

Prebiotic Chemistry in Clouds

Verne R. Oberbeck,¹ John Marshall,² and Thomas Shen³

¹ NASA Ames Research Center, Moffett Field, CA 94035, USA

² Arizona State University, Tempe AZ 85287, USA

³ SETI Institute, Moffett Field, CA 94035, USA

Summary. In the traditional concept for the origin of life as proposed by Oparin and Haldane in the 1920s, prebiotic reactants became slowly concentrated in the primordial oceans and life evolved slowly from a series of highly protracted chemical reactions during the first billion years of Earth's history. However, chemical evolution may not have occurred continuously because planetesimals and asteroids impacted the Earth many times during the first billion years, may have sterilized the Earth, and required the process to start over. A rapid process of chemical evolution may have been required in order that life appeared at or before 3.5 billion years ago. Thus, a setting favoring rapid chemical evolution may be required. A chemical evolution hypothesis set forth by Woese in 1979 accomplished prebiotic reactions rapidly in droplets in giant atmospheric reflux columns. However, in 1985 Scherer raised a number of objections to Woese's hypothesis and concluded that it was not valid. We propose a mechanism for prebiotic chemistry in clouds that satisfies Scherer's concerns regarding the Woese hypothesis and includes advantageous droplet chemistry.

Prebiotic reactants were supplied to the atmosphere by comets, meteorites, and interplanetary dust or synthesized in the atmosphere from simple compounds using energy sources such as ultraviolet light, corona discharge, or lightning. These prebiotic monomers would have first encountered moisture in cloud drops and precipitation. We propose that rapid prebiotic chemical evolution was facilitated on the primordial Earth by cycles of condensation and evaporation of cloud drops containing clay condensation nuclei and nonvolatile monomers. For example, amino acids supplied by, or synthesized

during entry of, meteorites, comets, and interplanetary dust would have been scavenged by cloud drops containing clay condensation nuclei. Polymerization would have occurred within cloud systems during cycles of condensation, freezing, melting, and evaporation of cloud drops. We suggest that polymerization reactions occurred in the atmosphere as in the Woese hypothesis, but life originated in the ocean as in the Oparin–Haldane hypothesis. The rapidity with which chemical evolution could have occurred within clouds accommodates the time constraints suggested by recent astrophysical theories.

Key words: Prebiotic chemistry — Primordial soup — Oparin hypothesis — Evolution — Impact catastrophism

Introduction

According to the Oparin–Haldane hypothesis for the origin of life, and refinements developed in the many years following its introduction, monomer synthesis occurred in the atmosphere through the action of ultraviolet light and/or electrical discharge. Monomers were transported to the ocean and were concentrated in water where they participated, over a long period of time by a variety of mechanisms, in the eventual production of the first living cell. Polymers may have been produced by the attachment of monomers to clays; polymerization occurring as a result of the catalyzing electrochemical surface properties of the clay minerals in combination with cycles of wetting and drying of the monomers. Some of the biochemical compounds produced would themselves have been capable of catalyzing even

more complex reactions. Eventually, life originated through a progression of increasingly complex and selective organic chemical processes. In the Oparin hypothesis, the first life is anaerobic/heterotrophic, which depletes the oceanic store of energy-rich organic compounds. As a result, life evolved into photosynthetic organisms.

In 1979, Woese questioned the Oparin hypothesis for several reasons and proposed chemical evolution in atmospheric water drops. Because life existed on Earth 3.5 billion years ago, Woese suggested that there was insufficient time for the protracted accumulation and the long series of reactions between organic compounds in a dilute ocean. According to Woese, life in the Oparin model originated in a nonbiological way; energy sources for chemical evolution included ultraviolet light and electrical discharges that are also destructive to biological systems. In the traditional view, life that evolved consumed the organic compounds from which it originated. Woese maintained that the classic experimental approaches to chemical evolution represents *de facto* rejection of chemical evolution in the ocean because biochemical polymerization results mostly from dehydration reactions and thus polymerization could not reasonably have occurred in the oceans.

In this paper, we reexamine the potentially beneficial effects of atmospheric droplet chemistry for polymerization of prebiotic monomers because new impact cataclysm studies show that there may have been only a short time period available for the origin of life, but there would have been sufficient time for concentration of amino acids in periods of days or weeks and resulting polymerizing cycles of hydration and dehydration in cloud systems containing water-monomer solutions. An atmospheric mechanism may be especially significant because all prebiotic reactants, including amino acids, were supplied by electric discharge, shock heating, or extra-terrestrial sources such as meteoroids and comets. Reactants were supplied to the atmosphere and they were brought into contact first with moisture in the atmosphere.

