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# Prebiotic organic chemistry and the origin of life

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Prebiotic synthesis of organic compounds such as amino, hydroxy and aliphatic acids, urea, imidazoles and synthesis of amino acids, co-enzymes, nucleosides under primitive earth conditions have been reviewed.

**Key-words**—Prebiotic earth, Evolution, Organic synthesis.

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## सारांश

जीवितापूर्व कार्बनिक-रासायनिक अध्ययन एवं जीवन की उत्पत्ति

दीवान सिंह भाकुनी

इस शोध-पत्र में अमीनो, हाइड्रोक्सी एवं एलीफेटिक अम्लों, यूरिया, इमिडाजोल के जीवितापूर्व संश्लेषण तथा आदिकालीन भू-परिस्थितियों में अमीनो अम्लों, सह-विकरों एवं न्यूक्लिसाइडों के संश्लेषण की समीक्षा की गई है।

LIVING system, according to the modern paradigm, arose through a lengthy process of chemical evolution that began with the prebiotic synthesis of simple organic compounds in the atmosphere and surface environments of the primitive earth. The physical-chemical evolution of the planet, which would have determined the temperature, pressure and chemical composition of environments above, below and at its surface as a function of time must have influenced the prebiotic syntheses. Although chemical evolution of organic matter is very much an integral part of the evolution of a planet, its scope is not restricted to planets only. In fact, it includes all non-biological processes that produce organic compounds occurring in any environment in space and time.

Chemical and Darwinian evolutions are quite different processes. In Darwinian evolution reproduction, mutation and natural selection are important processes which did not occur before the development of the first living organisms. In chemical evolution non-biological processes are involved. This point is of great significance because of the continuity it implies for the transformation of lifeless into living matter. Evolution of organic matter towards life must have been intimately intertwined with the evolutionary development of the

Earth itself. Careful studies of the geological record of 3.5 Ga has revealed the presence of diverse types of microscopic organisms. But there is no clearcut evidence when life first emerged from non-living matter. Models for chemical evolution on Earth, and available data on the early history of the Solar System by the existing record of biological and geological events on Earth are providing sound foundation for scientific basis of the origin of life. The state of carbon, hydrogen, nitrogen, and oxygen, the principal elements involved in the chemistry of organic matter and the atmospheric setting within which the primary prebiotic synthesis of organic matter has taken place are of basic importance in the chemical evolution process. There are strong differences of opinion about the origin of life. These differences are expected to emerge since the controversy cannot be resolved readily by direct observation. An excellent review on the subject covering references till 1983 is given in the book, "Earth's earliest biosphere : its origin and evolution" (Edited by Schopf, 1983).

## THE MODELS OF THE PREBIOTIC EARTH

### The Oparin Model

Oparin (1938) postulated that the prebiotic milieu where organic compounds were initially synthesized had hydrogen, ammonia ( $\text{NH}_3$ ), methane, and other hydrocarbons and water. In this model, a reducing environment lacking molecular oxygen ( $\text{O}_2$ ) is a prerequisite for the prebiotic synthesis of organic compounds. Oparin noted that in stars, comets, meteorites, and in Jupiter and Saturn, carbon occurs in elemental form and is bound with nitrogen as cyanide ( $\text{HCN}$ ) and with hydrogen as hydrocarbons. Oparin considered the presence of carbon dioxide on Earth and Venus to be of secondary origin. The presence of carbon dioxide in Mars's atmosphere was unknown at the time. Earlier writers believed that prebiotic atmospheric carbon existed in the form of carbon dioxide. In 1919, Osborn expressed the view (cited in Oparin, 1938) that the "Earth was still uninhabited by living creatures and thickly blanketed with an atmosphere containing much water vapour and carbon dioxide. This carbon dioxide served as the source of carbon for the formation of organic substances from which organisms developed by a long process of evolution."

