and Viking 2 detected dichloromethane. However, these chlorohydrocarbons were all considered to be terrestrial contaminants, although they had not been detected at those levels in the blank runs. Therefore, the conclusion was drawn that no organic compounds of Martian origin were detected (Biemann et al. 1976, 1977). This null result strongly influenced the interpretation of the reactivity seen in the Viking biology experiments (Levin and Straat 1977, 1979, 1981). It led to the conclusion that life was not present and, instead, that there was some chemical reactivity in the soil (Biemann 1979; Klein 1977).

Recently, however, a new twist has been added to the story of organic molecules on Mars. The detection of perchlorates in the Martian soil by instruments on the Phoenix lander (Hecht et al. 2009) and the reports of methane in the Martian atmosphere (Formisano et al. 2004; Mumma et al. 2009; Webster et al. 2014) suggest that it may be time to reconsider the presence of organic compounds on the red planet. The earlier Martian atmospheric methane data have been heavily debated (*e.g.* Zahnle et al. 2011). New measurements taken by the Sample Analysis at Mars (SAM) instrument suite onboard the Curiosity rover at the Martian surface (Webster et al. 2013; 2014) indicate a baseline value of 0.07 ppb, which is consistent with the expected source of meteoritic organic material falling onto the surface of Mars (Flynn and McKay 1990) and degrading to release methane (Keppler et al. 2012; Moores and Schuerger 2012; Schuerger et al. 2012), which is then photochemically destroyed with a 300-year lifetime (Wong et al. 2003). An unexpected result, however, is the detection of a 7 ppb methane plume that lasted 60 days (Webster et al. 2014), which has been ruled out to be an instrument artefact. Neither the source nor the sink of this plume have been established as of yet. Still, neither of the methane results observed on the surface by Curiosity is consistent with the comparatively very large amounts observed from Earth (Mumma et al. 2009). Therefore, methane may still not be the best marker in the search for organic compounds on Mars.

Perchlorates on the other hand tell a different tale. Perchlorate itself on the Martian surface is harmless for organic compounds. Its radiolysis products on the other end are strong oxidants on the Martian surface (Quinn et al. 2013). Even if there is an organic residue present on the Martian surface, taking all other surface removal processes into account (ten Kate 2010), perchlorate has another negative side effect. The high-temperature oxidizing properties of perchlorates promote combustion of organic compounds in pyrolytic experiments and may have affected the ability of both Phoenix's organic analysis experiment and the Viking mass spectrometer experiments to detect organic molecules (Navarro-Gonzalez et al. 2010; Quinn et al. 2013; Steininger et al. 2012).

A primary focus of the Curiosity/Mars Science Laboratory (MSL) mission is the detection and identification of organic molecules by means of thermal volatilization, followed by gas chromatography–mass spectrometry—similar to the technique used by the Viking mission. The Sample Analysis at Mars (SAM) instrument suite is dedicated to this analysis (Mahaffy et al. 2012). To enhance organic detectability, some of the samples will be processed with derivatization reagents which will dissolve organic molecules from the soil before pyrolysis, and may separate them from the soil perchlorates (Mahaffy et al. 2012). The first measurements with SAM have provided similar results to those of both the Phoenix and Viking missions. In the first measurements SAM detected an abundance of oxygen in combination with chlorine, which is interpreted as perchlorate (Glavin et al. 2013; Leshin et al. 2013). This detection is comparable to the previous measurements made by

Phoenix (Hecht et al. 2009). Chlorinated hydrocarbons were also detected (Ming et al. 2014), which strongly points towards the presence of organic compounds. At least part of this organic component has been attributed to a leak of the derivatization reagents, *i.e.* terrestrial organics (Glavin et al. 2013) while another fraction should have a Martian origin (Freissinet et al. 2015). The Martian contribution to this organic budget is currently still unknown.

6.1.2 Is Mars Still Habitable?

The ESA Mars Exploration Program has developed multiple strategies to search for evidence of extinct or extant life on Mars and this effort has recently resulted in the definition of future Mars instrument payloads as described in the ExoMars Science Management Plan.[1] Thanks to observations collected by ESA's Mars Express orbiter, as well as NASA's Spirit and Opportunity rovers, the ancient history of Mars has been entirely revised during the last decade (Bibring et al. 2006).

The primary hypotheses driving the current exploration of Mars for habitability and signs of life rely on the notion that the planet was warmer and wetter during the Noachian and early Hesperian Eons when conditions were more favorable for the formation of life (Morris et al. 2010; Poulet et al. 2005).

