LIFE IN THE SOLAR SYSTEM

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ABSTRACT

Life, defined as a chemical system capable of transferring its molecular information via self-replication and also capable of evolving, must develop within a liquid to take advantage of the diffusion of complex molecules. On Earth, life probably originated from the evolution of reduced organic molecules in liquid water. Organic matter might have been formed in the primitive Earth's atmosphere or near hydrothermal vents. A large fraction of prebiotic organic molecules might have been brought by extraterrestrial-meteoric and cometary dust grains decelerated by the atmosphere. Any celestial body harboring permanent liquid water may therefore accumulate the ingredients that generated life on the primitive Earth. The possibility that life might have evolved on early Mars when water existed on the surface marks it as a prime candidate in a search for bacterial life beyond the Earth. Europa has an icy carapace. However, cryovolcanic flows at the surface point to a possible water subsurface region which might harbor a basic life form. The atmosphere and surface components of Titan are also of interest to exobiology for insight into a hydrocarbon-rich chemically evolving world. One-handed complex molecules and preferential isotopic fractionation of carbon, common to all terrestrial life forms, can be used as basic indicators when searching for life beyond the Earth.

ORIGIN OF LIFE ON THE PRIMITIVE EARTH

Primitive life probably appeared with the first chemical systems able to transfer their molecular information via self-replication and to evolve in liquid water. Unfortunately, the direct clues which may help chemists to identify the molecules which participated in the emergence of life on Earth about 4 billion years ago have been erased by plate tectonics, the permanent presence of running water, the unshielded solar ultraviolet radiation and by oxygen produced by life. By analogy with contemporary life, it is generally believed that primitive life originated from the processing of reduced organic molecules by liquid water. Primitive life may also have started based on mineral crystals. This idea has been developed by Cairns-Smith (1982) but still needs to be supported by experiments.

Liquid Water

It is generally thought that life on Earth emerged in liquid water. For this reason, water is considered as one of the prerequisites for life to appear and evolve on a planet. In contemporary living systems, water participates as a solvent in the organization of biopolymers in three-dimensional structures and as a chemical partner in most of the biochemical pathways. According to its molecular weight, water should be a gas under standard terrestrial conditions by comparison with CO₂, SO₂, H₂S, etc. Its liquid state is due to its ability to form hydrogen bonds. This is not restricted to water molecules since alcohols exhibit a similar behavior. However, the polymeric network of water molecules created via H-bonds is so tight that the boiling point of water is raised from 40 °C (temperature inferred from the boiling point of the smallest alcohols) to 100 °C. Hydrogen bonds are formed between water molecules and organic molecules, providing that the latter contain -OH, -NH, -SH groups in addition to carbon and hydrogen. As a consequence of this affinity many CHONS organic molecules are soluble in water. Hydrocarbons cannot form hydrogen bonds with water molecules and are consequently insoluble in water. In addition to the H-bonding capability, water exhibits a large dipole moment (1.85 debye) as compared to alcohols (<1.70
debye). This large dipole moment favors the dissociation of ionizable groups such as -NH₂ and -COOH leading to ionic groups which can form additional H-bonds with water molecules, thus improving their solubility. Water is also an outstanding dielectric with a high dielectric constant, ε, of 80. When oppositely charged groups are formed, their recombination is unfavored because the attraction force for reassociation is proportional to 1/ε. Abiotic organic molecules can be divided into two families: hydrocarbons and CHONS containing molecules. When brought into the presence of liquid water, hydrocarbons try to escape the water molecules while CHONS have some affinity for water, especially those that bear ionizable groups. When these two species are forced to coexist within the same molecules, the duality generates interesting topologies. When they are separated by long distances - such as in fatty acids or phospholipids - micelles, vesicles, or liposomes are formed due to clustering of the hydrophobic groups. Over short distances, hydrophobic and ionizable groups generate chain conformations that depend strongly on the sequence, i.e. the distribution of the group along the chains.

Water molecules are widely spread in the universe as grains of solid ice or as very dilute water vapor. Liquid water is a fleeting substance that can persist only above 0 °C and under an atmospheric pressure higher than 6 mbars. Therefore, the size of a planet and its distance from the star are two basic characteristics that will determine the presence of liquid water. If a planet is too small, like Mercury or the Moon, it will not be able to retain any atmosphere and, therefore, no liquid water. If the planet is too close to the star, the mean temperature rises due to starlight intensity. Any seawater present would evaporate delivering large amounts of water vapor 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 photodissociation by ultraviolet light would break the molecules into hydrogen, which would escape into space, and oxygen, which would recombine into the crust. If a planet is far from the star, it may host liquid water providing that it can maintain a constant greenhouse atmosphere. However, water would provoke its own disappearance. The atmospheric greenhouse gas, CO₂ for instance, would be dissolved in the oceans and finally trapped as insoluble carbonates by rock-weathering. This negative feedback would lower the surface pressure and the temperature to an extent that water would be largely frozen. A volcanically active planet could recycle the carbon dioxide by breaking down subducted carbonates. The size of the Earth and its distance from the sun are such that the planet never experienced either a runaway greenhouse or a divergent glaciation.

Terrestrial Production of Reduced Organic Molecules

Oparin (1924) suggested that the small, reduced organic molecules needed for primitive life were formed in a primitive atmosphere dominated by methane. The idea was tested in the laboratory by Miller (1953; 1998) when he exposed a mixture of methane, ammonia, hydrogen, and water to electric discharges. In his initial experiment, he obtained four of the twenty naturally occurring amino acids, via the intermediary formation of hydrogen cyanide and formaldehyde. 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 primitive Earth's atmosphere remains difficult to define. The source of the primitive terrestrial atmosphere can be found in a combination of the volatiles CO₂, N₂, H₂O, trapped in the rocks that made the bulk of the planet's mass ("internal reservoir") and a late accreting veneer of extraterrestrial material ("external reservoir"). The formation of the internal reservoir is a natural consequence of the accretion of the planet. Wetherill (1990) suggested that collisions with planetary embryos on eccentric orbits should have thoroughly homogenized the rocky composition of Venus, Earth, and Mars. The late-accreting veneer contributed by some combination of volatile-rich meteorites and comets should also have been uniform from planet to planet. A volatile-rich veneer may have replaced the atmosphere produced by the planet's early accretion, which was subsequently blown off by the giant impact between the Earth and a Mars-sized planetary embryo that generated the Moon and caused the early atmosphere to undergo massive hydrodynamic loss. The abundance and isotopic ratios of the noble gases neon, argon, krypton, and xenon suggest that meteorites alone or in combination with planetary rocks could not have produced the Earth's entire volatile inventory and that a significant contribution from icy planetesimals was required (Owen and Bar-Nun, 1995; Owen, 1998).

