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SHOCK WAVES AND THE ORIGIN OF LIFE

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by

Akiva Bar-Nun

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c. Shock waves

An energy source which was certainly abundant on the primitive Earth is the electrical energy of lightning. Lightning is produced when a potential difference is built up between the clouds and the ground or between adjacent clouds. The potential difference is created by separation of charges of water droplets and ice crystals in the clouds and possibly also by the transfer of ions formed near the ground into the clouds (20). Regardless of the exact mechanism, updrafts are essential for charge separation and these in turn are caused by the solar heating of the surface. In most cases the humidity of the air is of great importance as well as other factors (20), all of which prevent us from determining the frequency of thunderstorms on the primitive Earth. Although there is reason to believe that this frequency was larger on the primitive Earth, a conservative estimate will be the contemporary value of 100 lightning strokes each second over the whole Earth (21).

In the familiar process of lightning (Figure 1), huge currents (10,000 to 100,000 amperes) flow through a few mm-thick channel in the atmosphere. This huge number of electrons which collide with the gas molecules cause dissociation excitation ionization, and an increase in the kinetic energy of the particles. Typical temperatures of the plasma range from 10,000 to 30,000°K (20). The incandescent gas radiates both in the visible and in the ultraviolet, thus releasing some of the energy. Of the initial energy input of about 10^5 joules/m only a few percent are converted to dissociation, excitation ionization, and radiation, while most of it goes into the thunder shock-wave (22).

In the lightning channel, the temperature of the gas is raised very rapidly and a huge pressure is built up. The hot, high-pressure gas expands outward from the core and, in a very short time, forms at its front a supersonic blast wave, i.e., a sharp wave front across which pressure, temperature and density rise discontinuously. The process is schematically illustrated in Figure 2. This blast wave was termed (23) thunder shock-wave.

The thunder shock-wave can be approximated by the so-called cylindrical 'blast wave theory' (22, 24) for a single lightning stroke. The 'theory' is based on the assumption that most of the lightning energy is concentrated in an infinitesimally slender cylindrical column and is discharged instantaneously into the gas. As the shock front passes into the atmospheric gas it compresses and heats it, causing dissociation, excitation, ionization and chemical reactions all of which absorb energy and lower the gas temperature behind the shock (25). In order to calculate the actual temperature, the time dependent behaviour of these processes should be taken into account, for which unfortunately there is not enough information at the present. Alternatively, chemical and thermodynamic equilibrium are assumed to exist at all times, although this assumption is not valid for short periods (of the order of 1 μ s) immediately behind the shock front. The computed temperatures therefore are quite lower than the actual ones. Using an average energy input of 10^5 J/m into the gas and assuming an initial.

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Summary

The current views on the origin of life on Earth are discussed briefly, with special emphasis on the chemical evolution of the Earth's primitive atmosphere which was the opening step towards the origin of life. The various forms of shock-waves in the atmosphere: thunder, meteorite shocks and explosive volcanic eruptions are shown to have been of major importance in the atmospheric evolution, because of their very high efficiency in changing the atmospheric composition and in the formation of the building blocks of life.

TABLE OF CONTENTS

	<u>Page</u>
Acknowledgements	ii
Summary	iii
 1. INTRODUCTION	 1
a. Some historical notes	1
b. On Panspermia	2
c. The rebirth of an inquiry	2
 2. THE PRIMITIVE EARTH AND ITS ATMOSPHERE	 3
a. A time scale for chemical evolution and the antiquity of terrestrial life	3
b. Some properties of the planets	4
c. The Earth's primitive atmosphere	4
 3. ENERGY SOURCES ON THE PRIMITIVE EARTH	 5
a. A timescale for atmospheric evolution	5
b. Energy sources	6
c. Shock-waves	7
 4. THE CHEMICAL EVOLUTION OF THE PRIMITIVE ATMOSPHERE AND THE VERSATILITY OF BIOMONOMERS	 9
a. The formation of biomonomers and their precursors	9
b. Meteorites, comets, Jupiter and the interstellar molecules	10
c. Shock-wave production of biomonomers	11
d. The rate of chemical evolution of the primitive atmosphere	12
 5. POLYMERIZATION AND ORGANIZATION	 12
a. Polymerization of biomonomers	12
b. Some notes on replication	13
 6. ON EXTRATERRESTRIAL LIFE	 13
Mercury	13
Venus	13
Mars	14
Jupiter	15
Saturn, Uranus, Neptune and Pluto	15
Titan	15

	<u>Page</u>
7. CONCLUDING REMARKS	16
BIBLIOGRAPHY	17
TABLE 1	21
TABLE 2	22
TABLE 3	22
FIGURES	

1. INTRODUCTION

a. Some historical notes

The problem of man's beginning has intrigued him since remotest antiquity. Of more recent origin - and of perhaps greater fascination - is the question of life on other worlds beyond the Earth. It is our immense good fortune to live at the first moment of history when these tantalizing issues can be approached with some rigor and detail. It is certainly not a mere coincidence that our understanding of the processes which led to the emergence of life on Earth has advanced so rapidly in the last decades along with man's first ventures into space, where the theory can be finally tested.

Historically, the question of how life originated received the answer which was contemporarily available within the framework of theology, philosophy and science. One of the earliest is the detailed description of the reation in Genesis 1, in which God created the world and its inhabitants in pretty much the same order as suggested by modern science. Similar views are also found in the ancient Sumerian creation myths. At a later age the question of the origin of life was trivial. Life was arising all the time, at least for lower animals; not quite from nowhere, but mice from the mud of the Nile, maggots from putrefied meat and lice from sweat, as the most elementary observation seemed to show. The spontaneous origin of lower animals was accepted without question by ancient Greek philosophers and later by Aristotle (1), whose ideas dominated the human mind for almost two thousand years. Thus, major figures in the history of thought such as Thales, Plato, Epicurus, Democritus, Cicero, Plutarch, St. Augustine, St. Thomas Aquinas, Alexander Neckham, Cardinal Damien, Paracelsus, Goethe, Copernicus, Galileo, Harvey, Francis Bacon, Descartes, Hegel and Shelling, all accepted the spontaneous generation of plants and lower animals as a fact and differed only in their theoretical interpretation of the phenomenon (2). The idea of spontaneous generation however, already started to erode during the Renaissance, by experimenters such as the Italian physician Francesco Redi (3) who, in 1665, demonstrated that putrefied meat fails to generate maggots when covered with a gauze. About a decade after Redi disproved the spontaneous generation at the level of the house fly, a Dutchman, Antony van Leeuwenhoek, discovered microorganisms and thereby extended the debate on spontaneous generation for another two centuries. Experiments in which microorganisms were "generated" in virtually any sort of fermenting or decomposing water extract of plant or animal material were abundant (2,4). It was not until 1861, two years after the publication of Darwin's "The Origin of Species," that the theory of spontaneous generation was finally disproved by Louis Pasteur. In a series of exceptionally lucid experiments, which were described in his "Memoir on the Organized Corpuscles which exist in the Atmosphere: A Study of the Doctrine of Spontaneous Generation" (5), Pasteur showed unequivocally that in a sterilized solution in contact with sterilized air, even microorganisms are not generated.

Thus, by the 1860's it was no longer possible to hold that contemporary organisms, no matter how simple, spontaneously arise from non-living precursors. By this time Darwin had provided an intellectual framework in

which the development of complex organisms from simpler ones by natural selection could be understood. Yet, the problem of the origin of the first organism remained.

b. On Panspermia

In this intellectual climate, the Swedish chemist Svante Arrhenius in 1907 proposed the Panspermia hypothesis (6). Arrhenius suggested that terrestrial life did not originate on Earth and imagined that simple living forms may have drifted from world to world propelled by the pressure of radiation from the stars. Although this hypothesis can not be totally disproved, it faces very severe difficulties on account of the immense distances between the stars: Geometrical considerations make it highly improbable that such a "bug," randomly travelling through space, will be planted on Earth, unless our galaxy is densely populated and the planets eject considerable masses of these "bugs" into space (7). A more severe difficulty is posed by the destructively high dose of radiation which such organisms encounter while journeying unshielded through space. If some sort of shielding has to be provided against radiation damage, the organism becomes far too heavy to be ejected from the solar system by the star's radiation pressure (7). Another sort of planetary seeding, as proposed by Thomas Gold of Cornell University (7), invokes accidental contamination of direct seeding of the Earth by some advanced civilization capable of space travel. As Gold vividly describes it, the visitors having a picnic on the virgin planet, left their refuse behind and the microbial resident of the primordial cookie crumb may be the ancestor of us all. While this garbage theory of the origin of life on Earth understandably lacks appeal, it should not be excluded altogether. However, it is difficult to say much more about such a possibility. The panspermia theory does not indeed change much the nature of the problem, but merely shifts the origin to another locale. Since there is only an extremely remote chance of it being valid, we must finally come to grips with the problem of an indigenous origin of life on our own planet.

c. The rebirth of an inquiry

Pasteur's work was followed by a long period of experimental pessimism, during which many eminent scientists believed that the question of the origin of life could not be profitably studied by the scientific method. However, during the late nineteenth and early twentieth centuries a vast amount of detailed information about the chemistry occurring in the living cells has been accumulated (8). Namely, the identification of cell constituents such as proteins, polysaccharides, nucleic acids and lipids, as well as their building blocks, the amino acids, sugars, purine and pyrimidine bases, fatty acids and many others. Along with the identification of these substances, their roles in the complex and highly interlocking reaction sequences in the cell were gradually revealed. This progress in the understanding of the living cell on a molecular basis was accompanied by a fast increase in the understanding of the non-living world, through chemistry, physics, astronomy and geology. It became thus quite inevitable that the question of how life originated be reopened and examined again in view of the newly acquired knowledge. The major driving force behind the rebirth of the inquiry was naturally Darwin's evolutionary theory, of which the origin of life was a logical extension.

