

SYNTHESIS AND ANALYSIS IN CHEMICAL EVOLUTION

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ABSTRACT. In the first part we examine the synthesis of the fundamental complex molecules of life (aminoacids and their polymerization to proteins, lipids, sugars, purines and pyrimidines, and nucleic acids) from simple molecules (H_2O , CH_4 , NH_3 , HCN , CO_2 , etc) under a variety of natural and laboratory conditions and sources of energy. In the second part we examine the analysis of the data that confirm the early appearance of life on Earth and the presence of complex organic compounds in a variety of environments (carbonaceous chondritic meteorites, the atmospheres of Jupiter and Titan, interstellar space, etc.) All these results confirm the universal effectiveness of chemical evolution.

I. SYNTHESIS

1.1 The Raw Material

The raw material from which the building blocks of life have evolved consists of the chemical elements of the periodic table. Examination of the crust of the Earth, the oceans, and the atmosphere provides us with the information about the abundance of these elements on the Earth. Data on the elemental composition of matter beyond the Earth come from several sources. The spectroscopic analysis of light from stars reveals the nature of the elements in them. The development of radio astronomy has provided us with the microwave technique of detecting various elements and excited species in interstellar space. Cosmic ray particles can supply us with samples of extraterrestrial matter. Meteorites and lunar samples have given us valuable knowledge of the composition of our Solar System. A reasonable and consistent picture of the abundance of the elements in the Universe can thus be obtained.

Hydrogen is by far the most abundant element. It makes up 93% of the total number of atoms in the Universe, and 76% of the Universe by weight. The theories of Gamow and Hoyle have attempted to outline the processes by which the elements were built up in a stepwise manner. Neutron capture, hydrogen fusion, and helium burning have been invoked

to explain the process of nucleosynthesis. There is a parallel between the gradual formation of the elements of the periodic table and the evolutionary development of the stars. The atomic abundance of some of the elements found in the Sun are shown in Table 1.

TABLE I: COMPOSITION OF THE SUN

Hydrogen	87.0	%
Helium	12.9	
Oxygen	0.025	
Nitrogen	0.020	
Carbon	0.010	
Magnesium	0.003	
Silicon	0.002	
Iron	0.001	
Sulphur	0.001	
Others	0.038	

The composition of the Sun may be taken to represent the average composition of the Solar System. Hydrogen, helium, carbon, nitrogen, and oxygen are the most abundant elements. With the exception of helium, these are the very elements which constitute 99% of living matter.

1.2 The Nature of The Primitive Atmosphere

A true understanding of the nature of the Earth's primitive atmosphere is a logical starting point for any discussion of the problem of the chemical origin of life. While it is difficult to answer by direct observation the questions that arise, evidence available from a number of sources indicate that a reducing atmosphere gradually gave way to the oxidizing atmosphere of today (1). Information gleaned from astronomy, astrophysics, chemistry, geology, meteoritic studies, and biochemistry can be used to elucidate this problem. The present rarity of the noble gases in the Earth's atmosphere in comparison to their distribution in the Universe indicates that the primitive atmosphere of the Earth was lost, and that the atmosphere that is generally described as primitive was secondary in origin. This atmosphere was outgassed from the interior of the Earth during planetary heating and it is the one which would be considered in our discussion of the primordial atmosphere of the Earth. The study of chemical equilibrium sheds some light on the nature of the reactions which should have taken place in a primordial reducing atmosphere. The thermodynamic properties of carbon, carbon dioxide, methane, ammonia, and water are very well known (see Table II).

TABLE II: EQUILIBRIUM CONSTANTS (K at 25 C)

$C + 2H_2 \rightarrow CH_4$	$8 \cdot 10^6$
$N_2 + 3H_2 \rightarrow 2NH_3$	$7 \cdot 10^5$
$H_2 + 1/2 O_2 \rightarrow H_2O$	$4 \cdot 10^4$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	$7 \cdot 10^6$
$S + H_2 \rightarrow H_2S$	$6 \cdot 10^{11}$

Composition of equilibrium mixtures of these materials has been satisfactorily determined. The equilibrium constants for the formation of methane from carbon and hydrogen, or water from oxygen and hydrogen, and ammonia from nitrogen and hydrogen are all of considerable magnitude. It is reasonable to suppose, then, that in the presence of a large excess of hydrogen, the elements carbon, nitrogen and oxygen existed in their reduced forms.

