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THE ORIGIN AND EARLY EVOLUTION OF LIFE ON EARTH

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PERSPECTIVES AND SUMMARY

Although during the first decades of the twentieth century Darwin's explanation of the causes of evolution had fallen out of favor among biologists, his ideas provided the essential framework for the development of a large body of thought devoted during that period to the question of the origins of life. Of all the hypotheses that were suggested (Farley 1977, Kamminga 1988), fcw were as fruitful as those of Oparin (1924, 1936), who proposcd a long period of chemical abiotic synthesis of organic compounds as a necessary precondition for the appearance of the first life forms. The first forms of life would then have been anaerobic heterotrophic microorganisms. Similar ideas were suggested independently by Haldane (1929).

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In Table 1 a list of some of the major discoveries and scientific developments directly or indirectly related to the origin of life is given.

Following the model of Oparin's reducing primordial terrestrial atmosphere developed by Urey (1952), Miller (1953) showed that a number of protein amino acids and a diverse assortment of other small organic molecules of biochemical significance could be made in the laboratory under environmental conditions thought to be representative of the Hadean or early Archean Earth. Since then, a wide variety of organic compounds of biochemical significance have been experimentally formed from simple molecules such as water, methane, ammonia, and HCN (Miller 1987). The results of these experiments have been highlighted by the discovery of a large variety of organic molecules in the interstellar clouds of the Milky Way and other galaxies, in comets, and in carbonaceous chondrites (Oró & Mills 1989). These findings have been complemented with information from comparative planetology, Archean geology, and Precambrian micropaleontology. Nevertheless, it is unlikely that the early Archean geological record will provide evidence of the transition from the prebiotic organic molecules to the first cells. Therefore, to recon-

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Table 1 Some scientific discoveries and developments related to the origin and early evolution of life on Earth

Discovery or development	Reference(s)
1. Concept of chemical and prebiological evolution	Oparin 1924, Haldane 1929
2. Quantitative models of the Earth's reducing atmosphere	Urey 1952
3. Prebiotic synthesis of amino acids	Miller 1953
4. Founding of Precambrian micropaleontology (Gunflint microfossils, 2000 Ma)	Tyler & Barghoorn 1954
5. Prebiotic synthesis of adenine	Oró 1960
6. Cometary contribution to the primitive Earth	Oró 1961
7. Swaziland microfossils (3400 Ma)	Barghoorn & Schopf 1965
8. Prebiotic synthesis of pyrimidines	Sanchez et al 1966
9. Early biological evolution and the origin of eukaryotes	Sagan (Margulis) 1967, Margulis 1970, pp. 45–68
10. Racemic mixtures of meteoritic amino acids	Kvenvolden et al 1970
11. Template-directed polymerization reactions of nucleotides	Orgel & Lohrmann 1974
12. Phylogenies based on ribosomal RNA	Woese & Fox 1977
13. Catalytic activity of RNA	Cech et al 1981
14. Warrawoona microfossils (3500 Ma)	Awramik 1981, Awramik et al 1983
15. Stereoselective aminoacylation of RNA	Usher & Needels 1984, Lacey et al 1988
16. Template-directed synthesis of novel nucleic acid–like structures	Schwartz & Orgel 1985

struct the possible characteristics of the first living systems, we must rely on studies of prebiotic chemistry as well as on information in contemporary biological systems. These include studies of macromolecular sequence data from proteins and nucleic acids of different organisms, and from comparisons of metabolic pathways and their phylogenetic distribution (Margulis & Guerrero 1986, Lazcano 1986, Woese 1987, Lazcano et al 1988a, Berry & Jensen 1988). A brief discussion concerning the time of the origin of life has been undertaken somewhat recently by Oró & Lazcano (1984). Oberbeck & Fogleman (1989) have calculated the maximum time required for life to originate and evolve to the level of complexity represented by the oldest microfossils; in short, most available calculations and evidence seem to indicate that the emergence of life occurred approximately 3.85 Gyr ago (e.g. Carlin 1980).

We do not have a detailed knowledge of the processes that led to the appearance of life on Earth. In this review we bring together some of the most important results that have provided insights into the cosmic and primitive Earth environments, particularly those environments in which life is thought to have originated. To do so, we first discuss the evidence bearing on the antiquity of life on our planet and the prebiotic significance of organic compounds found in interstellar clouds and in primitive solar system bodies such as comets, dark asteroids, and carbonaceous chondrites. This is followed by a discussion on the environmental models of the Hadean and early Archean Earth, as well as on the prebiotic formation of organic monomers and polymers essential to life. We then consider the processes that may have led to the appearance in the Archean of the first cells, and how these processes may have affected the early steps of biological evolution. Finally, the significance of these results to the study of the distribution of life in the Universe is discussed.

There are many books on the origins of life. We cannot mention all of them here, but among those that discuss aspects of interest to Earth scientists are the books by Calvin (1969), Kenyon & Steinman (1969), Rutten (1971), Miller & Orgel (1974), as well as those edited by Kvenvolden (1974), Ponnamperuma (1977), Halvorson & Van Holde (1980), Holland & Schidlowski (1982), Nagy et al (1983), and Schopf (1983).

THE ANTIQUITY OF TERRESTRIAL LIFE

"To the question of why we do not find rich fossiliferous deposits belonging to these assumed earliest periods prior to the Cambrian system," wrote Darwin in *On the Origin of Species by Natural Selection*, "I can give no satisfactory answer." The answer was provided almost a century later, when Tyler & Barghoorn (1954) and Barghoorn & Tyler (1965) published

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their description of the 2000-Myr-old microfossils from the Gunflint Formation. Thus the field of Precambrian micropaleontology was born, demonstrating that life is indeed a very ancient phenomenon on our planet. Some of the major problems in Precambrian paleobiology were discussed in this series some time ago by Schopf (1975) and, more recently, in the *Annual Review of Microbiology* by Knoll (1985), who emphasized Proterozoic microbial evolution.

The Archean Era (4.55–2.5 Ga) is generally divided into three main intervals: the Hadean, which comprises the initial period after the formation of the Earth (4.55–3.9 Ga); the early Archean (3.9–2.9 Ga); and the late Archean (2.9–2.5 Ga) (Ernst 1983). We have no definitive evidence of Hadean life, and evidence of early Archean life is sometimes contradictory and difficult to accept (Schopf & Walter 1983). For instance, the biological nature of the structures previously described as fossil prokaryotes by Barghoorn & Schopf (1965) in South African 3000-Myr-old sediments has been disputed (Schopf 1976). Previous reports of yeastlike microfossils (Pflug 1978, Pflug & Jaeschke-Boyer 1979) in the 3800-Myr-old carbonate-rich metasedimentary rocks of Isua, West Greenland (Moorbath et al 1973), are now considered to correspond to structures having nonbiological, inorganic origins [probably fluid inclusions (Bridgwater et al 1981)].

Ratios of stable carbon, nitrogen, and oxygen isotopes in the Isua metasediments have been interpreted to imply the existence of an Archean carbon cycle driven by photosynthetic microbes (Schidlowski et al 1979, 1983). However, since the $^{13}C/^{12}C$ values would have been deeply affected by high-grade metamorphic processes that have modified the Isua Supracrustal Belt samples (Awramik 1982, Knoll 1986), at the present time it is not possible to assert the existence of microbial communities based on photoautotrophs 3800 Myr ago, although such organisms may have existed then.

Nevertheless, there is ample morphological evidence documenting the existence of a complex microbiota in nonmetamorphosed sediments from the early Archean. It consists of many different morphotypes of structurally well-preserved fossil bacteria from the 3500-Myr-old Australian Warrawoona Group (Awramik 1981, 1982, Awramik et al 1983, Schopf 1983, Schopf & Packer 1987) and from 3400-Myr-old South African sediments from the Zimbabwe craton (Knoll & Barghoorn 1977). This evidence is further supported by several Archean occurrences of stromatolites, which are organo-sedimentary structures in whose formation microbial communities play an active role (Margulis et al 1980). The oldest known stromatolites from Archean sequences date back to 3500-Myr-old sediments in the Pilbara Group in northwestern Australia (Walter 1983).

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Possible stromatolites have been reported by Byerly et al (1986) in 3300-Myr-old rocks from the Fig Tree Group in South Africa, and Orpen & Wilson (1981) have found structures in sediments of the Mushandike Sanctuary (Zimbabwe) that could also correspond to 3500-Myr-old stromatolites.