Thus, in 1927, J.B.S. Haldane suggested (9), based on the common initial steps of metabolic breakdown of sugar by anaerobic (not requiring molecular oxygen) and aerobic organisms, of which the latter group are much more advanced in utilizing the energy in the sugar, that the anaerobic organisms were the ancestors of the aerobic ones. He proposed therefore that the early organisms were anaerobic because the Earth's primitive atmosphere lacked free oxygen and was probably reducing (hydrogen rich). Further, based upon the many laboratory syntheses of organic molecules of biological importance which were studied by then, Haldane felt that their formation upon the Earth in the prebiological era could have proceeded much more easily if the atmosphere were reducing. At the time his suggestion was radical, since it was not yet known that the universe is made up mostly of hydrogen.

A few years earlier, in 1924, the Russian biochemist A.I. Oparin (10) had drawn the same conclusion from supposed abiogenic origin of petroleum. In 1929 it was found by spectroscopic studies that the universe is made up mostly of hydrogen and in 1934 methane and ammonia (the most reduced forms of carbon and nitrogen) were found spectroscopically on Jupiter. Two years later, Oparin published a book entitled "The Origin of Life" in which, based upon this evidence, the reducing nature of the Earth's primitive atmosphere was well established (10). Both Oparin and Haldane went further and suggested that under these reducing conditions a large variety of organic molecules were formed on the primitive Earth which, after a large span of time, gave rise to the first living organism. This prediction, known as the Haldane-Oparin hypothesis, does not contradict Pasteur's conclusions that life can not emerge on the Earth under the present conditions, since in the presence of free molecular oxygen most of the organic molecules of biological importance can not be formed outside a living body.

2. The primitive Earth and its Atmosphere

a. A time scale for chemical evolution and the antiquity of terrestrial life

Before proceeding with a detailed description of the processes which occurred on the primitive Earth, including the role played by shock waves in the emergence of life, it is necessary to form a time scale for the various events. Absolute age determination of the Earth's crust by the method of radioactive dating (11) suggests that the crust had solidified about 4.5 billion years ago. Not surprisingly, the moon and various meteorites were found to have approximately the same age.

The antiquity of terrestrial life was determined by radioactive dating of various precambrian rock formations and by searching them for fossils of ancient organisms (12). Whereas well defined microfossils are abundant in relatively young rocks, having an age of about 1.9 billion years, they are more scarce in the older rocks and resemble less the contemporary microorganisms. Nevertheless, it seems quite certain the microorganisms resembling rod-shaped bacteria existed already 3.1 billion years ago (12). Confirmation that these are fossils of living organisms can be obtained also from a variety of organic molecules, found in these rocks, which are distinctly associated with living organisms (13).

Around 1.4 billion years elapsed therefore between the formation of the Earth's crust and the appearance of microorganisms similar to the contemporary rod-shaped bacteria, which are far more advanced than the first primitive living system. Consequently, the chemical evolution which led to the first living system must have occurred within less than one billion years. This chemical evolution is the topic of the next chapters.

b. Some properties of the planets

It is assumed that our solar system was formed from a cloud of gas and dust similar to the ones which are so abundant in interstellar space. This cloud, upon reaching a certain density started to contract, either by gravitational forces or by weak chemical attraction forces, to form the central sun and the disk or solar nebula, from which the planets were formed. Although the exact mechanism of the process is still under debate it is apparent that the solar nebula was almost uniform, except for minor changes in the chemical composition as a function of the distance from the sun. Why is it then that the terrestrial planets Mercury, Venus, Earth and Mars are so different from the Jovian planets Jupiter, Saturn, Uranus and Neptune, which are constituted mainly of hydrogen and helium? The reason for this difference lies in their masses and proximity to the sun: The outermost region of a planetary atmosphere, the exosphere, is the layer from which gases escape from the planet into space, provided that their velocity is large enough to enable them to overcome the planet's gravitational pull. Since at any given temperature all the molecules have the same average kinetic energy, the lighter ones among them have a larger velocity. Thus, at a high enough exospheric temperature, the lightest elements: hydrogen and helium will be the first ones to escape into space. Because the terrestrial planets are closer to the sun their exospheric temperatures (except for Mercury which has no atmosphere left) are higher than those of the Jovian planets. On the other hand, their masses and consequently their gravitational pull are smaller. Therefore, hydrogen and helium are almost completely absent from their atmospheres. Mercury is so close to the sun that it has lost all of its atmosphere, while Mars has a small enough mass that enables even energetic oxygen and nitrogen atoms to escape. In photographs of the Earth's upper atmosphere in short ultraviolet light, even today one can see a huge cloud of hydrogen escaping into space. This process explains why, unlike Jupiter, the Earth's atmosphere has no free hydrogen, although both were formed from the same hydrogen-rich solar nebula.

c. The Earth's primitive atmosphere

Table 1 (14) shows the abundance of the elements in the Earth's crust, the Sun's surface and the average for the universe. From this Table it is clear that the Earth is not only deficient in hydrogen and helium but also in carbon, nitrogen, oxygen and the noble gases argon, krypton and xenon. This implies that not only hydrogen and helium escaped from the Earth, but also all the other volatile materials, even those much heavier than hydrogen. Whether this occurred after the formation of the Earth, because of a very large luminosity of the sun (7) or at a normal solar

luminosity before the accretion of the Earth was completed, can not be currently determined. Nevertheless, it is evident that the Earth was at some early stage devoid of an atmosphere and acquired one by exhalation of trapped gases from the interior. These gases should have originally been completely reduced as in the solar nebula, or on Jupiter where the oxygen, nitrogen and carbon are in the form of water, ammonia and methane respectively. But, since they were exhaled from the interior of the Earth, their composition was strongly dependent upon its temperature and composition. The currently accepted theory holds that the Earth was accreted from gas, dust and planetesimals of various sizes and was cold at the beginning. It warmed up gradually by contraction and release of gravitational energy and by the release of energy through radioactive decay. Eventually, in order for the iron to sink into the core and the lighter elements to migrate upward, the Earth's interior should have become hot enough ($\sim 1000^{\circ}\text{C}$) to melt the mantle. The gases which were exhaled while the Earth was cold should have been completely reduced, i.e., methane, ammonia and water vapour. If the exhalation continued when the interior became hot and molten, the gases should have gone through chemical reactions at high temperatures and emerged at a different state. Ammonia is not stable at elevated temperatures and decomposes to nitrogen and hydrogen. Methane is pyrolyzed to ethane and acetylene and to some larger species. It can be also oxidized by water vapour to carbon monoxide and carbon dioxide with the liberation of hydrogen (15). The oxidation however, can be slowed down if hot elemental iron is abundant, as indeed it was before sinking into the core, since the iron is oxidized more easily than hydrocarbons. Consequently, the composition of the gases emerging from the interior changed gradually, along with the variation in temperature and free iron content of the mantle. At the beginning they were mostly methane, ammonia, water vapour and hydrogen. Later exhalation consisted of methane, ethane, ethylene, acetylene and other hydrocarbons, nitrogen, water vapour and hydrogen. While finally, when the elemental iron sank almost completely by gravitation into the core and the mantle temperature was high, carbon monoxide and carbon dioxide, nitrogen, water vapour, and hydrogen were exhaled. The rate of exhalation at each temperature regime is not known and therefore we do not know what fraction of the atmospheric carbon was initially in the form of hydrocarbons and what fraction was in the form of carbon monoxide and carbon dioxide. The same also holds for nitrogen and ammonia. But, since the formation of carbon oxides from methane and nitrogen from ammonia is accompanied by the liberation of hydrogen, these exhaled gases contained free molecular hydrogen and the initial mixture was always reducing. This hydrogen escaped through the exosphere and its residence time in the atmosphere can not be determined with certainty.

In addition to the changes in atmospheric composition by the varying conditions in the interior, major changes occurred through various sources of energy in the atmosphere. Eventually, the two processes altered the composition of the atmosphere in the same manner, as will be seen later.