The surface temperature of the early Earth was very much dependent upon the partial pressure of CO₂ in the atmosphere. The dominant view in recent years has been that the early atmosphere was a weakly reducing mixture of CO₂, N₂, and H₂O, combined with lesser amounts of CO and H₂ (Kasting, 1993;
Kasting and Brown, 1998). An efficient greenhouse effect induced by a high CO$_2$ partial pressure was the most likely mechanism capable of compensating for the faint young Sun, the luminosity of which was about 30% lower than today. The dominant sink for atmospheric CO$_2$ was silicate weathering on land and subsequent formation and deposition of carbonate sediments in the ocean. However, a negative feedback system probably maintained the Earth’s surface temperature above freezing: if the temperature were to drop below freezing, silicate weathering would slow down and volcanic CO$_2$ would accumulate in the atmosphere. Walker (1985) suggested that the CO$_2$ partial pressure could have been as high as 10 bars prior to the emergence of the continents because of limited silicate weathering and storage in continental carbonate minerals. Under these conditions, the early Earth could have been as hot as 85 °C. Recent analysis of samarium/neodymium ratios in the ancient zircons indicate that the continents grew rapidly, so a dense CO$_2$ atmosphere may have been restricted to the first few hundred million years of the Earth’s history.

In a weakly reducing gas mixture of CO$_2$, N$_2$, and H$_2$O, the production of amino acids appears to be very limited (Schlesinger and Miller, 1983). More recently, Wächtershäuser (1994; 1998) suggested that the carbon source for life was carbon dioxide. The energy source required to reduce carbon dioxide was provided by the oxidative formation of pyrite (FeS$_2$) from troilite (FeS) and hydrogen sulfide. Pyrite has positive surface charges and bonds the products of carbon dioxide reduction, giving rise to a two-dimensional reaction system, a “surface metabolism.” Recent experimental laboratory work is about to legitimize this new hypothesis (Heinen and Lauwers, 1996; Huber and Wächtershäuser, 1997; 1998).

Deep-sea hydrothermal systems may also represent likely environments for the synthesis of prebiotic organic molecules (Holm and Andersson, 1995; 1998) and perhaps for primitive life (Stetter, 1998). Experiments have been carried out in order to test whether amino acids can be formed under conditions simulating the hydrothermal vents. Yanagawa and Kobayashi (1992) treated methane and nitrogen under simulated hydrothermal vent conditions (325°C and 200kg/cm$^2$) and obtained glycine and alanine in low yields (10$^{-4}$%). Hennet et al. (1992) obtained glycine, alanine, serine, aspartic and glutamic acids, isoleucine, when treating mixtures of hydrogen cyanide, formaldehyde and ammonia at 150°C and 10 bar in the presence of pyrite-pyrrhotite-marquetite. The amino acid diversity is roughly similar to that reported for electric discharges but the yields are significantly higher (6.9 % for glycine). Hydrothermal vents are often disqualified as efficient reactors for the synthesis of bio-organic molecules because of the high temperature. However, the products that are synthesized in hot vents are rapidly quenched in the surrounding cold water. When fluid containing glycine repeatedly circulated through the hot (225°C) and cold (0°C) regions in a laboratory reactor that simulated a hydrothermal system, glycine peptides up to hexaglycine were obtained (Imai et al., 1999).

Extraterrestrial Delivery of Organic Molecules to the Earth

Comets show substantial organic material. According to Delsemme’s analysis (1991), dust particles ejected from the Comet Halley nucleus contain 14% organic carbon by mass (Delsemme, 1991). About 30% of cometary grains are dominated by light elements C, H, O, and N, and 35% are close in composition to carbonaceous chondrites (Kissel and Knieger, 1987; Langevin et al., 1987). Among the molecules identified in comets are hydrogen cyanide and formaldehyde. The presence of purines, pyrimidines, and formaldehyde polymers has also been inferred from the fragments analyzed by Giotto Picca and Vega Puma mass spectrometers. However, there is no direct identification of the complex organic molecules present in the dust grains and in the cometary nucleus. Many chemical species of interest for exobiology have been detected in Comet Hyakutake in 1996, including ammonia, methane, acetylene (C$_2$H$_2$), acetonitrile (CH$_3$CN) and hydrogen isocyanide (HNC) (Irvin et al., 1996). In addition to hydrogen cyanide and formaldehyde (H$_2$CO), seen in several earlier comets, the Comet Hale-Bopp was also shown to contain methane, acetylene, formic acid (HCOOH), acetonitrile, hydrogen isocyanide, isocyanic acid (HNCO), cyanoacetylene (HC$_3$N$_2$), and thioformaldehyde (H$_2$CS). Cometary grains might, therefore, have been an important source of organic molecules delivered to the primitive Earth (Oró, 1961; Chyba et al., 1990; Greenberg, 1993; Delsemme, 1998).

