# Chapter 1
# Chemical Biosignatures at the Origins

**André Brack**

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

## 1.1 Introduction

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

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

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## 1.2 Chemical Prerequisites

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

### *1.2.1 Liquid Water*

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

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

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

### 1.2.2 *Organic Molecules*

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

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

#### 1.2.2.1 Production of Organics in the Atmosphere

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

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

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

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

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

#### 1.2.2.2 Submarine Hydrothermal Systems

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

#### 1.2.2.3 Delivery of Extraterrestrial Organic Matter

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

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

The Stardust mission collected samples of Comet Wild 2 and returned them to Earth in January 2006 for laboratory analysis. Unexpectedly, most of the comet's rocky matter formed inside the Solar System at extremely high temperature. The grains contain organic functions (alcohol, ketone, aldehyde carboxylic acids, amides, nitrile). The protein-building amino acid glycine has also been discovered. Cometary grains may therefore appear as an important source of organic molecules delivered to the primitive Earth (Ehrenfreund and Charnley 2000; Despois and Cottin 2005). However, it is unlikely that whole comets could have safely delivered organics to the Earth. They would either have exploded while crossing the atmosphere or when impacting the Earth's surface.

The ESA Rosetta robotic spacecraft performed the most detailed study of a comet ever attempted (Glassmeir et al. 2007). Launched in March 2004, the spacecraft reached Comet 67P/Churyumov–Gerasimenko in August 2014. It consisted of two main elements: the Rosetta space probe orbiter and the Philae robotic lander. The orbiter featured eleven instruments. Among them, ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) measured the deuterium-to-hydrogen ratio of water vapour emanating from the comet and found it to be more than three times greater than for Earth's oceans (Altwegg et al. 2015). The discovery fuels the debate on the origin of Earth's oceans. The instrument also made the first measurement of molecular nitrogen for a comet, providing clues about the temperature of the environment in which the comet formed (Rubin et al. 2015). Moreover, ROSINA detected volatile glycine, accompanied by methylamine and ethylamine, in the coma, confirming the results of the Stardust mission. Together with the detection of phosphorus and a multitude of organic molecules, this result demonstrates that comets could have played a crucial role in the emergence of life on Earth (Altwegg et al. 2016).

The Philae robotic probe landed on Comet 67P/Churyumov–Gerasimenko on 12 November 2014, achieving the first-ever soft landing on a comet nucleus. It hosted nine instruments. Among them, COSAC (Cometary Sampling and Composition experiment) was designed to detect and identify complex organic molecules from their elemental and molecular composition. SD2 (Sample and Distribution Device) was designed to drill more than 20 cm into the surface, collect samples and deliver them to different ovens or for microscope inspection. When the Philae lander successfully touched down on the comet, it unfortunately bounced twice to finally settling in a location and layout preventing the solar panels from charging the batteries. After a year of silence from the craft, the European Space Agency began to power down the systems.

Philae nonetheless provided interesting results for astrobiology. Just after the first comet touchdown, COSAC mass spectrometer took a spectrum in sniffing mode of the ejected material. The spectrum displayed a suite of 16 organic compounds, including methyl isocyanate, acetone, propionaldehyde, and acetamid (Goesmann et al. 2015).

Meteorites—Carbonaceous chondrites also delivered organic materials to the early Earth. They contain between 1.5% and 4% carbon, for the most part as organic materials. One hundred kilograms of the Murchison meteorite, a CM2 type carbonaceous chondrite that fell in Australia in 1969, have been extensively analysed

(Pizzarello 2007; Pizzarello and Shock 2010). Murchison organic materials are generally classified according to their solubility in water and organic solvents. Insoluble and soluble components represent respectively 70% and 30% of the total carbon components. The insoluble organic material is a poorly identified macromolecular material of complex composition with average elemental abundances of $C_{100}H_{46}N_{10}O_{15}S_{4.5}$. NMR, IR and pyrolysis analyses suggest the presence of aromatic ring clusters bridged by aliphatic chains, with peripheral branching and functional groups. The insoluble organic material releases a variety of aromatic and heteroatomic hydrocarbons as well as a suite of alkyl dicarboxylic acids up to C18 chain length under conditions similar to those of hydrothermal vents (Yabuta et al. 2007).