3. Energy Sources on the Primitive Earth

a. A time scale for atmospheric evolution

Before dealing with the processes which caused the composition of

the primitive atmosphere to change from reducing to oxidizing (containing free oxygen), we should look for a geological indication of the transition point. Such indication indeed exists in the form of the minerals uranite- UO_2 and the sulphides of iron, zinc and lead. If these minerals were exposed during their deposition even to a minute concentration of free oxygen, they should have been transformed to other, more oxidized minerals. These reduced minerals are all found in the South-African gold-uranium reefs which were determined to be 1.8 to 2.5 billion years old (16). It can be concluded then that the Earth's atmosphere contained no free oxygen until around 2 billion years ago. The free oxygen in the contemporary atmosphere is definitely a result of photosynthesis, with a small contribution from dissociation of water molecules by ultraviolet light in the upper atmosphere, which is accompanied by the escape of hydrogen. The appearance of free oxygen either by water photodissociation or already by photosynthesis is however the final stage of the atmosphere's evolution when, according to the fossil record, life was already abundant on the Earth. It is the early stage of atmospheric evolution which is pertinent to the origin of life. Unfortunately, there is no geological indication to the change in atmospheric composition between hydrocarbons and carbon dioxide.

Let us return then to the primitive atmosphere and, based upon the previous arguments, assume that it consisted at the beginning mainly of methane, ammonia and nitrogen, water vapour and some hydrogen sulphide and follow the chemical changes which were caused in it by atmospheric reactions. As water vapour is even today the major constituent of volcanic emanations, large quantities of water were exhaled and soon liquid water was accumulated in seas and oceans. Both ammonia and hydrogen sulphide are readily soluble in water and only small concentrations of these compounds remained in the atmosphere. The same low atmospheric concentration should have been maintained also for carbon dioxide, if any was present already at this early stage. The major atmospheric constituents were then methane and nitrogen. Since methane is stable at the atmospheric temperature range, it required an input of energy in order to change.

b. Energy sources

The energy available from the various sources on the primitive Earth can be fairly well estimated from contemporary values, which are presented in Table 2 (17). The flux of solar radiation 4.5 billion years ago was estimated from the course of the Sun's evolution, to be only about 60 percent of the current value (18). For the initiation of chemical changes in the atmosphere only the short ultraviolet range in the solar spectrum should be considered, as only photons at wavelengths shorter than $\sim 2800 \text{ \AA}$ can be absorbed by some of the atmospheric constituents, while most of them absorb at much shorter wavelengths. The flux of cosmic rays was probably similar to the contemporary one, while radioactivity was 3 to 4 times greater than at the present because of the decay of the radioactive elements during 4.5 billion years (19). The energy released by volcanic eruptions on the primitive Earth is hard to estimate, since it is not known if the geological conditions then were more favourable or less so for this phenomenon.

c. Shock waves

An energy source which was certainly abundant on the primitive Earth is the electrical energy of lightning. Lightning is produced when a potential difference is built up between the clouds and the ground or between adjacent clouds. The potential difference is created by separation of charges of water droplets and ice crystals in the clouds and possibly also by the transfer of ions formed near the ground into the clouds (20). Regardless of the exact mechanism, updrafts are essential for charge separation and these in turn are caused by the solar heating of the surface. In most cases the humidity of the air is of great importance as well as other factors (20), all of which prevent us from determining the frequency of thunderstorms on the primitive Earth. Although there is reason to believe that this frequency was larger on the primitive Earth, a conservative estimate will be the contemporary value of 100 lightning strokes each second over the whole Earth (21).

In the familiar process of lightning (Figure 1), huge currents (10,000 to 100,000 amperes) flow through a few mm-thick channel in the atmosphere. This huge number of electrons which collide with the gas molecules cause dissociation excitation ionization, and an increase in the kinetic energy of the particles. Typical temperatures of the plasma range from 10,000 to 30,000°K (20). The incandescent gas radiates both in the visible and in the ultraviolet, thus releasing some of the energy. Of the initial energy input of about 10^5 joules/m only a few percent are converted to dissociation, excitation ionization, and radiation, while most of it goes into the thunder shock-wave (22).

In the lightning channel, the temperature of the gas is raised very rapidly and a huge pressure is built up. The hot, high-pressure gas expands outward from the core and, in a very short time, forms at its front a supersonic blast wave, i.e., a sharp wave front across which pressure, temperature and density rise discontinuously. The process is schematically illustrated in Figure 2. This blast wave was termed (23) thunder shock-wave.

The thunder shock-wave can be approximated by the so-called cylindrical 'blast wave theory' (22, 24) for a single lightning stroke. The 'theory' is based on the assumption that most of the lightning energy is concentrated in an infinitesimally slender cylindrical column and is discharged instantaneously into the gas. As the shock front passes into the atmospheric gas it compresses and heats it, causing dissociation, excitation, ionization and chemical reactions all of which absorb energy and lower the gas temperature behind the shock (25). In order to calculate the actual temperature, the time dependent behaviour of these processes should be taken into account, for which unfortunately there is not enough information at the present. Alternatively, chemical and thermodynamic equilibrium are assumed to exist at all times, although this assumption is not valid for short periods (of the order of 1 μ s) immediately behind the shock front. The computed temperatures therefore are quite lower than the actual ones. Using an average energy input of 10^5 J/m into the gas and assuming an initial.

atmospheric pressure of one atmosphere and a composition of 72% methane, 25% ammonia and 3% water (by volume), the shock velocities and distances from the core as a function of time shown in Figure 3A were obtained (23). Note that about 1 μ s after the lightning discharge the shock-wave is 2 cm from the core and has a velocity of 10 km/s; at 60 μ s, the shock has moved to about 15 cm and has slowed down to about 1 km/s. Simultaneously, the temperature of the gas compressed by the passage of the shock wave drops by about 5000°K, immediately behind the shock (see dashed line, Figure 3B). This rapid deceleration of the shock wave is the result of a constant amount of energy being distributed into a fast growing mass of atmospheric gas (as the square of the shock radius) and, also, into changing the chemical composition of the compressed gas. The equilibrium temperature and composition right behind the shock wave in a reduced gas mixture consisting of methane, ammonia and water vapour are shown in Figure 4. Following the high temperature, the hot compressed gas is cooled by expansion (23) at a rate of between 0.5 and 5×10^7 °K/s as shown in Figure 3B. Thus, an element of fluid 2 cm away from the lightning column is traversed by the shock 1 μ s after the lightning discharge and the subsequent temperature history is given by the solid line labelled $t_s = 1$. Similarly, temperature histories are shown for those elements traversed by the shock after 2, 3 and 6 μ s. As will be shown later, this rapid heating to high temperatures which is followed by rapid cooling is very efficient in altering the chemical composition of the atmosphere.

Another source of shock waves are meteoroids which travel through the atmosphere at supersonic speeds - 11.3 to 70 km/s (26). While all incoming bodies are called meteoroids, those that impact on the ground are called meteorites. Figure 5 shows a schematic of a hypersonic flow around such a meteoroid. About 99 percent of the kinetic energy expended by the meteoroid is dissipated through the shock-wave, by compressing and heating the gas around it to temperatures of several tens of thousands of degrees. Similar to thunder shock-wave heating, the gas entering the bow shock is heated very rapidly. The hot gas then, flows mainly into and about the wake and is quenched at a slower rate than behind a thunder shock-wave. As will be shown later, the slower quenching of the hot gas is disadvantageous for some of the chemical reactions which lead to the formation of molecules of biological importance. Occasionally, a large meteorite with its very hot gases in the stagnation and bow shock regions hits water and the various chemical species generated at the high temperature have a chance to react with steam and water droplets (26). It is not clear however, whether the quenching in this case is much faster.

An additional source of meteorite energy is the shock-wave generated upon its impact with the ground. During the impact, its kinetic energy is suddenly released explosively and a good part of the meteorite and the ground where it strikes are evaporated. There are about 50 circular features on Earth, ranging up to 56 km in diameter that were caused by meteoritic impact (25). Obviously, many more such markings were erased from the surface of the Earth by weathering during the eons. Contrary to the Earth, both the Moon and Mars, as well as Phobos and Deimos, the Martian moons, are very heavily cratered from meteoritic impacts. Since most meteoroids originate in the asteroid belt located between the orbits of Mars and Jupiter, roughly the same number of meteorites should have been swept by Mars, the moon and the Earth. However, since the moon has no atmosphere, the meteorites reaching it were neither ablated nor slowed

down while approaching the surface and a much larger number has reached its surfaces. In addition, the lack of weathering has preserved these craters. The ablation and deceleration of meteorites in the rarified Martian atmosphere were also considerably smaller than in the case of the Earth. The craters on the Moon and Mars attest therefore to the huge number of meteorites which entered the Earth's atmosphere since its formation.

