

THE ROLE OF COMETARY PARTICLE COALESCENCE IN CHEMICAL EVOLUTION

V. R. OBERBECK*, C. P. MCKAY*, T. W. SCATTERGOOD**,
G. C. CARLE*, and J. R. VALENTIN*

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Abstract. Important prebiotic organic compounds might have been transported to Earth in dust or produced in vapor clouds resulting from atmospheric explosions or impacts of comets. These compounds coalesced in the upper atmosphere with particles ejected from craters formed by impacts of large objects. Coalescence during exposure to UV radiation concentrated organic monomers and enhanced formation of oligomers. Continuing coalescence added material to the growing particles and shielded prebiotic compounds from prolonged UV radiation. These particles settled into the lower atmosphere where they were scavenged by rain. Aqueous chemistry and evaporation of raindrops containing monomers in high temperature regions near the Earth's surface also promoted continued formation of oligomers. Finally, these oligomers were deposited in the oceans where continued prebiotic evolution led to the most primitive cell. Results of our studies suggest that prebiotic chemical evolution may be an inevitable consequence of impacting comets during the late accretion of planets anywhere in the universe if oceans remained on those planetary surfaces.

1. Introduction

Traditional theories for the origin of life involve, as the initial step, the production of complex monomers such as amino acids. The classic experiments of Miller (1953) produced amino acids when mixtures of CH_4 , NH_3 , and H_2O were exposed to electric discharge. Thus, lightning discharges in such a highly reducing atmosphere on primitive Earth would have been important for chemical evolution. Subsequent studies suggest that the early atmosphere on Earth did not contain CH_4 for extended periods and was not highly reducing. Any methane initially present could have been oxidized to CO_2 by reaction with OH radicals formed from the photolysis of water vapor (Kasting *et al.*, 1983). The atmosphere contained up to 20 bars (Holland, 1984) or 10 bars of CO_2 (Walker, 1985) which persisted for at least several hundred million years after accretion when continents appeared (Walker, 1985). Thus, there is sustained interest in the theory of Oro (1961), who proposed that comets frequently supplied Earth with compounds like NH_3 , H_2O , and HCN which would have been concentrated near the impact site and spontaneously reacted to form complex organic compounds necessary for prebiotic chemical evolution.

Recent measurements of comet Halley suggest that HCN (Schloerb *et al.*, 1986), NH_3 (Allen *et al.*, 1987) and CH_4 (Krankowski *et al.*, 1986) are present. Water is known to be a major component of comets and H_2CO may also be present (Delsemme, 1981) as indicated by the recent discovery of polyoxymethylene (Huebner, 1987). Amino

* NASA Ames Research Center, Moffett Field, CA 94035, U.S.A.

** State University of New York at Stony Brook, NY 11794, U.S.A.

acids have been found in carbonaceous chondrite meteorites which are related to comets. Formaldehyde and complex organic monomers may have also formed in interstellar grains which also have been related generically to comets (Greenberg, 1981; Agarwal, 1985; d'Hendecourt *et al.*, 1986). Thus, complex organic compounds of prebiotic importance could also have been supplied to Earth in interstellar grains and in comets. Interstellar grains, about 0.2 μm in diameter, would not have been heated enough during atmospheric entry to destroy prebiotic compounds. They would have stayed in the upper atmosphere until they coalesced with other particles. Carbonaceous material is also found in interplanetary dust which enters the atmosphere and is now being recovered from the stratosphere (Sandford, 1987; Brownlee, 1985).

It is well recognized that heating many organic compounds of prebiotic interest above about 550°C will destroy them. However, it is not true that heating reduced organic compounds like those present in comets to temperatures much higher than 550°C cannot produce useful organic compounds and monomers. The classic experiments of Miller (1953) show that amino acids were produced during cooling of very high temperature electrical discharges in NH_3 , CH_4 and water vapor. Bar Nun *et al.* (1971) exposed NH_3 , CH_4 , C_2H_6 , and H_2O vapor to temperatures up to 3500°K during high pressure shock tube experiments. In these experiments, the organic compounds were first fragmented by the temperature pulse and then, upon rapid cooling, the excited radicals combined to produce HCN and aldehydes which then reacted to form amino acids. Theoretical modeling by Jones and Lewis (1987) show that when equal amounts of CH_4 and NH_3 , with up to 35% water vapor, are shocked to 2300°K and rapidly quenched, HCN and other compounds are produced. Compounds as complex as amino acids were not included in the models. Experimental shocking of dry mixtures of CH_4 and NH_3 produced HCN in agreement with these results (McKay *et al.*, 1988). Hochstim (1971) also proposed that high pressure-high temperature shock waves produced during impact can convert organic compounds to polymers.

Comets, containing CH_4 , NH_3 , H_2O and other simple organic compounds, would have been vaporized during shock heating from explosions in the atmosphere and impact with the Earth's surface. Temperatures of the vapor clouds would have been as high or higher than those in the high temperature events described above. Thus, useful organic compounds and monomers could have been produced during rapid cooling of these vapor clouds. In this case, prebiotic material would have been supplied by comets impacting at hypervelocity as well as by the low velocity comets considered by Clark (1988).

Calvin (1969) suggested that amino acids, polypeptides, and purines must have already been produced prior to four billion years ago. Based on lunar cratering, the period before 3.8 billion years ago represents the late bombardment of the Earth when the rate of cometary impacts would have been higher than at any time since that period (Murray *et al.*, 1981). During this period, compounds as complex as amino acids could have been transported to or produced in the stratosphere as a result of cometary entry in quantities larger than would have been produced after that time.