Haldane (1929) agreed with Oparin's ideas on the emergence of life from a reservoir of organic matter in a reducing prebiotic atmosphere. He adopted Oparin's methane postulate in his later writings (Haldane, 1954). Although Osborn did not explain the steps involved in the transformation of lifeless to living matter, his brief description of the setting in which the process of chemical evolution began is supported with the evidence now available from the most ancient representation of the rock record.

According to Oparin (1938) the Earth was formed by the condensation of super-heated gases released from the Sun. The cooling gases might have condensed into droplets on iron and its alloys. Carbon and nitrogen dissolved in the metal had formed carbides and nitrides. Eruptions of deep-seated metal from the core to the planet's surface were suggested as the means to bring metal, carbides and nitrides into contact with hot water in the atmosphere. The water was believed to decompose carbides and nitrides to yield hydrogen ( $\text{H}_2$ ), hydrocarbons, and ammonia. Reactions in the hot atmosphere between gaseous ammonia, water and unsaturated hydrocarbons could have yielded more complex organic compounds which eventually "rained" into the primordial sea where they

underwent further transformation to form a "broth" of organic matter which ultimately spawned the first living systems. According to Oparin, thermal energy and the chemical free energy of metastable organic compounds provided the driving force for chemical evolution. However, he did not take into account till 1957 the importance of sunlight, electric discharges in the atmosphere and other natural energy sources. In subsequent years he realised that astrophysics, the cosmochemistry of the other bodies in the solar system, the geology and geochemistry of the Earth, and the biochemistry and molecular biology of past and present life on Earth all contribute to an understanding of the origin of life. He has given in detail his concept of chemical evolution and has placed the problem of origin of life in a universal cosmochemical and planetological framework (see Schopf, 1983).

### The Urey Model

According to Urey (1952), the prebiotic Earth was, more or less, a homogeneous mixture of metal and silicates overlain by the primordial sea and atmosphere. Carbon occurred predominantly in the form of carbides and elemental carbon, nitrogen as nitrides and ammonium chloride, and hydrogen as hydrated minerals. The heating during impact released water from chemical-bound sites which reacted with some of these minerals (including metallic iron and sulfides) to produce  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{H}_2\text{S}$ . During these changes the temperature of Earth never exceeded  $1200^\circ\text{K}$ . As the atmosphere and surface of Earth were cooling, nitrogen in the presence of  $\text{H}_2$  was thought to be converted into  $\text{NH}_3$ . Urey further postulated that as  $\text{H}_2$  continued to escape from Earth, the methane, ammonia, and water could be converted into oxidized species due to atmospheric electric discharges and photochemical processes involving ultraviolet sunlight. The oxidized species would have dissolved in the primitive oceans and undergone further chemical evolution along the paths as thought by Oparin.

Urey's model of prebiotic Earth was a forerunner of a class of "homogeneous accretion" models for Earth.

### The Rubey Model

Rubey (1951), during his investigations into the origin of seawater, observed that weathering of the pre-existing rocks over geological time could account for the major rock-forming elements (e.g., Al, Ca, Fe, K, Mg, Na, Si). But the abundance of volatile species and elements (e.g., C as  $\text{CO}_2$ , H as  $\text{H}_2\text{S}$ , N, Cl, S, Ar) in the atmosphere, hydrosphere, and sediments greatly exceeded the amount

attributed to rock weathering. He believed that the excess volatiles must have gradually accumulated over a time at a more or less steady rate by outgassing of Earth's interior since the apparent composition of "excess volatiles" was remarkably similar to that of magmatic gases released from the interior of Earth by fumaroles, hot springs, and volcanoes.

Rubey did not believe that prebiotic atmosphere was composed predominantly of  $H_2$ ,  $CH_4$ ,  $NH_3$  and  $H_2O$ . According to Rubey (1955) life originated in an environment resembling the present-day surface of Earth but lacking from oxygen ( $O_2$ ). Thus, the pre-Oparin conception of a primordial atmosphere containing  $CO_2$  as the dominant carbon source was finally supported by scientific facts.