The Woese Hypothesis for Atmospheric Chemical Evolution and Review of the Hypothesis

Surface conditions may have been different than assumed in traditional theories for chemical evolution, Woese (1979) proposed that the early Earth was still bombarded by meteoroids and planetesimals, it was partly molten and subject to an early runaway greenhouse effect, and this made organic compounds unstable on the surface. The atmosphere would have exhibited large atmospheric tem-

perature differentials that generated massive convection currents. Winds sweeping the hot dry planetary surface would have produced violent dust storms that carried mineral particles high into the atmosphere where they served as nuclei for condensation of water vapor. A thick cloud layer of water drops containing salts in solution veiled the planet. Woese suggested that CO_2 and H_2 reacted to produce useful prebiotic materials. Thus, in his view, visible light was the energy source for prebiotic synthesis and the first organisms were photoautotrophic. The primary chemistry was associated with interfaces that enhanced reaction rates because of the enormous surface area available in droplets. He speculated that the giant reflux columns processed prebiotic reactants and produced macromolecules at droplet surfaces. The processes that gave rise to life were the same that exist in living systems. Eventually droplets served as protocells. Photoabsorbers, concentrated at droplet boundaries, converted electromagnetic energy into chemical energy. Membranes selected reactants from the surrounding environment. Woese went so far as to suggest that protocells capable of metabolism originated in the atmosphere. In this hypothesis, methanogenic metabolism converts CO_2 to methane and this led to the breakdown of the greenhouse effect.

Scherer (1985) stated that the hypothesis of Woese was not a reasonable alternative to prebiotic chemistry in the ocean for several reasons. Scherer pointed out that the strong convection currents in the Woese model would have continuously mixed stratospheric oxygen and ozone into the lower atmosphere (troposphere); biological macromolecules produced in the reflux columns would have been destroyed by oxidation and ultraviolet radiation after disruption of the ozone layer. Oxygen is produced in the present stratosphere by photodissociation of water vapor. However, Kasting and Ackerman (1986) suggest that the stratosphere of early Earth was very dry with a water vapor mixing ratio less than 10^{-7} for all reasonable CO_2 partial pressures. Their results predict little, if any, production of oxygen through photodissociation of water. They conclude that this argues against the possibility of an oxygenic prebiotic atmosphere. Therefore, from this model it can be assumed that an oxygenated atmosphere would not have existed and macromolecules could not have been destroyed by oxygen as suggested by Scherer (1985).

However, if there were no ozone layer in the primordial atmosphere, the atmosphere would have been continuously exposed to ultraviolet radiation. This would have prevented the long-term existence of replicating entities in the atmosphere as noted by Scherer (1985), but not the prebiotic droplet chemistry proposed by Woese. Oberbeck et al. (1989)

have calculated that the attenuation of ultraviolet light would be large in species like ammonia and formaldehyde and higher molecular weight compounds believed to be supplied by comets, to coalescing particles. Macromolecules adsorbed in clay lattices in particles in cloud drops would also escape prolonged exposure to ultraviolet radiation. Thus, macromolecules could survive in cloud drops that scavenged them until they were deposited in the ocean. Therefore, while it would be difficult for organisms to exist permanently in an atmosphere, unprotected by an ozone layer, prebiotic reactions in droplets could have been possible and perhaps enhanced by short-term exposure to some ultraviolet light.

Scherer (1985) was correct to note that any molecules synthesized in the Woese hypothesis reflux column would have been carried by the convective cells to the surface of the Earth where high temperatures, created by Woese's runaway greenhouse effect, would have sterilized the droplets. However, Kasting and Ackerman's (1986) results now suggest that the early Earth was not subject to a runaway greenhouse effect and surface temperatures would not have exceeded 100°C. Therefore, macromolecules were, according to the Woese hypothesis, synthesized in the atmosphere, and could have survived on the primordial planet's surface as it is now perceived. According to Scherer (1985), there would have been insufficient time for replication of atmospherically suspended proto-organisms before they were pyrolyzed at the surface. Although this remains a valid criticism of the Woese hypothesis, which included a runaway greenhouse effect, it does not apply to the cooler primordial atmosphere, which is now hypothesized to have been present. Finally, Scherer (1985) noted that pure monomer solutions would not have been available in the mechanisms available in the Woese hypothesis. Even though this is true, no natural environment, including the primordial soup of the ocean, has yet been proposed to adequately explain the presence of optically pure reactants.