In this paper, we examine the entry of comets, interplanetary dust, and carbonaceous meteoroids in the Earth's early atmosphere. We examine the formation of organic

compounds during cometary entry and by photolysis during particle growth in the upper atmosphere. We also consider the protection of the oligomers and other products from prolonged UV radiation as the particles fall into the lower atmosphere. The results of our studies suggest that particles up to 2 μm in radius, containing important prebiotic organic compounds, could have formed due to coalescence of material from the vapor clouds resulting from the entry of comets. Growth rates early in particle formation were high enough to protect prebiotic materials produced before and during entry or by photolysis from prolonged ultraviolet exposure. As particles containing prebiotic organic compounds settled into the lower atmosphere, they became condensation nuclei for rain droplets. Some of the simple monomers would have dissolved in the droplets. Some of the droplets fell into regions of higher temperature and lower relative humidity. These would have evaporated and organic compounds would have been oriented and concentrated at liquid-gas interfaces where oligomerization would have been enhanced. Acidification of the lower atmosphere by shock formation of HNO_3 from cometary entry in a $\text{CO}_2\text{-N}_2$ atmosphere would not have prohibited this prebiotic evolution.

2. Entry of Cometary Materials into the Primitive Earth's Atmosphere

Cometary objects entering the Earth's atmosphere are crushed when the aerodynamic pressure, ρV^2 (ρ = atmospheric density and V = entry velocity), on the front surface of the comet exceeds the crushing strength of the comet (Brownlee, 1985). From Jones and Kodis (1982) the loss of kinetic energy of a comet entering the atmosphere may be computed from the following expression:

$$dE/E = 1.5 \text{ C.D.}/\rho d, \quad (\text{cgs units})$$

where dE/E is the fraction of energy lost by the object of density ρ and diameter d as it passed through a portion of the atmosphere with column density C.D. Although fragmentation typically occurs at high altitude, most of the deceleration occurs in the lower atmosphere. For example, Bronsten (1983) reports that icy objects will first fragment and then later spread out during maximum deceleration where vaporization and explosion occurs. Jones and Kodis (1982) suggested that the Tunguska catastrophe in Russia was the result of entry of a 40 km s^{-1} comet followed by loss of most of the kinetic energy and consequent explosion between 5 and 10 km altitude. It may be shown that the above expression for loss of kinetic energy gives results in agreement with the observed stopping point and explosion for the Tunguska event.

Results of recent modeling suggest that the partial pressure of CO_2 in the early atmosphere was 10 bars (Walker, 1986). As a model for the density profile of this atmosphere, we take the current density profile above 29.5 km above Venus' surface, where the pressure is 10 bars (Keating, 1980; Seiff *et al.*, 1980). Using this density profile and a compressive strength of 10^4 dynes cm^{-2} for comets, we find that comets would have been crushed at an altitude greater than 75 km above the surface of the primitive Earth. A substantial amount of the fragmented material would have been a few tenths μm in diameter because failure of aggregate materials commonly results in

particles of the same sizes as those of the original grains (Hamilton and Knight, 1958). Note that comets were probably made from gentle accretion of submicron interstellar grains. The fraction of cosmic dust believed to be of cometary origin is indeed a mixture of submicron grains of organic materials and silicate minerals (Brownlee, 1985). Some of these grains could have conceivably survived in the upper atmosphere.

Bronshthen (1983) reviewed the effects of vaporization combined with fragmentation for icy objects and concluded that the rate of vaporization increases with fragmentation and this could lead to an explosion at the end of the trajectory as fine fragments spread and vaporize very rapidly. Applying the analysis of Jones and Kodis (1982) to projectiles passing through a 10 bar primitive atmosphere, we find that a 150 meter diameter icy object with a density of 1 gm cm^{-3} would have stopped, exploded, and vaporized just as it reached the surface of the Earth. All smaller objects would have stopped, exploded and vaporized in the atmosphere. Vaporized material from comets exploding in the atmosphere would have been launched to high altitudes. This happens because the kinetic energy per gram of comets entering at 40 km s^{-1} is about 100 times the chemical energy per gram of common high explosives.

A crushed comet nucleus larger than 150 meters in diameter would have impacted against the Earth's surface as a unified mass, but the vaporized comet would have been separated from the crater ejecta. In order to explain the enrichment of iridium in Cretaceous-Tertiary clay deposits associated with the biologic extinctions at that time, O'Keefe and Ahrens (1982) modeled the impact dynamics of very large bodies. They found that impact of a 10 km diameter object would result in widespread distribution of material enriched in extraterrestrial material because the high speed, early ejecta, consisting primarily of the vaporized projectile, was lofted much higher than the slower speed late stage crater ejecta which was deposited near the point of impact. An amount of crater ejecta from Earth's crust, consisting of particles less than $1 \mu\text{m}$ in diameter, equal to one tenth of the comet nuclei mass would have been launched into the stratosphere.

