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Origin of Biological Macromolecules on the Young Earth

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The crux of the riddle of the origins of life on this Earth lies in understanding how the first biopolymers were formed. The synthesis of a host of biologically essential macromolecules – the proteins, carbohydrates, DNA, RNA, lipids, etc. – without the intervention of a cell, is astounding. It is a question of how the egg came without the hen. The answer will be of immense significance not only for understanding origin of life on our planet but also for clearly assessing the possibility of life in other regions of the universe.

Conditions on the early Earth were obviously favourable for the synthesis and stabilisation of biopolymers. What were these conditions ? The scenario must be examined from many different angles before even a hazy picture is formed, of the possible mode of the origin of biopolymers.

Key Words : Prebiotic, Evolution, Organics, Biomolecules

The Young Earth

Origin of the Earth

Radiometric evidence from meteorites and the moon indicates that the formation of the solar system was initiated @4.6Ga (Ga=10^9 years) ago. The gravitational collapse of interstellar matter produced, initially, an accretion disc containing mainly hydrogen, helium and stellar dust (heavier elements) from Nova and Supernova explosions of stars from earlier generations. The greatest mass became concentrated near the centre resulting in the formation of the Sun. In the outer regions, condensation led to the formation of planetesimals which further accreted within 10^6 to 10^8 years to form the protoplanet Earth (Condie 1989). Accretion was probably homogeneous rather than inhomogeneous. As accretion continued, the kinetic energy of the impacting planetesimals increased the temperature of the Earth to a point at which iron oxides were reduced. Further accretion caused melting of the iron which moved towards the center of the Earth forming the core. This highly exothermic process resulted in fusion and separation of a metal core and a molten silicate mantle. The early reducing atmosphere was either lost or blown away by solar winds from the Sun during its T-Tauri stage of evolution (Condie 1989, Stevenson 1983).

Evolution of the First Life Forms

Although planetary accretion was completed by 4-5 Ga, the Earth and other planets were subjected to intense meteorite bombardment till about 3.9 Ga. The bombardment would have penetrated to about 100-200 km of the crust and destroyed the pre-existing crust. No life could have survived such conditions (Ernst 1983, Pichamuthu 1985, Maher & Stevenson 1988). Any life which could have formed during the relatively quiescent periods would have been totally destroyed until a little before 3.8Ga (Maher & Stevenson 1988, Oberbeck & Fogleman 1989a, 1990). Evidence from the oldest known sedimentary rocks, the Isua supracrustal sequence in Greenland, which is dated around 3.8Ga old (Moorbath et al. 1973, Compston et al. 1986) suggests the presence of a significant biomass by this time (Schidlowski 1988). Even though there are no fossils in the Greenland rocks, the presence of apatite and the enrichment of ^{12}C over ^{13}C provides a

'chemical signature' for the evidence of life prior to 3.8Ga (Mojzsis et al. 1996). However, evidence for Archaean microfossils as old as 3.46Ga is available in a carbonaceous chert from Warrawoona Group in Western Australia, as stated by Schopf (1993). Archaean cellular microfossils suggest that the earliest organisms were prokaryotes. The most primitive group were the archaebacteria which used RNA for the synthesis of proteins, followed by eubacteria which had advanced replication processes and could probably photosynthesise. The first autotrops appeared as cyanobacteria, which is evidenced in the Warrawoona stromatolite formations (Condie 1989, Moorbath 1994). From the existing evidence, it is now more or less accepted that the unbroken evolution of life had commenced by 3.8 Ga (Eigen et al. 1989, Moorbath 1994). The process probably took about 10 Ma (Ma=10^6 years) to 25 Ma (Oberbeck & Fogleman 1989b, Lazcano & Miller 1994). The time required for the first appearance of biopolymers has not been evaluated but it certainly must have occurred within a much shorter span of time.

Composition of the Atmosphere

The composition of the atmosphere around the period 3.8 Ga has been the subject of some controversy. Three possible sources are considered for the Earth's atmosphere -- residual gases remaining after the Earth's accretion, extraterrestrial sources and degassing of the Earth. A significant depletion in rare gases in the Earth compared to carbonaceous chondrites and the Sun, indicates that the primitive atmosphere has been lost, probably due to a T-Tauri solar wind. Most investigators, therefore, agree that the present atmosphere originated by degassing of the mantle and crust (Condie 1989). However, due to various uncertainties, the possible range of compositions for the primitive atmosphere vary widely. These range from a highly reducing one containing CH_4, NH_3, H_2, He and H_2O (Oparin 1957) to a non-reducing CO_2-N_2-H_2O atmosphere as proposed by Rubey (1951). Holland (1984) developed a multistage model for the evolution of the Earth's atmosphere, wherein he concluded that the primordial atmosphere was mildly reducing and dominated by H_2O, H_2 and CO. Abelson (1966) proposed that the prebiotic atmosphere could have been CO, H_2 and N_2. However, regardless of whether the carbon was released as CH_4, CO or CO_2, photochemical reactions would have resulted in rapid oxidation to form CO_2 (Kuhn & Atreya 1979, Kasting et al. 1983). The partial pressure of CO_2 could have been as high as 10 bars (Walker 1985). This would decrease with time by deposition of marine carbonate sediments (Condie 1989).