1.3 Energy Sources

The energies available for the synthesis of organic compounds under primitive Earth conditions are ultraviolet light from the Sun, electrical discharges, ionizing radiation, and heat. It is evident that Sunlight is the principle source of energy. Solar radiation is emitted in all regions of the electromagnetic spectrum. A great deal of this radiation, especially in the ultraviolet region, is shielded today by the ozone layer in the upper regions of the atmosphere. Since reaching the main sequence, our Sun has been very stable. The temperature of the Sun's surface four and one half billion years ago was almost as high as it is today. With this information, the solar flux at different wavelengths has been calculated. These figures clearly demonstrate the dominant role that ultraviolet light must have played among primitive energy sources.

The ultraviolet light should be considered as far more important than all other sources of energy that have been used in simulation experiments in the laboratory. However, on account of the intrinsic difficulties that have been involved in using short wavelength ultraviolet light, not many experiments have been performed with this energy source. The absorption of methane extends to 1450 angstroms, water to 1650, and ammonia to 2200. The quantum yield for the photolysis of ammonia is approximately 0.5, for water 0.3, and for methane about 0.5. The dissociation of these molecules takes place within the shorter wavelength region. However, the dissociation products may absorb at higher wavelengths.

Next in importance as a source of energy are electrical discharges such as lightning and corona discharges from pointed objects. These occur close to the Earth's surface, and therefore could have effectively transferred the reaction products to the primitive oceans. Since lightning can be easily simulated in the laboratory, many experiments have been performed using this form of energy.

The principal radioactive sources of ionizing radiation on the Earth are potassium-40, uranium-238, uranium-235, and thorium-232. Potassium-40 seems to be quantitatively more important than the other three sources at present. Presumably, therefore, it must have been more important in the past. The energy of potassium-40 is in the form of penetrating beta and gamma rays. In contrast, almost 90% of the energy from uranium-238 and thorium-232 is evident as alpha particles, which may not be penetrating enough to have a significant effect.

Calculations show that the decay of potassium-40 in the Earth's crust today gives rise to 3×10^{19} calories per year. Two billion years ago this would have been 12×10^{19} calories. By comparison, this is only 1/30-th of the energy available from short wavelength ultraviolet light.

The distribution of energy is a matter of importance. Most radiation from radioactive sources is absorbed in solid matter. Since the Earth's crust is about 30 km thick, this type of radiation could not have made a contribution to the synthesis of organic matter in the primitive oceans. However, local regions of high radioactivity might have existed in the past. There may have been micro-environments where the catalytic action of the metals present favored condensation reactions of the first molecules synthesized by ionizing radiation.

Heat from volcanoes was another form of energy which may have been effective. It is reasonable to expect that volcanic activity was more prevalent on the primitive Earth than today. The figure in Table III has been calculated on the assumption of one cubic km of lava emission per year at 1000°C . Besides, heat would also have been available from hot springs around boiling mud pots.

TABLE III: ENERGY SOURCES

Radiation from the Sun (all wavelengths)	260,000 cal/cm ² yr	
Ultraviolet light $\lambda < 2500 \text{ \AA}$	570	"
$\lambda < 2000 \text{ \AA}$	85	"
$\lambda < 1500 \text{ \AA}$	3.5	"
Electric discharges	4	"
Cosmic rays	0.0015	"
Radioactivity (to 1.0 km depth)	2.8	"
Heat from volcanoes	0.13	"
Meteoritic impacts	0.1	"

Chemosynthesis by meteoritic impacts on planetary atmospheres has been suggested as a possible pathway for primordial synthesis of organic matter (2). The reaction is probably a result of the intense heat generated momentarily in the wake of the shock wave following the impact.

EXPERIMENTAL WORK IN THE LABORATORY

Students of chemical evolution have tried to recreate Darwin's "warm little pond" in the laboratory. In other words, most of these different energy sources that have been considered to be possible have been used in the laboratory to see whether, when they act upon the Earth's primitive atmosphere, organic molecules are formed.