The idea that the Cretaceous-Tertiary deposits became enriched with iridium-rich projectile material due to ejecta separation is supported by laboratory studies of impact cratering. Oberbeck and Morrison (1976) showed that an expanding conical ejecta sheet develops when impact craters are formed in vacuum. Ejecta cone boundaries represent the locus of points along trajectories of individual particles at given times after impact. Initially, the highest speed material was located at ground zero. In this region, shock pressures and particle velocities were the highest and vaporized material would have been formed. Consequently, this material was found at the highest points in the conical ejecta curtain and at the greatest distances from the crater. The low speed ejecta material, launched from positions at the greatest distance from the impact point within the growing crater, were found at the lowest positions in the ejecta curtain and were deposited nearest to the crater rim. Schultz and Gault (1982) studied ejecta curtains of impact craters formed beneath an atmosphere and found similar behavior. They discussed a variety of mechanisms related to ejecta curtain development which would have isolated the vaporized projectile from the bulk of the crater ejecta and insured survival of the signature of the projectile on a global scale. Jones and Sandford (1977) found that for a 1

$\times 10^{25}$ erg explosion, which is about the kinetic energy of a 150 meter comet with the mean cometary velocity of 40 km s^{-1} , the vapor cloud would have expanded to an altitude well above 47 km. The vapor from larger comets would have expanded to higher altitudes. Therefore, the cometary volatiles and condensates contained in the vapor clouds of vaporized comets would have retained their identity by being separated from the crater ejecta containing mostly target material and would have been launched as high as, or even higher than, the present day stratosphere. Transient and isolated high temperature atmospheres, containing primarily cometary compounds needed for synthesis of prebiotic compounds, would have been produced by impacting comets.

3. Synthesis and Transport of Organic Monomers during Entry of Cometary Material

Lazcano-Araujo *et al.* (1983) suggested that cometary collisions with Earth would have produced organic compounds during shock heating of cometary compounds and the volatiles of comets would have supplied reduced gases which favored synthesis and prevented degradation of useful organic products. Based upon recent measurements of Halley's Comet which show that silicates, water, NH_3 and various carbon compounds like CH_4 , CO_2 , HCN, and H_2CO are present, we adopted a comet model containing 25% silicates, 25% carbon and nitrogen compounds and 50% water. Bar-Nun *et al.* (1971) carried out shock tube experiments in which NH_3 , C_2H_6 , CH_4 , and H_2O vapor were exposed to high shock pressure and temperature conditions. In these experiments, sample heating up to $3500 \text{ }^\circ\text{K}$ fragmented most of the molecules. Amino acids were produced during rapid cooling as active radicals reassembled. The internal energy of the test samples in these experiments was $\approx 4 \times 10^{11}$ ergs mole $^{-1}$. O'Keefe and Ahrens (1982) modeled the impacts of high velocity comets (see above) and showed that the internal energy of the vapor clouds produced was about 1.2×10^{12} ergs gm $^{-1}$. Thus, using an average molecular weight of 30 gm mole^{-1} for our model comet and using the value just mentioned, the molar internal energy of the vapor cloud produced by impact of the comet would have been about 3.7×10^{13} ergs mole $^{-1}$. Based upon the experiments of Bar-Nun *et al.* (1971), the internal energy of cometary vapor clouds should have been high enough to form radicals which could have re-combined during cooling to form useful prebiotic compounds like amino acids. Amino acids have also been produced (Hattori *et al.*, 1984) when mixtures of CH_4 and CO_2 in the same ratios as observed in the coma of Comet Halley (Kankowsky *et al.*, 1986) were subjected to electrical discharges. Thus, CO_2 in comets would not have prevented the production of amino acids and other useful organic compounds. Upon consideration of impact mechanics and of organic compound synthesis studies, it seems likely that useful prebiotic material could have been produced in the atmosphere during cooling of high-temperature transient and isolated cometary vapor clouds.

Other researchers results indicate that complex organic compounds can be formed in space and, because the host particles were not severely heated, they survived entry into the Earth's atmosphere. According to Greenberg (1981), the relative velocity between the

solar system and interstellar clouds during early encounters with the primitive Earth was about 10 km s^{-1} . During such encounters, complex organics of prebiologic significance in small interstellar grains may have been supplied to Earth. Oro (1965) simulated the interstellar medium by exposing icy mixtures of H_2O , CH_4 , N_2 , and NH_3 to ionizing radiation and produced water soluble biochemical compounds and nonvolatile polymers. Greenberg (1981) and Agarwal *et al.* (1985) simulated the production of mantles on interstellar grains by exposing mixtures of frozen CH_4 , NH_3 , H_2O and CO to ultraviolet light at 10 to 15 K and reported formation of more complex organic species. d'Hendecourt *et al.* (1986) reported that formaldehyde and more complex molecules were formed when CH_4 and NH_3 were deposited at 10 K and exposed to ultraviolet light.

Organic compounds are now being delivered to the Earth's atmosphere in small cosmic dust particles. Low velocity $10 \text{ }\mu\text{m}$ diameter interplanetary dust particles collected from the stratosphere were heated to less than $550 \text{ }^\circ\text{C}$ during entry in the present Earth's atmosphere (Sandford, 1988). Compounds in the dust should be similar to those found in comets because comets are the sources of much of the cosmic dust. Using the equations for heating of particles during entry into the atmosphere and the assumed velocity of 15 km s^{-1} for cosmic dust given by Brownlee (1985), we find that a $0.1 \text{ }\mu\text{m}$ radius particle of 1 gm cm^{-3} reached a maximum temperature of 365 K in the primitive atmosphere and lost its cosmic velocity 86 km above the primitive Earth's surface. Small (less than $0.2 \text{ }\mu\text{m}$ radius) particles entering at high velocity will still have contained pristine organic material after entry. Therefore, these particles and the low velocity larger particles could have contained useful prebiotic organic material that formed in space and survived entry. The physics of aerosol formation indicates that organic rich particles from interplanetary and interstellar dust, vaporized cometary material, and carbonaceous chondrites would have coalesced with each other and with fine grained ejecta of large craters to form larger particles that eventually settled out of the atmosphere.