EXTRATERRESTRIAL ORGANIC COMPOUNDS

Interstellar Molecules

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Although the hypothesis of a period of abiotic chemical syntheses of organic compounds prior to the emergence of life that Oparin (1924, 1936) and Haldane (1929) suggested was originally received with considerable skepticism, contemporary evidence clearly shows that organic molecules not only formed before the appearance of life, but even before the origin of the Earth itself. The existence of simple carbon combinations (C_2, CN, CH, CO) in the atmospheres of relatively cool stars had been known for a long time, and neutral molecules could be presumed to exist in interstellar space (Oró 1963a), but it was not until 1969 that microwave techniques led to the detection of interstellar ammonia, water, and formaldehyde, the first organic molecule to be discovered in space (Snyder et al 1969). Ever since, more than 80 different molecular species have been detected in interstellar or circumstellar clouds. A significant percentage of these compounds are organic, and they include most of the functional groups of biochemical compounds, with the exception of those involving phosphorus (Lazcano-Araujo & Oró 1981). Recent discoveries include the detection of phosphorus nitride (PN) achieved simultaneously by Ziurys (1987) and by Turner & Bally (1987), as well as cyclic C_3H (cf. Irvine 1989). The detection of the linear $HC_{11}N$ (Bell et al 1982) and C_3 molecules (Hinkle et al 1988) in the circumstellar spectrum of the carbon star IRC+10°216 shows that in our Galaxy, cool carbon stars are a source of complex interstellar molecules that are ejected by means of various processes into space.

Among the interstellar compounds, there are many that have been used in prebiotic organic synthesis to obtain most of the biochemical monomers found in contemporary living systems (Irvine 1989). However, as of May 1989, no interstellar amino acid, nucleotide derivative, or other metabolite has been reported. Searches for interstellar cyclic furan and imidazole (De Zafra et al 1971), pyrimidines and pyridines (Simon & Simon 1973), and glycine (Brown et al 1979, Hollis et al 1980) have been unsuccessful. A large number of interstellar emission lines in the 3–6 mm wavelength remain to be identified, and it is possible that some of them may correspond to biochemical compounds. This possibility is made plausible by the results

of several laboratory simulations of the interstellar environment. In these studies, icy mixtures of water, methane, carbon dioxide, ammonia, and nitrogen have been irradiated by ionizing radiations (Oró 1963b, Lazcano-Araujo & Oró 1981) and ultraviolet light (Greenberg 1981, d'Hendecourt et al 1986), yielding, upon hydrolysis, significant amounts of amino acids, hydroxy acids, nitrogen bases, and other nonvolatile organic molecules, including polymers.

Although it is very unlikely that interstellar molecules played a direct role in the origin of life, the presencc in interstellar space of a large array of many molecules of prebiotic importance, combined with the fact that their synthesis must differ from the chemical pathways that were possible in the primitive terrestrial environment, implies that some molecules are particularly easily synthesized when radicals and ions recombine.

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Comets and Carbonaceous Chondrites

Since most of the interstellar organic compounds have been observed in dense, cool interstellar clouds where star formation is taking place, it is reasonable to assume that the primordial solar nebula had a somewhat similar composition. This hypothesis suggests that a certain amount of interstellar organic compounds, most likely incorporated on cosmic dust particles, became part of comets and planetesimals (Delsemme 1984, Kerridge & Anders 1988). This conclusion is supported by the observation of a number of organic molecules and radicals (C_2, C, CH, CO, CS, HCN, CH_3CN) and other simple chemical species (NH, NH_3, OH, H_2O) in cometary spectra. As shown by the recent observations of Comet Halley, cometary nuclei are relatively small bodies with diameters of a few kilometers in which frozen water comprises approximately 80% of the total volatile ices. The remaining 20% of the volatiles includes formic acid, formaldehyde, carbon dioxide, carbon monoxide, HCN, acetylene, and cyclopropenylidene in various proportions (Delsemme 1988, Oró & Mills 1989).

A recent detailed discussion of the chemistry of comets, including an analysis of elemental abundances in Comet Halley, has been given by Delsemme (1988), who argues that most of the chemical elements appear to exist in their cosmic abundances, with the exception of hydrogen (and, perhaps, of helium and neon), which is depleted by a factor close to 10^3. Cometary nuclei thus appear to be the most pristine bodies in the solar system. Rccent analysis by Kissel & Krueger (1987) of the dust mass spectra of Comet Halley suggests that cometary dust has an organic component that includes adenine and other purines, together with other heterocyclic compounds and organic polymers. As argued by Matthews & Ludicky (1987), it is possible that the low albedo and other features of

Comet Halley could be explained by the presence of HCN polymers. A discussion of the possible routes of formation in cometary nuclei of these and other organic compounds of prebiotic significance may be found in Oró & Mills (1989). The biochemical monomers and properties that can be derived from interstellar and cometary molecules are summarized in Table 2.

The abiotic synthesis of biochemical compounds during the time of formation and early evolution of the solar system, or even during presolar events, is further indicated by the large array of proteinic and nonproteinic amino acids, carboxylic acids, purines, pyrimidines, hydrocarbons, and other molecules that have been found in carbonaceous chondritic meteorites. The earlier evidence has been reviewed by Hayes (1967) and Nagy (1975). Results on extraterrestrial D and L amino acids were published by Kvenvolden et al (1970, 1971) and Oró et al (1971a,b), and data on nucleic acid bases (Anders et al 1974, Stoks & Schwartz 1981) and amphiphilic compounds (Deamer 1985) have also been published. Of the 74 amino

Table 2 Biochemical monomers and properties that can be derived from interstellar and cometary molecules[a]

Interstellar and cometary molecules	Formulae	Biochemical monomers and properties
1. Hydrogen	H_2	Reducing agent
2. Water	H_2O	Universal solvent
3. Ammonia	NH_3	Catalysis and amination
4. Carbon monoxide	$CO(+H_2)$	Fatty acids
5. Formaldehyde	CH_2O	Ribose and glycerol
6. Acetaldehyde	$CH_3CHO(+CH_2O)$	Deoxyribose
7. Aldehydes	$RCHO(+HCN$ and $NH_3)$	Amino acids
8a. Hydrogen sulfide	H_2S(+ other precursors)	Cysteine and methionine
8b. Thioformaldehyde (interstellar)	CH_2S	
9. Hydrogen cyanide	HCN	Purines and amino acids
10. Cyanacetylene (interstellar)	HC_3N(+ cyanate)	Pyrimidines
11. Cyanamide (interstellar)	H_2NCN	Condensing agent for biopolymer synthesis
12a. Phosphorus nitride (interstellar)	PN	
12b. Phosphine (Jupiter and Saturn)	PH_3	Phosphates and nucleotides
12c. Phosphate[b]	PO_4^{3-}	

[a] From Oró et al (1978, 1990). With the exceptions of phosphine (PH_3) and phosphate (PO_4^{3-}), all other molecules have been detected in interstellar clouds, and most have also been detected in comets. Molecules that have only been detected in interstellar clouds are indicated by "(interstellar)." With the exception of the monosaccharides and some of the lipids, the prebiotic formation of the biochemical compounds (amino acids, purines, pyrimidines, etc) requires the participation of HCN or its derivatives.

[b] Found in meteorites and interplanetary dust particles.

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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). All the meteoritic alpha amino acids are found as racemic mixtures, including the α-alkyl, α-amino acids such as isovaline, which cannot be racemized. This demonstrates that these compounds are indigenous to the meteorite and not terrestrial contaminants.

Recent studies on the chemical and isotopic compositions of the amino acids in the Murchison meteorite by Epstein et al (1987) and Cronin (1989) have provided major insights into their origins and probable mechanisms of synthesis. Although a comparison between the relative abundances of the α-amino acids found in the Murchison meteorite with those formed by electrical discharges in a Miller-Urey type of synthesis suggests that the latter process can account for their origin (Wolman et al 1972), an analysis of the deuterium/hydrogen ratio of the meteoritic amino acids shows that these compounds are highly enriched in deuterium compared with the average solar system D/H value (Epstein et al 1987, Cronin 1989).

From these measurements it seems likely that the amino acids could not have been formed from gasses of the solar nebula, but rather are more likely to have formed from highly deuterium-enriched molecules from presolar interstellar clouds. Accordingly, Oró & Mills (1989) have suggested that the aldehyde or ketone precursors to the amino acid R groups were part of a presolar interstellar cloud with a high D/H ratio, which became part of the material that condensed in the meteorite parent body (presumably a primitive dark asteroid). Further thermal evolution of these parental bodies may have led to transient hydrothermal phases during which the amino acids were synthesized following the Strecker-cyanohydrin mechanism involved in the synthesis by electrical discharges. This pathway supports the hypothesis of a direct relationship between organic-rich interstellar grains, comets, dark asteroids, and carbonaceous chondrites (Cruikshank 1989).

THE ENVIRONMENT OF THE HADEAN EARTH

The Origin of Terrestrial Volatiles

One of the major problems in attempting to reconstruct the conditions of the Hadean environment is that of the origin and detailed chemical composition on the early terrestrial atmosphere. Since there is general agreement that the solar system formed 4600 Myr ago as a result of the condensation of the solar nebula, whose elementary abundances and molecular composition were comparable to those of the dense gas and dust regions found in the Milky Way, it would be tempting to assume that

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the early Earth inherited not only simple organic molecules from the solar nebula, but also the complex carbon compounds that appear to exist in interstellar grains and comets, as well as the polymers found in carbonaceous chondrites like the Murchison meteorite.