The study of meteorites, particularly the carbonaceous chondrites that contain up to 5% by weight of organic matter, has allowed close examination of extraterrestrial organic material delivered to the Earth. Eight proteinaceous amino acids have been identified in the Murchison meteorite among more than 70 amino acids found therein (Cronin et al., 1988; Cronin, 1998). These amino acids are asymmetric and the
two enantiomers, L and D, are generally found in equal proportions. Engel and Macko (1997) reported that L-alanine and L-glutamic acid were surprisingly more abundant than the corresponding D-enantiomers (L-enantiomer excesses of over 30 and 50%, respectively) in the Murchison meteorite. These large L-enantiomer excesses may be due to the presence of contaminant amino acids showing gas-chromatography retention times similar to those of the alanine enantiomers (Pizzarello and Cronin, 1998). In order to eliminate contaminant amino acids, which may potentially co-migrate with the target amino acids during gas chromatography (GC), Cronin and Pizzarello (1997) fractionated the Murchison extracts by reversed-phase liquid chromatography prior to GC. Under these conditions, they found 9% L-enantiomeric excesses for non biological amino acids which cannot be suspected to be the result of biological contamination. The presence of L-enantiomeric excesses in the Murchison meteorite suggests an extraterrestrial asymmetric synthesis of amino acids, asymmetry that is preserved inside the meteorite. These excesses may help to understand the emergence of a one-handed (homochiral) life. For example, proteins are built up with twenty different amino acids. Each amino acid, with the exception of glycine, exists under two enantiomeric forms, L and D, but proteins use only L ones. Proteins adopt asymmetrical rigid geometries, α-helices and β-sheets, which play a key role in the catalytic activity.

Fig. 1. β-pleated sheet structure (left) and right-handed α-helix (right). Both structures are stabilized by hydrogen bonds (-----) between NH groups (Hp) and CO groups (C=O).

Homochirality is now believed to be not just a consequence of life, but also a prerequisite for life, because stereo-regular structures such as protein β-sheets do not form with mixtures of amino acids of both handedness. 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 a neutron star remnant of a supernova (Bonner and Rubenstein, 1987). Strong infrared circular polarization, resulting from dust scattering in reflection nebulae in the Orion OMC-1 star-formation region, has been recently observed (Bailey et al., 1998). Circular polarization at shorter wavelengths might have been important in inducing chiral asymmetry in interstellar organic molecules that could be subsequently delivered to the early Earth. Whether the extraterrestrial organic material collected on Earth bears witness to the interstellar organic chemistry is still unknown. More information must be collected about the process of transferring organic material between the interstellar medium (ISM) (where more than 100 different molecules, the bulk of them organic, have been detected so far by radioastronomers (Irvine, 1998)), and the Earth, in order to better understand the global ISM-comets-planets ecosystem from an exobiological point of view.

Dust collection, both above the terrestrial atmosphere by Love and Brownlee (1993), and in the Greenland and Antarctic ice sheets by Maurette (Maurette et al. 1995; Maurette, 1998) show that the Earth captures interplanetary dust as micrometeorites at a rate of about 50-100 tons per day. About 99% of this mass is carried by micrometeorites in the 50-500 μm size range. This value is about 2,000 times higher than the most reliable estimate of the meteorite flux (about 0.03 tons per day) estimated by Bland et al. (1996). This amazing dominance of micrometeorites already suggests their possible role in delivering complex organics to the early Earth 4.2 to 3.9 Ga ago when the micrometeorite flux was enhanced by a factor of 1,000 (Anders, 1989). In the Antarctic micrometeorites, a high percentage of unmelted chondritic micrometeorites from 50 to 100 μm in size have been observed, indicating that a large fraction crossed the terrestrial atmosphere without drastic thermal treatment. In this size range, the carbonaceous micrometeorites represent 80% of the samples and contain 2% of carbon, on average. They might have brought about 1020 g of carbon over a period of 300 million years corresponding to the late terrestrial
bombardment phase. This delivery represents more carbon than that engaged in the surficial biomass, i.e. about $10^{18}$ g. Amino acids such as α-amino isobutyric acid have been recently identified in these Antarctic micrometeorites (Brinton et al., 1998). These grains also contain a high proportion of metallic sulfides, oxides, and clay minerals that belong to various classes of catalysts. In addition to the carbonaceous matter, micrometeorites might also have delivered a rich variety of catalysts having perhaps acquired specific crystallographic properties during their synthesis in the microgravity environment of the early solar nebula. They may have functioned as tiny chondritic chemical reactors when reaching oceanic water. Amino acids like those detected in the Murchison meteorite have been exposed to space conditions in Earth orbit onboard unmanned Russian satellites of the Fotons 8 and 11, free and associated with clay minerals. Free exposed aspartic acid and glutamic acid were partially photo-processed during exposure to solar UV. However, decomposition was prevented when the amino acids were embedded in clays (Barbier et al., 1998).

A Primitive Cellular Life

By analogy with contemporary living systems, it is generally believed that the first primitive life emerged as a cell-like organized system. This cell-like system required at least, boundary molecules able to isolate the system from the aqueous environment (a membrane), catalytic molecules providing the basic chemical work of the cell (enzymes), and information molecules allowing the storage and the transfer of the information needed for replication (RNA).

**Boundary Molecules.** Fatty acids are known to form vesicles when the hydrocarbon chains contain more than ten carbon atoms. Such vesicle forming fatty acids have been identified in the Murchison meteorite (Deamer, 1985). However, the membranes obtained with these simple amphiphiles are not stable over a broad range of conditions. Stable lipids can be obtained by condensing fatty acids with glycerol or with glycerol phosphate, thus mimicking the stable contemporary phospholipids (Deamer and Ord, 1980; Deamer, 1998). Primitive membranes could initially have also been formed by simple isoprene derivatives. From the analysis of organic molecular fossils in various sediments, Ourisson and Nakatani (1994) proposed a phylogenic classification of the terpenoids, from simple linear polyprenoids to complex ones like steroids, taxol or carotenoids. The simplest, and probably the most primitive, membrane-forming terpenoids are linear polyprenoids flanked by phosphate polar head groups. Such compounds have been synthesized and spontaneously give vesicles in water. The role of terpenoids in the origin of life will become granted when the prebiotic synthesis of polyprenyl precursors from ethylene and acetone will be documented.