Oceanic Conditions

Since life probably originated in the oceans, a knowledge of the early ocean environment can provide important clues to the origin of biological molecules. It is generally accepted that an initially acidic ocean would have rapidly reacted with rocks causing a rapid increase in *p*H. Therefore, the ocean water would probably have been slightly acidic or slightly alkaline (Holland 1972, 1973, Condie 1989). Sedimentological studies also suggest that average surface temperatures were neither above 60°C nor below a few °C (Walker et al. 1983, Pichamuthu 1985, Nisbet 1987). Limestones, which are found in some of the earliest sedimentary rocks (3.0 Ga), suggest that the surface water must have been saturated with respect to calcite (Holland 1973). Archean carbonates are, however, a rarity. Detrital quartz is abundant as are greywacke and argillite (Windley 1984, Pichamuthu 1985). The appearance of banded iron formations (BIF) at around 2 Ga suggests the transformation from an anoxygenic to an oxygenic atmosphere (Windley 1984). It may be inferred that the water in which the first biomolecules were synthesised were rich in silica, Ca^{2+}, Mg^{2+}, Fe^{2+} and other salts and had a *p*H close to 7.0.

Formation of the First Simple Biochemicals

A possible route for prebiotic synthesis of biochemicals was first demonstrated by Miller (1953) when he showed that an electric discharge passed through a mixture of CH_4, NH_3, water vapour and H_2 produced a variety of organic compounds, particularly amino acids. The key step was

apparently the formation of the HCN (Miller 1957). Various other sources of energy such as uv, radioactivity, volcanoes, shock waves, etc., may also have been responsible for the synthesis of such monomers (Miller 1987).

Oro (1960) first demonstrated the production of adenine under prebiotic conditions from NH_4CN. Ponnamperuma et al. (1963a) also obtained adenine after irradiating with electrons, a reducing Miller-type atmosphere. When the amount of NH_3 was less than that used by Miller (1953), a lower yield of amino acids was obtained but various other compounds like hydroxy acids, aliphatic acids, etc., were also formed (Wolman et al. 1972). Using only mildly reducing atmospheres, such as CO, N_2 and H_2, drastically lowered the amount of amino acids formed (Abelson 1966, Miller & Schlesinger 1983); similarly, a mixture of CO_2, H_2 and N_2 produced glycine and other amino acids in low yields.

Production of other biochemical monomers like guanine, cytosine and thymine using different starting materials like carboxamides, cyanoacetylene, etc., has been demonstrated (Oro & Kimball 1962, Miller & Orgel 1974). Imidazole was observed to form from glyoxal, ammonia and formaldehyde (Oro et al, 1984). All biological purines may be produced by condensation of imidazole derivatives with monocarbon compounds; thus, the reaction of 4-amino-imidazole-5-carboxamide with urea produced guanine and xanthine (Oro & Kimball 1962). Cytosine may be produced from cyanoacetylene and urea/cyanate; this may be subsequently deaminated to uracil (Miller & Orgel 1974); uracil can react with formaldehyde to produce thymine (Stephen-Sherwood et al. 1971). The production of other biochemicals such as sugars has also been demonstrated under prebiotic conditions. Sugars readily formed when formaldehyde polymerised under alkaline conditions (Decker et al. 1982); a complex mixture of more than 50 different pentoses, hexoses and other sugars were obtained (Decker et al. 1982). Exhaustive details regarding the formation of biochemical monomers are available in several review articles (Miller & Orgel 1974, Orgel & Lohrmann 1974, Fox & Dose 1977, Ferris & Hagan 1984, Oro et al. 1990).

These experimental results demonstrate that organic monomers can be synthesised in fair yields under a wide variety of conditions. As the oxidation state of the gases is increased from CH_4 to CO then to CO_2 and from NH_3 to N_2, both yield and product diversity decrease (Chang et al. 1983). However, in spite of many limitations to various proposed models, there is little doubt that prebiotic synthesis experiments have been notably successful. They have unequivocally demonstrated that the monomeric building blocks of proteins, nucleic acids and carbohydrates can be synthesised from reducing atmospheres or from intermediates and products obtained in the former. They also help in explaining the occurrence of such compounds in extraterrestrial sources such as meteorites, comets, etc.

Origin of Biological Macromolecules

In contrast to the clear picture available on the prebiotic formation of biological monomers on the young Earth, there is much ambiguity regarding the manner of synthesis of the macromolecules which are essential for the first life to evolve. In general, a variety of catalytic agents have been proposed to promote the polymerisation of the monomers to the more complex forms. Such polymerisation reactions have been studied not only in an aqueous medium (which is the most relevant prebiotic condition) but also in the dry state and in the gaseous state.

Catalysis by Organic Agents

Simulated primitive - earth experiments yield several compounds which are capable of acting as condensing agents. These include, hydrogen cyanate, cyanogen, cyanovinylphosphate, cyanoguanidine, amidinium carbodiimide, amino acid phosphoramide, etc. (Calvin 1969). Cyanamide, which was presumably synthesised on the primitive Earth from HCN, is considered as one of the best condensing agents. Condensation by cyanamide has been observed to yield significant

amounts of oligopeptides (Hawker & Oro 1981), oligonucleotides (Odom et al. 1982) and phospholipids (Rao et al. 1982). Thus, Ponnamperuma and Peterson (1965) exposed aqueous solution of glycine and leucine to uv light in the presence of cyanamide and obtained various dipeptides in 1% yield. Polymerisation products were also obtained when dicyandiamide was used (Steinman et al. 1965). Proteinoids may form from amino acids by thermal polycondensation when sufficient aspartic acid and glutamic acid or lysine are present (Fox & Harada 1960). The synthesis of oligonucleotides has also been achieved using imidazoles which have been demonstrated to form under primitive Earth conditions (Oro et al. 1984, 1990). Joyce et al. (1984) observed that imidazole derivatives that polymerise on a poly (C) template can give rise to oligo (G) nucleotides with chain lengths from 2-40. Oro et al. (1984) concluded that the charge relay group (-N-C-N-) present in imidazoles, carbodiimides, cyanamides, etc., is essential for the synthesis of phosphate-diester and pyrophosphate bonds.