It is unlikely, however, that the organic molecules from which it is assumed that the first living systems were formed were derived directly from the solar nebula. The amount of interstellar material trapped by the prebiotic Earth was very small, since the well-known terrestrial depletion of noble gases relative to solar abundances (Brown 1952, Suess & Urey 1956, Anders & Owen 1977, Cameron 1980) shows that the primordial atmosphere was almost completely lost, and that the Earth acquired a significant part of its secondary atmosphere from the release of internal volatiles (Walker 1977, 1986, Arrhenius 1987) and the late accretion of volatile-rich minor bodies such as cometary nuclei (Oró 1961, Lazcano-Araujo & Oró 1981).

According to the single-impact theory on the origin of the Earth-Moon system developed by Cameron and his collaborators (Benz et al 1986, 1987, Cameron & Benz 1989), a near-Mars-size body collided with the proto-Earth. Upon collision, all of the iron from the impactor was injected into the core of the proto-Earth. The impact of the collision was such that both the impactor and most of the Earth's mantle were melted, and a lump the size of the Moon was ejected into the Earth's orbit. This process explains the formation of the Earth-Moon system with all its physical and chemical characteristics, but it also implies that as a consequence of this very early catastrophic event the Earth must have lost into space practically all of the water and most of the biogenic elements (H, C, N, O, S, and P) that the protoplanet may have previously retained. Comets and other primitive solar system bodies captured by the primitive Earth must have been then the major source of the terrestrial volatiles (Oró 1961, Anders & Owen 1977, Lazcano-Araujo & Oró 1981, Delsemme 1984, Chyba 1987). Table 3 displays the various estimates of the amounts of cometary matter captured by the Earth.

In spite of all the uncertainties that exist in our current reconstruction of the first 800 Myr of the Earth (Chang et al 1983, Arrhenius 1987), most of the theoretical models developed to explain the formation of the terrestrial planets predict a molten early Earth (Wetherill 1980). This would produce an extensive pyrolysis of primordial organic compounds whose products would then form a gaseous mixture of CO_2, CO, CH_4, H_2, N_2, NH_3, and H_2O (Miller 1982). Moreover, the capture of large planetesimals—comparable both in size and in chemical composition to comets and dark asteroids—during the early and late phases of accretion would lead to their melting and complete vaporization at impact. The

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Table 3 Estimates of cometary matter captured by the Earth

Cometary matter captured	Time period	Reference
2×10^{14} to 10^{18}	Initial 2×10^9 yr	Oró 1961
1×10^{25} to 10^{26}	Late accretion period	Whipple 1976
4×10^{21}	Late accretion period	Sill & Wilkening 1978
1×10^{23}	Initial 2×10^9 yr	Oró et al 1980
1×10^{24} to 10^{25}	Initial 1×10^9 yr	Delsemme 1981
2×10^{24}[a]	Initial 2×10^9 yr	Frank et al 1986
2.3×10^{24} to 10^{26}	Initial 7×10^8 yr	Chyba 1987
6×10^{24} to 10^{25}	Initial 1×10^9 yr	Ip & Fernandez 1988

[a] Calculated by extrapolating from current estimates of 10^{15} g yr^{-1} of incoming mass.

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water vapor thus liberated would eventually condense, which implies that an atmosphere-ocean system was formed simultaneously with the increase of mass of the Earth (Arrhenius 1987). It is probable that a substantial fraction of the organic molecules present in the colliding volatile-rich minor bodies were destroyed due to the high temperatures and shock-wave energy generated during the impact with the Earth (Arrhenius 1987). However, under the anoxic conditions generally thought to prevail in the prebiotic atmosphere, the postcollisional formation of large numbers of excited molecules and radicals that are stable at high temperatures, such as CO, CN, and C_2 (Thomas et al 1989), could have led upon cooling to the formation of more complex organic compounds of biochemical significance (Lazcano-Araujo & Oró 1981, Mukhin et al 1989).

The Chemical Composition of the Archean Atmosphere

There is no general agreement on the detailed chemical composition of the Archean paleoatmosphere (Chang 1982, Holland 1984, Miller 1987). As shown below, there is considerable experimental evidence showing that the more reducing atmospheres (CH_4, NH_3, H_2O, H_2) yield a higher variety and amount of organic compounds than mildly reducing and nonreducing atmospheres, such as those in which CO and CO_2 are used instead of CH_4 (Schlesinger & Miller 1983a,b, Stribling & Miller 1987).

It is possible that if intense degassing took place during the accretional phase of our planet, then the Archean Earth could have had a highly reducing atmosphere (Pollack & Yung 1980). However, the presence of the 3800-Myr-old carbonate-rich metasedimentary rocks in Isua (Moorbath et al 1973) shows that even if methane was the predominant form of carbon in the prebiotic paleoatmosphere, a substantial amount of gaseous CO_2 was present in the Earth's atmosphere only 800 Myr after its formation

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(Schidlowski 1978, Lazcano et al 1983). This conclusion is supported by models of planetary formation in which a rapid core formation leads to a short-lived, highly reducing terrestrial secondary atmosphere (Holland 1984). Because of the restrictions that high CO_2 and low H_2 pressures put on abiotic synthesis, we have suggested elsewhere (Lazcano et al 1983) that the nonenzymatic syntheses of organic compounds occurred very rapidly in very low concentrations of atmospheric CO_2. This conclusion is in agreement with the analysis that S. L. Miller and his collaborators performed using several equilibrium and rate constants for the formation of amino-, hydroxy-, and dicarboxylic acids from the Murchison meteorite. Their results suggest that these organic compounds were synthesized in the meteorite parent body and in the primitive Earth in less than 10^4 yr (Peltzer et al 1984).

Additional localized reducing environments that could have included NH_3 and CH_4 would be maintained by local gas production from crustal reservoirs (Arrhenius 1987) and from gases originating in the trailing edges of Archean plates in midocean spreading centers (Lazcano et al 1983). The latter possibility is supported by the geological evidence that points to the existence of continental masses and oceanic basins, midocean ridges, subduction, and other indicators of an active terrestrial crust in which plate tectonics was probably operating since the early Archean (Bickle 1978, 1986, Compston & Pidgeon 1986, Nisbet 1987). As discussed elsewhere (Miller & Bada 1988), this hypothesis does not suggest at all that life originated in high-temperature hydrothermal systems, but only that the latter could have been a source of reduced gases and of chemical recycling in the Archean environment.

Free-Energy Sources

The direct sources of energy available for prebiotic organic synthesis are listed in Table 4 (Miller 1987). With the exception of cosmic rays, it is clear that in the prebiotic Earth the energy values were higher than those shown in Table 4, which represent current estimates for our planet. This is particularly clear in the cases of heat from volcanic sources, shock waves, radioactivity, and solar ultraviolet light. For instance, the evidence for intense geological activity in the terrestrial crust during the Archean (Nisbet 1987), the collisional events occurring during the late accretion phase of the Earth (Lazcano-Araujo & Oró 1981), and the higher concentrations of unstable isotopes (which had not yet decayed) all imply that the amounts of free energy available in the prebiotic environment from these processes were much higher than the contemporary values. Moreover, although Welch et al (1985) have argued that the Sun was perhaps never massive enough to have shown the enhancement of ultraviolet light during its early

Table 4 Present sources of energy averaged over the Earth

Source	Energy (cal cm^{-2} yr^{-1})	Energy (J cm^{-2} yr^{-1})
Total radiation from Sun	260,000	1,090,000
Ultraviolet light:		
<3000 Å	3400	14,000
<2500 Å	563	2360
<2000 Å	41	170
<1500 Å	1.7	7
Electric discharges	4[a]	17
Cosmic rays	0.0015	0.006
Radioactivity (to 1.0-km depth)	0.8	3.0
Volcanoes	0.13	0.5
Shock waves	1.1[b]	4.6

[a] 3 cal cm^{-2} yr^{-1} of corona discharge + 1 cal cm^{-2} yr^{-1} of lightning.
[b] 1 cal cm^{-2} yr^{-1} of this is in the shock wave of lightning bolts and is also included under electric discharges.

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stages of evolution that has been predicted by others (Gaustad & Vogel 1982, Canuto et al 1982), the absence of substantial amounts of free atmospheric oxygen and the subsequent lack of an ozone shield would account for the greater ultraviolet flux of the Hadean and early Archean (Lazcano et al 1983, Schopf 1983).

However, although it should be emphasized that neither a single energy source nor a single process can account for all of the organic molecules that were formed in the prebiotic Earth (Miller et al 1976), the importance of a given energy source is determined by the product of the energy available and its efficiency for synthesis of organic compounds or their intermediates, such as HCN (Oró & Lazcano-Araujo 1981, Miller 1987). Accordingly, the energy from the decay of radioactive elements was probably not an important energy source for abiotic organic synthesis, since most of the ionization events would have occurred in silicate rocks rather than in the reducing atmosphere (Miller 1987). Molten lava and other sources of volcanic heat have been suggested as playing a role in polymerization reactions (Fox & Dose 1977), but we believe that heat may have been important only in the pyrolytic synthesis of some amino acids (Friedmann et al 1971) and perhaps other organic compounds (Harada 1967). Ultraviolet light was certainly the largest source of energy on the primitive Earth but not necessarily the most effective one, since most of the photochemical synthetic reactions would occur in the upper atmosphere and the products formed would be decomposed by longer ultra-

violet wavelengths before reaching the oceans (Miller & Orgel 1974, Miller 1987).