#### **A multi-stage Model for early atmospheric evolution**

Holland (1962) developed a multi-stage model for the evolution of Earth's atmosphere that could reconcile the two contrasting hypotheses, the one by Oparin and Urey and the other by Rubey. He provided a unified model for the early evolution of Earth's atmosphere by accommodating a highly reducing primordial composition at the outset which then changed to a much less reducing one, consistent with the geological record of outgassing. Other workers such as Abelson (1966), Bada and Miller (1968) have also contributions to the debate.

#### **EVIDENCE IN SUPPORT OF THE CHEMICAL EVOLUTION**

The most compelling evidence for chemical evolution is probably provided by the record of biological evolution manifested in the chemistry of living organisms and preserved in geologic records. For direct evidence, extraterrestrial environments have been scrutinized for the presence of organic matter. Putative prebiotic conditions on Earth have been simulated to test pathways for organic synthesis in model environments.

#### **EXTRATERRESTRIAL EVIDENCE**

The occurrence of organic matter in the solar system and beyond supports the assumption that organic compounds necessary for life would have been formed by non-biological processes, before the origin of life.

Meteorites of the carbonaceous type were known since the early nineteenth century to contain organic compounds. Most of the organic matter was considered extraterrestrial in origin (Hayes, 1967;

Nagy, 1975). Unambiguous proof of the abiotic origin of amino acids in the Murchison meteorite is recorded (Kvenvolden *et al.*, 1970). This report is especially significant since amino acids play an important role in biochemistry, and are considered essential molecular building blocks in the process of chemical evolution. The presence of a variety of organic compounds such as amino, hydroxy, mono- and di-, carboxylic acids; urea and amines; ketones and aldehydes; hydrocarbons; alcohols; amines; and N- and S-heterocycles in the Murchison meteorite (Hayes, 1967; Nagy, 1975; Chang, 1979) leaves little doubt that the synthesis of organic compounds in extraterrestrial environment preceded the origin of life. Unfortunately, the chemical processes involved in the syntheses of these compounds and where they took place remain poorly understood (Miller *et al.*, 1976; Chang, 1979; Bunch & Chang, 1980).

The simple molecular species ( $CH$ ,  $C_2$ ,  $C_3$ ,  $CO^+$ ,  $CO_2^+$ ,  $NH$ ,  $NH_2$ ) observed in comets suggest the presence of organic compounds. Hydrogen cyanide ( $HCN$ ) and methyl cyanide ( $CH_3CN$ ) are complex cometary molecules (Delsemme, 1977). Similar sources may have supplied the organic matter in meteorites and comets (Delsemme, 1975; Chang, 1979; Buch & Chang, 1980). An interstellar origin for some of it appears very probable (Whittaker *et al.*, 1980; Hayatsu *et al.*, 1980; Oft *et al.*, 1981).

Presence of about 36 organic molecules containing C-H bonds is reported in a review on interstellar chemistry (Turner, 1980). Compounds, containing up to eleven atoms have been observed. The low temperature ( $\leq 100^\circ K$ ) and gas densities ( $\leq 10^6$  particles per cubic cm) of the environment of "dense" interstellar clouds appear inimical to chemical reactions, nonetheless the exotic condition exhibits a rich chemistry that manifests itself in the production of numerous types of organic compounds.

The presence of simple hydrocarbons in the atmosphere of Jupiter and the colours of its multihued clouds, are indications of active chemical processes. The occurrence of hydrocarbons can readily be explained as the products of solar ultraviolet photochemistry and lightning activity (Prinn & Owen, 1976; Bar-Nun, 1979). Saturn's moon, Titan, contains methane and small amounts of  $C_2$ -hydrocarbons in its atmosphere and exhibits a reddish colouration that may be caused by organic matter. The organic chemistry on Titan has been reviewed by Chang *et al.* (1979).