Direct synthesis of polymerised products from aqueous solution of ammonium cyanide was achieved by Lowe et al. (1963); molecular weights of the polyamino acids were in the range of 100-5000. Polymeric materials have also been obtained from hydrogen cyanide (Oro & Kimball 1962, Lowe et al. 1963, Harada 1967). Hydrolysis of these polymers results in amino acids but the exact nature of these polymers is still uncertain (Fox & Dose 1977).

Akabori (1959) proposed that the synthesis of protein may be visualised as occurring by progressive substitution of preformed polyglycine, referred to as fore-protein. In the first stage, HCHO, NH_3 and HCN react to form aminoacetonitrile; in the second stage, the nitrile polymerises on a solid surface to form polyglycine. Subsequently, various amino acid residues are produced. Later, Ponnamperuma and Woeller (1967) and Chadha et al. (1971a, b) demonstrated the formation of aminoacetonitrile by electric discharge through a mixture of CH_4 and NH_3. Mathews et al. (1984) proposed that heteropolypeptides could be formed directly from HCN and water; vapour phase polymerisation would produce polyaminomalonitrile; these would react further with HCN to produce heteropolyamides and then with water to form heteropolypeptides. On the other hand, Kawashiro et al. (1989) observed that methyleneaminoacetonitrile, formed by reaction of aminoacetonitrile with HCHO, produced various nitriles and glycine derivatives but did not produce compounds of biological significance, such as peptides and hydroxy amino acids. However, another compound, α-aminopropionitrile, produced polypeptides (Kawashiro et al. 1984). The coupling of amino acids into polypeptides may also be achieved by oxidative acylation with activated amino acids such as thioester derivatives (Liu & Orgel 1997).

For the formation of polymers of nucleotides, polymetaphosphate ethyl ester (PMP) appears to be quite efficient. This type of condensing agent is, however, unlikely to form under primitive Earth conditions (Fox & Dose 1977). Fox (1965) presented some arguments to show that PMP could indeed have formed on the young Earth. According to him, nucleosides as well as the polymers can be synthesised using sugars, bases and phosphates, in the presence of PMP. Fox (1965) also reported the formation of polyglycosides by heating monosaccharides at 50-60°C with PMP in organic solvents. Glycosyl phosphates could be formed from a solution of phosphate and glucose using cyanogen (Degani & Halmann 1971).

Template directed polymerisation reactions have been extensively studied by Orgel and his coworkers. They showed that oligonucleotides could act as templates to facilitate the synthesis of complementary oligomers from activated mononucleotides (Inoue & Orgel 1983, Joyce 1987). Ibanez et al. (1971) reported the polymerisation of TMP in aqueous solution using imidazole as a condensing agent; polymerisation with cyanamide in the presence of polyornithine as template was also reported, though yields were low in both cases. Oro and Stephen-Sherwood (1973) reviewed the literature on oligomerisation of nucleotides and observed that such reactions occur under drying conditions using various condensing agents but none of these

methods are representative of prebiotic conditions. It was suggested that oligonucleotides of 12 units length could serve as templates. However, according to James and Ellington (1997), nucleic acid replication via oligonucleotide ligation is extremely prone to errors and is an unlikely route for the origin of life. Joyce et al. (1984) observed polymerisation of 2-methyl-imidazole derivatives using random poly (C,U). A model for autocatalytic synthesis of a tetranucleotide analog has been presented by Zielinsky and Orgel (1987). Schwartz et al. (1987) observed that the acyclic analog 9-(1, 3- dihydroxy-2-propoxy)-methyl-guanine can polymerise in the absence of a template but that the reaction proceeded more efficiently in the presence of poly (C). According to Schwartz and Orgel (1985), this analog could have readily formed under prebiotic conditions from guanine, formaldehyde and glycerol. Later, Schwartz (1997) proposed that a backbone structure based on ribose-2,4-diphosphonic acid could have formed by simple reactions involving phosphonic acids. Rembold and Orgel (1994) reported that single-stranded regions of poly (G) could act as templates for oligo (C) synthesis. The first ancestral genetic system may, thus, have consisted of nucleic acid - like informational replicating macromolecules derived from prochiral monomeric units (Joyce et al. 1987, Joyce 1989).

A further step in this direction would be a general autocatalytic process in which the reaction product serves as the catalyst for its own synthesis by recognising and promoting coupling of reactants. One example of this for nucleic acid bases has been described above. However, the feasibility of molecular self-replication for peptides has not been clearly established (Orgel 1992). Only recently, an example of a self-replicating peptide has been reported (Lee et al. 1996). Lee et al. (1996) showed that a 32-residue α-helical peptide could act autocatalytically in templating its own synthesis in dilute aqueous solution.

A completely different viewpoint was advanced by Mehta (1986) who suggested that amino acids arranged around a prebiotically formed stable molecule could become linked to form a miniprotein. Later, deDuve (1991) proposed that prebiotic catalysts were organic oligomers formed by the random assembly of small abiotic building blocks. Bar-Nun et al. (1994), in a further development of this idea, tried to determine whether a non-random assembly of building blocks (amino acids) could occur. They observed that free amino acids could display catalytic activities and concluded that assemblies of amino acids were formed around substrate molecules through weak interactions. These could, in principle, catalyse many prebiotic reactions.