The present focus on the search for ancient biomarkers and evidence for extinct life contrasts with the search for extant life on Mars that was performed during the NASA Viking Missions (*e.g.*, Klein 1977). Viking biology experiments were designed to identify the presence of extant life in Martian soil and returned results that have never been fully explained (*e.g.* ten Kate 2010; Zent and McKay 1994). However, the results suggest that multiple types of reactive chemicals are present in the Martian surface and indicate that, in general, the surface environment may have low organic biosignature preservation potential (*e.g.* Quinn et al. 2013). This conclusion is supported by the apparent depletion of organic compounds in soils as indicated by Viking (Biemann et al. 1977), Phoenix (Ming et al. 2008), and MSL (Glavin et al. 2013) results.

Results from previous missions suggest that while in general Mars may be classified as a habitable planet (Jakosky et al. 2003; Stoker et al. 2010; Ulrich et al. 2012) and some terrestrial microorganisms have the potential to survive on Mars (de la Vega et al. 2007; de Vera et al. 2010; Nicholson et al. 2013; Schirmack et al. 2013; Wassmann et al. 2012), the surface radiation environment and lack of water may limit the possibility of life to subsurface niches. In these niches, water may be available due to the presence of salts, such as perchlorate, that can form cryobrines (which means water remains a liquid because of the high salt concentration) at temperatures down to 213 K at Mars' ambient pressure, well below the triple point of pure water (Chevrier et al. 2009; Moehlmann and Thomsen 2011). It has also been suggested that the presence of reoccurring slope lineae (dark coloured lines on the surface of slopes which change in step with seasonal and daily cycles) may indicate the presence of large seasonal flows of aqueous brines (McEwen et al. 2011, 2014). Additionally, the presence of interfacial water in the Martian soil formed through capillary forces or a solid greenhouse effect may produce biologically available water (Moehlmann 2011). Other parameters critical to habitability such as the presence of energy sources (*e.g.*, iron and sulfur rich minerals) are generally favorable (Bibring et al. 2006; Fairen et al. 2010; King and McLennan 2010).

[1] Available here: http://exploration.esa.int/jump.cfm?oid=46849.

It is possible that if life originated on Mars in the past when its climate was wetter and more moderate (Morris et al. 2010; Poulet et al. 2005), life might persist in some habitats (Fairen et al. 2010). For instance, it has been suggested that methane in the atmosphere of Mars may be due the presence of biological habitats, although the origin, presence and quantity of methane is highly debated (Mumma et al. 2003; Webster et al. 2013; Zahnle et al. 2011; Webster et al. 2014).

The possible persistence of life on Mars would depend on the capacities of putative Martian organisms to adapt to changing environmental conditions. Terrestrial prokaryotes, relatively simple organisms that might be analogs of the biology to be expected on Mars, show a remarkable evolutionary plasticity and flexibility. Prokaryotic adaptation processes can be very rapid (Wassmann et al. 2010) and facile compared to more complex life forms from the eukaryote domain. Horizontal or lateral gene transfer in prokaryotes (Jain et al. 2002; Koonin et al. 2001), along with their faster reproduction rates, which favor higher recombination and mutation rates might have allowed quick adaptation to the environmental changes that occurred during the transition from the Noachian to the Hesperian (Andrews-Hanna and Lewis 2011). Thus, based on current knowledge regarding of the adaptive capacities of microorganisms that are capable of survival under simulated Martian conditions (de la Vega et al. 2007; de Vera et al. 2010, 2014; Schirmack et al. 2013; Wassmann et al. 2012), the possibility that extant life is present in certain well-defined habitats on Mars cannot be completely excluded (Bauermeister et al. 2014).

A biosphere, possibly including Iron reducing and iron oxidizing bacteria, could thus be hidden in the Martian subsurface which cannot be easily detected from orbit. Most terrestrial microbes are not detectable from orbit around Earth. Therefore improved technologies for *in situ* life detection are needed in the near future.