Impact Conditions on the Early Earth May Have Required Rapid Chemical Evolution

Recent developments in impact catastrophism have focused our attention on the theory of Woese because the droplet chemistry included in this theory offers the possibility for rapid polymerization and thus rapid chemical evolution, and a large body of impact work in this area suggests that long continuous periods of low temperatures favoring stability of biomolecules for chemical evolution did not exist at the surface of Earth. Much less than one billion

years may have been available for origination of life between the formation of Earth and the age of the oldest fossils. It has been reported that magma oceans formed until Earth reached 90% of its present radius (Matsui and Abe 1986). Thus, biomolecules would not have been stable during this period. Hartmann and Davis (1975) proposed that a giant impact formed the Moon from matter ejected during collision of a Mars-size planetesimal with the Earth during this period of time. Stevenson (1987) concluded that this impact (10^{38} ergs kinetic energy) would have raised the global temperature by a few thousand degrees K and cooling time would have been as long as 10^3 to 10^4 years. The condition under which the Moon could have formed from the Earth has since been developed by Benz et al. (1986) and Cameron and Benz (1989). After about 35 million years (Myr) of the Earth's history, hotspots may have formed only around impact sites, but regions away from the impacting objects would not have been molten (Arrhenius 1987). Kasting and Ackerman (1986) point out that near-surface temperatures would have been about 100°C in the absence of intermittent impacts. However, based on the observation of giant impact basins of that age on the moon, the heavy bombardment of the Earth continued until about 3.8 billion years ago. Large impacting events (2×10^{35} ergs kinetic energy) would have vaporized the oceans and those with one-tenth this energy would have removed the photic zone of the ocean (Sleep et al. 1989). Maher and Stevenson (1988) suggested that large ocean-vaporizing impacts would have frustrated the chemical evolution of life for hundreds of millions of years.

Oberbeck and Fogleman (1989, 1990) have argued that impacts with kinetic energy sufficient to vaporize the oceans and interfere with the chemical evolution of life occurred with high probability as late as 3.8–4.0 billion years ago. The work of Sleep et al. (1989) suggests that it would have taken only on the order of a few thousand years for the oceans to recondense to new oceans after such impacts. Thus, it may have been required that life originated rapidly, from chemical evolution, between large ocean-vaporizing impacts in a time interval perhaps as short as 2.5 Myr (Oberbeck and Fogleman 1989).

Yet, it is part of the classical theory that, even with the most optimistic production rates for HCN by electric discharge in the atmosphere, it would have taken of the order of 10 Myr for HCN and aldehydes that were supplied to the ocean to produce amino acids by hydrolysis to levels ranging from 10^{-7} to 10^{-4} M concentrations in the oceans (Stribling and Miller 1987). Lahav and Chang (1976) reported that, with amino acid concentrations in the range of 10^{-7} M to 10^{-5} M, it is unlikely that condensation of amino acids to polymers would have

occurred in the open ocean, because the monomer density on mineral grains after adsorption would be too low. They proposed that, in tidal lagoons, cycles of flooding and evaporation of monomers on clay minerals would have promoted the formation of larger and larger oligomers faster than in systems lacking cycling. However, at the time preceding the origin of life, global oceans may have been present and there may have been no flooding and drying in tidal lagoons. Because it is certain that cloud droplets would have experienced cycles of wetting and drying, and because there may have only been a narrow time window for the development of life, it is important to reexamine the concept of droplet chemistry in clouds as a means of accelerating chemical evolution. It is therefore appropriate at this time to consider the possibility of prebiotic chemistry in clouds.

Prebiotic Reactants in Earth's Atmosphere

There are two major sources of monomers for prebiotic chemical evolution as described in a recent comprehensive review article (Oró et al. 1990). The classical sources are gases of the primitive atmosphere. Another very important source is extraterrestrial material supplied in interplanetary dust, comets, and carbonaceous chondrites. For the first source, the dominant energy sources for synthesis of prebiotic monomers existed in the atmosphere and monomers synthesized would have occurred in the atmosphere. Reactants supplied or synthesized from material supplied from extraterrestrial sources would have been present first in the atmosphere because this material passed through the atmosphere before deposition in the oceans or on the Earth's surface. Thus, there is reason to believe that chemistry in clouds might have been important for chemical evolution.