In calculating the energy input by meteoroids into the primitive atmosphere, distinction should be made between meteorites and micrometeorites. Above an altitude of about 90 km, most micrometeorites and cometary meteors have been either completely ablated or thermalized so the remnants float down like a fine rain (27). The distribution function of incoming particles is a power law strongly weighted towards the smaller particles. On the primitive Earth a larger flux, particularly of cometary debris may be expected, since by now a large fraction of the interplanetary debris has been swept by the Earth, which is estimated to lower their density around its orbit by about a factor of 3 every $\sim 10^8$ years (28). A conservative estimate of the mass flux for the primitive Earth is 2×10^{-14} g/cm²s, with arrival velocities of some 35 km/s (29). The corresponding energy flux is therefore ~ 0.1 cal/cm²yr.

Volcanic eruptions were mentioned earlier as a source of thermal energy. Occasionally, a very large pressure of gases and water vapour is built up inside the volcano before eruption. An explosion then takes place which gives rise to shock-waves in the atmosphere. The eruption which resulted in the explosive disappearance of two thirds of the island of Karakatoa in 1883 is estimated to have been equivalent to 5000 megatons of TNT (25), giving rise to shock waves which were heard at a distance exceeding 4500 km. A more recent explosive eruption occurred in Iceland's Heimaey Island, fortunately without loss of life.

Yet another source of energy arises from cavitation in water, owing to the action of ocean surface waves (30). Gas bubbles in the water collapse by impact of the waves, and are heated by compression to hundreds or even thousands of degrees. It is not clear however whether the heating is due to imploding shock-waves or to simple adiabatic compression. The energy available in cavitation has not been evaluated but, because of the great abundance of ocean surface waves, it is probably significant.

The estimated energy sources on the primitive Earth are summarized in Table 3.

4. The Chemical Evolution of the Primitive Atmosphere and the Versatility of Biomonomers

a. The formation of biomonomers and their precursors

When any of these energy forms, namely UV or ionizing radiation, high-energy particles, thermal energy, electrical discharges or shock waves are applied to a reduced gas mixture consisting of carbon, nitrogen, oxygen and hydrogen regardless of the exact composition, practically the same chemical reactions occur (31, 32, 33). The outcome of these reactions are, among others,

amines ($R-NH_2$), imines ($RCH=NH$) and hydrogen cyanide (HCN) of the carbon nitrogen compounds and of the carbon oxygen compounds alcohols (RCH_2OH), aldehydes ($RCHO$), organic acids ($RCOOH$), carbon monoxide (CO) and carbon dioxide (CO_2). Hydrocarbons like ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2) and other are also formed. The various energy forms produce only different relative concentrations of each of the products and vary in the energy efficiency. These products of the reactions in the primitive atmosphere react with each other to form the building blocks of life. Formaldehyde (CH_2O) polymerizes to form sugars $(CH_2O)_n$, hydrogen cyanide, ammonia and aldehydes condense together to form amino acids (34) - the building blocks of proteins; and hydrogen cyanide with ammonia condense to form some purines and pyrimidines - the basic units of ATP, DNA, RNA etc. A simple scheme showing the interrelations between some biomonomers and their precursors is presented in Figure 6. It is to be emphasized that these materials which are essential to any living system can be easily produced from any reduced gas mixture containing carbon, nitrogen, oxygen and hydrogen, utilizing a large variety of energy sources.

b. Meteorites, comets, Jupiter and the interstellar molecules

It is indeed rather surprising, although perhaps it should not be so, that these very compounds are abundant also outside the earth. A special class of meteorites, the carbon-rich carbonaceous chondrites, contain a large variety of hydrocarbons, carbon-nitrogen compounds and even yield upon hydrolysis some amino acids (35). As mentioned earlier the meteorites originate from the asteroid belt between the orbits of Mars and Jupiter and represent ancient chemical remnants from the solar nebula. Comets, which again belong to our solar system and are believed to be ices of various condensable gases (36) reveal by spectroscopic studies the species C_1 , C_2 , C_3 , CO and CN , CH , NH_3 , NH_2 and NH . Jupiter, which retained all of its original hydrogen has in its atmosphere, aside from the original methane, ammonia and water vapour, also ethane, acetylene (37), phosphine (38) and carbon monoxide (39). As will be shown later, both formaldehyde and hydrogen cyanide can be expected there as well. Upon leaving our solar system and reaching the vast interstellar medium, we also encounter a large variety of organic compounds. To mention only a few: carbon monoxide, formaldehyde, acetaldehyde, alcohols, ammonia, amines and imines, hydrogen cyanide, methyl acetylene, diacetylene, cyanoacetylene, cyanodiacetylene etc., (40). These interstellar molecules, which are being discovered at an amazingly fast rate, again attest to the versatility and great abundance of the carbon-nitrogen-oxygen-hydrogen compounds. They are indeed the very molecules which are formed in the laboratory from the reduced gas mixtures. But in the interstellar clouds they are being formed at very low gas and dust densities and at very low temperatures.

Thus, meteorites, comets, the Jovian planets and the interstellar clouds are all teeming with a huge number of chemical species, many of which are essential to living organisms or are precursors of the essential compounds. Moreover, all living organisms on Earth incorporate the very same chemical building blocks and function biochemically in an extremely uniform way. This rigid, uniform and nonvariable chemical system points unequivocally to the roots of the origin of life on Earth and makes life elsewhere an essential consequence. This realization of the amazing uniformity of the whole universe is perhaps our contemporary way of understanding the first chapter in the book of Genesis.

c. Shock wave production of biomonomers

The fact that compounds of biological importance, biomonomers, can be formed in a reducing atmosphere is not by itself sufficient for the emergence of life. Unless these biomonomers could be formed in quantities large enough to promote further chemical evolution and lead to life, they would have remained dissolved as such in the oceans. The quantity produced of each biomonomer during the period shortly after the formation of the Earth can be estimated from the energy efficiency of each of the energy sources which were then available. The energy efficiency of shock waves in producing aldehydes, hydrogen cyanide and amino acids is between 10^3 to 10^6 times larger than that of ultraviolet radiation (depending upon the UV absorber in the mixture) and about 10^3 times larger than that of electrical discharges (28). After the passage of a single shock through a reduced gas mixture, about a quarter of the reactants are converted to amino acids. This high energy efficiency of shock waves in converting the initial gases to biomonomers lies in the nature of the process. Namely, rapid heating of the gases to temperatures between 1000 to 3000°K, at which they reside for about a millisecond and the subsequent very rapid quenching of the hot gases. During the period of high temperature, the initial hydrocarbons are oxidized by water vapour into aldehydes (RCHO) and react with ammonia or nitrogen to produce hydrogen cyanide (HCN). The aldehydes condense in the gas phase with ammonia to form imines (RCH-NH), which add, again in the gas phase, hydrogen cyanide, to form aminonitriles $\left\{ \begin{smallmatrix} \text{RCH-CN} \\ | \\ \text{NH}_2 \end{smallmatrix} \right\}$. These upon hydrolysis in solution yield amino acids $\left\{ \begin{smallmatrix} \text{RCH-COOH} \\ | \\ \text{NH}_2 \end{smallmatrix} \right\}$ (34). The aldehydes can also condense by themselves in solution to form sugars; and hydrogen cyanide with ammonia yield in solution some of the purine and pyrimidine bases.

The fast chemical reactions which occur at the high temperatures provided by the shock wave are responsible for the high-energy efficiency of these processes. But, the short duration of the high-temperature regime and the rapid quenching are also essential, since if the gas is kept at the high temperature for a longer time, the aldehydes are oxidized further to carbon monoxide (CO) (15,34) which is of no value to the synthesis of amino acids or sugars.

In order to evaluate the contribution of each source of energy to production of biomonomers, the estimated amount of energy available has to be multiplied by the experimentally found energy efficiency with which it produces biomonomers. Upon doing so it becomes evident that shock waves were among the larger if not the largest contributor to the conversion of gases in the primitive atmosphere into biomonomers which, upon dissolution in the primordial oceans, become available for further chemical evolution. Based on the availability of thunder shock-waves on the primitive Earth, it was estimated (28) that during 10^9 years about 30 kg/cm^2 of organic material could have been generated. In addition to the continuous effect of thunder shock-waves, occasional large meteorites could have contributed very large quantities of organic matter locally. A meteorite 100m in diameter travelling at a velocity of 11 km/s could have provided 10^5 tons of organic matter (26) which, upon colliding with a small sea, could have raised the concentration in it to a very high level.

d. The rate of chemical evolution of the primitive atmosphere

By assuming that the frequency and energy of lightning strokes in the primitive atmosphere were similar to the contemporary ones, it was possible to calculate the rate in which the primitive atmosphere evolved from one composed mainly of methane and nitrogen to one composed of carbon dioxide and nitrogen (15). Figure 7 describes this process of atmospheric evolution by the effect of thunder shock waves. It was assumed, after Rubey (41), that most of the carbon, oxygen and nitrogen which are currently present in the Earth's atmosphere, hydrosphere and buried sedimentary rocks was accumulated by outgassing from the interior over approximately 5×10^8 years, while only a small fraction of them could be generated by rock weathering. When thunder at the current frequency and power was applied to the atmosphere of methane, nitrogen and water vapour using the experimentally obtained (15) energy efficiency and kinetic data, the nature and rate of the chemical changes in the atmosphere could be calculated. It is worth noting in this figure that huge amounts of both aldehydes and hydrogen cyanide were produced when the atmosphere evolved, giving rise to a large variety of biomonomers, such as amino acids, sugars, purine and pyrimidine bases etc. The rate of chemical evolution of the primitive atmosphere was of course larger, probably almost doubled, because of the additional effect of ultra-violet radiation from the sun (32, 42-44) and of lightning discharges (32, 45), which also increased the variety of the species produced.