1.4 Amino Acids

The greatest amount of work in the field of prebiological chemistry

concerns the origin of amino acids. This may be due to the fact that amino acids are readily formed. A second reason may be that the emphasis on nucleic acid chemistry is only of comparatively recent origin. The protein molecule formerly occupied a pre-eminent position in biochemistry, and it is not surprising that efforts were made to look for its constituents. The development of chromatographic techniques facilitated the detection of minute traces of amino acids in complex mixtures.

Amino acids have been synthesized under simulated primitive Earth conditions by the action of ultraviolet light, electric discharges, heat and ionizing radiation. In some cases, the starting materials were reactive intermediates. In one of the first experiments done simulating the synthesis of organic matter on the primitive Earth, Miller exposed a mixture of methane, ammonia, water, and hydrogen to an electric discharge from tesla coils for about a week. Several organic compounds were formed. Among them were the amino acids, glycine, alanine, β -alanine, aspartic acid, and glutamic acid. Of the initial carbon introduced as methane, 2.1% had been converted into glycine.

1.5 Purines and Pyrimidines

The first synthesis of purines under simulated primitive-Earth conditions was carried out by Oro, who demonstrated that adenine could be synthesized from a concentrated solution of ammonium cyanide (3). The overall reaction can be depicted as 5 molecules of hydrogen cyanide in the presence of ammonia giving rise to adenine. This synthesis has been confirmed by Lowe et al. Oro's detailed study has shown that 4 aminoimidazole-5-carboximide and formamidine were the probable intermediates in this reaction.

Adenine was also synthesized by Ponnampetuma et al. by the electron irradiation of methane, ammonia, and water (4). Since hydrogen cyanide has been detected in these reactions, the possible pathway may be the same, namely, the base catalyzed reaction of hydrogen cyanide. In the electron irradiation of methane, ammonia, and water, the yield was about 0.01% of the starting methane. This is considerable and is realistic under primitive-Earth conditions. The interesting observation was made that the production of adenine was enhanced by the absence of hydrogen. This is not surprising, since methane carbon must be oxidized in order to appear finally in the purines. In any event, the high concentration of organic matter on the prebiotic Earth probably arose when most of the hydrogen had escaped from this atmosphere. Although many efforts have been made, purines and pyrimidines have not been definitely identified in the end products of electric discharge experiments. Since a large amount of hydrogen cyanide is formed, it is difficult to understand why the purines could be absent in such experiments.

In further experiments, it was shown that when a dilute solution of hydrogen cyanide was exposed to ultraviolet light, both adenine and guanine were formed. The yields of adenine and guanine were small, but more adenine was formed than guanine. Urea was found in large yield (5).

Investigations by Sanchez, et al., have shown that aminomalononitrile is an important intermediate in the synthesis of adenine (6). The monoaminomalononitrile is transformed into 4-aminoimidazole-5-carboximide, either by direct reaction with formamidine or, what is most interesting for our studies, the photochemical rearrangement of the hydrogen cyanide tetramer. By hydrolysis, it gives the 4-aminoimidazole-5-carboximide, which can condense under milder conditions with aqueous cyanide, formamidine, or cyanogen to produce a variety of purines, adenine, hypoxanthine, diaminopurine, and guanine.

In recent experimental work in the laboratory, we have recreated the primitive Earth conditions using methane, ammonia, and water as our raw materials and electrical discharges as our energy source. All five of the genetic bases, adenine, guanine, cytosine, uracil, and thymine were identified in this experiment. This was done by separation with High Pressure Liquid Chromatography (HPLC) and confirming the individual separated components by High Resolution Mass Spectrometry. This exciting finding leads us to believe that the conditions for the generation of all the components required for the nucleic acids were prevalent in prebiotic times.

1.6 Monosaccharides

As early as 1861, Butlerow showed that aqueous formaldehyde will undergo condensation to a mixture of sugars in the presence of alkali. In addition to hexoses, the lower molecular-weight monosaccharides are also formed in this alkaline-induced condensation of formaldehyde. Glycolaldehyde has been isolated and is apparently the product of the condensation of two molecules of formaldehyde.