**Catalytic Molecules.** Most of the chemical reactions in a living cell are achieved by proteinaceous enzymes made of 20 different homochiral L-amino acids. Amino acids were most likely available on the primitive Earth as complex mixtures. The number of condensing agents capable of assembling amino acids into peptides in water is restricted, especially when looking for prebiotically plausible compounds. Carbodiimides, R-N=C=N-R, can be used in water providing a careful choice of the substituent R and of experimental conditions. Under selected conditions, Cavadore and Previero (1969) obtained long peptides in water up to 30 monomers long. The simplest carbodiimide, H-N=C=N-H, can be considered as a tautomeric form of cyanamide NHz-CN which is present in the interstellar medium. In water, cyanamide forms a dimer, dicyandiamide, which is as active as carbodiimides to form peptides. However, the reactions are very slow and do not proceed beyond the tetrapeptide. Diaminomaleonitrile, the tetramer of HCN, has been found to form diglycine in 3.1% yield.

Clays can also be used to condense amino acids in water. Alanyladenylates, mixed anhydrides between alanine and adenosine monophosphate, condense readily in the presence of montmorillonite (Paecht-Hörwitz and Eirich, 1988). When subjecting mixtures of glycine and kaolinite to wet-dry and 25-94 °C temperature fluctuations, Lahav et al. (1978) observed the formation of oligopeptides (short peptides) up to five glycines long. The drying/wetting cycle procedure was extended to alanine in the presence of silica, alumina and smectic clays (Budjak and Rode, 1997). White and Erickson (1980) studied the effects of the dipeptide histidyl-histidine in the polymerization of glycine during fluctuating moisture and temperature cycles on kaolinite. A turnover of 52 was observed, i.e. each molecule of dipeptide helps the polymerization of 52 molecules of glycine. Mutual catalysts of amino acids in the salt-induced peptide formation reaction has been demonstrated for the case of glycine/alanine (Siuwannaehot and Rode, 1998).
Efficient mineral-catalyzed (hydroxylapatite, illite clay) condensation of amino acids into long peptides have been recently reported (Ferris et al., 1996; Hill et al., 1998; Liu and Orgel, 1998).

Thermal condensation of amino acids has been described by Fox and Dose (1977). They have shown that dry mixtures of amino acids polymerize when heated at 130 °C to give “proteinoids.” In the presence of polyphosphates, the temperature can be decreased to 60 °C. High molecular weights were obtained when an excess of acidic or basic amino acids are present. In aqueous solutions, the proteinoids aggregate spontaneously into microspheres of 1-2 microns, presenting an interface resembling the lipid bilayers of living cells. The microspheres increase slowly in size from dissolved proteinoids and are sometimes able to bud and to divide. These microspheres are described as catalyzing the decomposition of glucose and work as esterases and peroxydases. The main advantage of proteinoids is their organization into particles but they represent a dramatic increase in complexity. When heating a mixture of selected L-amino acids, the resulting condensate is only 50% peptidic, the peptidic fraction is racemized, the peptide linkages are ambiguous since they include the α, β, and δ functions of the dicarboxylic amino-acids, and the sequences are multiple although not completely random.

Helical and sheet-structures can be modeled with the aid of only two different amino acids, one hydrophobic, the second hydrophilic. Polypeptides with alternating hydrophobic and hydrophilic residues adopt a water-soluble β-sheet geometry because of hydrophobic side-chain clustering (Brack and Orgel, 1975). Due to the formation of a β-sheet, alternating sequences gain a good resistance toward chemical degradation. Aggregation of alternating sequences into β-sheets is possible only with all-L or all-D polypeptides.

When hydrophobic and hydrophilic amino acids coexist within the same polypeptide chain, the duality generates interesting topologies such as stereoselective and thermostable β-sheet structures. Short peptides have also been shown to exhibit catalytic properties (Barbier and Brack, 1992; Brack, 1993). Chemical reactions capable to selectively condense the protein amino acids at the expense of the non-protein ones have been described (Brack, 1987). According to De Duve (1995; 1998), the first peptides appeared via thinesters.

Information Molecules. In contemporary living systems, the hereditary memory is stored in nucleic acids, long chains built from nucleotides. Each nucleotide is composed of a base (purine or pyrimidine), a sugar (ribose for RNA, deoxyribose for DNA), and a phosphate group. The accumulation of significant quantities of natural RNA nucleotides does not appear as a plausible chemical event on the primitive Earth (Schwartz, 1998). Purines are easily obtained from hydrogen cyanide or by submitting reduced gas mixtures to electric discharges. No pyrimidine synthesis from electric discharges has been published so far and hydrogen cyanide affords only very small amounts of this base. Condensation of formaldehyde leads to only very tiny amounts of RNA ribose among a large number of other sugars. The synthesis of purine nucleosides (the covalent combination of purine and ribose), and of nucleotides has been achieved by heating the components in the solid state. The yields are very low and the reactions do not lead to the
biological linkages. Interestingly, efficient clay-catalyzed condensation of nucleotides into oligonucleotides up to 55 monomers long has recently been reported (Ferris et al., 1996; 1998).

The synthesis of oligonucleotides is much more efficient in the presence of a pre-formed pyrimidine-rich polynucleotide acting as a template. Non-enzymatic replication has been demonstrated by Orgel and his co-workers. The pre-formed chains align the nucleotides by base-pairing to form helical structures which bring the reacting groups in close vicinity (Inoue and Orgel, 1982). Under special conditions, purine-rich strands can also act as templates (Sievers and von Kiedrowski, 1994; Li and Nicolaou, 1994).

The prebiotic synthesis of oligonucleotides remains an unsolved challenge. Each step of the chemical pathway has been achieved in the laboratory but the desired product is never dominant. It is always contaminated with by-products that are wastes or even poisons. Chemists have considered early living systems using simpler informative molecules. Spach (1989) proposed to replace the sugar by glycerol for the backbone and this idea was tested in the laboratory. The chemistry of these simplified informative molecules does not appear much easier (Vissher and Schwartz, 1990). The straightforward and selective formation of ribose diphosphates from glycolaldehyde phosphate suggests that pyranosyl-RNA may have been involved in the early forms of life. Intense experimental work is presently being performed in Eschenmoser's laboratory along this new and promising avenue (Bolli et al., 1997).