Catalysis by Polyphosphates

Several workers have proposed that polyphosphates could cause phosphorylation and condensation of biomolecules on the early Earth (Ponnamperuma et al. 1963b, Rabinowitz et al. 1969, Yamagata et al. 1982, Yamanaka et al. 1988). Rabinowitz et al (1969) reported that glycine could dimerise to glycylglycine in the presence of trimetaphosphate under alkaline conditions. Harada and Fox (1965) studied thermal condensation of amino acids with polyphosphoric acid at 70-130°C. Even at 100°C, polymers with molecular weights ranging from 5000-15000 could be obtained. Ponnamperuma and Chang (1971) pointed out that orthophosphates may be readily converted to condensed phosphates at relatively low temperatures and these could act as phosphorylating agents for nucleosides. Miller and Parris (1971) suggested that pyrophosphate, which can be readily synthesised by the reaction of cyanate with hydroxy apatite, may have played an important role in the polymerisation of organic compounds. Yamanaka et al. (1988) observed that diglycine condenses to tetra- and hexa-glycine in the presence of trimetaphosphate; maximum yields were obtained at around *p*H 7. Yamagata et al. (1982) showed that an aqueous solution of adenosine could be phosphorylated to AMP by phosphorus pentoxide, the major products being 2′- and 3′-AMP. Yamagata et al. (1991) later showed how water soluble polyphosphates could have formed in the early

Earth from volcanic gases. Further, the phosphate would be continuously recycled by volcanic processes causing a continuous production of polyphosphates. Keffe and Miller (1996) reported that although pyrophosphates could be produced from orthophosphates by nitriles, acid anhydrides, lactones, etc., these processes could not have been relevant in the prebiotic ocean. Kolb and Orgel (1995) observed that glyceric acid is phosphorylated to 2- and 3-phosphoglyceric acids in the presence of trimetaphosphates in alkaline solution. This reaction is particularly significant because it converts a simple prebiotic molecule into phosphate derivatives that are important to carbohydrate metabolism.

Mineral Catalysts

Goldschmidt (1945) was probably the first to suggest that complex organic molecules could have evolved on the Earth by adsorption on mineral surfaces. Bernal (1951) independently stressed the potential importance of clay minerals. He proposed that clays near the hydrosphere--lithosphere interface might have adsorbed organic molecules thereby providing protection from uv-radiation, increasing the concentration and facilitating condensation by surface catalysis. Degens and Matheja (1971) extensively studied the catalytic action of about 60 different mineral templates on amino acids, urea, glucose, purines, pyrimidines and carboxylic acids. They observed that at 80°C, polymers of amino acids formed in aqueous solution; in the absence of minerals, polymerisation did not take place. The peptide chains contain 7-15 amino acid residues. With nucleic acid bases as well as sugars, polymerisation did not occur. However, the addition of phosphates induced the formation of polynucleotides. Kaolinite was found to be a better catalyst than montmorillonite. Forced cycles of wetting and drying were observed by Lahav et al (1978) to cause the formation of oligo-peptides up to five residues in length. Cations at low *p*H enhanced the adsorption of amino acids and nucleic acid bases (Ponnamperuma et al. 1982). Lahav and White (1980) suggested that clays may contain some structural heterogenity which as a template may repeatedly produce certain sequences of amino acids in peptides. Cairns-Smith (1982) put forward a 'radical' mineral theory of the origin of life. He proposed that in the first organisms, the major control structures—the catalysts, membranes, genes— were all inorganic in nature and these were gradually replaced during the early phases of evolution as competence in the control of organic chemical reactions improved. Thus, it is possible that micas could have been the primitive genetic material, zeolites and sulphides the primitive catalysts, oxides/ hydroxides the primitive membranes, etc. (Cairns-Smith et al. 1992). So far, however, no experimental evidence in support of the mineral life hypothesis is available.

The mechanisms of catalytic actions of clay minerals have been studied in great detail over the years. In an early review of this topic by Fripiat and Cruz-Crumplido (1974), it was suggested that amino acid polymerisation on clay can proceed via carboxyl activation. Thus, an ionised carboxyl group can react with Al^{3+} on a kaolinite crystal, followed by attack of an amino group. Clays may also cause preferential polymerisation due to selective interaction with adsorbed monomers and steric factors. The zwitterion form of amino acid on the clay surface undergoes ready polymerisation on dry heating, e.g. at 140-244°C (Fripiat et al. 1966). Degens and Matheja (1971) also obtained polymers of molecular weights from 1000-2000, when clay-amino acid complexes were heated at 140°C. In studies on the effect of wetting/drying cycles, Lawless and Levi (1979) observed that cations on the clay may act as catalysts; the order of catalytic activity observed by them was $Cu^{2+} > Ni^{2+} > Zn^{2+} > Na^{+}$. In their review article, Ponnamperuma et al. (1982) suggested that clays do not act as catalysts or condensing agents in the polymerisation of free amino acids or nucleotides under aqueous conditions. Clays may act as Bronsted acids or Lewis acids by providing protons or accepting electrons. Clays do not affect the unfavourable energy of the dehydration reaction which must be lowered either by using activated monomers or condensing agents or adding energy. However,

since clays increase the concentration and degree of interaction of the reactants, the polymers formed in the presence of clays have longer chain lengths than those formed in their absence. Other theoretical and thermodynamic aspects of the role of clay minerals in prebiotic polymerisation processes have been considered in great detail by Coyne (1985) and Collins et. al. (1988).