5. Polymerization and Organization

a. Polymerization of biomonomers

The next step in chemical evolution was the reactions in the oceans, which utilized the dissolved materials produced in the atmosphere. The 30 kg/cm^2 of biomonomers which could accumulate during 10^9 years is obviously an overestimate since, as was seen earlier, a large fraction of the atmospheric carbon was completely oxidized and ended up as carbon dioxide buried in carbonate rocks (15). Further, even the amount of carbon which was converted into biomonomers could not accumulate indefinitely in the oceans. A large fraction of it was scavenged from the oceans by nonbiologically mediated chemical and physical processes, such as adsorption on sinking minerals, polymerization and aggregation to humic type polymers, or by aggregation to particulate matter through bubbling and sinking of this material to the ocean bottom (46). It is therefore hard to estimate the concentration of the solution of biomonomers in the oceans at each time. Nevertheless, it is obvious that in order to counteract the scavenging processes, a very large rate of production of biomonomers was necessary in order to maintain a large concentration of them in the oceans. This large rate of production is therefore the main contribution of shock waves to the process of chemical evolution.

Naturally, an increase in the degree of order had to follow, which could be achieved through polymerization of the various biomonomers into ordered polymers. Amino acids condense to peptides and proteins either thermally (47) or through the influence of clay minerals such as montmorillonite (48). Sugars, themselves the condensation products of formaldehyde, could condense further to polysaccharides under radiation (49). Similarly, radiation promotes the condensation of nucleotides to polynucleotides (50). Numerous

other modes of condensation of these biomonomers are described in detail elsewhere (32, 33).

b. Some notes on replication

Polymerisation is not sufficient for the emergence of life. One of the basic features of a living system is its replication. The only replication method known on Earth is via DNA which can replicate itself and build proteins according to a specific sequence of amino acids. This mechanism is rather elaborate and was most likely perfected over ages of trial and error. Presently, it is not known whether this was basically the original replicating system or a much simpler one existed, such as for instance the polymerization of amino acids on clay minerals like montmorillonite (48). This very complicated and yet unsolved problem is however beyond the scope of this review. But, once a self-replicating system has evolved, it could propagate without interruption, having the whole organic "soup" in the oceans as its food source. Indeed, one of the most challenging goals of exobiology is the discovery outside the Earth of a system in transition between a non-living and a living (replicating) state. An artist's conception of the entire life-development processes described in the foregoing is beautifully illustrated in Fig. 8.

6. On Extraterrestrial Life

At the time that this review is being written, Viking 1 is looking for life on Mars. This is the best possible proof of the state which the theory on the origin of life has reached. Not only has it allowed us to understand the events which led to the appearance of life on Earth, but it made it possible to estimate with some measure of certainty the chances of finding life on other planets, based upon the conditions prevailing on them and their past history.

Mercury, being very close to the sun is devoid of an atmosphere and is irradiated so intensely that life could not have evolved there.

Venus provides a somewhat more hospitable environment, but still quite hostile by comparison with Earth. The pressure at the ground level is about 100 atmospheres and the highest temperatures are around 700°K. The atmosphere of Venus consists mainly of carbon dioxide, with some water vapour and a haze of fine droplets of hydrated sulphuric acid - by no means a pleasant environment to live in. It is currently believed (51) that the atmospheres of Earth and Venus evolved in a similar way from highly reduced to ones dominated by carbon dioxide. The difference between the two planets lies in their proximity to the Sun. Venus is about 30 percent closer to the Sun than the Earth. Its surface temperature was therefore always higher than the boiling temperature of water and oceans could not be formed there. The vapour along with hydrocarbons and later carbon dioxide produced a strong greenhouse effect which kept heating and surface. The atmospheric gases allow solar radiation in the wavelength of the visible range to penetrate and heat the ground (like glass in a greenhouse). Most of the Sun's radiation is in the visible range, because of its high surface temperature. The ground is heated to several tens of degrees only and radiates therefore in the range of infrared wavelengths.

This radiation is absorbed by the gases in the atmosphere and cannot escape - thus heating the atmosphere and surface. Had it not been for this greenhouse effect, the surface temperature of the Earth would have been well below freezing. The carbon dioxide and water vapour produce together a strong greenhouse effect on Venus, raising the surface temperature to its high level. On the primitive Earth, where liquid water accumulated in the oceans, the carbon dioxide was dissolved in the oceans and precipitated as calcium and magnesium carbonates, forming the carbonate rocks. It is estimated (51) that the amount of carbon locked in carbonate rocks on Earth is comparable to the amount of carbon as carbon dioxide in the atmosphere of Venus. The discussion above suggests that the Venusian atmosphere has evolved along a path similar to the Earth's. The absence of liquid water on its surface might however have hindered further chemical evolution beyond the atmospheric reactions. Nevertheless, some primitive forms of life are still possible in the water clouds of in the somewhat cooler poles (52). The large temperature gradient in the Venusian atmosphere promotes updrafts which most likely produce thunderstorms, whose magnitude is presently unknown.

Mars was the first planet in our solar system to be chosen for a search for life, because it looked the most promising to harbour life as we know it. Its thin atmosphere, although only at a pressure of about 7 thousandths of our own, consists of carbon dioxide - the carbon source of most of Earth's living organisms, and some small amounts of carbon monoxide, water vapour, oxygen and a trace of ozone (53). Upon passage through the thin atmosphere, the mass-spectrometer on board the Viking Lander detected 3% of nitrogen, which is essential for life as we know it and also some 2% of argon (54). Because of the crucial role played by liquid water in life processes, the question whether there is water on the surface of Mars is of prime importance. Each of the Martian polar caps recedes quite rapidly at the beginning of summer, but a considerable area remains white all through the summer. It is suggested that this fraction of the cap is covered by water ice, while the easily removed fraction is solid carbon dioxide. It is also assumed that much water ice is locked beneath the surface all over the planet in the form of permafrost, like in Antarctica (53). The trench left by the Viking Lander's arm after removing a soil sample strangely enough resembles a trench in wet sand. Whether this indicates the presence of water is still undetermined (54). An indication that during some time in Mars' past, liquid water was flowing over the surface is provided by the Mariner 9 and Viking Orbiter pictures of the planet, in which are seen long and deep canyons and fully developed river valleys which are probably formed by fluid erosion. The mechanism for warming up the planet and release of the frozen water and carbon dioxide is still unknown. Possibly the changing angle between Mars' axis of rotation and the plane of its orbit around the sun provides every ~ 11,000 years conditions where neither of the two poles is cold enough to trap all the carbon dioxide and water vapour from the atmosphere. The released gases produce a large greenhouse effect, like the carbon dioxide and water vapour in the Earth's atmosphere, which enhance the warming up trend, thus releasing more of the frozen material. Another warming-up mechanism might be through very large, planet-wide dust storms, which increase the surface temperature. The Mariner 9 measurements indeed showed an increase in temperature by several degrees during the major dust storm on Mars (55).

Because of Mars' lower gravity, both oxygen and nitrogen can escape through its exosphere (56), in addition to hydrogen, which is the only escapable species from the Earth. From the argon content of the Martian atmosphere

(argon not being able to escape Mars), it can be calculated that Mars had in its past a much denser atmosphere (54).

Thus, there is good reason to believe that Mars once had conditions similar to those on the primitive Earth and possibly life could have originated there as well. Although conditions now are considerably harder for life by Earth standards, it is conceivable that life, once originated, would have adapted to these conditions.

While this review is being written, all three biology experiments on board the Viking Lander gave positive results with regard to the possible existence of microorganisms in the Martian soil. A more definite conclusion will be reached after repeating the results and running several control experiments with sterilized Martian soil. Conclusive evidence for the existence of life on Mars will obviously be of invaluable importance to the understanding of the processes which led to the emergence of life on Earth and possibly elsewhere.