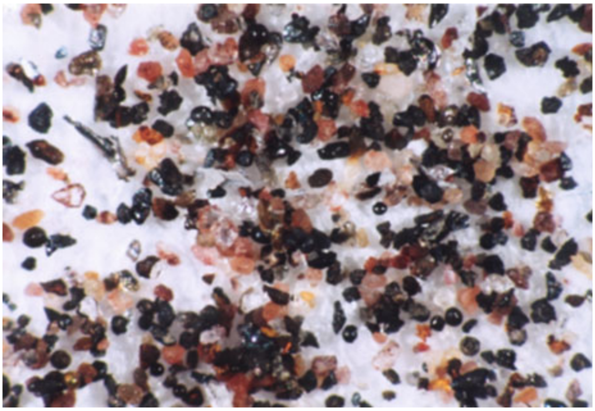
The soluble organic compounds of the Murchison meteorite represent a diverse and abundant group of organics that vary from small water-soluble compounds such as amino acids and polyols up to 30 carbon-long hydrocarbons. This diversity has been analysed in detail for the amino acids. The total number of meteoritic amino acids is about one hundred. All the possible α-amino alkylamino acids up to seven-carbon have been identified as well as large abundances of N-substituted, cyclic, β-, γ-, δ-, and ε-amino acids. Eight protein-building amino acids (glycine, alanine, proline, leucine, isoleucine, valine, aspartic acid and glutamic acid) have been found. Nucleic acid bases, purines and pyrimidines have also been noted in the Murchison meteorite (Stoks and Schwartz 1982; Callahan et al. 2011). No ribose, the sugar moiety linking together nucleic acid building blocks, has been detected in meteorites. Vesicle-forming fatty acids have been extracted from different carbonaceous meteorites (Deamer 1985, 1998).

A combination of high-resolution analytical methods, comprising organic structural spectroscopy FTICR/MS, UPLC-QTOF-MS and NMR, applied to the organic fraction of Murchison extracted under mild conditions allowed chemists to extend its indigenous chemical diversity to tens of thousands of different molecular compositions, and likely millions of diverse structures (Schmitt-Kopplin et al. 2010).

Most of the amino acids detected in the carbonaceous chondrites are chiral but present as racemates, i.e. L- and D-enantiomers are present in equal proportions. However, enantiomeric excesses have been detected, as described in Sect. 1.3.2.1. The discovery of a large number of meteorites since 1969 has provided new opportunities to search for organic compounds in CM type carbonaceous chondrites (Pizzarello et al. 2001; Glavin et al. 2006; Pizzarello and Shock 2010).

Micrometeorite. Micrometeorite collections in the Greenland and Antarctica ice sheet (Fig. 1.1) show that the Earth captures interplanetary dust as micrometeorites at a rate of about 20,000 tonnes per year. About 99% of this mass is carried by micrometeorites in the 50–500 μm size ranges. This value is about 2000 times higher than the most reliable estimate of the meteorite flux (about 10 tonnes per year). The amazing dominance of micrometeorites within impactors already supports their possible role in delivering complex organics to the early Earth between 4.1 to 3.9 Ga ago, when the flux of impacting objects was probably enhanced by several orders of magnitude. Antarctic micrometeorite flux measurements suggest that a huge mass ($\sim 5 \times 10^{24}$ g) of micrometeorites was accreted by the Earth during ~200 Ma of the late heavy bombardment (Maurette 1998, 2006).