A Primitive Life Based Only on RNA? Cech found that some RNA, the ribozymes, are able to act as catalytic molecules (Zaug and Cech, 1986). For example, they increase the rate of hydrolysis of oligoribonucleotides. They also act as a polymerization template since chains up to 30 monomers long can be obtained starting from a pentanucleotide. Since this primary discovery, the catalytic spectrum of these ribozymes has been considerably enlarged by directed test tube molecular evolution experiments initiated in Joyce's and Szostak's laboratories (reviewed by James and Ellington, 1995; 1998). Since RNA was shown to be able to act simultaneously as an information and a catalytic molecule, RNA has been considered the first living system on the primitive Earth (the "RNA world"). This is because it can simultaneously be the genotype and phenotype and can fulfill the basic cycle of life consisting of self-replication/mutation/selection. One should, however, remember that their synthesis under prebiotic conditions remains an unsolved challenge. It seems unlikely that life started with RNA molecules because these molecules are not simple enough. The RNA world appears as an episode in the evolution of life before the appearance of cellular microbes rather than as the birth of life.

Chemists are now tempted to consider that primitive replicating systems must have used simpler informational molecules than biological nucleic acids or their analogs. They are looking for simple self-sustaining chemical systems capable of self-replication, mutation, and selection. Rebek and co-workers have used nucleic base-like A-B templates able to form hydrogen bonded ternary complexes with individual A and B subunits and to catalyze the synthesis of new A-B molecules (Park et al., 1992). These experiments are illuminating examples of autocatalysis but they do not yet address the problem of self-replication of long linear sequences. Terfort and von Kiedrowski (1992) showed that simple A-B molecules unrelated to nucleotides can provide exponentially replicating autocatalytic models (reviewed by Burmeister, 1998). Luisi and co-workers (Bachmann et al., 1992) have demonstrated beautiful examples of autocatalytic micelle growth. However, these autocatalytic systems do not really store hereditary memory and cannot therefore evolve by natural selection.

The geological record also provides important information. The isotopic signatures of the organic carbon of the Greenland meta-sediments bring indirect evidence that life may be 3.85 billion years old (Mojzsis et al., 1996). Schidlowski (1987) has compiled the carbon isotopic composition of over 1,600 samples of fossil kerogen (a complex organic macromolecule produced from the debris of biological matter) with carbonates in the same sedimentary rocks. The organic matter has an average $\delta^{13}C$ of $-25\pm 7\%$ (where $\delta^{13}C$ expresses the permil deviation of the $^{13}C/^{12}C$ ratio of the sample relative to that of a conventional standard, the carbonate skeleton of a fossil cephalopod that has a $^{13}C$ ratio of 0.0112), whereas the carbonate varies by no more than about 2% around a mean of 0%o. The $-25-30\%$ shift is taken as an indication that biosynthesis by photosynthetic organisms was involved. In fact, this offset is now taken to be one of the most powerful indications that life on Earth was active nearly 3.9 Ga ago because the sample suite encompasses specimens right across the geologic time scale. Some organic matter in ancient sediments has been measured as being even more enriched in the light isotope of carbon which would
suggest involvement of methane utilizing organisms. This conclusion is fully consistent with the remarkable diversity of the 3.465 billion year old fossilized microflora reported by Schopf (1993; 1998).

Were the first replicators based on autocatalysis, on thioester chemistry, or on organic molecules adsorbed on pyrite? This exciting question is still open. A major problem lies in the fact that we remain ignorant of the true historical facts on Earth from the time when life started.

LIFE BETWEEN THE SUN AND MARS?

If one excepts life on Earth, the probabilities for habitability are quite low between the Sun and Mars.

Venus may perhaps have been Earth-like in its past so that its early environmental conditions may have been favorable for the emergence of life. Today, Venus is too hostile on the surface to harbor life. The high surface temperature (464 °C) and its permanent thick clouds of aqueous H$_2$SO$_4$ would impede the search for signatures of primitive life and may even have erased the signatures, if any (Colin and Kasting, 1992).

The Moon has been recently revisited by the Clementine and Lunar Prospector spacecrafts. In 1996, Clementine radar data suggested the possible presence of water ice on the lunar poles. The neutron spectrometer on board Lunar Prospector detected in 1998 high hydrogen concentrations at both poles, a telltale signature of the presence of water ice. Although other explanations for the hydrogen enhancement are possible, the data suggest that significant quantities of water ice are located in permanently shadowed craters in both polar regions. Each polar region could contain as much as roughly $3 \times 10^9$ metric tons of water ice (Feldman et al., 1998). The ice may have arrived as comets that plowed into the moon at or near the South pole, an area which never sees the sun. The water may have migrated south into a deep crater at the moon's darkest part. The presence of ice does not increase the chances to detect any lunar microbial life but rather opens the moon to cost-effective lunar and planetary exploration by providing water for life support and fuel for rockets.

LIFE ON MARS?