Jupiter's atmosphere (Figure 9) is still in its most reduced form. It is therefore a good model for the Earth's primitive reducing atmosphere, with one difference: There is about a 1000:1 ratio between the hydrogen and the carbon, nitrogen and oxygen. Despite the large excess of hydrogen, the highly hydrogen deficient acetylene was detected in the Jovian atmosphere (37). This acetylene can be formed under the Jovian conditions only through thunder shock waves (57), whose frequency or power were estimated to be some 10^4 times larger than on Earth (57). The carbon monoxide, which was also recently discovered on Jupiter (39), probably can be formed only through thunder shock waves (58) and supports the hypothesis of severe thunderstorms in the Jovian atmosphere. These thunderstorms will be looked for in the forthcoming mission to Jupiter (59) and are currently being investigated through the expected decametric radio noise (60). Based upon simulation studies (57,58) these Jovian thunder shock waves are expected also to produce hydrogen cyanide and formaldehyde which can, like on the primitive Earth, give rise to biomoners. Whether living systems can evolve in the Jovian water and ice cloud layer (61) is questionable. The lower atmospheric layers are extremely hot and dense and lack liquid water. Jupiter has no solid surface at all. Even if life does not exist there, finding biomoners and possible their condensation products in the Jovian atmosphere will be invaluable in enlarging our knowledge about similar processes in the Earth's primitive atmosphere. These findings however, have to await a Jupiter entry probe carrying a mass-spectrometer similar to the one on the Viking mission.

Saturn, Uranus and Neptune are quite similar to Jupiter but, because of their distance from us are harder to study. Like Jupiter, Saturn also has spots and bands, which again suggest thunderstorm activity and interesting prebiotic chemistry. Very little is currently known about Pluto, the outermost member of the solar system.

Titan, one of the Saturnian satellites is known to have an atmosphere, one component of which was identified as methane (62). Because of its smallness its hydrogen content is probably low, making it quite similar to the primitive Earth, and therefore worth studying with great care.

7. Concluding remarks

The experimental and observational evidence, part of which was described here, suggests a way by which life could have evolved on Earth. The scheme discussed here is certainly incomplete and probably inaccurate in many details. Nevertheless, it is believed that the general framework of the theory is correct.

Shock waves, having an energy efficiency several orders of magnitude larger than those of the other energy sources in producing biomonomers, have been no doubt a major driving force for chemical evolution.

Since the early stages of chemical evolution left no trace on the Earth, the way to confirm this theory is through planetary exploration where, hopefully, various stages of chemical and biological evolution might be studied. In the forthcoming years or even weeks, therefore, we can expect or at least hope that some of the clues to our origin on this planet will be found elsewhere in space.

Note added in proof:

While this review was being written, positive results were obtained from the three life detection experiments on the Viking landers. It was hoped that by the time the review was published, conclusive evidence as to the existence of living organisms on Mars would be found. However, further experiments did not clarify the matter and additional experiments both on Mars and on Earth are required in order to decide whether the results indicate some life form or merely special Martian soil chemistry. Fine accounts of the Viking results can be found in an article by W. D. Metz (Science, 194, 819, 1976) and in the two Science issues of August 27 and October 1, 1976.

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Table 1: Abundance of the elements [after (14)]

Element	gram atom/gram atom of Si		
	Earth's Crust	Sun's Surface	Total Universe
H	0.14	5.1×10^4	$4. \times 10^4$
He	7.5×10^{-8}	1.0×10^4	3.1×10^3
Li	4.3×10^{-4}		$1. \times 10^{-4}$
Be	2.2×10^{-5}		0.2×10^{-4}
B	$3. \times 10^{-5}$		0.24
C	2.7×10^{-3}	1.	3.5
N	3.3×10^{-4}	2.1	6.6
O	2.9	2.8×10^2	21.5
Ne	$<5. \times 10^{-9}$		8.6
Na	0.12	0.1	$4. \times 10^{-2}$
Mg	8.6×10^{-2}	1.7	0.91
Al	0.3	0.11	9.5×10^{-2}
Si	1.0	1.0	1.0
P	3.8×10^{-3}		1.0×10^{-2}
S	1.6×10^{-3}	0.43	0.38
Ar	$4. \times 10^{-7}$		0.15
Kr	$<5. \times 10^{-9}$		0.51×10^{-4}
Xe	$<5. \times 10^{-9}$		0.04×10^{-4}

Table 2: Free energy sources on the contemporary Earth (after 17).

Source	Energy Calories/cm ² yr
Total radiation from the sun*	260,000
Solar ultraviolet light	
$\lambda < 2500 \text{ \AA}$	570
$\lambda < 2000$	85
$\lambda < 1500$	3.5
Electric discharges	4
Cosmic rays	0.0015
Radioactivity (to 1 km depth)	0.8
Volcanoes	0.13

*Out of the total radiation from the sun, only the photons of the ultraviolet light are energetic enough to have caused changes in the chemical constitution of the primitive atmosphere.

Table 3: Estimated energy sources on the primitive Earth

Source	Energy
Solar ultraviolet radiation at the top of the atmosphere (31)	
$\lambda < 2900 \text{ \AA}$	7×10^{14} photons /cm ² s
$\lambda < 2600$	4×10^{14}
$\lambda < 2400$	9×10^{13}
$\lambda < 2000$	2×10^{13}
Cosmic rays	0.0015 cal/cm ² yr
Radioactivity	2.6
Volcanoes	0.13
Lightning	4
Thunder shock waves	2
Meteorite shock waves	0.1
Explosive volcanic eruptions and cavitation	?

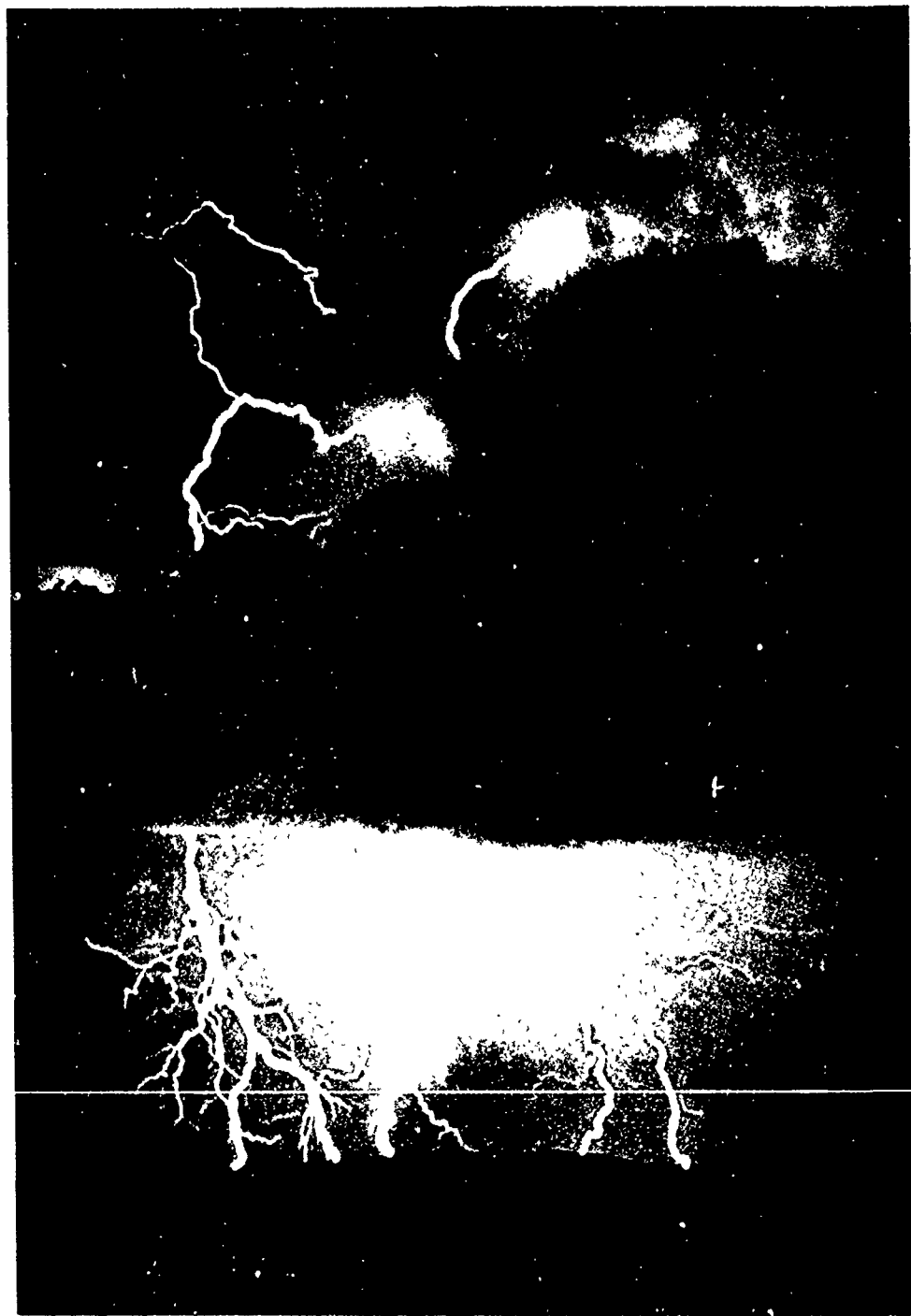


FIG. 1. LIGHTNING AND THE OIL FIELD (COURTESY: © AMERICAN PETROLEUM SOCIETY)