Formaldehyde has been reported in the products obtained when methane, ammonia, and water mixtures were subjected to an electric discharge, β -irradiation or γ -irradiation. Although sugars have not yet been detected in experiments using methane, ammonia and water as starting materials, the ultraviolet irradiation of formaldehyde can lead to ribose and deoxyribose as well as other sugars (7).

Several difficulties are encountered in proposing the use of formaldehyde as the precursor of monosaccharides. Horowitz and Miller have pointed out that the high concentrations of formaldehyde used in some of the experiments were unrealistic in primitive-Earth experiments. Objections have also been made to the use of very basic solutions.

In an effort to circumvent some of these objections, Gabel and Ponnampereuma have used a simulated hydrothermal spring as a reaction medium (8). Aqueous solutions of formaldehyde of various concentrations were refluxed over kaolinite. The products were separated into trioses, tetroses, pentoses and hexoses. At a formaldehyde concentration of 0.5M, only trioses, tetroses and pentoses were formed. When the concentration of formaldehyde was reduced to 10^{-2} M, hexoses were also formed. Ribose was identified in the end products. The simulation of the hydrothermal spring, although possibly occurring only in microenvironments on the primitive Earth, eliminates the need for

postulating a basic primitive ocean, and would have provided also an opportunity for the breakdown of the paraformaldehyde. The photochemical synthesis of sugars, however, needs further investigation and may provide another reasonable pathway for sugar synthesis.

1.7 Nucleosides and Nucleotides

The satisfactory synthesis of nucleic acid bases and sugars under primitive-Earth conditions have led some investigators to explore the abiogenic formation of nucleosides and nucleotides. When ribose, adenine, and phosphate in dilute aqueous solution 10^{-3} molar was exposed to ultraviolet light, adenosine was formed (9). The phosphate appears to have acted as a catalyst in this reaction. The mechanism has not been investigated. However, it appears that a sugar-1-phosphate is formed and the phosphate is then replaced by the purine.

In the synthesis of nucleotides, the heterogeneous reactions which may have taken place on a dried-up ocean bed have also been examined. In simulating these conditions, an intimate mixture of the nucleosides was heated with an organic phosphate. Several phosphates were used in this reaction. Among them were disodium monohydrogen, trisodium, sodium ammonium monohydrogen, ammonium dihydrogen, diammonium monohydrogen, monocalcium, and tricalcium monophosphates and phosphoric acid (10). When the intimate mixture of the nucleosides and the phosphate was heated, phosphorylation took place. The mononucleotides were identified in the end products. The best yields in this reaction were obtained at about 160° . However, a small yield was obtained at temperatures as low as 50° . These experiments simulate an environment with a relative absence of water. However, water is not incompatible with this reaction and does not hinder it unless present in large excess. The conditions under which this reaction proceeds may therefore be described as hypohydrous. Among the monophosphates that were formed there were equal amounts of the 2', 3', 5', and cyclic monophosphates. It is possible that the presence of certain amino acids might direct the synthesis preferentially to yield a particular isomer.

1.8 Polypeptides

Simulated primordial syntheses of polypeptides have received more attention than the syntheses of other biological polymers. This is probably due to the great emphasis that has been placed on the primordial origin of amino acids. Fox has long been an exponent of the anhydrous or hypohydrous thermal origin of all primordial organic compounds. Fox and Harada have shown that in the presence of a proportionally large amount of glutamic acid or aspartic acid, an intimate mixture of all 18 amino acids normally present in proteins can be thermally polymerized at a temperature of 180° - 200°C . These polymers have been described as proteinoids. The molecular weights increased from 3600 in a proteinoid made at 160° to 8600 in one made at 190° . The maximum molecular weight which has been obtained is 80,000.

The polymers give a positive biuret test, can be hydrolyzed back to amino acids and are attacked by various proteolytic enzymes.

It has been argued that the energy available from volcanic activity is quite small compared to the other available sources of energy. Nevertheless, it cannot be denied that organic reactions, including polymerization of amino acids with the formation of peptide bonds, would occur under conditions simulating a volcano. A glaring weakness in this type of pathway for the origin of polypeptides is the necessity of postulating highly concentrated, intimate mixtures of the amino acids which are to be polymerized.