**Fig. 1.1** Micrometeorites, 50–100 μm in size, collected in Antarctica ice. Source: Image courtesy of M Maurette



At least about 20 wt.% of the micrometeorites survives unmelted upon atmospheric entry. As their insoluble organic fraction represents about 2.5 wt.% of carbon, this amounts to a total mass of carbon of ~$2.5 \times 10^{22}$ g on the early Earth surface. This is equivalent to a ~30 m thick global layer deposited during ~200 Ma (Maurette and Brack 2006). This delivery represents more carbon than that present in the biomass of the present day Earth ($10^{18}$ g). One amino acid, α-amino isobutyric acid, has been identified in Antarctic micrometeorites (Brinton et al. 1998; Matrajt et al. 2004). These grains also contain a high proportion of metallic sulphides, oxides and clay minerals, a rich variety of inorganic catalysts which could have promoted reactions of the carbonaceous material leading to the origin of life. Analysis of the dust grains collected by the Cosmic Dust mission supports a cometary origin for the micrometeorites collected in Antarctica.

A collection of CONCORDIA Antarctic micrometeorites recovered from ultra-clean snow close to Dome C provided the most unbiased collection of large cosmic dust available. Many similarities can be found between Antarctic micrometeorites and Wild 2 samples, in terms of chemical, mineralogical, and isotopic compositions, and in the structure and composition of their carbonaceous matter (Dobrica et al. 2013). The cometary origin has been confirmed by a zodiacal cloud model based on the orbital properties and lifetimes of comets and asteroids, and constrained by Infrared Astronomical Satellite observations of thermal emission, but is also qualitatively consistent with meteor observations, with spacecraft impact experiments, and with the properties of recovered micrometeorites (Nesvorny et al. 2010).

## 1.3 Chemical Biosignatures

Two different kinds of chemical biosignatures can be considered: an overrepresentation of organics and long strands of homochiral sequences, such as homochiral poly amino acids.

## *1.3.1 Over Representation of Organics*

Any extraterrestrial explorer searching for life on Earth would probably be struck by the overabundance of organics by comparison to the composition of the mantle. Carbon, which constitutes 17.9% of the biomass, accounts for only 0.094% of the mantle. However, the presence of active carbon chemistry alone—or even associated with liquid water—does not necessarily generate life as illustrated by the case of Titan and also by the search for an alien form of life on Earth.

### 1.3.1.1 Titan

The Voyager 1 mission in 1980 first revealed the composition of Titan's atmosphere: 90% molecular nitrogen and about 1–8% methane. Further, a great number of trace constituents were observed in the form of hydrocarbons, nitriles, and oxygen-containing compounds, mostly CO and $CO_2$. Titan is the only other object in our Solar System to bear any resemblance to our own planet in terms of atmospheric pressure (1.5 bar) and carbon/nitrogen chemistry. It represents, therefore, a natural laboratory to study the formation of complex organic molecules on a planetary scale and over geological timescales.

The ISO satellite has detected tiny amounts of water vapour in the higher atmosphere, but Titan's surface temperature (94 K) is much too low to allow the presence of liquid water. Although liquid water is totally absent, the satellite provides a unique milieu to study, in situ, the products of the fundamental physical and chemical interactions driving planetary organic chemistry.

In 2004, the NASA/ESA Cassini-Huygens spacecraft launched in October 1997 arrived in the vicinity of Saturn and performed several flybys of Titan, taking spectroscopic, imaging, radar, and other measurements. On January 14, the European instrumented descent probe penetrated the atmosphere and systematically studied the organic chemistry in Titan's geofluid. For 150 min, in situ measurements provided analyses of the organics present in the air, in the aerosols, and at the surface. The GC-MS of the Huygens probe measured the chemical composition and the isotopic abundances from an altitude of 140 km down to the surface (Niemann et al. 2005; Israël et al. 2005). The main findings were:

1. nitrogen and methane are the main constituents of the atmosphere;
2. the isotopic ratio $^{12}C/^{13}C$ suggests a permanent supply of methane in the atmosphere;
3. the surface is "wetted" by liquid methane and rich in organics (cyanogen, ethane);
4. the presence of $^{40}Ar$ suggests the existence of internal geological activity.

Unfortunately, the Huygens probe had no specific instruments to detect any potential autocatalytic systems leading to non-stochastic chemicals such as homochiral molecules (Brack and Spach 1987).