The most widely used sources of energy for laboratory simulations of prebiotic synthesis are electric discharges, including spark, semicorona, arc, and silent discharges (Figure 1). Electric discharges are very efficient in synthesizing hydrogen cyanide, whereas ultraviolet light is not. Furthermore, since electrical storms occur close to the surface of the Earth, the organic molecules and their intermediates thus formed could reach the oceans before being photodissociated (Miller & Orgel 1974). This quenching and the protective steps are critical, since the organic compounds are destroyed if subjected continuously to the energy source (Miller 1987).

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CHEMICAL SYNTHESES OF MONOMERS

The wide variety of energy sources and chemical precursors that have been used in experiments simulating prebiological organic synthesis have been reviewed in considerable detail elsewhere (Abelson 1966, Miller & Orgel 1974, Lazcano et al 1983, Chang 1982, Chang et al 1983, Ferris & Usher 1983, Miller 1987, Ferris 1987). Several of these experiments have been performed under extreme concentrations of precursors, under high inputs of energy (Miller & Van Trump 1981, Chang 1981, 1982), or (in the case of the Fischer-Tropsch synthesis of fatty acids) under conditions of pressure and temperature that, although they may have been present in the solar nebula, are more difficult to envisage on the prebiotic Earth

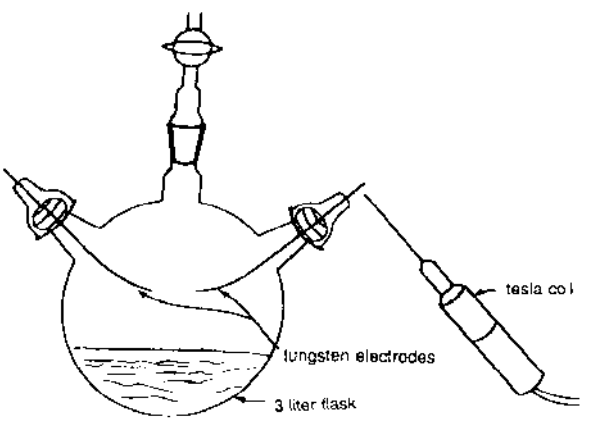

Figure 1 Electric discharge apparatus used to synthesize amino acids at room temperature. The 3-liter flask is shown with two tungsten electrodes and a spark generator (after Miller 1953, Oró 1963b).

(Miller et al 1976). In principle, however, the results of the laboratory nonenzymatic synthesis of organic compounds indicate that comparable processes took place on the early Earth, leading eventually to the accumulation of a complex heterogeneous mixture of monomeric and polymeric organic compounds.

Prebiotic Synthesis of Amino Acids

The first successful synthesis of organic compounds under plausible prebiotic conditions was accomplished by the action of electric discharges acting for a week over a mixture of CH_4, H_2, H_2O, and NH_3 (Miller 1953). Several amino acids, hydroxy acids, and other molecules were formed. A more detailed study of the electric discharge experiments demonstrated that essentially all the protein and nonprotein amino acids found in a sample of the Murchison meteorite were present among the products of the electric discharge (Ring et al 1972, Wolman et al 1972). Perhaps one of the most remarkable results of this comparison is that the ratios of amino acids relative to glycine in the Murchison sample are quantitatively similar to those found in the spark discharge experiments.

Miller (1957) has shown that the mechanism of synthesis of amino acids is the Strecker condensation, where HCN and aldehydes formed by the electrical discharges condense with each other in the presence of ammonia, forming the amino nitriles that upon hydrolysis yield the amino acids (Figure 2*a*). A similar mechanism can account for the synthesis of the reported hydroxy acids (Figure 2*b*). The study of the rate and equilibrium constants of these reactions (Miller & Van Trump 1981) has shown that both amino acids and hydroxy acids can be synthesized even at high dilutions of HCN and aldehydes in a primitive hydrosphere. The half-lives for the hydrolysis of the amino and hydroxy nitriles are less than 10^3 yr at 0°C (Miller 1987). Following previous studies on the formation of imidazole from glyoxal, ammonia, and formaldehyde (Oró et al 1984), and of imidazole-4-glycol and imidazole-4-acetaldehyde under prebiotic conditions (Shen et al 1987), Shen et al (1990a) have recently performed

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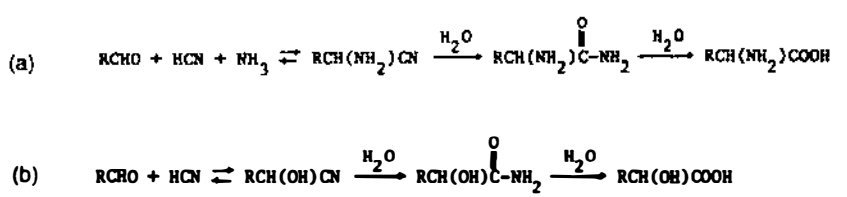

Figure 2 Strecker synthesis of (*a*) amino acids and (*b*) hydroxy acids (after Miller 1957).

the nonenzymatic synthesis of histidine from erythrose and formamidine followed by a Strecker synthesis.

Additional routes for the abiotic synthesis of amino acids have also been suggested (Sanchez et al 1966, Ponnamperuma & Woeller 1967); a very important one appears to be the condensation of HCN from NH_4CN into polymers, which upon hydrolysis yield glycine, alanine, aspartic acid, and several other amino acids (Oró & Kamat 1961). The base-catalyzed condensation of HCN yields a very heterogeneous brown polymer. Hydrolysis of this polymer produces many of the α-amino acids commonly found in proteins (Lowe et al 1963, Harada 1967, Friedmann & Miller 1969). Moreover, Ferris et al (1978) have shown that at pH 9.2, dilute solutions (0.1 M) of HCN condense into oligomers, which upon hydrolysis yield several protein and nonprotein amino acids as well as purines and pyrimidines.

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Prebiotic Synthesis of Bases, Sugars, and Their Derivatives

Several possible prebiotic routes for the formation of all the components of nucleic acids have been suggested. For instance, sugars are readily formed when formaldehyde polymerizes under alkaline conditions (Butlerow 1861). However, it is difficult to explain the presence of only ribose and deoxyribose in the prebiotic environment by this mechanism (Reid & Orgel 1967). Under the slightly basic conditions of the Butlerow synthesis, a complex mixture of more than 50 different pentoses, hexoses, and many other sugars is obtained (Decker et al 1982). Furthermore, under the reaction conditions in which it is formed, ribose tends to decompose into acidic compounds (Socha et al 1981). Accordingly, at the present time it is difficult to understand how ribose could have accumulated and separated from other sugars of abiotic origin in the prebiotic environment (Shapiro 1984, 1988, Ferris 1987).

Adenine, a purine that plays a central role in genetic processes and energy utilization, was first shown by Oró (1960) to form under prebiotic Earth conditions from HCN. When aqueous ammonia solutions containing large concentrations of HCN (1–10 M) are refluxed, adenine is formed together with other purines and biochemical compounds, including amino acids and pteridines (Oró 1960, Oró & Kimball 1961, 1962). The synthesis of adenine is thought to take place by a series of condensation and cyclization reactions involving imidazole derivatives. The overall reaction can be represented simply as five molecules of hydrogen cyanide producing one molecule of adenine (Figure 3).

There are other alternative pathways that have been suggested for the prebiotic synthesis of adenine. These include direct consecutive condensation of hydrogen cyanide (Oró & Kimball 1962), photochemical

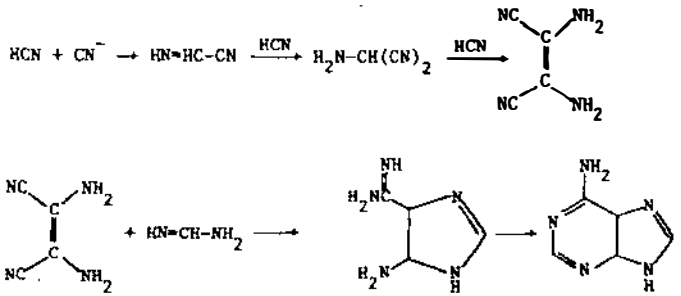

Figure 3 Prebiotic synthesis of adenine (after Oró 1960).

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isomerization of *cis*-diaminomaleonitrile (which is one of the HCN tetramers) and condensation with formamidine (Sanchez et al 1966), as well as a more complex sequence of reactions in which no isomerization of the *cis*-diaminomaleonitrile is required (Schwartz & Voet 1984). It is likely that more than one of these different pathways may have occurred under the variable conditions of the primordial environment (Basile et al 1985).