The synthesis of peptides directly from dilute solutions of amino acids has also been accomplished through the use of such condensing agents as cyanamide and dicyanamide. Both compounds are known to be formed upon ultraviolet irradiation of aqueous solutions of hydrogen cyanide or through the irradiation of a mixture of methane, ammonia and water (11). Ponnampereuma and Peterson have reported that glycylleucine and leucylglycine were formed from a dilute aqueous solution of glycine and leucine subjected to ultraviolet irradiation in the presence of cyanamide at pH 5. Mechanistically, ultraviolet radiation probably increased the concentration of carbodiimide, a tautomer of cyanamide, which can act as a condensing agent for amino acids.

II. ANALYSIS

2.1 The Origin of Life on Earth

The laboratory studies have established that the molecules necessary for life can be made in the laboratory. A question of paramount importance is whether this process did indeed take place on the Earth or elsewhere in the Universe. Can we go back in time to the earliest stages of the Earth, or the Solar System, and dig up some evidence for the presence of prebiologically synthesized organic molecules? Many attempts have been made to resolve this problem. When did the transition occur from the chemical to the biological systems? As the biological record is pushed farther, the period in which chemical evolution could have taken place is compressed. The base of the Cambrian is 600 million years ago. At one time it was thought that no life existed before the Cambrian. Paleontologists had argued that there were no skeletons, and therefore there was no life. However, the work of the micropaleontologists has pushed the presence of life much further back than 600 million years ago. At one billion years ago we have the Bitter Springs formations in Australia, in which microstructures have been observed. From three to three and a half billion is the Swaziland sequence in South Africa.

There are only three locations on the Earth which are indisputably recognized as older than 3.6 billion. There is the Isua region of West Greenland, the Saglefjord region of the Nain Province of Northern Labrador, and the Sighbhum granitic complex of eastern India.

The first evidence for life older than the Cambrian is the discovery of microfossils in thin sections from the Gunflint chert by Barghoorn and Tyler in 1954. Since then, many deposits from the

Proterozoic have been found which yield microfossils. The preservation of fine structural features as permanent comparisons of extant species and ecological patterns has resulted in the unequivocal acceptance of many Proterozoic microfossils as true remains of Precambrian organisms.

Among the earliest microfossils which meet rigorous criteria are the simple spheroids which have been found in the 3.4 billion year old Swarthoppic chert which immediately overlies the Upper Onverwacht of South Africa. The microfossils which have recently been found in the Pilbara Block of Western Australia appear to be of less certain origin. These appear to be poorly defined and resemble some of the microstructures found in the Onverwacht cherts. It is unlikely that they would even be considered as biogenic if they were not associated with stromatolites. While it seems possible and perhaps likely that at least some of the early Archean microstructures are true microfossils of once-living organisms, the evidence is still equivocal. At present, while such techniques as size distributions are applicable to a limited extent, the signs of micropaleontology cannot differentiate between those fossils which are from primitive living organisms and those which may have been abiotic.

2.2 Micropaleontology

Stromatolites are macroscopic sediments formed from the trapping and binding of detrital and precipitated minerals by sheaths of algae mats. These mats represent a complete ecology. The trapping of sediments by cyanophytes form a compact and opaque layer which forces the community to migrate up. As the process continues, layer upon layer of detritus is deposited between layers of organic debris and trapped microorganism. While present day stromatolites are limited in size and to harsh environments which exclude Metazoan grazers, stromatolites flourished in the Precambrian time.

Although some non-biological sedimentary processes can result in similar layered structures, stromatolites may be considered the best indication of life in the Archean. There are several known examples. The Bulowayan stromatolites are dated at about 2,700 million years old (12). Somewhat older are those in the Pangola supergroup of South Africa. More spectacular are those dated at 3.4 billion years, from western Australia (13). More recently, similar stromatolites have been described in Zimbabwe by Wilson and Orpen (14). Although metamorphosed to lower greenschist facies, the characteristics of these early Archean stromatolites are incredibly similar in appearance to younger, definitely biogenic stromatolites, and they constitute the best evidence of life at 1.2 billion years old and older.