Mars mapping by Mariner 9 and by Viking 1 and 2 revealed channels resembling dry riverbeds. Three major classes of channels were identified: (i) dendritic run off channels and valleys primarily associated with cratered terrain older than 3.8 Ga and which are generally associated with fluvial water erosion; (ii) outflow channels suggestive of large-volume flows in cataclysmic events; and, (iii) fretted channels which are steep-walled with smooth flat floors suggestive of erosion by debris flows. The inventory of the total amount of water that may have existed at the surface of Mars is difficult to estimate and varies from meters to several hundred meters. The climatic conditions required for the formation of the valley networks are also poorly understood. The most plausible explanation is a relatively thick CO$_2$ atmosphere (1 to 5 bars) in the early history of Mars, giving rise to a greenhouse effect which would have allowed for mean global surface temperature to remain above the freezing point of water. Carr (1995) suggested recently that the valley networks, like the fretted channels, formed mainly by mass wasting, aided by groundwater seepage into the mass-wasted debris, between 3.8 and 3.7 Ga ago. Therefore, it is generally considered that liquid water has been restricted to the very early stages of martian history. By about 3.8 Ga ago, most of the atmospheric CO$_2$ was probably irreversibly lost due to carbonate formation and pressure and temperature declined. However, the presence of extensive coastlines at the border of the northern lowlands where the «Valles» flow supports the presence of a large ocean in the Northern Hemisphere (Baker et al., 1991). Several features suggest the intermittent presence of water on the surface of Mars. Outflow channels have been active in Maja and Ares Valles (~2.2 Ga), in Kasei (~1.6 Ga) and Mangala (~0.6 Ga) Valles, and at Elysium (~0.3 Ga). Lacustrine deposits show the same range of age (ESA Exobiology Science Team, 1998).

The early histories of Mars and Earth clearly show similarities. Geological observations collected from martian orbiters suggest that liquid water was once stable on the Mars surface, attesting to the presence of an atmosphere capable of decelerating carbonaceous micrometeorites. Therefore, chemical evolution may have been possible on Mars (McKay, 1998). The Viking 1 and 2 lander missions were designed to address the question of extant life on Mars. Three experiments were selected to detect metabolic activity such as photosynthesis, nutrition, and respiration of potential microbial soil communities. The results were
ambiguous since although "positive" results were obtained, no organic carbon was found in the martian soil by gas chromatography-mass spectrometry. It was concluded that the most plausible explanation for these results was the presence, at the martian surface, of highly reactive oxidants like $\text{H}_2\text{O}_2$ which would have been photochemically produced in the atmosphere (Hartman and McKay, 1995). The Viking lander could not sample soils below 6 cm and therefore the depth of this apparently organic-free and oxidizing layer is unknown. Bullock et al. (1994) have calculated that the depth of diffusion for $\text{H}_2\text{O}_2$ is less than 3 meters. Direct photolytic processes can also be responsible for the dearth of organics at the martian surface (Stoker and Bullock, 1997).

The alpha proton X-ray spectrometer (APXS) on board the rover of the Mars Pathfinder mission in 1997 measured the chemical composition of six soils and five rocks at the Ares Vallis landing site. The analyzed rocks were partially covered by dust or a weathering rind similar in composition to the dust. Some rocks are similar to terrestrial andesites but it is not certain that these rocks are igneous. The textures of other rocks are difficult to interpret and might be sedimentary or metamorphic (Rieder et al., 1997).

Although the Viking missions were disappointing in the first instance for exobiology, in the long run the program has proven extremely beneficial for the investigation of the possibility of life on Mars. Prior to Viking it had been apparent that there was a small group of meteorites, all of igneous origin, called the SNC (after their type specimens Shergotty, Nakhlia, and Chassigny) that had comparatively young crystallization ages equal to or less than 1.3 Ga (Jagoutz and Waenke, 1986). One of these meteorites, EETA 79001, was found in Antarctica in 1979. It had gas trapped within glass pockets, which both compositionally and isotopically matched, in all respects, the make-up of the martian atmosphere, as measured by the mass spectrometer utilized for assessing the soil for the presence of organic compounds (Bogard and Johnson, 1983; Becker and Pepin, 1984; Carr et al., 1985). The data provide a very strong argument that at least that particular SNC meteorite comes from Mars, thus supporting the circumstantial conclusion that materials of young age must have derived from a planetary-sized body. There are now twelve SNC meteorites known in total; others were found more recently on the Antarctic Ice Cap including one, ALH 84001, of much older age. They can all be shown to be related by comparing their oxygen isotopic compositions. Only these twelve specimens (out of a total of ~20,000 meteorites) define a correlation line of slope one half on a plot of $\delta^{18}\text{O}$ versus $\delta^{17}\text{O}$ with $\Delta^{17}\text{O} = 0.321 \pm 0.013\%$, i.e. displaced from the Earth's reference line.

The two SNC meteorites EETA 79001 (Wright et al., 1989) and ALH 84001 (McKay et al., 1996; Grady et al., 1994) supply new and highly interesting information. A sub-sample of EETA 79001 excavated from deep within the meteorite has been subjected to stepped-combustion. The CO$_2$ released between 200-400 °C suggests the presence of organic molecules. The carbon is enriched in $^{12}\text{C}$ with $\delta^{13}\text{C}$ of about ~27%. The difference between organic matter and carbonates in martian meteorites is greater than the shift seen on Earth which could also be indicative of biosynthesis but some as yet unknown reason cannot be ruled out. McKay et al. (1996) reported the presence of PAHs, carbonates globules and ovoid features which may represent a signature of relic biogenic activity on Mars. From a list of observations about the carbonates and PAHs, the authors stated: "when considered collectively we conclude that [these phenomena] are evidence for primitive life on early Mars." Taken individually, the observations about the carbonates and PAHs can, however, be explained by non-biological means. For instance, there are conflicting values for the formation temperature of the carbonates: major-element chemistry implies a temperature of more than 500 °C (Harvey and McSween, 1996) incompatible with bacterial life, whereas oxygen isotope composition gives less than 100 °C. PAHs are not synthesized in any biological system but are produced by metamorphism of marine plankton and early plant life. Their presence in the unmetamorphosed ALH 84001 cannot therefore be taken as a convincing biomarker. No analysis of the composition of the ovoid feature edges has been performed to show whether they contain carbon or not. The carbonates that contain the microfossils are found in igneous rock rather than in a sediment (Grady et al., 1996).