Guanine and xanthine are formed by the condensation of 4-aminoimidazole-5-carboxamide with urea (Oró & Kimball 1962). It should be noted that these imidazole derivatives can all condense with monocarbon compounds to generate all biological purines (Oró 1965). The prebiotic synthesis of adenine was confirmed by Lowe et al (1963) and by Ponnamperuma et al (1963), who found adenine after irradiating a Miller-Urey type of reducing atmosphere (CH_4, NH_3, H_2O, and H_2) with an electron beam. The kinetics and mechanisms of HCN oligomerization, as well as the potential role of the HCN trimer and tetramer for purine synthesis, have been extensively studied by Ferris & Orgel and their coworkers (1965 et seq), who confirmed that the above sequence of reactions follows the same direction: first imidazole formation, and then pyrimidine cyclization, as in the biological synthesis of purines.

Pyrimidines can be formed under plausible prebiotic conditions by the condensation of cyanoacetylene with either urea or cyanate (Sanchez et al 1966), a method that yields considerable amounts of cytosine. Cytosine is readily converted into uracil by deamination (Miller & Orgel 1974). Thymine was produced in small yields from the reaction between uracil and formaldehyde in the presence of hydrazine, which acts as a reducing agent (Stephen-Sherwood et al 1971). As noted above, Ferris et al (1978) have found that orotic acid (the common biochemical precursor of pyrimidinic bases in contemporary organisms) is released by the hydrolysis of HCN oligomers, together with purines and amino acids. A detailed summary of

recent work on the abiotic synthesis of both purines and pyrimidines may be found elsewhere (Ferris & Hagan 1984, Basile et al 1985).

Prebiotic Synthesis and Activation of Nucleotides

Although additional studies are required to demonstrate the prebiotic formation of nucleotides (Ferris 1987), the phosphorylated forms of the nucleosides of purine and pyrimidine bases can be produced nonenzymatically in the presence of linear and cyclic phosphates. However, a detailed discussion of the formation and subsequent activation of mononucleotides from individual sugars, phosphates, and bases is beyond the scope of this review and has been discussed elsewhere (Joyce 1989). Suffice it to say, as Joyce does, that "it is a long and difficult road from HCN and H_2CO to the activated mononucleotides" capable of providing a substrate for template-directed oligomerization (discussed below). In fact, evidence of a number of cross-inhibition phenomena occurring between mononucleotide isomers in template-directed syntheses attempted in various laboratories have led Joyce (1989) to the interpretation that life did not start with nucleotide polymers. Instead, there may have been a simpler genetic system that preceded nucleotides. As discussed in a later section of this review, this has led some researchers to a new area of research involving the study of polymerization reactions of nucleic acid–like molecules that might have preceded RNA. We return to a more detailed discussion of template-directed synthesis of nucleotides and their analogues following a brief but necessary discussion of the prebiotic synthesis of coenzymes and the role of prebiotic condensing agents.

Prebiotic Synthesis of Coenzymes

One of the most ubiquitous coenzymes in metabolic pathways is nicotinamide-adenine dinucleotide (NAD). This coenzyme functions as an electron and proton carrier and is required for activity by many mainstream metabolic enzymes. The functional part of this coenzyme is a nicotinamide ring, and the prebiotic synthesis of this cyclic nitrogen–containing vitamin has been achieved previously and is discussed by Miller & Orgel (1974). Additional significant work on the prebiotic synthesis of a number of coenzymes includes the synthesis of nitrogenous base derivatives such as the coenzymes adenosine diphosphate glucose, guanosine diphosphate glucose, uridine diphosphate glucose, and cytidine diphosphoenthanolamine (Mar et al 1987, Mar & Oró 1990). These syntheses were carried out by reaction of individual constituents under aqueous conditions, at moderate temperatures for short periods of time, using urea and cyanamide as condensing agents. The ease by which the synthesis of

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these compounds can be achieved supports the hypothesis of their presence in the prebiotic environment.

Prebiotic Synthesis of Other Compounds

There are a number of additional compounds that have been synthesized under possible primitive Earth conditions, but space limitations do not permit a lengthy discussion here. These include the mono-, di-, and tricarboxylic acids, branched- and straight-chain fatty acids (C_2–C_{10}, etc), and a number of membrane-forming lipids, to name a few. Of particular interest to the origin and early evolution of life is the synthesis of amphiphilic membrane-forming phospholipids through the condensation of fatty acids, glycerol, and phosphate under primordial conditions (Hargreaves & Deamer 1978a, Eichberg et al 1977, Epps et al 1978). However, a thorough discussion of the prebiotic formation of some of the specific phospholipids found in contemporary membranes, as well as a discussion of the role of membranes in the processes that led to the origin of life, is deferred until later in this review.

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PREBIOTIC CONDENSATION REACTIONS

Prebiotic Condensing Agents

Several mechanisms for the condensation of amino acids and nucleotides have been studied under abiotic conditions (Oró & Stephen-Sherwood 1974). These include coupling reactions using activated derivatives, condensation reactions using polyphosphates, thermal polymerization, and condensation reactions using organic condensing agents derived from HCN, such as cyanamide (Oró 1963a, Hulshof & Ponnamperuma 1976, Oró & Lazcano-Araujo 1981). Cyanamide, which has been detected in the interstellar medium and was presumably synthesized on the primitive Earth from HCN, is one of the best condensing agents. The evaporating pond model provides a geologically plausible and realistic model by means of which cyclic changes in humidity and temperature in the presence of cyanamide may have yielded significant amounts of oligopeptides (Hawker & Oró 1981) [including the catalytic dipeptide histidyl-histidine (Shen et al 1990b,c)], oligonucleotides (Odom et al 1982), and phospholipids (Rao et al 1982). The prebiotic condensing reactions leading to the synthesis of other membrane components have been reviewed extensively by Oró et al (1978) and by Hargreaves & Deamer (1978a).

Some of the major prebiotic pathways that may have been responsible for the nonenzymatic synthesis of oligomers and polymers on the prebiotic Earth have been reviewed elsewhere (Miller & Orgel 1974, Hulshof & Ponnamperuma 1976, Oró & Lazcano-Araujo 1981). The use of cyanamide

and other condensing agents in the polymerization of ribonucleotides yields a significant amount of "unnatural" 2′–5′ bonds in the phosphodiester backbone of the resulting oligomer (Hulshof & Ponnamperuma 1976, Odom et al 1982). However, the hydration/dehydration cyclical pathways for the nonenzymatic synthesis of polynucleotides suggested by Usher & McHale (1976) and Usher (1977) would have led to the preferential hydrolysis of the 2′–5′ bonds and the subsequent accumulation of molecules linked by 3′–5′ bonds.

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Template-Directed Polymerization Reactions

Polynucleotide formation has been extensively studied by L. E. Orgel and his collaborators, who have shown that the nonenzymatic template-directed synthesis of activated nucleotides (Lohrman et al 1980) can occur in the presence of metallic ions. Of all the cations used, Zn^{++} leads to an extremely efficient incorporation of complementary bases (Bridson & Orgel 1980, Bridson et al 1981). This result is quite interesting from a biological point of view, since many DNA- and RNA-polymerases are known to be Zn-metalloenzymes (Mildvan & Loeb 1979). Since Orgel and his group have found no evidence for the direct activation of the 3′-OH group, they have suggested that the Zn ion functions by coordination with the N-7 position of guanine, thereby changing the detailed stereochemistry of the double helical complex (Inoue & Orgel 1981). A favorable orientation of the double-helix complex was also achieved using a nucleotide activated with 2-methyl-imidazole (Inoue & Orgel 1982). In the absence of metals, guanosine-5′-phospho-2-methyl imidazole derivatives that polymerize on a poly(C) template can give rise to over 90% of 3′–5′ linked oligo(G) nucleotides, with chain lengths from 2 to 40 bases (Joyce et al 1984). A simplified model of this system is shown in Figure 4. The kinetics and molecular evolutionary implications of these reactions have been studied and discussed recently by Kanavarioti and coworkers (Kanavarioti & White 1987, Kanavarioti et al 1989). A possible prebiotic synthesis of imidazole and the 2-methyl imidazole derivative has also been achieved (Oró et al 1984). However, the complete nucleotide containing the imidazole derivative together with sugar, phosphate, and nitrogenous base, such as in the guanosine-5′-phospho-2-methyl imidazolide mentioned above, has yet to be synthesized under reasonable prebiotic conditions. Condensation reactions involving deoxyribonucleotide substrates are much less efficient (Lohrmann & Orgel 1977). The polymerization of 2-methyl-imidazole derivatives using random poly(C,U) (Joyce et al 1984) and random poly(C,G) copolymers and templates has also been achieved (Joyce & Orgel 1986). From the point of view of simple chemical models, not necessarily prebiotic, an elegant demonstration of an autocatalytic

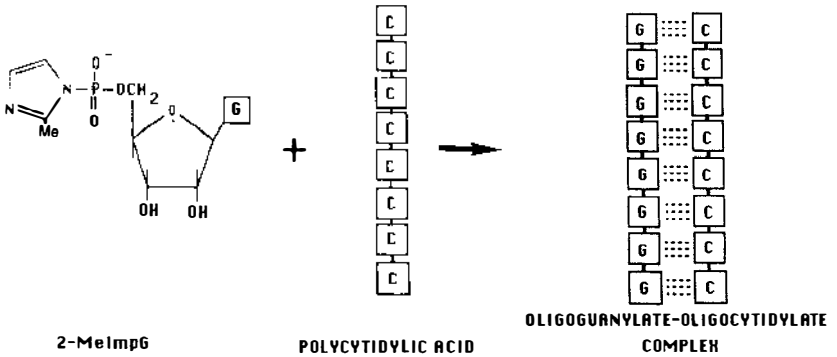

Figure 4 Template-directed oligonucleotide polymerization model.