#### 1.3.1.2 Alien Life on Earth

Life, being basically an autocatalytic chemical system, should be a reproducible process, if the starting conditions are identical. Therefore, the emergence of one or more types of alien terrestrial life, including a mirror-image life, coexisting with known life, should be conceivable (Davies and Lineweaver 2005). So far, no fossils of such a terrestrial alien life have been found. As for the emergence of a modern alien life, the insatiable appetite of bacteria, which have squatted in all habitable terrestrial sites, would probably prevent any de novo origin of life.

### *1.3.2 One-Handedness*

The carbon atom occupies the centre of a tetrahedron and when the four substituents at the four summits are different, the carbon atom becomes one-handed and shows two mirror images, a left-handed form and a right-handed form.

Present terrestrial life uses proteins, which catalyse biochemical reactions, nucleic acids, which carry genetic information, and phospholipids, which form the semi-permeable membranes around cells. Most of the constituents, amino acids, sugars and lipids, contain at least one asymmetric carbon atom. Life is one-handed so only one enantiomer of each chiral biomolecule is present in living systems. For example, each amino acid, with the exception of glycine, exists in two enantiomeric forms, L and D, but proteins use only L forms (Fig. 1.2).

Proteins adopt asymmetrical rigid geometries, α-helices and β-sheets, which play a key role in the catalytic activity. Homochirality is now believed to be not just a consequence of life, but also a prerequisite for life, because stereoregular structures such as protein β-sheets, for example, do not form with mixtures of monomers of both handednesses (Brack and Spach 1981). The use of one-handed biomonomers also sharpens the sequence information of the biopolymers. For a polymer made of $n$ units, the number of sequence combinations will be divided by $2^n$ when the system uses only homochiral monomers. Taking into account the fact that enzyme chains are generally made of hundreds of monomers, the tremendous gain in simplicity offered by the use of monomers restricted to.

Any chemical reaction performed in a symmetrical environment that forms chiral molecules yields a racemic mixture i.e. a mixture of equal quantities of right- and left-handed enantiomers. Theoretical models show that autocatalytic systems fed with both left- and right-handed molecules must become one-handed in order to survive. The problem of the generation of homochirality thus has two parts, the origin of a prevalent enantiomer and its further amplification until the appearance of life. The amplification of enantiomeric excesses of a few percent has been well documented in the laboratory using crystals, crystallization processes or biopolymers. Shibata et al. (1998) have clearly demonstrated that an excess of one enantiomer can be induced by the presence of few per cent of a chiral initiator and this

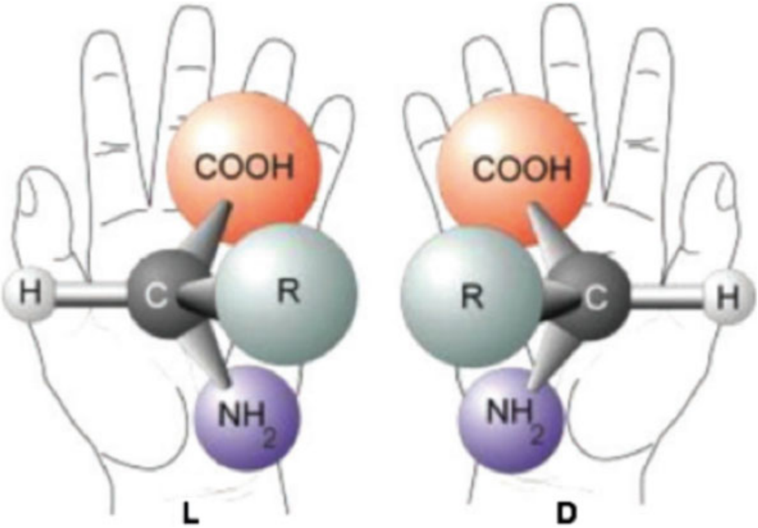


**Fig. 1.2** L-form and D-form, mirror image enantiomers of a generic chiral amino acid. Source: credit ESA

excess can be dramatically amplified by asymmetry autocatalysis. The source of the chiral initiator could be extraterrestrial, as already mentioned.