The occurrence of organic matter in the solar system supports the view that chemical evolution is a natural consequence of the evolution of matter. The pathways for the chemical evolution of organic

matter may be different but specific to the environment. Progress towards the origin of life would have been diverted at different stages depending on the physico-chemical constraints imposed by each environment. The occurrence of organic matter in extraterrestrial environments does provide evidence that chemical evolution occurs naturally, but it does not give any information regarding the particular circumstances involved in prebiotic syntheses of organic compounds on the primitive Earth.

### ORGANIC SYNTHESIS UNDER SIMULATED PREBIOTIC CONDITIONS

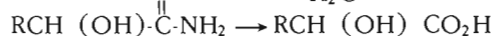
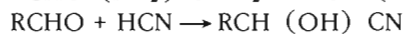
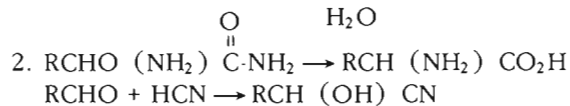
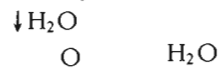
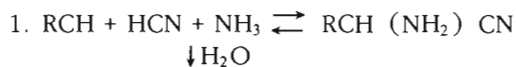
Beutner (1938) suggested that prebiotic organic matter might have been formed by electric discharges. When electric discharges were passed through carbon-containing gases like methane and carbon dioxide in the hope of synthesizing sugars, a complex inseparable mixture of compounds was obtained.

In the first half of the twentieth century, attempts were made to simulate the prebiotic synthesis of organic compounds related to the products of plant photosynthesis. Ultraviolet irradiation of CO<sub>2</sub> and H<sub>2</sub>O in the presence/or absence of oxygen proved largely unsuccessful (see Rabinowitch, 1945). Experiments that consistently yielded small amounts of formaldehyde required the presence of hydrogen or another reductant. Formic acid; and formaldehyde were obtained in low yields when aqueous solutions of CO<sub>2</sub> and ferrous sulphate were irradiated by 40 MeV helium ions. Although these early experiments supported the view that a reducing environment was necessary for the initial stages of the chemical evolution of organic matter, they neither denied nor affirmed the importance of ammonia and CH<sub>4</sub> or other hydrocarbons on Oparin's and Urey's models.

Miller (1953, 1955, 1957) passed an electric discharge through a mixture of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub> and achieved the facile synthesis of a variety of organic compounds, particularly amino acids. The ease with which the syntheses were accomplished under conditions similar to those originally postulated by Oparin (1938) and Urey (1952) stimulated experimentation by other workers (see Day, 1979).

Passage of an electric discharge through a mixture of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub> (representing a strongly reducing atmosphere) resulted in the first laboratory prebiotic synthesis of amino acids (glycine, 2% yield), together with hydroxy acids, aliphatic acids, and urea (Miller, 1953, 1955, 1957).

Many of the compounds produced were of biological importance. The mechanism of formation of these compounds is given below.



The compounds mentioned above can also be produced by the thunder shock waves associated with lightening discharges (Bar-Nun & Shaviv, 1975).

Irradiation of the mixture of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub> with short wavelength ultraviolet light < 150 nm produced amino acids in lower yield (Groth & Von Weysenhoff, 1960). If H<sub>2</sub>S or formaldehyde is added to the gas mixture, amino acids were obtained at relatively long wave lengths (≤ 230 nm) (Sagan & Khare, 1971; Bewcker *et al.*, 1974). In the presence of titanium dioxide as photo-catalyst, irradiation of CH<sub>4</sub> and NH<sub>3</sub> in water with near ultraviolet and visible light yielded amino acids (Reiche & Bard, 1979).