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self-replicating system (hexadeoxynucleotide) has been presented by von Kiedrowski (1986). A similar reaction with a tetranucleotide analogue has been reported by Zielinsky & Orgel (1987). Recent results on the nonenzymatic template-directed synthesis of polynucleotides have been reviewed by Joyce (1987).

As discussed above, it is extremely difficult at present to assert the presence of ribose in the prebiotic environment. This has led Orgel and his associates to a whole new area of rcscarch involving the study of polymerization reactions of nucleic acid–like molecules that could have preceded both RNA and DNA. These experiments have been recently discussed by Schwartz et al (1987a) and include polymerization reactions of nucleic acid analogues with unusual backbones, such as the Pb^{++}-catalyzed formation of 2′–5′ phosphodiester-linked oligoguanylic acid (Lohrmann et al 1980), the 3′–5′-linked phosphoramidates that result from the polymerization reaction of 3′-amino-3′-deoxynucleoside-5′-phosphoimidazolides (Zielinski & Orgel 1985), and the pyrophosphate-linked products of the abiotic condensation of deoxynucleoside-3′,5′-diphosphates (Schwartz & Orgel 1985).

The acyclic analog 9-(1,3-dihydroxy-2-propoxy)-methyl-guanine can polymerize in the absence of a template (Schwartz et al 1987b), but the reaction proceeds more efficiently in the presence of poly(C). This analogue is one of particular interest, since it could easily form under prebiotic conditions from guanine, formaldehyde, and glycerol (Schwartz & Orgel 1985). These results support the idea that the first ancestral genetic systems may have consisted of nucleic acid–like informational replicating macromolecules derived from prochiral monomeric subunits (Joyce et al 1987, Joyce 1989).

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THE ORIGIN OF THE FIRST CELLS

Needless to say, there is no detailed scheme of the mechanisms that led gradually—but not necessarily slowly—from the prebiotically formed monomers and polymers we have described above to the earliest cells. Attempts to solve this problem have sometimes relied on the assumption that life arose as a result of the spontaneous formation of a single substance that embodied within itself all of the fundamental properties associated with life (Troland 1914 et seq, Muller 1955). But there is no such thing as a living molecule. Biology has been unable to produce a wholly satisfactory definition of life, but at least on phenomenological grounds it is clear that one cannot reduce (the catalytic properties of RNA molecules notwithstanding) all characteristics of living systems to a particular substance that arises suddenly by a lucky combination of atoms or simple monomers (Lazcano 1986).

The Origins of Replication and Translation: Two Major Unsolved Problems

How the first biological systems capable of replication and translation emerged is one of the major problems in the study of the origins of life. It is even possible that the genetic code was established prior to the origin of RNA itself (Orgel 1987). It has been hypothesized that a replicative system could have resulted from the interaction between abiotically synthesized polynucleotides and simple catalytic peptides such as His-His (Shen et al 1990c), inside liposomes (Oró & Lazcano-Araujo 1981, 1984). However, the mere coexistence of small peptides and polynucleotides (or nucleic acid–like molecules) does not guarantee by itself that protein synthesis will develop.

In fact, even if we assume that an extremely rich supply of abiotic polypeptides with the catalytic and structural characteristics necessary for the maintenance and reproduction of systems based on polyribonucleotide replication were available in the primitive environment, in the absence of some mechanism of translation sooner or later these polypeptides would be exhausted and eventually hydrolyzed. Regardless of how many catalytic polypeptides were formed abiotically in the primitive Earth, protein synthesis would not have evolved without a replicating mechanism ensuring the maintenance, stability, and diversification of its basic components. In other words, the synthesis of peptide bonds took place via the intermediate formation of aminoacylated oligoribonucleotides, which were presumably ancestral to contemporary aminoacylated tRNAs. The primitive tRNAs, or proto-tRNAs, could translate the information coded in the base sequence of nucleic acid molecules (ancestral to messenger RNAs), which

until then had been only templates for nonenzymatic polynucleotide replication (Lazcano 1986).

The ease with which amino acids and their polymers are formed under plausible prebiotic conditions has led to the idea that the first replicating systems consisted of polypeptides (Fox & Dose 1977, Dyson 1982, Kauffman 1986), but this possibility appears to us to be extremely unlikely (Miller & Orgel 1974, Orgel 1987). A counterview is represented by the hypothesis that early biological systems based both their reproduction and their metabolism in RNA molecules, an idea that was first suggested some 20 years ago (Woese 1967, Crick 1968, Orgel 1968, Sulston & Orgel 1971).

The idea of the primordial primacy of nucleic acid molecules has received considerable attention due to the discovery of catalytic and autocatalytic properties of RNA molecules (Pace & Marsh 1985, Zaug & Cech 1986, Cech 1987). These findings led Alberts (1986), Gilbert (1986), and Lazcano (1986) to suggest that there was no prebiotic translational synthesis of proteins—i.e. that although there are many experiments in which the abiotic formation of peptide bonds has been demonstrated, translational processes mediated by tRNAs and ribosomes evolved in RNA cells in which reproduction and metabolism had been dependent until then on catalytic RNA molecules.

The RNA World

The idea that RNA preceded DNA as genetic material has been expressed independently by many authors (cf. Lazcano 1986). This hypothesis is supported by several lines of evidence, including (*a*) the central role that different RNA molecules play in protein biosynthesis (Crick 1968), and (*b*) the well-known fact that this process can take place in the absence of DNA but not of RNA (Spirin 1986). Additional support is provided by (*c*) the existence of replicating biological systems such as viroids (Diener 1982) and RNA viruses (Reanney 1982) that use either single- or double-stranded RNA molecules to store genetic information; and by (*d*) the fact that the biosynthesis of deoxyribonucleotides always proceeds via the enzymatic reduction of ribonucleotides, i.e. all dexoyribonucleotides are formed directly or indirectly (as in the case of dTTP) from a cellular pool of ribonucleotides (Sprengel & Follmann 1981, Lammers & Follmann 1983).

The existence of a primordial replicating and catalytic apparatus devoid of both DNA and proteins and based solely on RNA molecules was suggested some time ago by Woese (1967), Crick (1968), and Orgel (1968). Such a possibility has received considerable support from the recently discovered catalytic properties of RNA (Cech 1987) and led Gilbert (1986) to propose the existence of what he has termed the RNA world. Evidence

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supporting the hypothesis that catalytic RNA molecules preceded proteins includes (*a*) the involvement of the 2′-OH group of ribose in several prebiotically plausible phosphorylation (Halmann et al 1969), hydrolytic (Usher & McHale 1976), and condensation reactions (White & Erickson 1981); and (*b*) the ubiquity of pyridine nucleotide coenzymes and similar ribonucleotide cofactors in metabolic pathways, which has led to several independent suggestions that coenzymes represent pregenetic code catalysts that were employed by early Archean cells before the appearance of proteins (Sulston & Orgel 1971, White 1976, 1982).

Although it is not known how protein synthesis appeared, Alberts (1986), Gilbert (1986), and Lazcano (1986) suggested that the basic selective pressure for the origin and stabilization of the primitive translation apparatus (genetic code, tRNAs, ribosomes) was the enhancement of the catalytic activities of RNA-based cells in order to increase their dynamic stability and survival (see also Joyce 1989, Orgel 1989, and references therein). However, these models should be updated. They should be revised following an in-depth study of the catalytic and replicative nucleic acid–like molecules (Cech 1987) and should consider the difficulties in the synthesis of prebiotic RNA discussed by Joyce et al (1987).

The Appearance of Membranes and Liposomes

If the origin of life did not depend on the chance appearance of a single molecule but on the gradual evolution of systems formed by sets of different compounds of biochemical significance, then it is obvious that a mechanism for keeping them together was required from the very beginning, i.e. a decisive step toward the origin of life must have been the early appearance of membrane-bound polymolecular systems (Oparin 1936 et seq, Haldane 1954).

Although some authors have argued that the formation of membranes occurred after the development of a replicating system (Eigen & Schuster 1978), the lack of compartments would not only severely limit the possible cooperative interaction between the different molecules forming the replicating apparatus but would also lead eventually to their dispersal. Membranes are essential to life, not only because they allow cells to maintain an internal microenvironment different from the exterior, but also because any self-replicating systems lacking them would be unable to undergo preferential accumulation and, eventually, differential replication (Oparin 1972, 1975, Oró 1980, Ferris & Usher 1983, Oró & Lazcano-Araujo 1981, 1984).