There is evidence in the geologic record that amino nitriles were produced during impact, processed in the atmosphere, and deposited in the ocean. Amino acids were reported in the sediments at the Cretaceous-Tertiary boundary and they are believed to have been formed in space (Zhao and Bada 1989) or synthesized during cometary entry. Oro (1961) has for many years argued that comets supplied important prebiotic compounds to the primordial Earth. Lazcano-Araujo and Oro (1981) suggested that transient vapor clouds of impacting comets would have provided an environment for the synthesis of new organic compounds of use to prebiotic chemical evolution. Oberbeck et al. (1989) examined the physics of hypervelocity impact of comets and concluded that synthesis during cooling

of such vapor clouds was the dominant mode of supply of organic compounds associated with cometary entry. See also Oro et al. (1990) for a comprehensive review of the ideas concerning synthesis of organic compounds associated with cometary entry. The recent discovery of amino acids at the K/T boundary is graphic confirmation of this long-held view that comets were important sources of prebiotic reactants for the origin of life on Earth (Oro 1961).

Muhkin (1989) reported production of 1.5×10^{17} molecules of HCN and one-fifth this amount of acetic aldehyde for impact vaporization of each gram of ordinary L-5 chondrite. These studies suggested that the HCN and aldehydes were produced in the hot inner parts of the vapor clouds of impacting chondritic meteoroids and the type of compounds produced in the inner part of the vapor cloud were insensitive to the composition of the ambient atmosphere. Oberbeck and Aggarwal (1990) showed that this production rate is insufficient to account for the amino acids column density at the K/T boundary and concluded that the K/T impactor was not a chondrite.

There is evidence suggesting that amino nitriles might have been produced during quenching of the vapor cloud formed during impact of the K/T comet. Shock tube experiments, in which methane, ethane, ammonia, and water vapor (compounds found in comets) are used, result in the formation of amino nitriles that are quenched from the shocked material. Amino acids were formed at room temperature by acid hydrolysis of amino nitriles after the experiment (Barak and Bar-Nun 1975). Even large amounts of oxygen did not prevent formation of amino nitriles in the shock tube experiments. Barak and Bar-Nun (1975) point out that quite large amounts of oxygen in experiments in which air was included in the shocked material (O/C ratio of shocked samples was 2.5) did not lower by much the amounts of amino acids produced later. The average ratio of O/C in comets is 2.5 according to Delsemme (1989). Oberbeck and Aggarwal (1990) showed that the shock tube yield reported by Barak and Bar-Nun for samples that are analogs for O/C compositions of volatiles in comets (O/C 4.3) is 1.6×10^{21} molecules of amino acids per kg of comet. This was found to be sufficient to produce the observed column density of amino acids at the K/T boundary. In this study, it was determined that amino acid concentration would have, in days or weeks, reached levels exceeding those produced by electric discharge in the atmosphere and hydrolysis of the compounds in the ocean during 10 Myr. Subsequently, polymerization of amino acids could have occurred during innumerable cycles of wetting and drying in cloud drops containing them.

Prebiotic Chemistry in Clouds

Only in the earliest stage of Earth's history would the surface have been continuously inhospitable for life. Matsui and Abe (1986) reported that during the first tens of millions of years, molten magma oceans existed. After about 35 Myr, hotspots may have formed only around impact sites whereas regions away from the impacting objects would not have been molten (Arrhenius 1987). Kasting and Ackerman (1986) estimated a surface temperature of only about 100°C, with pressures in the range of 10–20 bar after the first several hundred million years. Their results suggest that very low water content existed in the stratosphere but up to 10% of the entire atmosphere consisted of water. Therefore, clouds containing water droplets could have existed in the troposphere in the presence of a dry stratosphere. Inhospitably high surface temperatures proposed by Woese appear to be ruled out. Although temperatures higher than at present existed at any given altitude above the surface, meteorologic processes in the primitive atmosphere may have been quite similar to those in the present atmosphere and should have been favorable for chemical evolution. Weather fronts, buoyant air parcels, and convective cloud systems were present and would have contained water droplets.