Pyrolysis of CH<sub>4</sub> and NH<sub>3</sub> at 1073° to 1473°K followed by addition of water gave amino acids in low yield (Lawless & Boynton, 1973). Pyrolysis of CH<sub>4</sub> and other hydrocarbons produced benzene, phenyl-acetylene, and other hydrocarbons in moderate concentrations. It can be shown that phenylacetylene can be converted into phenylalanine and tyrosine by model pathways possible in the primitive seas (Friedmann & Miller, 1969). Similarly, tryptophan can be synthesized from indole which is produced by the pyrolysis of the hydrocarbons in the presence of NH<sub>3</sub>.

Passage of an electric discharge through a mixture of CH<sub>4</sub>, N<sub>2</sub> and traces of NH<sub>3</sub> and H<sub>2</sub>O (Earth's prebiotic atmosphere of Oparin's and Urey's models) yielded amino acids in low yield, but the products formed were more diverse (Ring *et al.*, 1972; Wolman *et al.*, 1972). Hydroxy acids, low molecular weight aliphatic acids, and dicarboxylic acids were produced along with the amino acids. In this experiment 10 of the 20 amino acids that occur commonly in proteins were synthesized.

Sparking of three types of mixtures: (i) CH<sub>4</sub> + NH<sub>3</sub>, (ii) CH<sub>4</sub> + N<sub>2</sub>, (iii) CH<sub>4</sub> + H<sub>2</sub>O separately produced nitriles in (i) and (ii); aldehydes, ketones, acids and alcohols in (iii); and hydrocarbons in all three. Hydrogen cyanide was probably the most important intermediate first formed which was then transformed into amino acids and purines in the

primitive seas. Additional products included cyanoacetylene, which subsequently might have been converted to pyrimidines and aspartic acid. Cyanamide and cyanogen might have served as dehydrating agents suitable for promoting condensation-polymerisation reactions. Ultraviolet irradiation (185 nm of CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>O mixtures furnished hydrocarbons, alcohols, aldehyde, and ketones (Ferris & Chen, 1975).

Electric discharges on the mixture of CO, N<sub>2</sub> and H<sub>2</sub> (mildly reducing atmosphere) in which the ratio of H<sub>2</sub> to CO was greater than one (Abelson, 1966; Miller & Schlesinger, 1983) produced glycine in fair yield. Large amounts of formaldehyde and HCN were also obtained in the reaction, which are important intermediates for the prebiotic synthesis of sugars and purines.

A mixture of CO and H<sub>2</sub> is used in the Fischer-Tropsch reaction to make hydrocarbons. The reaction requires a catalyst, usually Fe or Ni supported on silica, a temperature of 673°K, and a short contact time. Depending on reaction conditions, aliphatic and aromatic hydrocarbons, alcohols, and acids can be produced. If NH<sub>3</sub> is added to the CO + H<sub>2</sub> mixture, amino acids, purines, and pyrimidines can be formed (Studier *et al.*, 1968; Hayatsu *et al.*, 1972).

Irradiation of a mixture of CO + H<sub>2</sub>O with ultraviolet light ( $\leq 184$  nm) produced formaldehyde and other aldehydes, alcohols, and acids in fair yields (Bar-Nun & Hartman, 1978).

Irradiation of a mixture of CO<sub>2</sub> + H<sub>2</sub>O in the presence of Fe<sup>2+</sup> gave formic acid, oxalic acid and other simple products in fairly high concentrations (Gedtoff *et al.*, 1960).

The experimental results summarised above demonstrate that a wide variety of organic compounds can be produced in strongly reducing atmospheres. Apparently, solar ultraviolet irradiation cannot produce C-N bonds when nitrogen occurs as N<sub>2</sub> in the atmosphere, regardless of whether carbon is present as CH<sub>4</sub>, CO, and CO<sub>2</sub>. Calculations suggest that in the presence of H<sub>2</sub>, H<sub>2</sub>O CO and CO<sub>2</sub> lightening converts N<sub>2</sub> to nitric oxide (NO) which could then be converted to HNO, HNO<sub>2</sub> and HNO<sub>3</sub> and dissolved in primitive seas as nitrite and nitrate (Yung & McElkor, 1979; Chameides & Walker, 1981; Kasting & Walker, 1981). A thermochemical-hydrodynamic model has been used to predict rates of carbon and nitrogen fixation by lightening in the prebiotic atmosphere (Chameides & Walker, 1981).