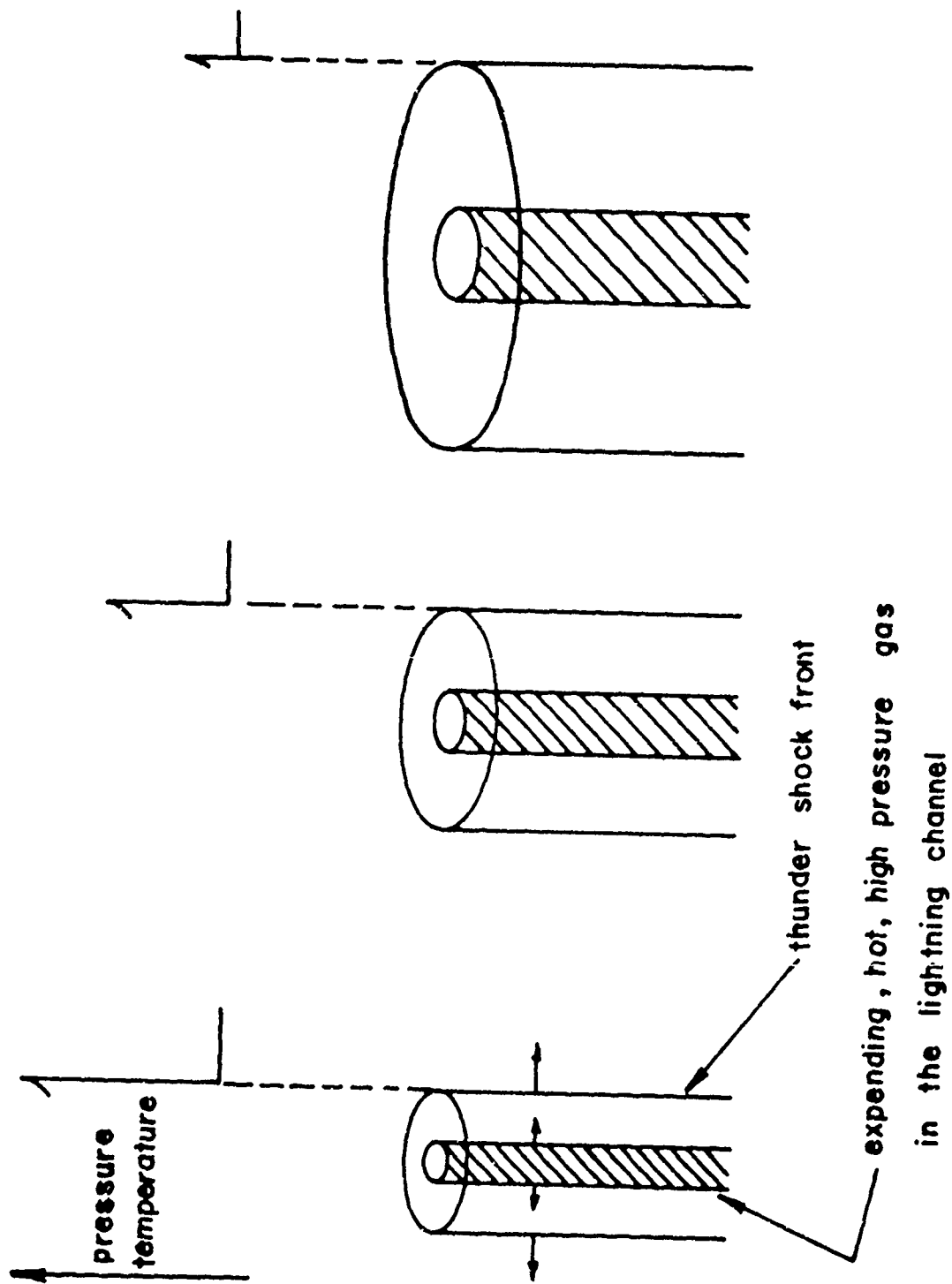


FIG. 2 A SCHEMATIC DRAWING OF A CYLINDRICAL THUNDER SHOCK WAVE

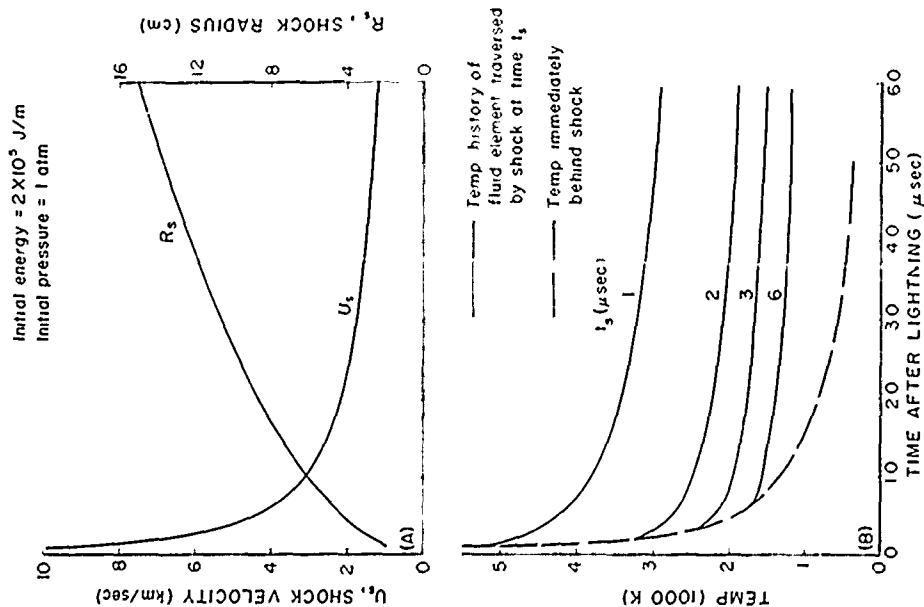
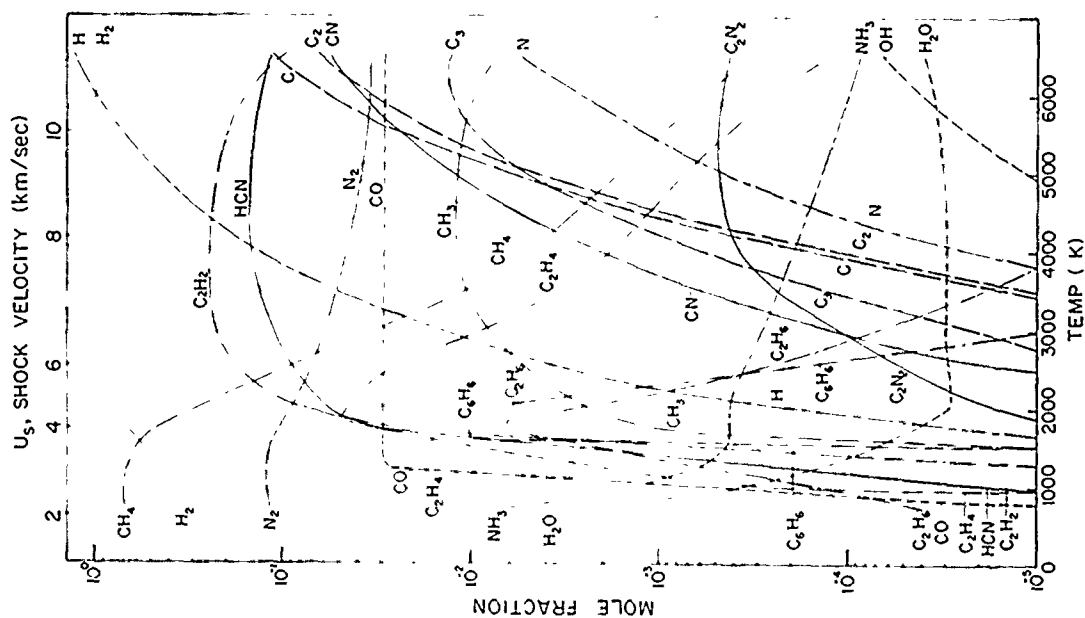


FIG. 3 APPROXIMATE RADIATIONAL BEHAVIOR OF A LIGHTNING-PRODUCED SHOCK WAVE: (A) VARIATION OF SHOCK-WAVE VELOCITY AND RADIUS WITH TIME. (B) TEMPERATURE HISTORIES IMMEDIATELY BEHIND SHOCK-WAVE AND OF FLUID ELEMENT OF FLUID [AFTER (23)]