4. Coalescence of Cometary Material in the Atmosphere

In order to examine the growth and fate of particles from all extraterrestrial sources in the early atmosphere, the fluxes of comets, interplanetary dust, and interstellar dust must be estimated. Lazcano-Araujo and Oro (1981) reviewed estimates of cometary mass captured by Earth. These estimates range from 3.5×10^{21} grams to 10^{25} grams (10^{-10} to $10^{-14} \text{ gms cm}^{-2} \text{ s}^{-1}$) for the first 500 million years of Earth's history. Chyba (1987) used lunar crater and basin populations to calculate that the Earth would have acquired an exogenous ocean of water with a mass of 10^{24} gm if 10% or more of the objects impacting the Earth between 4.5 and 3.8 billion years ago were comets containing 50% water. Organic and inorganic compounds included in the remaining half of the comets would amount to 10^{24} gm (corresponding to a delivery rate of $10^{-11} \text{ gm cm}^{-2} \text{ s}^{-1}$) which is near the upper bound of the range of mass estimates given above.

From data provided by Grün *et al.* (1985), we estimated the flux for $0.05\text{--}0.15 \text{ }\mu\text{m}$ radius interplanetary dust now entering the atmosphere. Dust as large as $0.15 \text{ }\mu\text{m}$ would have contained organic material unaffected by heating during even high velocity entry

into Earth's atmosphere. For this size range the flux is 1.54×10^{-3} particles $\text{m}^{-2} \text{s}^{-1}$. If 40% of these dust particles are of low density (Grün *et al.*, 1985), we obtain a flux of 6.2×10^{-4} particles $\text{m}^{-2} \text{s}^{-1}$. Adjusting this number to account for the higher cometary flux early in Earth's history (Weissman, 1982), we obtain a flux for small interplanetary dust particles containing pristine organic compounds intercepting primitive Earth of 10^7 gm year^{-1} (6×10^{-20} gm $\text{cm}^{-2} \text{s}^{-1}$). Greenberg (1981) estimated that 10^9 – 10^{10} gm year^{-1} (6×10^{-18} – 6×10^{-17} gm $\text{cm}^{-2} \text{s}^{-1}$) of interstellar dust should have been supplied to Earth early in its history. Note that these values are orders of magnitude smaller than those values expected for small particles produced from impact of comets between 4.5 and 3.8 billion years ago.

To model coalescence of cometary particles in the atmosphere, we have modified a coagulation-sedimentation model developed by McKay *et al.* (1988) for the organic haze of Titan's upper atmosphere. This model assumes that particles enter uniformly in time globally. We have observed that organic particles condensed from high temperature sparks are typically less than or equal to 0.1 μm radius. In the model, cometary mass was input as either 0.1 μm radius particles or as smoke particles less than 0.1 μm in radius. In both cases the material was considered to be a combination of simple compounds found in comets, monomers formed in vapor clouds, and silicates. Cometary material was injected over a range of altitudes equivalent to 10^{-1} to 10^{-7} bars pressure in both models in order to adequately simulate the range of comet explosion altitudes.

The results of the modeling are shown in Figure 1. Figures 1a and 1b show introduction of 0.1 μm radius particles or smoke at around the 10^{-7} bar level (86 km) for five different flux values. While small comets would have exploded at lower altitudes in the atmosphere and large comets would have impacted the surface, the vaporized cometary material would have been launched to very high altitudes, as discussed in Section 2. Regardless of flux and the initial size of the material, particles grow to the same final size (0.5–2 μm) at about the same time (0.5–3 years) in the atmosphere as they settle to about 30 km altitude. Smoke particles, much smaller than 0.1 μm radius, would have had small fall velocities and high concentrations, allowing for more rapid growth than for the case where all the mass is injected as 0.1 μm particles. Thus, 0.1 μm particles in the presence of smoke can grow, independent of flux, to 0.5 μm in several minutes (Figure 1b). After reaching 0.5 μm radius, a few tenths μm more material is added to the smoke particles during periods of days to months (depending on flux) in the atmosphere. Material initially in the form of 0.1 μm particles only coalesce slowly to 0.5 μm in about 10 days to 3 years depending upon the flux. Twenty days to 3 years are required to add another few tenths μm thickness to particles grown from the 0.1 μm population.

Figures 1c and 1d show the effect of injection altitude on growth of particles and smoke for the 10^{-12} gm $\text{cm}^{-2} \text{s}^{-1}$ flux case. More rapid particle growth occurs when either smoke or particles are injected at high altitudes (corresponding to 10^{-7} bar). The altitude of injection had the greatest effect for smoke. Note that as particles grow to their final sizes reported here, no scavenging by rain (see end of Section 6) is possible during their growth because, for all fluxes considered, particles remained above 30 km altitude.