6.2 Life in Icy Moons of the Outer Solar System?

The numerous satellites of the outer solar system are striking in their diversity and evolution (Schubert et al. 2010). Most of them are covered by an icy surface but some moons may also harbor liquid oceans in their interior as shown in Fig. 9. With respect to exobiology, the most attention has been given to the Galilean moons of Jupiter: Io, Europa, Ganymede and Callisto. Observations by the Galileo spacecraft suggest that oceans exist within the latter three. In the case of Callisto and Ganymede those oceans are probably sandwiched between ~150 km thick ice layers (Spohn and Schubert 2003). Europa has been studied for decades as an intriguing object in the outer solar system because below the ice crust, a large ocean is directly in contact with a rocky mantle (Sotin et al. 2002). In the Saturnian

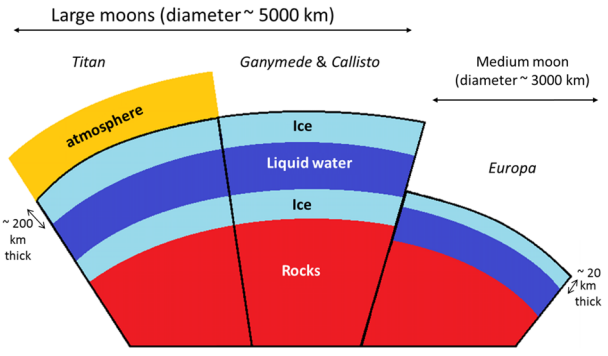


Fig. 9 Schematic view of the internal structure of icy satellites in the outer Solar System: Titan, Ganymede and Callisto, and Europa. Liquid water layers inside the first three moons are deeply embedded between two thick icy mantles, while oceans in Europa could be "only" a few tens of kilometers below the surface, and directly in contact with a rocky mantle

system, Enceladus and Titan are the centers of attention. For Titan, the Cassini/Huygens mission has revealed a very active world with rivers and lakes made of hydrocarbons, dunes, impact craters, mountains and cryo-volcanic flows. Titan stands apart in having a dense atmosphere, a methane cycle (akin to Earth's hydrologic cycle), and a surface inundated and heavily modified by liquid hydrocarbons (Raulin et al. 2012).

Europa, Enceladus, and Titan are central objects in astrobiology research representing modern habitats in the outer solar system with conditions that may favor complex organic chemistry and possible life, since liquid water and organic compounds both occur. The subsurface oceans of Jupiter's moon Europa and Saturn's moon Enceladus are considered by many scientists to have the greatest possibility of harboring life elsewhere in the solar system. Europa's ocean is in direct contact with the moon's rocky seafloor, where interior heat may be released to contribute to organic syntheses similar to mechanisms occurring in terrestrial hydrothermal vents. Based on new observations it has been suggested that material from Europa's liquid ocean bubbles up and reaches the frozen surface (Hand and Brown 2013). Enceladus harbors an ocean below the ice that likewise reaches the surface. Plumes ejecting complex organic compounds into space were observed by the Cassini mission (McKay et al. 2008). The underlying mechanism is known as cryo-volcanism. The identification of salts implies expulsion of liquid water that has interacted with rock. Saturn's moon Titan reveals the presence of liquid hydrocarbon oceans and river deltas, apart from complex organic molecules on the surface and in its dense atmosphere. Models of Titan's evolution and interior dynamics suggest the presence of an ammonia-rich water ocean below the ice crust that could interact with the organic rich surface environment (Tobie et al. 2005). Titan presents the richest known planetary laboratory for studying abiotic organic synthesis in our solar system.

Space missions to Europa confirming the presence of an interior ocean, characterizing the satellite's ice shell, and understanding its geological history have been envisaged through many scenarios but not yet realized. The ESA JUpiter ICy moons Explorer Mission (JUICE) will be launched in 2022 with an arrival at Jupiter in 2030. The spacecraft will spend at least three years making detailed observations of the giant gaseous planet Jupiter and three of its largest moons, Ganymede, Callisto and Europa (Grasset et al. 2013). This mission will be a first step in obtaining a better understanding of the Jovian moons, but will not provide a detailed structural characterization of Europa's subsurface. Europa is important for investigating how far organic chemistry can evolve in extreme environments and key to our understanding of the origin and evolution of water-rich environments in icy satellites. In that context, the recent exploration of subglacial aquatic areas in Antarctica is worth mentioning. Samples from Lake Vostok are currently under investigation by Russian scientists (Siegert et al. 2011; Sinha and Krishnan 2013). In 2012 the WISSARD (Whillans Ice Stream Subglacial Access Research Drilling) project recovered water and sediment samples from the subglacial Lake Whillans that showed clear signs of life (Fricker et al. 2011). Microbial life at −13 °C was recently detected in the ice cover of Lake Vida that encapsulates a cryogenic brine ecosystem (Murray et al. 2012). The outer solar system may harbor unexplored treasures on one of dozens of icy moons, or even inside Kuiper belt objects (Desch et al. 2009).

6.3 Around Other Stars?

In recent years, efforts have been made to detect rocky planets around other stars. These searches for exoplanets have yielded a diversity of candidates, some of which are in the habitable zone (Borucki et al. 2012, 2013), and some are similar to Earth in size (Quintana

et al. 2014). A major focuses for astrobiology in the 21st century will be to investigate them for signs of life.