Although heat is the most natural 'condensing' agent, chemical agents such as cyanate derivatives or polyphosphates also initiate condensation. Flores and Leckie (1973) obtained dipeptides on heating cyanate, apatite and glycine in the solid state at 95°C. Condensation was probably brought about by the formation of an aminoacylphosphate intermediate. Paecht- Horowitz et al. (1970) and Paecht-Horowitz (1971) studied amino acid polymerisation in the presence and absence of montmorillonite, using aminoacyladenylates. The presence of montmorillonite resulted in a higher yield and chain length of polymers and a discrete series of peptides which was not found in the absence of clay. According to Paecht-Horowitz (1973), clays catalyse polymerisation only when the amino acid is small enough to enter between the sheets of the clay. Paecht-Horowitz (1984) further observed that peptides adsorbed on the clay, prior to polymerisation, influence the reaction. Adsorption prior to reaction produces a certain order in the aggregates of the clay particles which might induce better reaction results. White et al. (1984) proposed that periodically dried minerals provide catalytically active surfaces for the formation of peptides; this is an *in situ* activation which does not necessitate the accumulation of hydrolytically unstable activating agents. Budjak et al. (1995) studied polymerisation of peptides, adsorbed on Ca^{2+}- and Cu^{2+}-montmorillonites, at 80°C. Much higher yields of oligomers were obtained with Ca^{2+}-montmorillonite rather than with the Cu^{2+}- form. Paecht-Horowitz and Eirich (1988) observed spontaneous polymerisation of amino acid adenylates on Na^{+}-montmorillonite in dilute neutral suspension after peptides were adsorbed on the clay. They found that the degrees of polymerisation of the peptides obtained depended on the amounts of polypeptides that were pre-adsorbed. Yanagawa et al. (1984) obtained glycine polymers with an average chain length of 12 when glycinamide was subjected to wetting -drying cycles at 80°C; the resulting polymers had leaf-like structures. Ferris et al. (1996) studied the condensation of nucleotides and amino acids on montmorillonite, illite and hydroxyapatite in the presence of imidazole and carbodiimide derivatives; oligomers upto 55 monomers long were obtained. They concluded that when monomers are successively 'fed' to the system, polymerisation is more efficient; polymerisation takes place on the mineral surfaces in a manner akin to solid-phase synthesis of biopolymers. Formation of polypeptides in the presence of salts alone has also been achieved. Thus, heating amino acids in a 'modified sea medium' resulted in formation of polymers (Okhiana 1982). The presence of Cu^{2+} was also reported to catalyse polymerisation (Rode & Schwendinger 1990, Schwendinger & Rode 1992).

In studies on the catalytic activity of silica surfaces, Basiuk et al. (1991) and Basiuk (1992) observed that when amino acids were sublimed in the presence of silica, the main products are diketopiperazines. Basiuk et al. (1995) also studied the thermodynamics of the adsorption of small biological molecules on silica. Carboxylic acids (including amino acids and peptides) showed very weak adsorption; nucleosides and their phosphates exhibited much higher adsorbability. Sugar phosphates were reported to be formed by the catalytic activity of several metal hydroxide minerals on glycolaldehyde phosphate in dilute weakly alkaline solution; the major products were aldotetrose-2,4-diphosphates and aldohexose-2,4,6-triphosphates (Pitsch et al. 1995).

Reactions of nucleotides and nucleosides at mineral surfaces have also been extensively studied. Ferris and Hagan (1986) observed that 3′-AMP adsorbed on montmorillonite was converted to 2′,3′-cyclic AMP by surface catalysis. Adsorption studies with several purine and pyrimidine nucleotides, at various *p*H, on montmorillonite were

done (Lawless et al. 1985). The results showed preferential adsorption that is dependent on the *p*H and the nature of the exchangeable cation. Similar studies were also carried out by Banin et al. (1985) and Ferris et al. (1989a) using montmorillonite, by Hermes-Lima et al. (1990) using calcium phosphate and by Orenberg et al. (1985) using calcium sulphate.

The formation of oligonucleotides from TMP by reaction on montmorillonite in the presence of cyanamide at 90°C was reported by Ibanez et al. (1971). Polymerisation of AMP adsorbed on basalt surfaces, by the action of γ-rays, was observed by Ortoshchenko et al. (1985). Ferris and Kamaluddin (1989) obtained oligomers when deoxyribonu-cleotides adsorbed on Na^+-montmorillonite were treated with a water soluble carbodiimide. However, no catalytic activity was observed with a Cu^{2+}-montmorillonite although adsorption of AMP was very strong (Ferris et al. 1989b). Na^+-montmo-rillonite was also found to catalyse the polymerisation of 5′-phosphorimidazole of uridine in aqueous solution to give polymers as long as 7-mers (Ding et al. 1996). Later Ertem and Ferris (1996) demonstrated that heterogeneous oligocytidylates, formed by montmorillonite-catalysed condensation of monomers, could serve as templates for the synthesis of oligoguanylates. Furthermore, oligocytidylates with the unnatural 2′,5′-linkages could also direct synthesis of oligoguanylates. A radically different viewpoint was presented by Orgel (1986) who proposed that mononucleotides, adsorbed on the surfaces of microcystals of inorganic phosphates such as hydroxyapatite, could act as templates to assemble complementary mononucleotides from solution and the phosphate groups of the assembled nucleotides could facilitate nucleation of a second hydroxyapatite cystal. This would provide a mechanism of replication that is subject to natural selection. This proposal is somewhat on the lines of Cairns-Smith's (1982) suggestion that the first replicating objects were clay crystals.