Calculations were also made for coalescence of interplanetary and interstellar dust

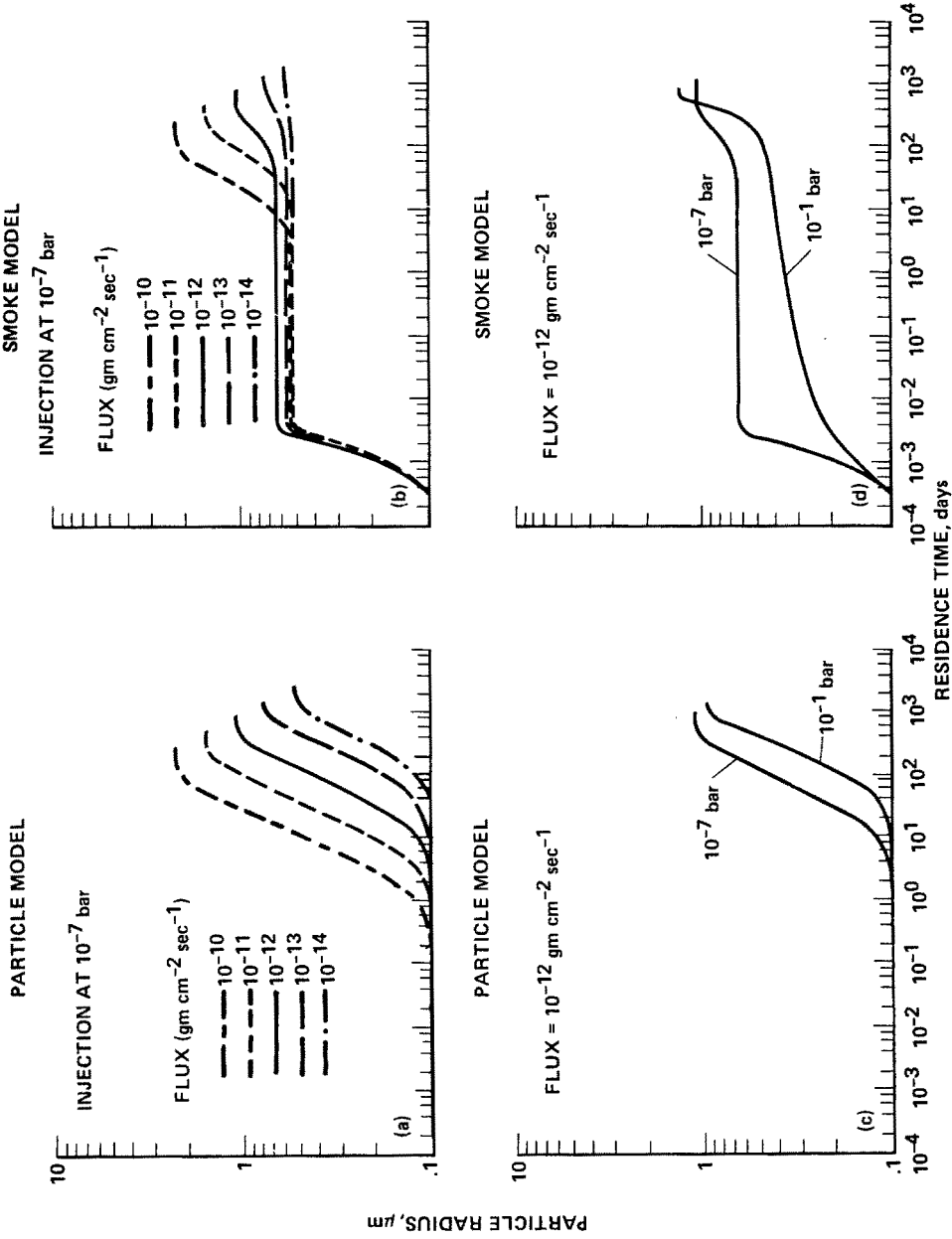
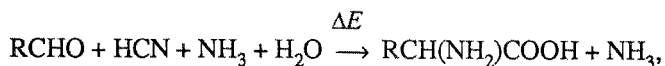


Fig. 1. Growth of sub- μm particles as a function of their residence time in the primitive Earth's atmosphere. The 'particle' models start with 0.1 μm size particles whereas the 'smoke' models start with particles smaller than 0.1 μm . Figures (a) and (b) show the effects of mass flux on growth and (c) and (d) show the effect of injection altitude (pressure level).

alone. The injection altitude of interplanetary dust and interstellar grains was taken to be at the 10^{-7} bar pressure level (86 km) where interplanetary grains were stopped. The initial size of the material in the models was $0.1 \mu\text{m}$ radius. Particles must have grown only by accretion because no vaporization occurred as the particles entered the atmosphere. We find that in our model simulations little, if any, particle growth occurred and it would have taken years for the particles to settle, by themselves, into the lower part of the atmosphere. Of course, these particles would have coalesced with particles condensed from vaporized comets and then sedimented to the Earth's surface. Thus, interstellar and interplanetary dust could have contributed simple compounds and monomers formed in space to the growing particles. Results shown in Figure 1 predict the fate of these particles as well because addition of such small fluxes to those of cometary particles would not affect the outcome. Model results show that this material, crater ejecta, and particles that condensed from the vapor clouds of comets would have coalesced and formed particles which settled to the lower atmosphere. While this model represents only an approximation to reality because it assumes a steady state flux, we included orders of magnitude variation in the assumed cometary mass flux to compensate for this assumption. Future work is planned to model single event impacts of different sizes.

5. Synthesis of Prebiotic Organic Compounds During Particle Coalescence

As discussed above, organic compounds useful for prebiotic evolution might have been produced in space and many of these compounds could have been formed again during cooling of cometary vapor clouds. We now use the coalescence model to see if organic synthesis could also have occurred during growth of cometary particulates in the atmosphere. Starting with simple organic molecules such as CH_4 , NH_3 , H_2O and H_2CO believed to exist in dust and comets, more complex species, like amino acids, may have been formed by UV photolysis (Oro, 1965). Such amino acids might have been synthesized by the well known Strecker synthesis (see *e.g.* Miller and Orgel, 1974) which is:



where R can be H, CH_3 , etc. If R is H, the RCHO is formaldehyde and the product is glycine, the simplest amino acid.