2.3 Analysis of Lunar Samples

The Apollo missions provided a unique opportunity for the analysis of samples brought back from the Moon. Samples from the Apollo missions 11-16 were analyzed in the laboratory. These studies included an

examination of the lunar material for total carbon, the organic carbon isotope fraction, microfossils, and mineralogy. Sequential treatment of this sample by benzene, methanol, water, and hydrochloric acid provided extracts for examination by chromatographic and spectrometric methods. To minimize contamination, the analyses were carried out in a clean laboratory with filtered air, and the entire sequence of a solvent extractions of the lunar dust was accomplished in a single glass vessel. The total carbon determined by measuring the volume of CO_2 evolved when a one gram sample was outgassed at 150° at a pressure of less than one micron, and then burned at $1,150^\circ$. The values ranged from 140 and 160. The amount of carbon which could be converted into volatile carbon-hydrogen compounds was determined by pyrolyzing about 30 mg of the dust in an atmosphere of hydrogen and helium. The resulting involatile compounds were estimated by hydrogen flame ionization detector. The average value obtained was 40 micrograms per gram. Isotope measurements on the total sample gave us a $\delta^{13}\text{C}$ value of +20, relative to the PDB standard. These figures are considerable higher than those reported for intact meteorites (15).

Observations of dust, surfaces of microbreccias in this sections made by light and electron microscopy yielded no evidence of indigenous biological structures. To detect extractable organic compounds, some of the lunar dust was treated with a mixture of benzene and methanol. Fluorescence excitation and emission spectra of these extracts are suggestive of porphyrins. But similar responses have been obtained in exhaust products from the tests of the lunar descent rocket engines. It is possible that these porphyrins were formed from components of the rocket exhausts.

Capillary gas chromatography showed that any single normal alkane from C^{12} to C^{13} was not present at concentrations above 2×10^{-5} micrograms/gram. When the sample was treated with 6-HCL, hydrocarbons from C^1 to C^4 were identified, suggesting that carbides were present in the samples. Although the limits of detectability of the techniques employed were in the nanogram range, normal alkanes, isoprenoids, hydrocarbons, fatty acids, amino acids, sugars, and nucleic acid bases were not present at this level of concentration. It is readily understood that the surface samples of the Moon were exposed to high intensity ultraviolet light and micrometeorite bombardment, and carbon-carbon bonds would have easily broken under such conditions.

2.4 Carbonaceous Chondrites

For over a century, meteorites have been examined for the presence of organic compounds. The Alais meteorite was analyzed by Berzelius, the Kaba by Wohler, and the Orgueil by Berthelot. It is now generally agreed that carbonaceous chondrites do contain polymeric organic matter. However, results obtained in the past have been ambiguous as to the origin of the detected extractable organic matter. Was it truly extraterrestrial in origin, or was it a result of terrestrial contamination? The analysis of the Murchison meteorite provided the first unambiguous and conclusive evidence for the presence of

extraterrestrial organic compounds in meteorites. The Murchison Type-2 carbonaceous chondrite fell on September 28, 1969, near Murchison, Victoria, Australia. Several pieces were collected soon after the fall, and later during the months of February and March, 1970. The stones selected for analysis were those with the fewest cracks, the least exterior contamination and of massive appearance. The samples used in the study contained 2% by weight of carbon and 0.16% of nitrogen.

In these samples, aliphatic hydrocarbons were identified. The samples were symmetrical in distribution with a maximum retention time of C18. Comparison with hydrocarbons produced from a spark discharge experiment showed a great similarity. Both appeared to be saturated alkanes containing the same dominant analogous series. These similarities suggest that the hydrocarbons in the Murchison meteorite may have originated abiogenically. Studies on the aromatic hydrocarbons reveal a similar result (16). The benzene extracts were analyzed by gas chromatography and gas chromatography combined with mass spectrometry. A thermal origin for the aromatic hydrocarbons in the Murchison meteorite is suggested by the resemblance to the aromatic synthesized during the pyrolysis of methane. In both groups of aromatics, polynuclear compounds containing an even number of carbon atoms predominated. The relatively simple composition of the aromatic hydrocarbon fraction is of interest in view of the more complex nature of the aliphatic hydrocarbons.