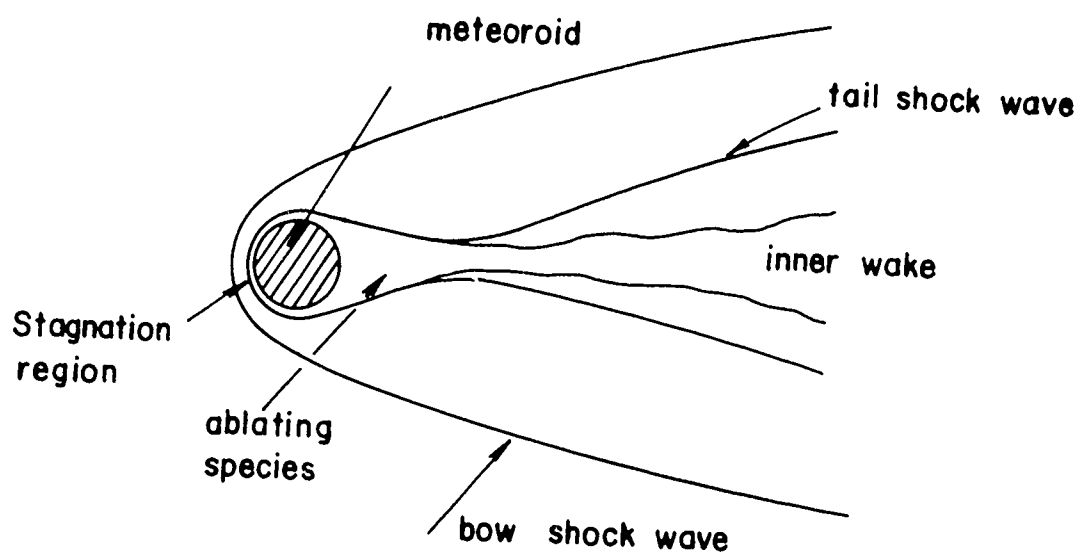


FIG. 5 SHOCK-WAVES GENERATED BY METEOR I EN [A DE (2)]

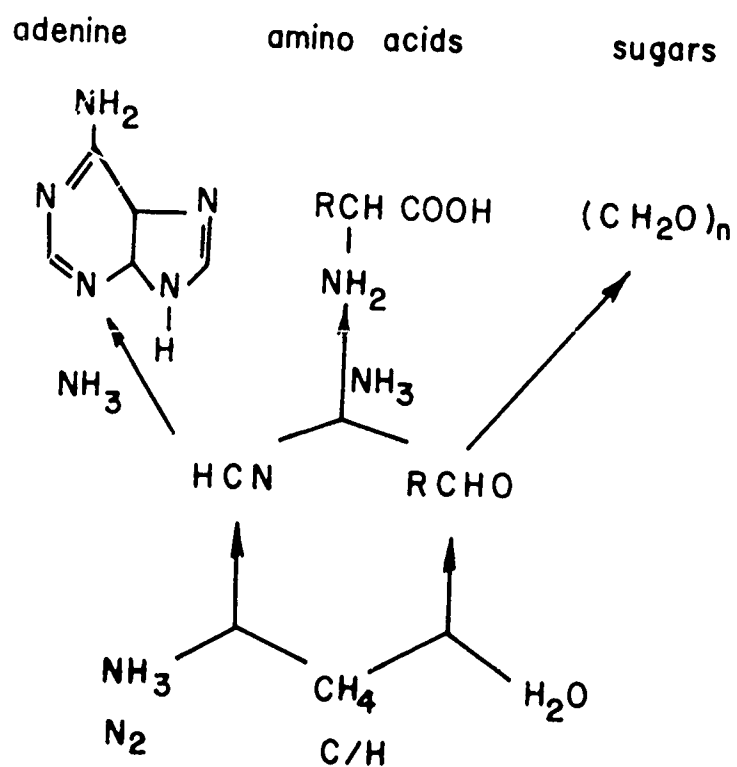


FIG. 6 A SCHEME OF CHEMICAL EVOLUTION OF BIOMONOMERS

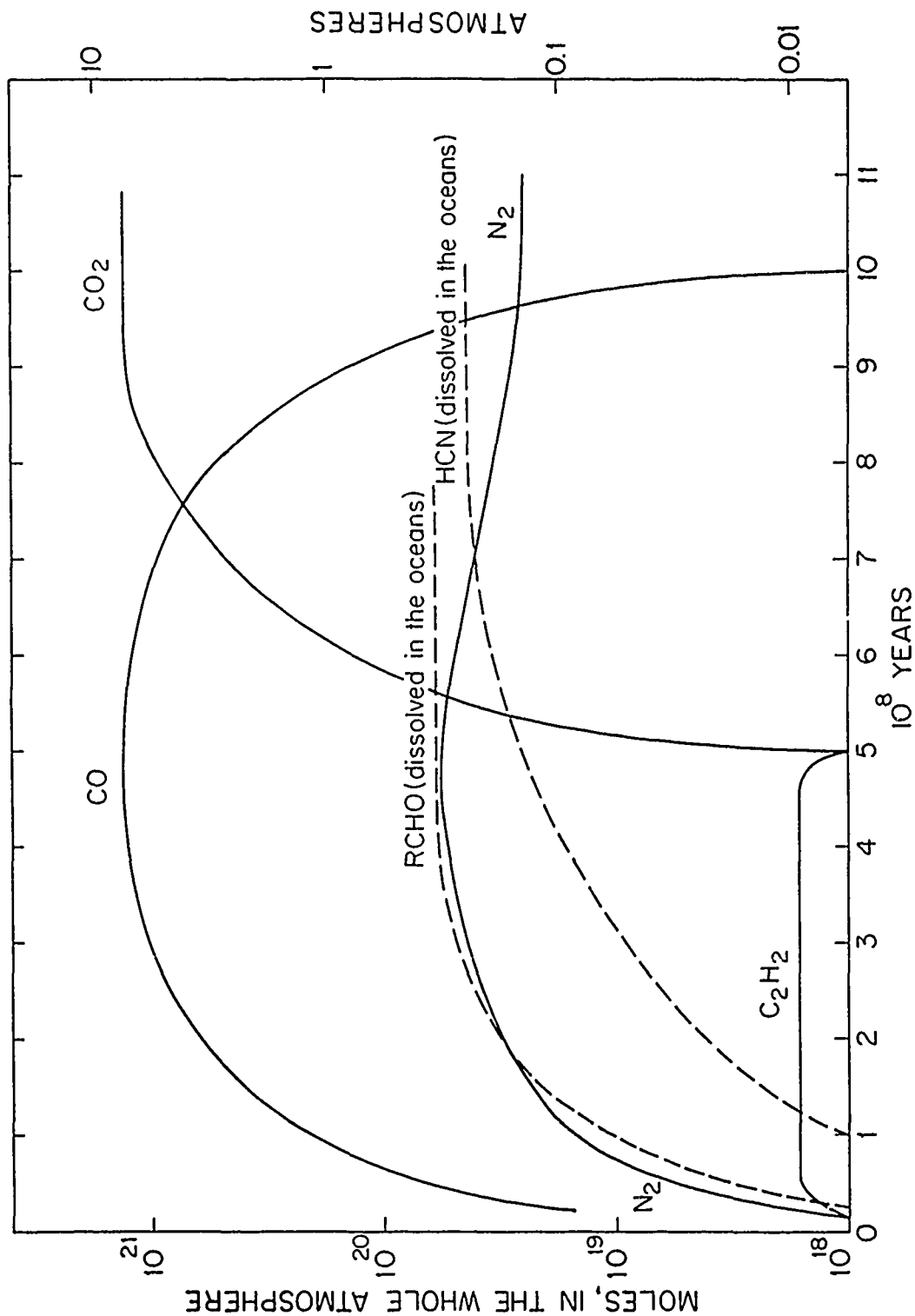


FIG. 7 VARIATION WITH TIME OF THE CONCENTRATION PROFILES OF THE MORE ABUNDANT SPECIES IN THE REDUCING ATMOSPHERE AS A RESULT OF THUNDER SHOCK WAVES, WHEN THE GREENHOUSE EFFECT OF ACETYLENE AND WATER VAPOUR WAS TAKEN INTO ACCOUNT. A STEADY RATE OF EXHALATION DURING $5 \times 10^8/\text{YR}$ AND A SURFACE TEMPERATURE OF 60°C WERE ASSUMED [AFTER (15)]



FIG. 8 AN ARTIST'S VIEW OF THE PROCESS OF CHEMICAL EVOLUTION (COURTESY: © NATIONAL GEOGRAPHIC SOCIETY)



FIG. 9 A VIEW OF JUPITER WHERE PRIMITIVE CLUES TO THE ORIGINS OF LIFE MAY BE FOUND. JUPITER'S RED SPOT AND A SHADOW OF THE MOON PLUS JUPITER'S CLOUD STRUCTURE CAN BE SEEN. THE PHOTOGRAPH WAS TAKEN AT 11.02 P.M. ON DECEMBER 1, 1973, AS NASA'S PIONEER 10 SPACECRAFT WAS ABOUT 2,500,000 KM FROM THE SURFACE.



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