As pointed out by Levine (1985), it is probable that there was no ozone layer in the primordial stratosphere. Levine has given hypothetical temperature profiles that show no tropopause because there was no ozone and thus no stratospheric heating due to ozone. This implies that even higher convective cloud systems existed in the primordial atmosphere than exist in today's atmosphere. Convective instability arises due to surface warming, which causes air to rise and cool and cloud drops to form when water vapor condenses on condensation nuclei. Latent heat of condensation increases the cloud temperature relative to surrounding ambient air and consequently enhances the cloud buoyancy. In the absence of a tropopause in the primordial atmosphere, buoyant air would have risen above the present location of the tropopause. It has been noted by Knupp and Cotton (1985) that condensation of rain drops on salt and mineral grains occurs in updrafts of convective clouds and this is followed by evaporation of rain in downdrafts. Downdrafts can be enhanced by entrainment of ambient undersaturated air at the cloud boundary followed by evaporation of cloud drops and cooling of cloud air. It is worth discussing the formation and fate of rain and ice in convective clouds in order to evaluate the potential role of clouds in prebiotic chemical evolution.

Figure 1 shows our concept using a convective

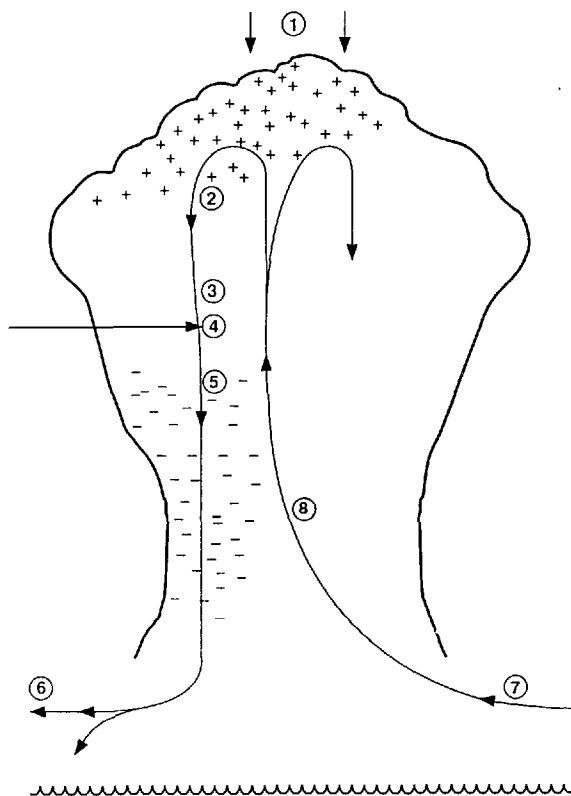


Fig. 1. Chemical evolution in convective clouds. (1) Extraterrestrial monomer sedimentation; (2) raindrops freeze and scavenge monomers and polymers; (3) ice crystals melt; (4) monomers are entrained and are scavenged by raindrops; (5) raindrops evaporate and new polymers form; (6) polymers transported to new cloud and ocean; (7) polymers from another cloud; and (8) raindrops condense on salt crystals and clay particles with polymers, polymers redistributed.

cloud as an example, but any cloud with condensing, freezing, melting, and evaporating water drops would be applicable. A characteristic feature of convective clouds in the present atmosphere is condensation of water on nuclei including clay particles at low altitudes and freezeout of water vapor directly onto kaolinite clay particles high in convective clouds. Most cloud drops evaporate and most ice crystals, which form sediment and melt at low altitudes and then evaporate. At temperatures between -5°C and -25°C in the present atmosphere, the saturated vapor pressure over water becomes greater than that directly. The difference in saturated vapor pressure exceeds 0.2 mb at temperatures below -15°C and the common clay mineral, kaolinite, becomes an active nucleus for freezeout of water vapor at -9°C (Barry and Chorley 1989). Lahav and Chang (1976) pointed out the advantages of cycles in temperature and water content in the presence of minerals including kaolinite for enhancing prebiotic chemical evolution. Clay particles would have been common constituents of the primordial atmosphere.

Clay minerals are common in breccia meteorites that are believed to originate on hydrated ancient planetary surfaces (Bunch and Chang 1980). Because all terrestrial planetary surfaces were heavily cratered by impacting planetesimals, comets, and asteroids in the time previous to the origination of life, impact craters would have ejected clay particles into the atmosphere at the same time impactors supplied amino acids. O'Keefe and Ahrens (1982) approximate that about 1% of the ejecta of large impact craters would have been less than $0.1 \mu\text{m}$ radius. This material has very low sedimentation velocity in the atmosphere and would remain aloft for a considerable time. Monomers and phyllosilicate minerals in dust from comets, carbonaceous chondrites, and IDPs from space sedimented into clouds and mixed with clay particles, ejecta of impact craters, minerals from dust storms, and volcanic eruptions. Therefore, monomers would have been exposed to cycles of wetting, drying, and freezing in the presence of clay particles in clouds.