Theoretical models for the existence of the slightly prevalent enantiomer excess on Earth can be divided into two classes, those which call for a chance mechanism and those which call for a determinate mechanism resulting from an asymmetrical environment.

#### 1.3.2.1 Enantiomeric Excess Via a Chance Mechanism

The proponents of the chance mechanism hypothesis argue that the notion of equimolarity of a racemic mixture is relative, and random fluctuations may favour one enantiomer over the other. For instance, for a population of ten million molecules, which is about the amount of chiral constituents of the smallest living cell, the probability to find an excess of 0.02% or more in one enantiomer, is about 50% (Spach and Brack 1988). In a rather simple kinetic model proposed by Frank (1953), an open flow reactor, running in far from equilibrium conditions, is fed by prochiral compounds and forms two enantiomers reversibly and auto catalytically. If the two enantiomers can react to form an irreversible combination flowing out the reactor (by precipitation, for instance), and if certain conditions of fluxes and concentrations are reached, the racemic production may become metastable and the system switches permanently toward the production of either one or the other enantiomer, depending on a small excess in one enantiomer. The Frank model has inspired a further model described as a theoretical framework, based on the stereo-selective reactivity of pre-existing chiral monomeric building blocks (polymerization, epimerization, and depolymerisation) maintained out of equilibrium by a continuous energy income, *via* an activation reaction. It permits the self-conversion of all monomeric subunits into a single chiral configuration (Plasson et al. 2004). A model featuring enantiomer cross-inhibition and chiral bias has been used to study the diffusion equations controlling the spatiotemporal development of left- and right-handed domains in the context of autocatalytic polymerization reaction networks (Gleiser 2007). A fully self-contained model of homochirality has been proposed that contains the effects of both polymerization and dissociation (Brandenburg et al. 2005).

Spontaneous resolution on crystallization represents the most effective means of chiral symmetry breaking by chance mechanism. Kondepudi et al. (1990) demonstrated a total spontaneous resolution by crystallization. Sodium chlorate crystals are optically active although the molecules of the compound are not chiral. When crystallized from an aqueous solution while the solution is not stirred, statistically equal numbers of L and D crystals were found. When the solution was stirred, almost all the $NaClO_4$ crystals (99.7%) in a given sample had the same chirality, either L or D. Quartz, known as an asymmetric adsorbent and a catalyst, may have undergone such a spontaneous resolution during crystallization when it cooled down on the primitive Earth. Close examination of over 2700 natural quartz crystals gave 49.83% L and 50.17% D, i.e. an almost even distribution. Beautiful enantio-separations have been obtained by the Lahav and colleagues with crystals, crystallites and crystalline self-assemblies at the water surface (Weissbuch et al. 1988, 1997; Zepik et al. 2002; Rubinstein et al. 2005).

Enantio-enrichment of a variety of amino acids has also been obtained by sublimation of near-racemic samples (Fletcher et al. 2007; Perry et al. 2007; Tarasevych et al. 2013, 2015).

#### 1.3.2.2 Determinate Mechanisms

In terms of determinate mechanisms, parity non-conservation has raised many hopes and caused many disappointments. There is an extremely small parity-violating energy difference in favour of L-amino acids in water and in favour of D-sugars (Nordén et al. 1985). The energy difference is about $3 \times 10^{-19}$ eV corresponding to one part in $10^{-17}$ for the excess of L-molecules in a racemic mixture at thermodynamic equilibrium at ambient temperature. This fundamental asymmetry of matter has been examined from various aspects such as circularly polarized photons emitted by the slowing down of longitudinally polarized electrons (Bremsstrahlung), inducing degradation reactions or stereo selective crystallization of racemic mixtures. No experiment has convincingly supported these theoretical considerations for the origin of a dominant enantiomer on Earth. Either the results were shown to be artefacts or so weak that they are doubtful (Mac Dermott 1995).