The two methods by which this will be done are by searching for surface signatures of life in the reflectance spectra and by searching spectral signatures of gases which could be biologically produced within the atmosphere of these planets.

The first method relies on surface-dwelling life having molecules that absorb in regions of the spectrum to yield spectral features not expected from known abiotic materials (Hegde and Kaltenegger 2013; Kiang et al. 2007a, 2007b). A particularly strong candidate is the red edge of chlorophyll, which is a distinctive surface feature of vegetation on planet Earth (Seager et al. 2005; Tinetti et al. 2006) indicating complex life form which were however not present on the early Earth. Other signatures might be detectable depending on the characteristics of organisms on the planetary surface and the chemistry and absorption of their pigments (Kiang et al. 2007a, 2007b). These characteristics might be quite different from those of terrestrial life and, if this extraterrestrial life is photosynthetic, influenced by the spectrum of the host star.

In the case of atmospheric gases, the method relies on identifying gases that are thought to be derivable only from biological processes (Des Marais et al. 2003; Leger et al. 1993; Lovelock 1975; Owen 1980; Raven and Wolstencroft 2004).

Among the promising gases that are signatures of life are the products of oxygenic photosynthesis: oxygen and its photolytic product, ozone (Leger et al. 1993; Raven 2007). Atmospheric ozone produces a strong absorption in the infrared spectrum of light (at 9.6 μm) emitted from a planet. Models show that this has been the case for the Earth since the beginning of the Proterozoic (Kaltenegger et al. 2007). Atmospheric models show that the atmosphere of any planet that contains concentrations of oxygen comparable to the Earth, but subjected to the different radiation outputs of other stars, is likely to contain ozone (Kasting 1997). Thus, ozone is considered a robust biosignature of life on a temperate planet where the abiotic production of O_2 by H_2O and CO_2 photolysis can be excluded. The abiotic production of ozone is thought to be confined to dry planets (Segura et al. 2007; Selsis et al. 2002), which would not be considered to be favourable environments for life, reducing the chances of the false positive detection of life. But it has to be taken into consideration that oxygenic photosynthesis is certainly a process used by quite evolved forms of life, and it emerged on Earth quite late. Then, in the first billions of years of the history of our planet, when life was already present, it would not have been detected by remote sensing technics analyzing the atmospheric composition. So oxygen and ozone could be used as indicators for already developed life.

Other potential biogenic gases are methane (CH_4) and nitrous oxide (N_2O), both of which are within the resolving power of space-based telescopes. Although gases such as CH_4 and N_2O might indicate the presence of life, oxygenic photosynthesis is of special interest because the presence of oxygen in an atmosphere implies the possibility of aerobic respiration which is thought to be a prerequisite for the large-scale biological productivity necessary for the development of multi-cellular complexity and ultimately intelligence (Vermeij 1995).

7 Conclusion

Two additional papers will discuss the two main focuses and conclusions of the topical team. They contain the recommendations for the next programmatic steps in astrobiology research.

The face of astrobiology has been remodeled since the beginning of the new millennium. Theories, technologies, and discoveries have opened a promising window of opportunities for interdisciplinary research activities. The study of the origin and limits of life on Earth are informing the search strategy for life elsewhere in the Solar System and beyond.

However, we should be wary of being overly optimistic about discovering life beyond Earth. Aside from sensational media announcements that could result into weariness and discouragement in the public opinion if not validated, the astrobiology science community should maintain a rational and patient approach. We may find clues in the future of potential extraterrestrial life, but clues are not a proof. The quote popularized by Carl Sagan in the Cosmos TV program in the 1980s "extraordinary claims require extraordinary evidence" must be embroidered into the astrobiology research community's approach. Scientists have still not managed to reach a consensus about a definition of life (see for instance Bersini and Reisse 2007; Gayon et al. 2008), thus a consensus about an announcement regarding the discovery of extraterrestrial life may be similarly difficult.

The words of Alexander Ivanovitch Oparin regarding the study of the origin of life (Oparin 1953) are still relevant and invite us to exercise great caution and realism in our research: "*We are faced with a colossal problem of investigating each separate stage of the evolutionary process as it was sketched here*. (. . .) *The road ahead of us is hard and long but without doubt it leads to the ultimate knowledge of the nature of life. The artificial building or synthesis of living things is a very remote, but not an unattainable goal along this road*". The same can be said about the search for extraterrestrial life.

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