Some of the minerals from terrestrial sources may have been carried to the cloud top by updrafts (1, Fig. 1). As the clay particles from both sources enter the cloud tops, they act as ice crystal nuclei because, in this part of the cloud, the concentration of water vapor exceeds that allowable by the vapor pressure. There is a phase change from vapor directly to ice which nucleates (in the present atmosphere) on kaolinite clay particles (Barry and Chorley 1989). Cloud drops carried by updrafts scavenge monomers and freeze in this region and ice crystals will scavenge monomers (note that cloud regions containing ice crystals typically exhibit positive electrical charge, 2). Ice crystals then settle and melt (3). Ambient undersaturated air, containing monomers supplied from space or produced in the atmosphere, are entrained into the cloud and drops scavenge monomers (4). Note that in this region of the cloud, where the temperature exceeds the melting point of ice, the electrical charge is typically negative (Johnson 1960). Undersaturated entrained air causes cloud drops to evaporate, nonvolatile monomers to concentrate, and polymers to form during evaporation (5). Polymers on clay and salt particle nuclei are transported to the ocean and to new clouds (6). Polymers on clay and salt nuclei enter new adjacent clouds and are carried in the updraft (7). Raindrops condense on clay, salt, and polymer substrates as warm moist air is cooled aloft; polymers are redistributed on clay and salt substrates (8). Sea salts would have been available in raindrops because they would have acted as condensation nuclei. Soluble salts would have been ideal substrates for attachment of reaction products because they come out of solution during evaporation of droplets, act as substrates for formation of polymers, and during the next wetting

cycle, go rapidly into solution and quickly redistribute reaction products (Lahav and Chang 1982). Updrafts carry raindrops with polymers and clay-salt nuclei aloft and drops freeze. These ice crystals, together with those formed earlier on clay particles at the cloud top, scavenge new monomers, grow, sediment, and melt. The water redistributes monomers and polymers on the clay substrate. Then, entrainment of ambient air causes droplet evaporation and a new generation of more complex polymers forms. The cloud mechanism may be applicable to other monomers like sugars and bases as well, but we only evaluate amino acid concentration and polymerization.

It has been pointed out by Scott (1983) that hydrated electrons produced by exposure of water molecules to UV would have been ubiquitous on the primordial Earth but would have been repelled by other negatively charged materials. For this reason, he suggested that hydrated electrons would have acted over geologic time to select useful macromolecules, which also tend to be negatively charged. That part of the convective electrically active cloud with rain is negatively charged (Johnson 1960), as shown in Fig. 1. In storm clouds, useful macromolecules would tend to be naturally protected because they produced in this negatively charged region. Although some polymers produced in one cloud could have been destroyed by hydrated electrons in regions of positive charge in a second cloud, some polymers produced in the first cloud would have entered the ocean before entering a new cloud and some polymers that entered new clouds would not have been carried to the cloud tops before cloud drops evaporated and produced new polymers. Cycles of condensation, scavenging of monomers, and droplet freezing and evaporation could have occurred many times in clusters of clouds. Over long periods of time there may have been a slight bias on survival of biochemically useful polymers.

Because the amino nitriles hydrolyzed to amino acids in acid solutions, it could have been possible for them to hydrolyze to amino acids in primordial cloud drops in an atmosphere acidified by the impact. Subsequently, cloud drop chemistry could have polymerized them before polymers were finally scavenged by rain to the ocean. The amino nitriles, quenched from the vapor cloud of a comet, would have been available very quickly to water drops once they entered the cloud. Amino nitriles are very soluble in water and would have a high scavenging coefficient.