In the search for amino acids, interior pieces of the meteorite were pulverized, extracted with boiling water, and analyzed by gas chromatography combined with mass spectrometry. A large number of amino acids were identified in the Murchison meteorite, including glycine, alanine, valine, proline, glutamic and aspartic acid. In addition, there were a number of non-protein amino acids, *n*-methyl glycine, β -alanine, 2-methyl alanine, α -amino butyric acid, β -amino butyric acid, and γ -amino butyric acid. Of the amino acids with assymmetric centers, both *d* and *l* enantiomers were detected. The presence of non-protein amino acids and amino acids with equal amounts of *d* and *l* enantiomers strongly suggest that these amino acids were prebiotic in origin. These provide us with the first conclusive results concerning extraterrestrial amino acids (17).

The studies similar to those undertaken on the Murchison meteorite have been applied to the Murray, which fell in Kentucky in 1951, and to the Mighei, which fell in Odessa in 1966 (18). These meteorites have been contaminated by exposure and by handling. The techniques of gas chromatography and mass spectrometry enable us to separate the indigenous amino acids and hydrocarbons from terrestrial contamination. Thus far, three examples were found which showed amino acids of extraterrestrial origin.

More recently, the exploration of the Antarctic gave a new impetus to the study of meteorites. The Japanese geologist Kenzo Yanai, on an expedition to the Yamato highlands of the Antarctic, discovered eight pieces of meteorite outside his tent in 1971. When these meteorites were studied he found they happened to be eight different meteorites. The following year 300 were identified, in a subsequent year 600, and now, over the years 4000 new meteorites have been brought back from the

Antarctic. Of these, about 40 fall into the category known as "carbonaceous chondrites." Two of these have been analyzed in the laboratory, the Alan Hills and the Yamato, and they provide supportive evidence of the observations made on the Murchison, the Murray, and the Mighei (19).

A striking feature of the Antarctic meteorites is that they are uncontaminated. The exterior and interior have the same amount of amino acids. Short of going to the asteroid belt, these are the best meteorites that are available to us for analysis.

The questions of the presence of the bases of the nucleic molecule in meteorites has been under discussion. Conflicting results from a variety of laboratories have raised questions about their presence in carbonaceous chondrites. However, recent work in this laboratory, using the techniques of HPLC combined with high resolution mass spectrometry have unequivocally confirmed the presence of the five genetic bases in the Murchison meteorite. Further work is now in progress to ascertain whether they are present in other carbonaceous chondrites.

2.5 Jupiter, Saturn and Titan

The study of the giant planets from ground-based observatories has given us a fair knowledge of the composition of these atmospheres. They appear to be highly reduced, containing large amounts of hydrogen, helium, and the hydrocarbons. The Voyager mission, with its number of experiments, especially the infrared observations, has given us a further handle to the composition of these giant planets and their satellites. It is clear that if hydrocarbons, such as methane and acetylene, ammonia, and phosphates are available, many organic reactions could take place. Simulation studies in the laboratory have shown very clearly that a large number of the organic molecules that were postulated as prebiotic could be synthesized under these conditions (20). As a matter of fact, their colored material -- the red spot of Jupiter, for example -- could be explained by the formation of organics from methane and ammonia. The presence of organic molecules in the giant planets has, therefore, been established by the observations of the Voyager spacecrafts and by laboratory simulation studies.

Of great interest to us is the possible reactions that may be taking place on Titan, the giant satellite of Saturn. Titan appeared in the pictures sent back to Earth by the Voyager mission as a fuzzy, orange ball. The analytical data point out to an atmosphere consisting mainly of nitrogen, and up to about 2% of methane. Furthermore, for the first time, hydrogen cyanide has been observed in a planetary atmosphere. When the data obtained from the Voyager mission gave us an atmosphere of 98% nitrogen and 2% methane, a large number of experiments were done where this mixture was exposed to a variety of energy sources. A whole range of organic molecules was synthesized (21), which correspond very largely to those identified in the Voyager mission. The data available to us have clearly established the presence of organic molecules in the giant planets and the satellite of Saturn, Titan.

As regards to life, the conditions may be such that the convection would take the synthesized molecules deeper into the planet to high temperatures and perhaps break them down. The chances of life originating under such conditions may be minimal. In the case of Titan, though it has an atmosphere, the temperature is probably so bitterly cold that the chances of any of the molecules coming together may be small. Still the process of prebiotic evolution may be taking place under these conditions.

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