Pavlovskaya and Pasynskii (1959) exposed formaldehyde and ammonium nitrate or ammonium chloride in aqueous solutions to ultraviolet light and produced amino acids in 20 hours. The intensity of the light in the experiment was similar to that a similar sample would have been exposed to in the atmosphere. If ammonium compounds were present in the atmosphere and formaldehyde was supplied by comets, amino acids might have been formed within the growing particles following cometary entry. Figure 1 shows that, depending upon the assumed fluxes, the surfaces of particles less than $0.5 \mu\text{m}$ in radius would have been exposed to UV light for periods of days to months before other materials covered the outer surfaces. These periods would have been long enough for amino acids (and other organic compounds) to have formed in the growing particles

provided the reactants did not evaporate before synthesis occurred. Hence, amino acids might have been formed within growing particles by photolytic reactions of organic compounds. Organic monomers important in prebiotic evolution may have been produced in space, upon entry or in the atmosphere by a variety of mechanisms. The next step for chemical evolution was the production of oligomers from these materials.

Various geophysical and geochemical mechanisms have been proposed to enhance oligomerization reactions necessary for chemical evolution. Bernal (1951) first suggested that clays may have played an important role in chemical evolution because they would have provided surfaces for concentrating the monomers. The research over the preceding 30 years on the effects of clay surfaces in chemical evolution has been reviewed by Ponnampetuma *et al.* (1982). It was concluded that clay minerals facilitated synthesis of prebiologic monomers in the primordial atmosphere, that clays adsorb and concentrate by several orders of magnitude monomers in aqueous solutions and that clays probably promote polymerization of monomers by concentrating them and protecting the products in lattice spaces. Ponnampetuma *et al.* (1982) concluded that clays may have promoted reactions producing at first monomers and then polymers simply by concentrating organic molecules and bringing the reactants in close proximity to each other. Clays also provide a surface upon which reactants and products can be redistributed during wetting and drying cycles commonly found in clay environments.

Clays are probable components of crater ejecta on the primitive Earth because they are products of alteration of silicate minerals in an aqueous environment. Oceans present in the first hundreds of millions of years were exposed to heavy bombardment of accreting impactors, the larger of which would have penetrated the oceans and crushed the surface. Thus, an ideal environment for clay mineralization, in which silicate material was crushed in the presence of water, existed at the Earth's surface after the first 50–100 million years. This concept is supported by discovery of phyllosilicate minerals, like chlorite, in carbonaceous chondrites which are believed to be the products of aqueous alteration of the regoliths formed during late accretion of parent bodies (Bunch and Chang, 1980). Thus, cratering in the crust would have ejected clay minerals into the stratosphere. O'Keefe and Ahrens (1982) estimated that the amount of material less than 1 μm that was ejected into the stratosphere by large impacts was about one tenth the mass of the impacting body. Hence, significant amounts of the particles coalescing in the atmosphere may have contained clays which may have aided oligomerization reactions. Phyllosilicate minerals have also been discovered in carbonaceous chondrites (Brownlee, 1985) that are similar to materials found in interplanetary dust (Sandford, 1988). It should be noted, that clays would have been useful for enhancing prebiotic reactions, but they would not have been required for prebiotic reactions to have taken place during particle coalescence.

Coalescence of condensates in vapor clouds, interstellar and interplanetary dust, and crater ejecta would have brought monomers and other species in close proximity to each other. During impact of large objects, the concentration of particles in the atmosphere can increase so much that global cooling from attenuation of sunlight by the particles can occur (Toon *et al.*, 1982). Finally, the particles are cleansed from the atmosphere by

coalescence with other particles until they become large enough to settle by gravity to the lower atmosphere where they are either scavenged by rain or settle to the surface. The results of our model (see Figure 1) show that cometary particles accumulated in the early atmosphere in sufficient concentrations to cause particle coalescence and sedimentation. Thus, any monomers in these small particles would have been concentrated and mixed with other monomers by the process of aerosol growth. This increase in concentration in the presence of UV radiation would have favored the development of oligomers, especially for particles that contained clay cores from crater ejecta and interplanetary dust.

6. Production of Oligomers in the Lower Atmosphere

Lerman (1986) suggested that aerosols, produced by bubbles bursting at the sea surface, would have promoted prebiotic chemical reactions by concentrating monomer solutions, by creating surfaces, and by permitting aqueous chemistry, all of which are conducive for formation of oligomers. Gaines (1966) pointed out that many organic compounds have a tendency to form monolayers at liquid-gas interfaces, where reactions are enhanced. Carothers (1936) noted the importance of interfaces in polymerization of amino acids. He noted that two different paths are possible in amino acid polymerization. Purely chance encounters of amino acid molecules should produce mostly cyclic polymers but chain polymers, of interest in biological reactions, are often formed instead. Carothers explained this behavior by pointing out that on surfaces (interfaces), the reactant molecules cannot easily assume the sterically favored cyclic configuration because they are fastened at the head, middle and tail to the surface. Thus, surfaces of aqueous solutions also could have been important in prebiotic chemistry.