There has been no lack of theoretical and experimental models developed to study the properties of putative precellular systems. To cite just a few, this list includes coacervates (Oparin 1936), protenoid micro-

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spheres (Fox & Dose 1977), and sulphobes (Herrera 1942). However, all of these systems are formed under conditions that tend to produce the condensation of small molecules into polymers (Deamer & Oró 1980), and their choice as laboratory models of prebiotic systems has rested mainly upon the idiosyncratic assumptions about the nature of early life made by each researcher. A critique of these and other models has been carried out by Day (1984), whose detailed analysis led him to give considerable support to liposomes as the best contemporary laboratory models of precellular systems. The experimental evidence leading to this view has been presented by Oró et al (1978), Hargreaves & Deamer (1978a), Deamer & Oró (1980), Stillwell (1980), Ferris & Usher (1983), and Oró & Lazcano (1984).

Liposomes are spheres with diameters of 5–50 μm whose amphiphilic components self-assemble into vesicles with a double-layered membrane in the absence of any polymerization process (Deamer & Oró 1980). Although the prebiotic formation of lipids has not been studied as extensively as that of amino acids or nitrogen bases, their presence in the prebiotic environment is indicated by the nonenzymatic synthesis of neutral lipids, including fatty acids up to C18 synthesized by a modification of a Fischer-Tropsch process that produces several hydrocarbons (Nooner & Oró 1979). The prebiotic synthesis of lipids, including the amphiphilic phosphatidic acids (Epps et al 1978), phosphotidylcholine (Rao et al 1982), and phosphotidyl ethanolamine (Rao et al 1987), has been summarized and discussed by Oró et al (1978) and Hargreaves & Deamer (1978a). This liposome hypothesis will receive additional support if isotopic analysis confirms the extraterrestrial origin of the nonpolar membrane-forming molecules that have been extracted from samples of the Murchison carbonaceous chondrite (Deamer 1985, Deamer & Pashley 1989).

Since a C10–C12 linear fatty acid is the minimum size required to form a bilayer membrane (Deamer 1986), it is possible that the first liposomes that formed in the prebiotic oceans were relatively simple structures comparable to those described by Hargreaves & Deamer (1978b). Encapsulation of DNA within liposomes of more complex chemical nature has been achieved by dehydration-hydration cycles that may have occurred in intertidal settings in the prebiotic Earth, as they do today (Deamer & Barchfeld 1982). The evidence supporting the hypothesis that RNA molecules preceded contemporary DNA cellular genomes (Alberts 1986, Gilbert 1986, Lazcano 1986, Lazcano et al 1988b) led Baeza et al (1986) to study the encapsulation of polyribonucleotides within liposomes. The efficiency of encapsulation of poly(C) and poly(U) was not affected by the presence of a number of prebiotic condensing and catalytic agents, such as urea, cyanamide, and Zn^{++} (Baeza et al 1987). As indicated by liposome models of primordial cells, basic polypeptides of abiotic origin may have

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played an important role in the encapsulation of nucleic acid–like molecules within the lipidic boundaries (Jay & Gilbert 1987).

Models of transport of amino acids, nucleotides, and sugars inside a liposome have been developed by Stillwell (1980) using simple lipid-soluble carriers that may have existed in the prebiotic hydrosphere. Unfortunately, very little is known about the origin and early evolution of transport mechanisms and membrane-bound bioenergetic systems (Holden 1968, Wilson & Maloney 1978, Morowitz et al 1988). In our view, this is an area that requires intense study in order that we may develop an understanding of the origin of ion pumps and bioenergetic processes and the development of metabolism (Maloney & Wilson 1985, Maloney 1986).

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EARLY BIOLOGICAL EVOLUTION

The Origin of the Genetic Code

A direct correlation has been found between the hydrophobicity ranking of most amino acids and their anticodons (Weber & Lacey 1978, Lacey & Mullins 1983). Four codon assignments, corresponding to Trp, Tyr, Ser, and Ile, do not fit into this scheme, which has led Lacey et al (1985) to suggest that these amino acids are later additions to the code. This idea is consistent with Wong's (1981) hypothesis of a coevolution of the genetic code and amino acid biosynthesis, which proposes that the code evolved to accommodate new amino acids that were not present in the prebiotic terrestrial environment. The monophyletic origin of the triplet-based genetic code is supported by its universal distribution among contemporary forms of life. The minor exceptions to the code that have been detected among mycoplasms and protists and in animal, fungal, and plant mitochondria appear to be recent adaptations (Jukes 1983, 1984, Fox 1987). The synthesis of proteins is one of the most complex biochemical processes occurring in living systems. It requires the participation of a complicated translation apparatus (ribosome), three kinds of RNAs, and many structural proteins, enzymes, and cofactors. One can only conceive the emergence of the translation apparatus through a gradual sequence of steps that go from the relatively simple activation of amino acids to ever more complex phases of structural and functional molecular evolution. In one of its simplest expressions, the RNA-directed synthesis of proteins could be visualized by the interaction of a polynucleotide (acting as mRNA) with the loop regions of short hairpin oligonucleotides (acting as tRNAs), each having a carboxyl-activated amino acid at the 3′-OH group of the terminal adenosine (CCA). If the proximity of two of the neighboring activated amino acid derivatives (AA-proto-tRNA) were of the order of molecular interatomic distances, then the formation of a peptide bond

could take place by a combined transesterification-transpeptidation, which is an isoergonic process.

Studies on different aspects of this process from a prebiotic point of view have been carried out by several investigators. We know from the work of Usher & Needels (1984) and more recently of Lacey et al (1988) that the chirality of the sugar (D-ribose) determines the preferred chirality of the incorporated amino acid (L-amino acid) in the activated 3′-OH position. We also know from modeling studies by Kuhn & Waser (1981) that the hairpin oligonucleotides, acting at the same time as adaptors and activators of the amino acids, can be quite small (5–10 units) and still be able to assemble into a three-dimensional structure that may facilitate the formation of the peptide bond. A recent review by Orgel (1989) on the origin of polynucleotide-directed protein synthesis discusses the evolution of the adaptor moeity of these hairpins to eventually produce a triplet code.

Another detailed scheme based on RNA molecules and simple basic peptides has been developed by Maizels & Weiner (1987) to explain the origin of protein synthesis. They suggest that tRNA-like molecules initially evolved as tags at the 3′-ends of primordial replicating RNA genomes, which implies that the first proto-tRNAs and tRNA synthetases emerged prior to the other components of the protein biosynthetic system. It is also possible that primitive tRNAs with catalytic activity acted as their own synthetases, in which case vestigial evidence of this activity could still be detected under modified laboratory conditions (Lazcano 1986).

A somewhat different model has been developed by Orgel (1989), who suggests that prior to protein synthesis the attachment of amino acids to the 2′ (3′) termini of RNA templates favored initiation of replication at the end of a template instead of at internal sequences. These aminoacylated RNA molecules would become the evolutionary ancestors of later tRNAs. A second step leading to triplet-coded protein synthesis would be the pairwise association of the aminoacylated RNA molecules in such a way as to favor noncoded synthesis of peptides.

The Early Evolution of Protein Biosynthesis

Contemporary organisms contain information on their origins and evolutionary development in the form of informational macromolecules (Zuckerkandl & Pauling 1965) and biochemical pathways (Berry & Jensen 1988). The development of nucleic acid sequencing techniques applied to the study of ribosomal RNA has provided evidence of an early divergence among microorganisms that led to archaebacteria, eubacteria, and eukaryotes (Woese & Fox 1977, Pace et al 1986). The universal distribution among all contemporary forms of life of what is essentially the same

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genetic code, together with all the other highly conserved features of DNA replication and protein biosynthesis that are shared by archaebacteria, eubacteria, and eukaryotes, imply that the basic features of both genome replication and gene expression were established before the three major cellular lines diverged. Therefore, features in common found in these three cellular lines must have been present in their common ancestor (Woese & Fox 1977, Margulis & Guerrero 1986, Pace et al 1986).

The above appears to be the case for the protein synthetic molecular machinery, which may have been originally dependent on ribosomes in which no proteins were present and RNA played all the catalytic and structural roles (Crick 1968, Woese 1980). Protein biosynthesis is today a complex process in which a large number of molecules participate in a highly orderly manner (Spirin 1986), but a Darwinian view of the molecular processes of living systems implies that primitive translation could not have been as complex and efficient as in contemporary cells (Spirin 1976). This conclusion is supported by a number of observations, including several experiments that have shown that under in vitro conditions a simplified process of protein biosynthesis can take place in the absence of elongation factors, initiation components, and several ribosomal proteins (Spirin 1986).