As a means of comparing the potential of the cloud drop mechanism to the classical methods of monomer concentration and polymerization in the ocean, we compare the efficiency of cloud drops in scavenging, concentrating, the polymerizing amino

acids supplied by the K/T impactor to the efficiency of open ocean concentration and polymerization of monomers produced in the atmosphere by electric discharge. Whether the amino acids in the K/T sediments were initially in the asteroid or comet or if they were synthesized in the atmosphere shortly after entry of the asteroid or comet, the amino acids would have been dissolved in cloud droplets. The typical maximum water content of cloud drops in clouds is of the order of 1 g/m^3 (Johnson 1960). If we assume clouds cover about 25% of the surface of Earth and that the average cloud occupies 25% of the height of the troposphere (cumulonimbus clouds can extend from about 1 km altitude to the tropopause and other types of clouds may occupy only a kilometer or so of the troposphere), then we can estimate, from the concentration of amino acids found at the K/T boundary sediments, an average concentration of amino acids in cloud droplets that cleansed the amino acids from the atmosphere. From the above considerations, a volume of the atmosphere roughly 16 times that of the cloud volume would have been cleansed by cloud drops. Within-cloud scavenging of gases and small particles is very fast and would have occurred within a period of weeks after the impact. Zhao and Bada (1989) give a surface area concentration of AIB amino acids of about $5 \times 10^{-5} \text{ g/cm}^2$ in the K/T boundary sediments, which implies $2.5 \times 10^{14} \text{ g}$ of AIB amino acids (2.5×10^{12} moles) were supplied to the atmosphere worldwide. Given that these amino acids in the entire atmosphere would have been scavenged from cloud drops in only $1/16$ of the volume of the atmosphere with water content of 1 g/m^3 , the concentration of AIB amino acids in the cloud drops would have been $7.8 \times 10^{-3} \text{ M}$. Locally much higher concentrations are reached during cloud drop evaporation. Thus, these concentrations of amino acids in cloud drops would have been reached in days, whereas a maximum concentration of 10^{-4} M would have been reached only after 10 Myr in the oceans as a result of atmospheric electric discharge, deposition, and hydrolysis in the ocean (Stribling and Miller 1987). This demonstrates the potential that clouds have for producing high concentrations of amino acid solutions quickly and for exposing them to cycles of flooding and evaporation that could have facilitated polymerization.

Conclusion

Organic monomers that were useful for chemical evolution were present in the atmosphere from three sources: (1) in situ production by lightning, impact shock processes, or photochemical reactions; (2)

fragments produced by aerodynamic or impact stresses acting on large comets or on carbonaceous chondrites of any size and material synthesized during cometary entry; and (3) sedimentation of interplanetary and interstellar dust. Prebiotic monomers were produced either in space or in the atmosphere. Monomers should always have been present in the atmosphere, but copious amounts would be expected immediately after cometary entry. New discoveries of amino acids in the K/T boundary sediments are graphic evidence that amino acids from space or those synthesized in the vapor clouds of comets would have contacted moisture first in the atmosphere because asteroids and comets contacted the atmosphere first. Clay particles and other minerals were supplied to the atmosphere by impact crater formation, dust storms, and volcanic eruptions. Salts were supplied to the atmosphere from sea spray. Those monomers with very low vapor pressures like amino acids would have been concentrated during cloud drop and rain drop evaporation. Cloud systems are characterized by fluctuations in temperature and pressure that result in condensation, freezing, and evaporation of water in the presence of salts and clay particles and, because clouds scavenge gases, aerosols, and dust from the present atmosphere, clouds would have removed salts, clays, and monomers from the primordial atmosphere. Fluctuations in temperature and water content in the presence of clays and salts in clouds are therefore plausible causes of polymerization on the primordial Earth.

There have been only a few studies exploring the advantages of atmospheric prebiotic chemistry in cloud drops and precipitation. Woese (1979) proposed the atmospheric reflux convection cells, Lerman (1986) emphasized the importance of aerosols formed in breaking waves and possibility of precipitation chemistry, and we outline the role of cloud drops and precipitation. Despite the continued emphasis placed on prebiotic chemistry in the ocean, atmospheric cloud drop and precipitation chemistry offers advantages over prebiotic chemistry in the ocean. A pronounced advantage of the cloud environment is that monomer concentration would be greater and could have occurred faster in the atmosphere than in the ocean because monomers are scavenged very quickly by small cloud drops, and aqueous solutions of nonvolatile monomers can be concentrated to dryness in seconds in cloud drops. During cycles of wetting, drying, freezing, and evaporation, polymerization could have occurred many times, in time intervals as short as days or weeks. Our mechanism for prebiotic chemical evolution in the atmosphere does not lead to origination of life in the atmosphere. It only provides a means for polymerization, a step that profits from dehydration

and interfacial catalytic chemistry offered by chemistry in cloud drops and rain drops.

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