Other chiral force fields that could have been acting on the Earth surface have been considered. Asymmetric synthesis and degradation have been achieved using circularly polarized light. On Earth, the classical electromagnetic interactions such as circularly polarized light or other fields would probably never result in a very high yield of optically pure compounds. They would also probably cancel on a time and space average.

The possibility to induce a chiral effect by submitting a suitable chemical reaction to a magnetic field first attempted by Pasteur has received experimental support in Rikken and Raupach (2000). The authors used a chiral chromium complex, which is unstable in solution and spontaneously dissociates and re-associates. The dissociation is accelerated by the absorption of light. In the presence of an unpolarised laser beam travelling parallel to a static magnetic field, a small excess of one enantiomer is produced and maintained. On reversing the magnetic field direction, the mirror-image enantiomer is obtained. Magnetochiral photochemistry therefore appears to be a possible source for biological homochirality. This is especially pertinent to hypotheses suggesting that complex organic molecules could evolve in the ice mantles of dust grains in interstellar space, because magnetic fields and unpolarised light are more common in the cosmos than circularly polarized light.

#### 1.3.2.3 Extraterrestrial Homochirality

Most of the amino acids detected in carbonaceous chondrites are asymmetric, with L- and D-enantiomers present in equal proportions. However, Cronin and Pizzarello (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000) found small L-enantiomer excesses in six α-methyl-α-amino alkanoic acids from the Murchison (2.8–9.2%) and Murray (1.0–6.0%) carbonaceous chondrites. Enantiomeric excesses up to 18% have been measured for isovaline, 2-methyl-2-aminobutyric acid. These amino acids are either unknown or rare in the terrestrial biosphere and cannot therefore be attributed to terrestrial contamination (Pizzarello 2007). In addition, the indigeneity of D- and L-isovaline enantiomers is supported by carbon and hydrogen isotopic data (Pizzarello et al. 2003; Pizzarello and Huang 2005). The Renazzo-type (CR) chondrites found in Antarctica revealed natal enantiomeric excesses of up to 60% (Pizzarello et al. 2012).

The excess of one-handed amino acids found in the Murchison meteorite may result from the processing of the organic mantles of interstellar grains by circularly polarized synchrotron radiation from the neutron star remnant of a supernova (Bonner 1991). Strong infrared circular polarization, resulting from dust scattering in reflection nebulae in the Orion OMC-1 star-formation region, has been observed (Bailey et al. 1998) and circular polarization at shorter wavelengths might have been important in inducing chiral asymmetry in interstellar organic molecules that could have been subsequently delivered to the early Earth (Bailey 2001).

## 1.4 Conclusions

On Earth, life probably appeared about 4 billion years ago, when some assemblages of organic molecules in a liquid water medium began to transfer their chemical information and to evolve by making a few accidental transfer errors. The number of molecules required for those first assemblages is still unknown. The problem is that, on Earth, those molecules have been erased. If life started on Earth with the self-organisation of a relatively small number of molecules, its emergence must have been quick; therefore the chances for the appearance of life on any appropriate celestial bodies are real. On the contrary, if the process required thousands of different molecules, the event risks being unique and restricted to the Earth. The discovery of a second independent genesis of life on a body presenting environmental conditions similar to those which prevailed on the primitive Earth, such as Mars (Westall et al. 2015), would strongly support the idea of a rather simple genesis of terrestrial life. More than just a societal wish, the discovery of a second genesis of life is a scientific need for the study of the origin of life. It will demonstrate that life is not a magic one-shot process but rather a common phenomenon. Many scientists are convinced that microbial life is not restricted to the Earth but such conviction now needs to be supported by facts. So far, chemists have been able to propose requirements for the origin of terrestrial, alien terrestrial and extraterrestrial life and put forward a certain number of chemical biosignatures. However, only joint efforts between astronomers, planetologists, geologists and geochemists will be needed to legitimize those prerequisites and evaluate chemical biosignatures.

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