Prebiotic syntheses of organic compounds despite some limitations have achieved a notable degree of success. Nearly all the building blocks of proteins and nucleic acids have been synthesized.

Considerable progress has been made for producing peptides and polynucleotides but the size of these molecules is still far from the size of biopolymers that are present in today's living systems.

A significant number of small molecules have been discovered in the interstellar medium. The largest molecule unambiguously detected was HC<sub>11</sub>N (Herbst, 1985). It has not been possible to decide whether the production of such complex gas phase molecules *in situ* occurs from atoms and smaller molecules followed by desorption into gas or by reaction in the gaseous phase.

Photolysis of CO : NH<sub>3</sub> : H<sub>2</sub>O gas mixture at 10 K have yielded alcohols, and fatty acids, and reaction pathways leading to the formation of these compounds is suggested (Agarwal *et al.*, 1985). Electric discharge experiments have been conducted in a plausible primitive earth atmosphere consisting of CH<sub>4</sub> : N<sub>2</sub> : H<sub>2</sub>O over an aqueous phase of ammonia-ammonium ion buffer solution. In some experiments, ions of metals such as Ca, Mg, Zn, Fe, etc. were introduced. It was found that in the presence of trace metal ions less organic compounds in gas phase and larger amounts of amino acids were synthesized (Kobayashi & Ponnampereuma, 1985). The importance of trace elements in chemical evolution has been reviewed.

Prebiotic synthesis of imidazole-4-acetaldehyde, imidazole-4-glycol and imidazole-4-ethanol (Shen *et al.*, 1986); synthesis of amino acids and imidazoles by proton irradiation of simulated primitive Earth atmosphere (Kobayashi *et al.*, 1990); chemical structure of a prebiotic analog of adenosine (Maurel & Convert, 1990); the synthesis of amino acids and sugars on an inorganic template from constituents of prebiotic atmosphere (Field & Spencer, 1990); copper-catalysed amino acid condensation in water—a simple possible way of prebiotic peptide formation (Rode & Schwendiner, 1990); prebiotic synthesis of orotic acid parallel to the biosynthetic pathways, (Yamagata *et al.*, 1990) have been reported.

Prebiotic phosphorylation of nucleosides has been studied (Havranek, 1989). The role of clay edges in prebiotic peptide bond formation has been discussed (Collin *et al.*, 1988). Prebiotic synthesis of pantoic acid, a constituent of acetyl co-enzyme A has been investigated (Schlesinger & Miller, 1986). A possible prebiotic synthesis of uracil from glycine by simultaneous irradiation with infrared rays and ultraviolet light is reported (Dioses, 1986). Formation of polypeptides (Yanagawa *et al.*, 1986) and polynucleotides (Otroshchenko *et al.*, 1986) under possible primitive Earth conditions has been studied.

Synthesis of the co-enzymes adenosine diphosphate glucose (ADPG), guanosine diphosphate glucose (GDPG) and cytidine diphosphoethanolamine (CDP-ethanolamine) under primitive earth conditions have been studied. These compounds have been synthesized from simple precursors under aqueous solutions, at moderate temperatures and short periods of time using urea and cyanamides as condensing agents (Mar & Oro, 1989).

The role of sulfur in prebiotic organic chemistry has been studied. Electric discharge experiments with  $H_2S$ ,  $CH_4$  and  $N_2$  over aqueous phase containing  $NH_3 \cdot NH_4Cl$  buffer yielded cysteine, cystine, methionine and several other amino acids. Higher yields of the amino acids were obtained when  $H_2S$  is replaced by  $Na_2S$  (Bhadra & Ponnampereuma, 1986).