Biochemical Synthesis in Hydrothermal Systems and Volcanic Environments

Corliss and coworkers were the first to study active submarine hydrothermal vents at an ocean ridge and identify mid-oceanic rift structures as likely sites for chemical evolution of organic compounds (Corliss et al. 1981). The fact that the most primitive organisms were thermophiles lent support to this theory. Hydrothermal systems provide a 'life-reactor' with large gradients of temperature, *p*H, concentration of chemical components and mineral catalysts. Non-equilibrium conditions are always maintained and a continuous flow of components connects different chemical environments. Various other models for the origin of life in hydrothermal systems have been summarised by Holm (1992). The major objections to this theory were advanced by Miller and Bada (1988) but all of their arguments have been shown to be invalid (Holm 1992). Baross and Hoffman (1985) also argued that the numerous physical and chemical gradients in hydrothermal vents provide the necessary multiple pathways for the abiotic synthesis of chemical compounds. They showed the analogies between contemporary and Archean hydrothermal systems and suggested several hypotheses for the evolution of life in Archean vents which can be tested in present day systems. Macleod et al. (1994) proposed that biomolecules and life forms could have evolved in non-volcanogenic, medium temperature, alkaline submarine hot springs. On the other hand, Podkletnov and Markhinin (1981) suggested that ash clouds produced by volcanoes could act as large chemical reactors with a wide range of temperatures and pressures, powerful electric discharges and a large catalytic surface. In volcanic eruption products investigated, 54 carbon containing compounds, including those of biological significance, could be identified. Basiuk and Gonzalez (1996) reaffirmed the importance of volcanic ash-gas clouds for the abiotic synthesis of organic molecules. They have reviewed the available data on this environment, its chemical and physical parameters and suggested experimental conditions for simulation studies.

Panspermia

Arrhenius (1908) first speculated that spores from another planetary system propelled by sunlight could have seeded the Earth. More recent panspermia theories suggest that life exists in outer space and is transported to planetary surfaces by meteorites, asteroids or comets (Hoyle & Wickramasinghe 1978). Thus, according to Wickramasinghe and Hoyle (1998), extraterrestrial microbes exist in the Kuiper belt as evidenced by the extreme redness of a class of objects present therein. Alternatively, life could have originated in another planet in our own solar system and have been transported to Earth by impact (Melosh 1988, Moreno 1988). Recent discovery (McKay et al. 1996) of what appear to be fossilised microbes (figure 1) in a piece of meteorite believed to have been a part of Mars blown out by impact, lends credence to this hypothesis, but this needs validation. According to the theory of Directed Panspermia, life may have been purposely spread through space from another planet through the action of intelligent beings (Crick & Orgel 1973, Crick 1981). The primary arguments against panspermia are the survival of the organisms in their journey through space and the availability of a suitable environment on Earth for their survival. It is interesting to note that Long Duration Exposure Facility experiments in space and laboratory simulations cannot rule out the possibility that bacteria and their spores could survive long transits in space (Horneck 1981, Weber & Greenberg 1985).

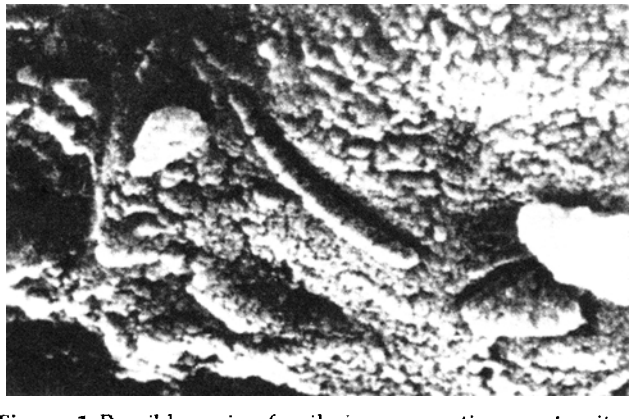

Figure 1 Possible microfossils in a martian meteorite (NASA release)

Exobiology : Information from Outer Space

An important source of information on how and why life originated on the early Earth, is the record of the early solar system as preserved in comets, asteroids, the Moon, Mars and a few other planetary bodies.

Interstellar and Circumstellar Dust in Prebiotic Chemistry

In interstellar and circumstellar regions, astronomers have identified gaseous organic molecules with up to 13 atoms [e.g., $H(C \equiv C)_5$-CN] and nearly 100 other molecules containing H, N or C atoms (Space Studies Board 1990, Irvine 1980, 1995). Evidence also suggests the presence of silicates, amorphous and graphitised carbon, polycyclic aromatic hydrocarbons, fullerene-type carbon clusters and highly branched macromolecular organic compounds (Basiuk & Gonzalez 1995). It is interesting to note that the key ingredients for prebiotic organic molecules, viz., H_2O, NH_3, HCN, H_2, etc., are found in the dust. Numerous silicate minerals are also present in the dust. Thus, interplanetary dust contains olivine, pyroxene, magnetite, etc.; cometary dust contains various silicates, oxides and hydroxides, carbonates, Na-, Ca- and Al-sulphates and Fe-sulphides (Basiuk & Gonzalez 1995). Such inorganic particles could catalyse organic chemical reactions. Transport of dust to the Earth would provide an important source of organic compounds and allow dust-driven catalytic formation of prebiotically important compounds (Basiuk & Gonzalez 1995, Whittet 1997).