Even if the evidence for ancient life in ALH 84001 is not conclusive, the two martian meteorites show the presence of organic molecules suggesting that the ingredients required for the emergence of a primitive life may have been present on the surface of Mars. Therefore, microorganisms may have developed on Mars until liquid water disappeared. Since Mars probably had no plate tectonics and since liquid water seems to have disappeared from Mars' surface very early, the martian sub-surface perhaps keeps a frozen
record of the very early forms of a terrestrial-like life. In 2005, the NASA Mars Sample Return mission will collect martian samples to be brought back to Earth for analysis in 2008. Drilling into the martian sediments and \textit{in situ} analysis of the cores will be a complementary way to explore the biological past of Mars and to search for organic remnants of meteoritic and cometary bombardment.

**LIFE BEYOND MARS?**

The atmospheres of the outer planets, from Jupiter to Pluto, contain methane as the main carbon-containing molecules. The atmospheres of the giant planets Jupiter, Saturn, and Uranus are mainly composed of hydrogen and helium with a noticeable fraction of methane and a lower contribution of ammonia (Pollack and Atreya, 1992). The situation is similar for Neptune but since the temperature is lower, the concentration of ammonia must be much lower (Gautier et al., 1995). The recent discovery of HCN in its atmosphere strongly suggests that nitrogen should be present as a main nitrogen atom source (Lellouch et al., 1994). In all these atmospheres, gas phase organic chemistry is dominated by methane photochemistry. The main products are saturated and unsaturated hydrocarbons. The coupling of methane and ammonia (or nitrogen) photochemistry can produce N-organics. On Saturn, the coupling of methane and phosphine (PH$_3$) photochemistry could produce HCP. Although the exobiological interest of these planets is limited, the study of their atmospheric organic chemistry can provide interesting examples of the wide variety of planetary organic processes.

**Europa**

Europa appears as one of the most enigmatic of the Galilean satellites. With a mean density of about 3.0 g cm$^{-3}$, the Jovian satellite should be dominated by rocks. Ground-based spectroscopy, combined with gravity data, suggests that the satellite has an icy crust roughly 150-km thick, and a rocky interior. The Voyager images showed very few impact craters on Europa's surface, indicating recent, and probably continuing, resurfacing by cryovolcanic and tectonic processes. The Voyager spacecraft also revealed that Europa's surface is criss-crossed by numerous intersecting ridges and dark bands. It has been suggested that Europa's thin outer ice shell might be separated from the silicate interior by a liquid water layer, prevented from freezing by tidal heating as the result of the variation of the gravitational field across the body of the satellite. Heat transfer from the core to the bottom of the ocean, similar to thermal vents in terrestrial oceans, is another possible source of thermal energy. Although the existence of such an ocean is still uncertain, the last images from Galileo showing evidence for mobile icebergs support the presence of liquid water at shallow depths below the surface, either today, or at some time in the past (Carr et al., 1998). If liquid water is present within Europa, it is quite possible that it includes organic matter derived from thermal vents. Terrestrial-like prebiotic organic chemistry and primitive life may therefore have developed in Europa's ocean (Reynolds et al., 1983; Oró et al., 1997). If Europa maintained tidal and/or hydrothermal activity in its subsurface until now, it is possible that bacterial activity is still present. Thus, the possibility of an extraterrestrial life present in the hypothetical ocean of Europa must be seriously considered (Abstracts Europa Ocean Conference, 1996). The most likely sites for extant life would be at hydrothermal vents below the most recently resurfaced area. To study this directly would require making a borehole through the ice in order to deploy a robotic submersible. On the other hand, biological processes in and around hydrothermal vents could produce biomarkers that would be erupted as traces in cryovolcanic eruptions and thereby be available at the surface for \textit{in situ} analysis or sample return. Mineral nutrients delivered through cryovolcanic eruption would make the same locations the best candidates for photosynthetic life.

**Ganymede**

An internal structure similar to that of Europa has been proposed for Ganymede, the largest satellite of Jupiter. Large tracts of Ganymede's surface have been resurfaced by some kind of tectono-volcanic process. Galileo images reveal that the ridge and groove patterns are repeated on a scale one order of magnitude smaller than that of those discovered by Voyager (Belton et al., 1996). However, the density of superposed impact structures indicates that this activity has long since ceased, probably longer than a billion years ago. Moreover, Ganymede's ice is probably over 1,000-km thick, so mineral nutrients are likely to be very deeply buried. Thus, although hydrothermally sustained life at the ice-rock interface could have been viable in the distant past, the prospects of finding biomarkers in the present surface ice are much poorer than for Europa.
Titan

Titan's atmosphere was revealed mainly by the Voyager 1 mission in 1980, which yielded the bulk composition (90% molecular nitrogen and about 1-8% methane). Also, a great number of trace constituents were observed in the form of hydrocarbons (acetylene, ethane, ethylene, etc.), nitriles (HCN, C$_2$N$_2$, HC$_3$N) and oxygen compounds (CO and CO$_2$). Titan is the only other object in our solar system to bear a resemblance to our own planet in terms of atmospheric pressure (1.5 bar) and carbon/nitrogen chemistry (Owen et al., 1992; Coll et al., 1998; Raulin, 1998). It represents, therefore, a natural laboratory to study the formation of complex organic molecules on a planetary scale and over geological times. The ISO satellite has recently detected tiny amounts of water vapor in the higher atmosphere, but Titan's surface temperatures (94 K) are 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 a planetary organic chemistry. Titan also serves as a reference laboratory to study, by default, the role of liquid water in exobiology.

The Cassini-Huygens spacecraft launched in October 1997 will arrive in the vicinity of Saturn in 2004 and perform several flybys of Titan making spectroscopic, imaging, radar and other measurements. A descent probe will penetrate the atmosphere and will systematically study the organic chemistry in Titan's geofluid. During 150 minutes, *in situ* measurements will provide detailed analysis of the organics present in the air, in the aerosols and at the surface (Lebreton, 1997).

CONCLUSIONS

Terrestrial life probably appeared between 4 and 3.8 billion years ago. The inventory of organic molecules of prebiotic interest which were likely to be present at that time is satisfactory except for the RNA sugar component, ribose, which cannot be synthesized in substantial amounts under prebiotic conditions. Delivery of extraterrestrial organic molecules is of special interest since it is a process which still occurs today. The existence of such an import process on the early Earth required only an atmosphere to decelerate the particles. Such an atmosphere existed 3.8 billion years ago as illustrated, for instance, by the Greenland sediments.