The discovery of catalytic ability in RNA has given fresh impetus to speculations that RNA plays a critical role in the origin of life. Many claims are recorded to support the idea that components of RNA were readily available on the prebiotic Earth. Shapiro (1988) has given a critical analysis of prebiotic ribose synthesis. He has reported that the evidences available do not support the availability of ribose in the prebiotic earth, except perhaps for a brief period of time, in low concentration, as part of a complex mixture, under circumstances that are unsuitable for nucleotide synthesis.

#### EVIDENCE OF CHEMICAL EVOLUTION IN THE GEOLOGICAL RECORD

Prior to life the main source of organic matter was presumably products of prebiotic organic syntheses, meteoritic and cometary debris. After life arose, biological organic matter eventually became the main source of reduced carbon preserved in sediments. Obviously the documentation in ancient sediments of the transition between prebiotic organic evolution and the origin of life would demonstrate convincingly the chemical evolution paradigm. The main difficulty here is to distinguish between abiotic and biological organic matter preserved in ancient rocks. Unfortunately, it is not possible to examine "fresh" organic matter in rocks of Early Archean and Hadean age, the time in Earth history when the origin of life must have occurred. The organic matter present in these rocks must have been altered by the ravages of time and temperature. Various methods have been tried for differentiating between biotic and biological organic matters, however, none of these techniques are very reliable.

#### PREBIOTIC ORGANIC SYNTHESIS

Oparin and Haldane postulated that the first organisms were chemoheterotrophs capable of utilizing preformed organic matter in their environment as the source both of energy and of cell building materials. It is difficult to imagine how the simplest cells of modern organisms, with their high degree of physicochemical complexity, intracellular, biochemical machinery, and sophisticated molecular organisation could have initially arisen without at least having small parts of the assemblage available preformed in the watery primordial medium. The formation of amino acids from  $CH_4$  and  $CO$  with ease provided strong support to heterotrophic origin of life. Further, it has been discovered that some heterotrophic microbes are evolved from autotrophic precursors (fox *et al.*, 1980).

Cosmochemical, geologic, and biologic evidence make viable atmospheric models involving  $CO_2$  and  $N_2$  as the primary sources of carbon and nitrogen with variable amounts of  $H_2$ . Prebiotic organic synthesis in these atmospheres may pose difficulties for reaction utilizing the three energy sources (lightning, thunder shock waves and sunlight) which are generally considered to have been most abundant on the prebiotic Earth. The syntheses of organic compounds in the seas and at the interfaces between the atmosphere and the surfaces of land and seas have been suggested by Gabel (1977), Baur (1978) and Walker (1980). It remains to demonstrate plausible pathways for organic synthesis in all environments consistent with available constraints.

#### PROBLEMS AND SCOPE FOR FUTURE RESEARCH

Although production of organic compounds in a highly reducing atmosphere has been demonstrated, the possibilities of a  $N_2$ - $H_2O$  atmosphere containing trace amounts of  $H_2$  and  $CO_2$  and a minor amount of  $CO$  remain relatively unexplored. Of the various energy sources, ultraviolet light ( $> 150$  nm), electric discharges, and thunder shock waves are generally believed to be the most significant on a global scale; there appears no compelling reason to assume a different situation existed in the primitive Earth. Gabel (1977) has pointed out the difficulties in reducing  $N_2$  to organic nitrogen and synthesizing key compounds such as amino acids in a  $N_2$ - $H_2O$  atmosphere. Ferris and Chen (1975) were unable to produce amino acids by irradiating a mixture of  $CH_4 + H_2O$  with ultraviolet light. Theoretical studies of the fixation of nitrogen by electric discharges

(and thunder shock waves) in a  $N_2$ - $H_2O$  atmosphere with minor amount of  $CO_2$  and  $H_2$  showed that nitric oxide could be formed in significant concentrations (Yung & McElroy, 1979; Chameides & Walker, 1981).