Our calculations show that monomers and oligomers in particles up to about 2 μm in radius would have settled into the meteorologically active lower atmosphere. In regions of the atmosphere saturated with water vapor, rain drops would have condensed on some of these particles because they served as condensation nuclei. Since rain drops falling from clouds often evaporate before reaching the ground, it is easy to imagine that conditions favorable for the production of polymers may have existed in the primitive atmosphere. Amino acids or other organic monomers in rain drops would have become insoluble at some point during evaporation so that monolayers of these compounds formed at interfaces where chain polymers could have easily been made (Carothers, 1936). For those drops which were completely evaporated, the condensation nuclei remaining would still contain non-volatile organic materials.

The surface temperature near the end of the first several hundred million years of Earth's history has been estimated to be in the range of 85–110 °C (Kasting and Ackerman, 1986). The atmospheric temperature at 5 km altitude would have been 65 °C, using a lapse rate of 4.5 °C km⁻¹ (Ackerman, personal communication, 1987). It has been reported that dry amino acids heated at 120 °C form proteinoids within one week (Fox and Dose, 1977) and in 80 days at temperatures as low as 65 °C (Rohlfing, 1976). However, Brack (1984) has pointed out that thermal polymerization of dry amino acids

can yield cross-linked polymers contaminated with by-products. Reaction of monomers on the surfaces of condensation nuclei may have inhibited the cross linking and produced higher yields of prebiotically useful compounds. Thus, it is probable that layers of organic compounds would have formed at liquid-gas interfaces as organic material came out of solution in the manner described by Gaines (1966) and that amino acids could have been polymerized in the manner proposed by Carothers (1936) or thermally as the rain droplets evaporated completely.

7. Survival of Prebiotic Compounds in the Atmosphere

It has been hypothesized that many complex organic compounds present in Earth's atmosphere would have been destroyed by continued exposure to ultraviolet light (Hull, 1960). Thus, we must consider the possibility of destruction of organic compounds by the processes described above. Bernal (1960) argued that natural processes, such as adsorption on clays or concentration in sea spray foams on the ocean's surface, would have protected prebiotic compounds from continued exposure to ultraviolet light. Addition of ultraviolet absorbing compounds on particle surfaces during coalescence of cometary and crater ejecta particles would also have protected synthesis products contained within. The attenuation of ultraviolet light with depth due to various compounds believed to be present in comets is shown in Figure 2. These curves were calculated using Beer's law. The materials chosen for these calculations include both pure compounds known or suspected to exist in comets and two model cometary mixtures, specifically a nominal model discussed by Delsemme (1981) with and without NH_3 . Ammonia has recently been detected in Comet Halley (Allen *et al.*, 1987). As can be seen from the figure,

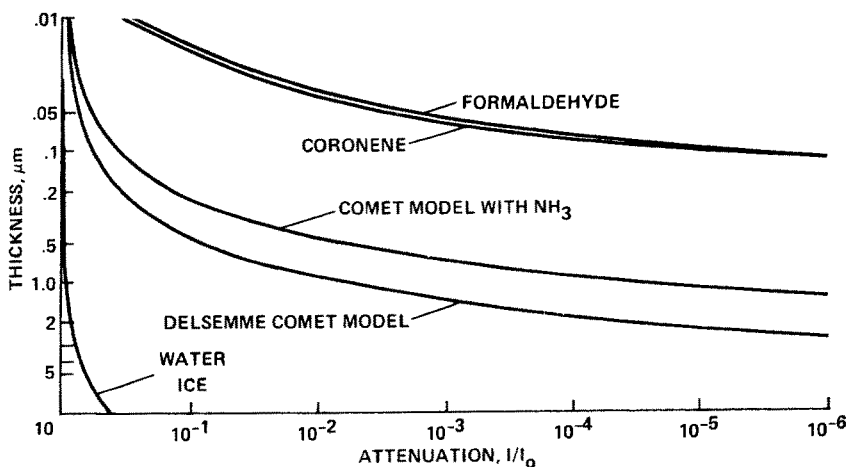


Fig. 2. Attenuation of ultraviolet light in cometary materials. The nominal comet model was taken from Delsemme (1981). The attenuation curves were calculated using extinction coefficients for the following wavelengths: H_2CO - 175 nm, coronene - 290 nm, NH_3 - 180 nm, comet model - 175 nm, H_2O ice - 170 nm.

relatively small thicknesses of some materials can strongly attenuate ultraviolet light. Thus, complex prebiotically important species produced in space, by comet vaporization, and by synthesis in the atmosphere should have been protected from photodissociation during long residence times in the upper atmosphere.

It has been proposed that impact of very large comets and asteroids, such as those which have been invoked to explain the Cretaceous-Tertiary extinctions, would have acidified the early atmosphere and oceans as a result of production of NO from shock waves produced in the atmosphere by the impacts of the objects with the surface. For example, the impact of a 26 km diameter comet with 65 km^{-1} impact velocity would have ejected material that shocked the atmosphere, producing NO, NO_2 , and finally HNO_3 in sufficient quantities to lower the pH of rain to 0–1.5 globally (Prinn and Fegley, 1987). Fegley *et al.* (1986) showed that NO is also produced when large objects form craters in surfaces beneath CO_2 rich atmospheres which are considered appropriate for the primitive atmosphere. Based on these studies, very large impacts may have destroyed life on Earth. However, after they stopped impacting smaller comets would have produced coalescing aerosol clouds which resulted in new cycles of prebiotic evolution.