Among these organic molecules processed by liquid water, some began to transfer their molecular information and to evolve by making a few accidental transfer errors. For the sake of simplicity - for chemists, prebiotic chemistry was simple - one is tempted to assume that the chemical information and the transfer machinery were provided by the same molecules. Self-replicating RNA molecules fulfill these requirements. However, RNA molecules are not really simple and whether they started life on Earth is still questionable. Self-replicating RNAs are, by definition, autocatalytic molecules that transfer their sequence information by an accurate residue-by-residue copying process, thanks to the template chemistry of complementary strands. This field of research is now opened to organic chemists and new results are eagerly anticipated.

Homochirality was probably a prerequisite for life. The enantiomeric excess of certain amino acids found in the Murchison meteorite seems to push the problem of the origin of biological chirality out into the cosmos. Most probably, there was never any racemic life using both L and D monomeric units in the chains. In the context of life's origin, the most relevant aspect of chirality is homochirality. The choice of the sign L or D may be just due to a chance event.

And importing life itself? The idea that life arrived on Earth from another star system, known as panspermia, was originally put forward by Richter and Arrhenius. Recent discoveries have given new support to the idea of panspermia. These are: (1) the identification of meteorites of lunar and probably also martian origin; (2) the probability of small particles reaching escape velocities by the impact of large meteorites on a planet; (3) the ability of bacterial spores to survive the shock waves of a simulated meteorite impact; (4) the high UV-resistance of microorganisms at the low temperature of deep space; and, (5) the high survival of bacterial spores over extended periods in space provided they are shielded against the intense solar ultraviolet radiation or are coated by a mantle of absorbing material which attenuates the solar UV radiation (Weber and Greenberg, 1985; Horneck, 1995). Even if panspermia is possible, it will not tell us how life started in another star system.
The clues which may help chemists to understand the emergence of life on Earth about four billion years ago have been erased by plate tectonics, the permanent presence of liquid water, the unshielded solar ultraviolet radiation and by life itself. However, the early histories of Earth and Mars show similarities. Liquid water was probably once stable on the surface of Mars attesting to the presence of an atmosphere capable of decelerating micrometeorites. Therefore, primitive life might also have developed on Mars. Liquid water seems to have disappeared very early from the martian surface, about 3.8 billion years ago, before life, if any, became very active. In addition, Mars probably had no plate tectonics. Mars may store some well preserved clues of a still hypothetical primitive bacterial life. The recent analysis of the martian meteorite ALH 84001 yielded some evidence, but not a convincing proof, of ancient microbial life on Mars. American, Japanese, and European space agencies have planned a very intensive exploration of Mars. The NASA program includes Mars Global Surveyor orbiting Mars since September 1997. In addition to the high-resolution imaging of the surface, the scientific objectives include the study of both the surface and the atmosphere. Mars Surveyor '98 Orbiter will monitor the daily weather and atmospheric conditions (wind, temperature profiles, water vapor, and dust) while the lander will record local meteorological conditions near the martian South pole and analyze samples of the polar deposits for volatiles (water, carbon dioxide). As part of the Mars Surveyor Program, NASA plans to send one or two spacecraft to Mars during both 2001 and 2003 launch windows, to support the return of samples using the 2005 opportunity and bring them to Earth in 2008. Mars Surveyor 2001 Orbiter will conduct mineralogical mapping of the entire planet. The corresponding lander will deliver a small rover to collect rock, soil, and gas samples for later return to Earth. Exobiology interests are included especially in the rover mission objective to characterize in situ sites where the environmental conditions may have been favorable for the preservation of evidence of possible prebiotic or biotic processes. The NASA Mars 2003 mission is expected to be a reconnaissance mission to prepare for a Mars sample return mission in 2005.

The Japanese Planet-B Mission was launched in July 1998. Its primary goal is to study the martian aeronomy with particular emphasis on the interaction of the upper atmosphere with the solar wind. ESA will launch Mars Express in June 2003. The orbiter will include instruments to study the surface mineralogy and the atmosphere. If the launch capability permits, landers will be designed to run exobiology studies of the subsurface.

Finding an extinct terrestrial-like life on Mars would be a major discovery. It would indicate that terrestrial life started with a rather simple set of autocatalytic molecules. If by a stroke of good fortune, it could be shown that the martian life used D-amino acids, for example, this would exclude any ancient panspermia from Mars to the Earth and would leave the sign of terrestrial homochirality to a pure chance event. Within the solar system, Europa may have an ocean of liquid water beneath its icy crust as suggested by data and theory. If submarine volcanism exists on Europa, the question arises of whether such activity could support life as on volcano-hydrothermal sites on the Earth's sea floor. New planets have been recently discovered beyond the solar system. On October 6, 1995, Mayor and Queloz (1995) announced the discovery of an extrasolar planet orbiting around a eight billion year old star called 51 Pegasus, forty-two light years away within the Milky Way. The suspected planet takes just four days to orbit 51 Pegasus. It has a surface temperature around 1,000 °C and a mass about 0.5 the mass of Jupiter. One year later, seven other extrasolar planets were identified. Among them, 47 Ursae Majoris has a planet with a surface temperature estimated to be around that of Mars (−90 to −20 °C) and the 70 Virginis planet has a surface temperature estimated around 70-160 °C. The latter is the first known extrasolar planet whose temperature might allow the presence of liquid water. How to detect extrasolar life will probably be a formidable challenge for astronomers and radioastronomers in the next century. The detection of water and ozone (an easy detectable telltale signature of oxygen) in the atmosphere will be a strong indication but not an absolute proof. The detection of an electromagnetic signal (via the SETI program) would be more convincing but probably more problematic. Such discoveries would over joy chemists, who suspect that life is universal because organic molecules and water are universal, but who need experimental proofs to claim it.

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