Organic Molecules in Comets and Meteorites

Observations of Comet Halley showed that cometary nuclei are small bodies in which frozen water comprises about 80% of the total volatile solids. The remaining 20% includes HCOOH, HCHO, CO_2, CO, HCN, C_2H_2, etc. (Delsemme 1988, Oro & Mills 1989). It was suggested that cometary collisions may have provided the primitive Earth with an important source of volatiles which subsequently may have been the precursors for the prebiotic synthesis of

biochemicals (Oro 1961). In fact, important biochemicals like adenine and other purines are probably present in comets as observed in Comet Halley (Kissel & Krueger 1987). Evidence for the presence of biological macromolecules is not yet available. However, it is now quite well recognised that comets represent an important source of both free-energy and volatiles for the Earth and may have created environments in which prebiotic synthesis may have occurred (Oro et al. 1992). Huebner and Boice (1992) reviewed information from recent spacecraft encounters and ground-based observations of cometary comae and concluded that complex organic molecules found in comets may be a source of abiotic molecules that led to the origin of life. Oberbeck and Aggarwal (1992) suggested that cometary agents could have been more important than endogenous ones for initial evolution of amino acids; they concluded that chemical evolution could have occurred even during periods of intense bombardment of the Earth before 3.8 Ga. Meteorites, which mostly originate in the asteroid belt and sometimes from the surfaces of Moon or Mars, are an important source of information on organic materials in the early solar history.One group known as the Type 1 carbonaceous chondrites (C1) is of particular interest in prebiological studies because of its high content of organic matter. Analysis of the Murchison meteorite revealed the presence of a wide variety of amino acids, mono- and di-carboxylic acids, urea, amides, ketones, aldehydes, alcohols, amines, N- and S-heterocycles (Hayes 1967, Kvenvolden et al. 1970, Nagy 1975). Of the 74 amino acids found in samples of the Murchison meteorite, 8 are present in proteins, 11 have other biological roles and the remaining 55 have only been found in extraterrestrial samples (Cronin 1989). Organic matter in carbonaceous chondrites can be separated into three fractions. One fraction is insoluble in chloroform and methanol. The two other fractions are chloroform-soluble hydrocarbons and methanol-soluble polar organics (Bunch & Chang 1980, Hartman et al. 1993). Hartman et al. (1993) proposed that the mechanism of formation of the polar organics on C1 carbonaceous chondrites may have also occurred during outgassing of the early Earth.

Samples of Orgueil meteorite contain about 5% by weight organic matter, the greater part of which is not extractable by organic solvents. Comparable aromatic substances are found on Earth in the form of kerogen (Sylvester-Bradley 1971). Hayatsu et al. (1968) proposed a Fischer--Tropsch type of pathway for the synthesis of a wide variety of hydrocarbons and nitrogenous compounds in carbonaceous chondrites. Wing and Bada (1992) proposed that polycyclic aromatic hydrocarbons in C1 and C2 carbonaceous chondrites are a product of high temperature synthesis rather than a thermal alteration product of pre-existing aliphatics. It is possible that the Earth's biologic precursors were delivered by late impacting meterorites and comets (Oro 1961, Lazcano & Oro 1981). Chemical reactions that produce organic compounds with greater thermal stabilities may occur during impact by condensation of the impact-produced vapour plume (Tingle et al. 1992).

Mineralogy of the carbonaceous chondrites indicates that alterations of minerals took place in the presence of water at low temperatures (Nagy et al. 1963, Clayton & Mayeda 1984). Phyllosilicates constitute the bulk of the matrix; carbonates, sulphides, ferrihydrite and spongy materials are also present (Barber 1981, Tomeoka & Buseck 1988). Many of these minerals are similar to those that are formed by aqueous weathering of rocks on the Earth.

Thus, it appears that many of the key ingredients for the formation of biological macromolecules are present in the meteorites --vital organic monomers, together with several of the proposed condensing agents, minerals which can act as catalysts, as well as water. In spite of this, there is no unequivocal evidence that life as such ever existed on the parent body or even that macromolecules of biological importance were ever found.

Biochemical Evolution on Other Planets

Knowledge of the processes that produce organic matter, wherever it occurs in the solar system, is central to our understanding of chemical evolution

on Earth. The planetary bodies and satellites in the outer solar system are of primary interest in this context because they are natural laboratories in which the chemical evolution of organic matter can be studied directly. The pathways for abiotic organic synthesis on the primitive Earth can be tested by studying the processes and products in other planets.

Mars is the extraterrestrial body which holds the greatest promise for answers to the origins of life. Public fascination with Mars as a home to extraterrestrial life began when the Italian astronomer, Giovanni Schiaparelli, studying Mars in 1877 drew a detailed map showing channels on its surface. Later, in 1903, Percival Lowell of USA suggested that numerous canals are present which have been excavated by denizens of the dying planet. This gave rise to numerous compelling tales of life on Mars. However, no unequivocal evidence for the existence of a martian biota were found from the earlier Mariner 4 and Mariner 6 images and from the later Viking Biology and Molecular Analysis experiments (Mazur et al. 1978, Space Studies Board 1990); also, no evidence of organic matter was found. However, Mars appears to have been particularly rich in water in the past as strongly evidenced by Pathfinder's images (figure 2), and had active volcanism, hydrothermal regions, anoxic conditions, cometary and meteorite impacts, etc. (Carr 1986, Pollack et al. 1987, Davis & McKay 1996). Thus, there are no conceptual obstacles to postulating that whatever led to the origin of life on Earth could also cause the origin of life on Mars (Oro & Mills 1989, Davis & McKay 1996). The latest piece of evidence in support of this hypothesis was obtained from a martian meteorite found in Antarctica. McKay et al. (1996) argued that the presence of polycyclic aromatic hydrocarbons and minerals like magnetite, gregite and pyrrhotite suggest the presence of life at about 3.6 Ga. Moreover, tubular and egg-shaped structures were also observed which appeared to be fossilised remains of martian microbes (figure 1). Their findings have, however, been disputed by Scott et al. (1997) who attributed all these characteristics to geological processes. More intensive studies on Mars, with samples from the Mars Rover Sample Return Mission, may greatly reduce the uncertainties about the origin of biomolecules and life (Space Studies Board 1990).