Prebiotic chemical evolution was certainly a continuous process and must have required cometary entry events frequent on the scale of geologic history if comets played a significant role. Size distributions of lunar craters indicate that the distribution of impacting objects early in Earth's history probably followed an inverse square power law. Since only the largest objects had any significant effect on global acidification and the impact frequency decreased with time, eventually the large impacts that may have destroyed life, would have stopped but smaller ones continued to produce coalescing clouds of material. Prebiotic reactions in these clouds could have led to development of new life on Earth. Thus, adverse affects of UV radiation or large impacts would not have frustrated relevant prebiotic evolution in coalescing particles.

8. Prebiotic Synthesis under Primitive Earth Conditions

Let us evaluate the cometary particle coalescence mechanism for prebiotic evolution within the framework of the geologic conditions that existed on Earth up to 4 billion years ago. According to Alfvén and Arrhenius (1976), the ocean may have started to form as early as 35 million years after the Earth started to accrete and reached its final mass in three hundred million years. Recent studies by Matsui and Abe (1986) give an accretion time of 50 million years to form the Earth. Their models show that surface temperatures were sufficiently high to maintain magma oceans until the Earth reached about 90% of its present radius at which time temperatures decreased rapidly. During the later stage of accretion enough water was supplied by volatile rich accreting bodies to suggest an impact origin for the atmosphere and hydrosphere. It now appears that oceans would have been stable even during the first several hundred million years of Earth's history (Kasting and Ackerman, 1986). Between 100 and 500 million years, when formation of monomers and oligomers useful for biologic evolution must have taken place, a global ocean may have existed. Geologic age dating of rocks indicates that 50% of the present continental

crust was present 1.75 to 2.00 billion years ago (Harley, 1987). It appears that little, if any, of the Earth's present continental crust may have been present during the first 500 million years (Patchett and Arndt, 1986). Therefore, if oligomers needed for biologic evolution were produced before 4 billion years ago (Calvin, 1969), then they probably were produced in the atmosphere or in the ocean and not on continental surfaces.

The rate of cometary impact would have been enhanced during the late bombardment of the Earth until about 3.8 billion years ago (Murray *et al.*, 1981). As discussed above, prebiotic monomers supplied by comets or produced in the atmosphere by cometary entry must have been concentrated in growing particles during their coalescence in the atmosphere. These particles would have combined with other particles before they became large enough to settle out of the atmosphere. This insured that monomers (and other organic reactants) would have been brought into contact with each other and with other types of inorganic and organic compounds during the time particles resided in the atmosphere (typically less than 3 years). This mechanism would have been very efficient when compared with other processes which required that monomers (and other precursor compounds) deposited directly in a global ocean had to be concentrated from dilute solutions. In the particle coalescence model, monomers first become concentrated in particles only 2 μm or less in radius. Then some of these compounds dissolved in rain drops. Evaporation of water resulted in concentrations of monomers much higher than those possible in the ocean. While dehydration of monomers dissolved in evaporating rain drops was possible, only those monomers near the surface of the global ocean and which were taken up by aerosols formed by bursting bubbles could have been dehydrated. Also, sediment-air interfaces on the Earth's surface where dehydration of monomer solutions might have occurred may not have existed before 4 billion years ago. While the cometary particle coalescence mechanism for polymerization does not rule out the previously proposed geologic polymerization mechanisms involving aerosol formation at the sea surface and on clay and other mineral surfaces at the Earth's surface, coalescence of cometary particles and aqueous chemistry in rain may have been more consistent with geologic conditions at the time and would have been a more efficient way for concentrated organic compounds and forming oligomers.

If a substantial portion of the starting compounds required for prebiotic evolution were supplied from space, aerosol formation and aqueous chemistry in the atmosphere would have been processes which enhanced chemical evolution. When deposited in the ocean, compounds remaining with the silicate particles would have been deposited and concentrated on the ocean bottoms and material dissolved in the ocean would have formed a surface scum and been concentrated by clumping. Oligomers made in atmospheric particles and then deposited in the ocean could have organized into microsystems like the coacervate droplets which form when high molecular weight oligomeric compounds are put in aqueous solutions (Yanagawa *et al.*, 1980). Further, gradual chemical evolution within either of these regimens could have given rise to biological compounds leading to the most primitive cells observed in the fossil record of 3.5 billion years ago.

9. Conclusions

The entry of comets into the atmosphere vaporized much of the cometary material producing excited organic species which combined upon condensation to form complex organic compounds of biological importance. Coalescence of these particles with interplanetary and interstellar dust and crater ejecta in the primitive atmosphere could have been an important process for chemical evolution. Particle coalescence concentrated and mixed organic compounds. Complex materials produced by impact processes or by photolysis during coalescence would have survived destruction from continued exposure to UV radiation and acids formed by large impacts. As the particles settled into the lower atmosphere, they became condensation nuclei for rain. Aqueous chemistry further promoted oligomerization reactions. Finally, the oligomers were deposited in the ocean where further concentration and subsequent reactions would have eventually produced microsystems and, later, the most primitive of cells.

If further study confirms that cometary entry in planetary atmospheres indeed enhanced chemical evolution, then chemical evolution may be viewed as part of the normal process of planetary formation anywhere in the universe. It is reasonable to believe that cometary objects containing simple organic compounds may have been common during development of many planetary systems and that cometary entry and impact would have been enhanced during the late stages of planetary accretion. Thus, prebiotic chemical evolution may be an inevitable consequence of impacting comets during the late stage of accretion of planets. This would imply that the probability for development of life elsewhere is high if water survived on planetary surfaces.

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