The presence of a reducing atmosphere ( $H_2$ ,  $CH_4$ , or  $CO$ ) is required if organic synthesis is to occur. Walker (1976) suggested the possibility that  $H_2$  could be produced by volcanic eruption by decomposition of  $H_2O$  in early tectonic processes and may have achieved 1 per cent concentration in the atmosphere on the early Earth. Whether or not this amount would have been sufficient to permit atmospheric organic synthesis remains to be evaluated. Calculations by Baur (1978) show that spontaneous formation of amino acids is thermodynamically possible in heterogeneous systems containing  $N_2$  and  $CO_2$  in the presence of ferrous iron-containing minerals and  $H_2O$ . There is need to investigate the potential pathways for organic synthesis in such heterogeneous systems.

Understanding of transport processes in the early atmosphere is very important since syntheses could occur in the atmosphere or in the oceans, at the interfaces between the atmosphere, bodies of water and land or beneath the seas at sea-floor. There are chemical reactions that act as "sinks" for organic matter. How much material in sinks is recycled is not known. Further, the production rates of organic compounds are also not known.

There is little doubt that organic chemical evolution must have occurred in a predominantly inorganic environment. The question is how did organic chemistry and mineralogy interact? Did the inorganic material act as a catalyst for organic reactions? How was phosphate utilized to produce nucleotides and polynucleotides?

Environment undergoes numerous fluctuations—day, night, seasons, tides, etc. In some experiments such environmental fluctuations have been simulated. Change of temperature and moisture contents have been studied, particularly in the syntheses of peptides from amino acids (Lahav *et al.*, 1978). The question remains, how important are such fluctuations for chemical evolution? The other day questions that need to be answered are: How was separation between an evolving organic system and the external environment achieved? How did membranes originate? How did the genetic code arise? What was the origin of chirality? Partial answers to some of these questions have come but more remains to be answered. To answer these and other questions, contributions from astronomy, astrophysics, atmospheric physics, geophysics, geochemistry, inorganic chemistry, organic chemistry and biology are essential.

## CONCLUSIONS

Living systems according to the modern paradigm arose through a lengthy process of chemical evolution that began with the prebiotic synthesis of simple organic compounds in the atmosphere and surface environments of the primitive Earth. Subsequent transformation in these environments converted the primary products into increasingly complex organic matter until the process culminated in the evolution of polymeric materials having the capability for primitive self-replication and other biochemical functions.

The characterization of organic compounds in meteorites, comets and atmospheres of the outer planets supports the hypotheses that prebiotic synthesis and chemical evolution of organic matter occur to varying degree throughout the cosmos. The processes that gave rise to such organic compounds and imposed limits on its chemical evolution are characteristic of each extraterrestrial environment. Prebiotic organic matter in ancient terrestrial rocks could have provided valuable information regarding chemical evolution but no reliable method is yet available to distinguish unambiguously between abiogenic and biogenic organic matter in ancient sediments.

Laboratory experiments indicate that prebiotic synthesis of organic matter would have occurred in strongly reducing atmospheres. Organic syntheses in mildly or non-reducing atmospheres have not been successful. Further investigation is needed. Prebiotic organic syntheses could have occurred on land, in the seas, in the atmosphere and at the interfaces between them. Theoretical and experimental studies suggest that primary synthesis of organic compounds may have occurred in heterogeneous systems. Investigations suggest that some metal ions and minerals (particularly clays) could have served as reactants, catalysts, and even templates for prebiotic organic synthesis. Their role in chemical evolution needs further exploration. Considerable success has been achieved in putative prebiotic syntheses of the monomeric and oligomeric building blocks of proteins and nucleic acids of today's living organisms. Whether these conditions differ from the actual condition existing in the prebiotic Earth is still uncertain.

The scientific study of the origin of life is still in its infancy considering the scope and magnitude of the problem. An interdisciplinary approach holds the greatest promise in understanding the problem.

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