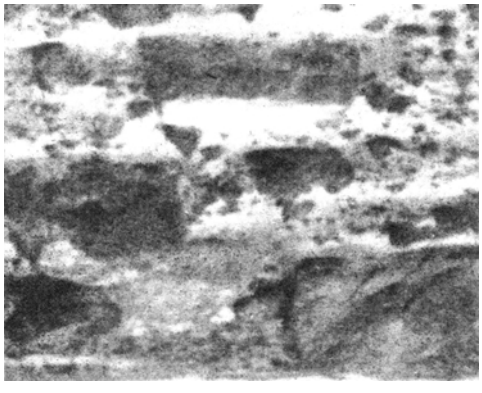

Figure 2 One of Pathfinders first images of Mars. Deposition of the boulders in a massive flood is indicated by their leaning in the same direction and their stacking against one another in the same way in which they lean (NASA release)

Titan, the largest satellite of Saturn, which has a dense N_2-CH_4 atmosphere rich in organics, is another likely region for evolution of biochemicals (Clarke & Ferris 1997). The absence of liquid water on Titan, the presence of oceans composed of liquid ethane, methane and nitrogen, together with liquid ammonia, suggests that there may be a pseudo-biochemistry going on in Titan's ocean where N-chemical groups substitute O-chemical groups; a tremendous richness of subsurface organic synthetic reactions is visualised (Oro & Mills 1989, Owen & Gautier 1989, Raulin et al. 1994). The Cassini-Huygens mission, which is expected to probe Titan's atmosphere, will provide an unique opportunity to study extraterrestrial abiotic organic processes with significant implications in the fields of exobiology (Raulin et al. 1994).

Suitable conditions for biomolecular synthesis may also exist on Europa and Ganymede, the satellites of Jupiter, which may have liquid water layer beneath a thin ice crust (Reynolds et al. 1987, Oro & Mills 1989). Hoyle and Wickramasinghe (1997)

postulate that the red coloration of planetary ices, for example, on the surface of Europa could be due to biological pigments. There is also speculation about life in liquid water clouds on Jupiter and Venus (Sagan & Saltpeter 1976, Davis & McKay 1996).

Further probes to the outer planets, comets and asteroids and beyond the planetary frontiers are expected to unravel pertinent questions concerning biochemical evolution and the origin of life on our planet. In particular, the Galileo spacecraft images of Jupiter and its moon Europa, the Pathfinder, Surveyor and the Sample-Return Mission (in 2005) probes on Mars, the Cassini spacecraft probe to Saturn and its moon Titan, the MUSES-C mission to an asteroid, Nereus, the Hubble Space Telescope and similar probes are likely to provide breakthrough information within the next decade. It is also not unlikely that intelligent life may be discovered, which has evolved in a manner similar to our own, in one of the innumerable galaxies that comprise the universe.

Concluding Remarks

In spite of the intensive studies that have been going on, it is rather surprising that there is as yet no clear picture of how biological macromolecules formed on the Earth. In fact, what emerges is a very confusing scenario, with an innumerable variety of compounds being strongly evidenced as possible prebiotic catalysts. Obviously all of these compounds did not function together to produce the biological macromolecules--a particular type or group of compounds were probably the main catalytic agents.

What is perhaps most necessary at this stage, is to short-list, from this wide array, a particular group or type of compounds as the most probable prebiotic catalysts. The basis of such short-listing would be to consider the whole range of conditions which would directly or indirectly influence macromolecular synthesis. Thus, atmospheric conditions, oceanic conditions, rock and ocean sediment mineralogy, organic and inorganic chemicals in air and water, UV light from the sun active volcanism, cometary and meteorite bombardment, etc., are some of the factors which need to be kept in mind in assessing prebiotic catalysts.

Although there is no consensus of opinion amongst the scientists regarding the environmental conditions of such macromolecular synthesis, certain inferences may be drawn based on logical extrapolation.

(1) Biological macromolecules would probably have formed in aqueous environments at sufficient depths to avoid the harmful effects of UV-rays. Consequently, dry environments such as exposed rocks and mineral surfaces would be unlikely locations for such synthesis.

(2) Organic catalysts would have to be stable in water and promote condensation reactions in aqueous media.

(3) If minerals had catalysed such reactions then synthesis would have occurred mostly at or near ocean floors.

(4) The nature of such mineral catalysts would be determined by the chemical composition of the oceans which in turn would depend on the rocks and its mineral constituents.

(5) Since the rocks were ultrabasic, the oceanic waters would be rich in cations, and minerals like smectite would form; other minerals such as kaolinite or hematite are, therefore, unlikely catalysts.

(6) If polyphosphates had been the prebiotic catalysts then synthesis could have only occurred in submarine volcanic regions and hydrothermal vents. Such environments should, however, be sufficiently mild to allow the accumulation of the products for long periods of time.

(7) The catalysts would be very broadly functional and capable of producing the whole range of macromolecules essential for the formation of the first cells.

(8) Although the catalyst itself may not be unique to this planet, the environmental conditions under which macromolecular synthesis occurred, must have been unique for the young Earth, since there is no evidence yet of biological macromolecular formation in other planets and their satellites, meteorites, comets, etc. studied so far.

It may be a worthwhile exercise for scientists from various fields including geologists, chemists, biochemists, mineralogists and space scientists to integrate their knowledge to a common base by including only compatible information and excluding those which are not. Thereby it will be possible to arrive at some consensus regarding the conditions for abiotic synthesis of biological macromolecules. Alternatively, it may be psssible to exclude certain environmental conditions and catalysts as untenable and unlikely. By removing such extraneous material and more clearly focusing our ideas within certain broad outlines, it may be possible to see through the haze and find the solution which has eluded us so far.

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