At least three major phases can be recognized in the evolution of cellular genetic material: first, genomes of nucleic acid–like molecules (Joyce et al 1987, Joyce 1989); second, genomes of RNA; and finally, double-stranded DNA genomes, such as those present in all contemporary cells and in many viruses (Lazcano et al 1988b). Thus, even if we do not know how protein synthesis originated, it is obvious that if RNA preceded DNA as an informational macromolecule, then RNA polymerase must be one of the oldest proteins (Lazcano 1986, Lazcano et al 1988a). Genes coding for RNA polymerases are present in many viruses and in all cells, and among the latter, several different types of DNA-dependent RNA polymerases may be recognized, depending on the number and size of their subunits, on their amino acid sequence, and on the type of RNA transcribed (Lazcano et al 1989). Can vestiges of the original replicase be identified among this large array of RNA polymerases?

The hypothesis that contemporary cellular RNA polymerases were originally RNA dependent, i.e. were replicases, is supported by the observation that under slightly modified laboratory conditions normally DNA-dependent eubacterial and eukaryotic RNA polymerases can use polyribonucleotides and RNA molecules as templates (Llaca et al 1990). This replicase activity in contemporary eubacterial RNA polymerases is interpreted as vestigial from before the appearance of double-stranded DNA molecules (Lazcano 1986, Lazcano et al 1988a, Llaca et al 1990). Based

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on the comparative immunological studies on contemporary eukaryotic, archaebacterial, and eubacterial DNA-dependent RNA polymerases performed by Zillig et al (1985), and on comparisons of the nucleotide sequence of the genes coding for the largest subunits of *Escherichia coli* and several archaebacterial and eukaryotic RNA polymerases, it has been argued that an important vestige of the original replicase is found in the contemporary eubacterial RNA polymerase β' subunit and its homologues (Lazcano et al 1988a, 1989). This hypothesis is strongly supported by the amino acid sequence analysis of a single-unit viral RNA-dependent RNA polymerase homologous to the eubacterial β' subunit (Roy et al 1988).

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The Biological Origin of DNA

The "RNA prior to DNA" hypothesis can be further developed by understanding the selective pressures that led to the appearance of the biosynthetic pathways of deoxyribose, thymine, and DNA-dependent DNA polymerases with proofreading activity (Lazcano 1986). The arguments supporting this idea have been critically reviewed elsewhere (Lazcano et al 1988b) and include (*a*) the increased stability to basic hydrolysis of the 2′-deoxy-containing phosphodiester backbone of DNA as compared with its ribo-equivalent (Ferris & Usher 1983); (*b*) the absence of proofreading activity in RNA polymerases, which leads to a higher rate of mutation in RNA genomes relative to DNA (Reanney 1982); (*c*) the tendency of genetic information to degrade in RNA genomes owing to the hydrolytic reaction that deaminates cytosine into uracil and the lack of a correcting enzyme (Kornberg 1980); and (*d*) the fact that ultraviolet irradiation produces a larger number of photochemical changes in RNA molecules relative to double-stranded DNA. Thus, the absence of atmospheric ultraviolet attenuation during the early Archean must have imposed an intense selection pressure favoring duplex DNA over other genetic information storage systems.

The universal distribution among the three main cellular lineages (Woese & Fox 1977, Pace et al 1986) of the biosynthetic pathways leading to deoxyribose and thymine, together with all the highly conserved features of DNA replication (DNA polymerases, DNA primases, DNA topoisomerases that couple the unwinding of double-stranded DNA with ATP hydrolysis, etc), imply a monophyletic origin for DNA. Moreover, since changes in the template specificity of RNA polymerases can be easily achieved in the presence of Mn^{++} ions (Llaca et al 1990), the evolutionary transition from the ancestral RNA-dependent RNA polymerase into the present day DNA-dependent enzymes must have required only minor modifications of the active site. The functional similarities between all

cellular nucleic acid polymerases (DNA- and RNA-polymerases, reverse-transcriptases, DNA primases) have been interpreted to imply that the genes coding for some of the proteins involved in DNA replication resulted from gene duplications and further differentiation from the ancestral replicase (Lazcano et al 1988b). This common origin is suggested by the high evolutionary conservation of regions of nucleotide sequences of the genes coding for these proteins (Lazcano et al 1989). Further evolutionary processes leading to contemporary differences in energy production, metabolism, morphology, and ecological setting among microbes are discussed elsewhere (Broda 1975, Margulis 1982, Margulis & Guerrero 1986, Woese 1987).

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LIFE IN THE UNIVERSE

We have no evidence of extraterrestrial life. However, in spite of all the uncertainties involved in our description of the processes that led to the emergence of biological systems on our planet, it is clear that life is neither a miracle nor the result of a chance event but rather the outcome of a long evolutionary process. Whether or not this process can take place in any other place in the Universe is a matter for speculation, but the cosmic abundances (Cameron 1980) of carbon, nitrogen, oxygen, and other biogenic elements (Oró 1963a), the existence of extraterrestrial organic compounds (reviewed above), and the processes of stellar and planetary formation are certainly suggestive that at least some of the requirements for life are met elsewhere in our Galaxy (Oró et al 1982, Oró 1988).

More than a decade has passed since the Viking landers investigated the possibility of life on Mars. The data concerning this question have been summarized elsewhere (Flinn 1977, Ezell & Ezell 1984); the primary conclusion was that the biology experiments found no unequivocal evidence for the existence of a martian biota (Mazur et al 1978, Oró 1979, Bieman et al 1976, 1977, Horowitz et al 1976).

Organic and biological analyses of several samples of the martian regolith found no evidence of organic matter at the two Viking spacecraft landing sites. No organic matter was found at either site by the pyrolysis-gas chromatograph–mass spectrometer (GC–MS) at detection limits of the order of parts per billion and for a few substances closer to parts per million (Bieman et al 1976, 1977). On the other hand, two of the experiments designed to investigate the possibility of microorganisms in the martian regolith—the labeled release (LR; Levin & Straat 1976) and the gas exchange (GEx; Oyama & Berdahl 1977) experiments—gave what appeared to be positive results. The pyrolytic release experiment gave data that were interpreted not to be biological in nature (Horowitz et al 1976).

Two different possible explanations were suggested for the positive results of the LR and GEx experiments: Either very active microbial metabolic processes were taking place, or else chemical oxidation processes brought about by a chemically active martian regolith were responsible for the oxidation of the radioactively labeled nutrients. The latter view has been found to account for most of the observations (Oró 1976). However, since Mars appears to have been particularly rich in water in the past (Carr 1986, Pollack et al 1987), it is quite possible that the formation of biochemical compounds took place in the primitive Mars environment during the first 800–1000 Myr of its history. A more detailed discussion of this possibility has been reviewed recently by Oró & Mills (1989).

It is possible that conditions suitable for the origin and evolution of life have existed elsewhere in the solar system and may still persist in some of its minor bodies, such as Europa (Oró & Mills 1989, Oró et al 1990). The exobiological implications of the ocean of liquid water that some believe may exist under the cracked, icy surface of Europa, one of the Galilean satellites of Jupiter, is critically discussed elsewhere (Oró et al 1990). Finally, it is possible that chemical evolution and synthesis of biochemical compounds have occurred and are occurring now in Titan (Oró & Mills 1989). Titan has a reducing atmosphere whose origin and chemical composition have been discussed in considerable detail by Owen and his collaborators (Caldwell & Owen 1984, Owen & Gautier 1989). Even though the origin of the CH_4, CO, and N_2 present in Titan's atmosphere remains unresolved, Owen & Gautier (1989) have developed the hypothesis that Titan's major constituents, other than being equilibrated with the gases of the proto-saturnian nebula, are original or derived from primordial interstellar matter that accreted and formed the bulk of this satellite. Whereas the essential lack of liquid water renders Titan's atmosphere an unlikely model for prebiological synthesis of oxygen-bearing biochemical compounds, this satellite provides an excellent "anhydrous" model for the study of atmospheric chemical evolution (Oró & Mills 1989). In contrast to the essentially anhydrous condition of its atmosphere, it is possible that a thin ocean of a water-ammonia mixture (87% and 13%, respectively) is present in the subsurface of Titan if the scenario described by Lunine & Stevenson (1987) prevails in this satellite. If oceans and dissolved organic matter exist both in Titan and in Europa, a tremendous richness of subsurface organic synthetic reactions could be visualized for these satellites, which may explain, in part, some of the darker spots observed in Europa's outer surface and more recently in Triton, the remarkable satellite of Neptune.

This has been discussed recently by Carl Sagan and other members of the Voyager team (see Sagan 1989) following the successful exploration of

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Neptune and its satellites by the *Voyager 2* robot spacecraft prior to its departure from the planetary frontiers of the solar system in search of other worlds.

This is indeed a fitting finale for the accomplishments of the National Aeronautics and Space Administration in this century. These accomplishments will include *Galileo* and other future missions to the terrestrial and outer planets, comets, and asteroids, and the long-awaited launch of the Hubble Space Telescope in a terrestrial orbit. Hopefully, the latter will enable us to see far-away stars and galaxies of our expanding universe.

Some of us hope to see the establishment of human colonies on the Moon and Mars by the next century in order for science to unravel pertinent questions concerning chemical evolution and the origin of life on our beautiful, blue terrestrial planet.

It is difficult to conceive from a scientific point of view that "intelligent" life on Earth is a singular phenomenon in the trillions of galaxies that comprise the observable universe.

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