

Atmospheric aerosols as prebiotic chemical reactors

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Aerosol particles in the atmosphere have recently been found to contain a large number of chemical elements and a high content of organic material. The latter property is explicable by an inverted micelle model. The aerosol sizes with significant atmospheric lifetimes are the same as those of single-celled organisms, and they are predicted by the interplay of aerodynamic drag, surface tension, and gravity. We propose that large populations of such aerosols could have afforded an environment, by means of their ability to concentrate molecules in a wide variety of physical conditions, for key chemical transformations in the prebiotic world. We also suggest that aerosols could have been precursors to life, since it is generally agreed that the common ancestor of terrestrial life was a single-celled organism. The early steps in some of these initial transformations should be accessible to experimental investigation.

Aerosol particles in the atmosphere have long been known to scatter and absorb sunlight and hence to have a substantial influence on the temperature of the Earth. Recent real-time observations of the chemical composition of individual aerosol particles have shown an unexpectedly and remarkably high content of organic molecules (1, 2). A conceptual model can account for this observation by an inverted micelle structure in which surfactants form a spherical monolayer enclosing an aqueous interior (3, 4). Analogies in size, form, and composition between these aerosols and single-celled organisms such as bacteria lead us to propose that similar atmospheric particles could have been the precursors of living systems on Earth. Large populations of aerosol particles would have provided an environment for the concentration of prebiotic molecular species and for their chemical transformation through exposure to the fluctuating fields of humidity, temperature, and sunlight available in the atmosphere at different altitudes and latitudes. Coagulation and division of the particles could have resulted in an increased diversity of molecular species and an early mechanism for reproduction and replication of successful molecular populations.

The most probable sequence of events in the evolution of living organisms on Earth started with either the terrestrial synthesis or the arrival from elsewhere in the universe of simple carbonaceous compounds (5). It was long ago recognized that hot water or steam would have reacted with metal carbides to form hydrocarbons as the Earth condensed from cooling gases (6). The precursors of biopolymers—amino acids, sugars, purines, and pyrimidines—as well as a range of surfactants such as long-chain carboxylic acids can be rationalized as prebiotic constituents by such means (7). Moreover, molecules of this type, including hydrocarbons with chain lengths in excess of C₁₀, have been found in the interior of carbonaceous meteorites (8). These building blocks are thought to have undergone polymerization and other reactions, and through a series of events to have formed structures of greater and greater complexity. The question of how such processes could occur in prebiotic times has been a subject of much investigation (7, 9, 10). In particular, key questions include how any such molecules could have reached sufficient concentrations to react in the presence of fluid mechanical dispersion aided by diffusion, making their concentration in the bulk oceans unlikely to have exceeded 10⁻⁶ M, and

how they could have had access to an energy source for their activation. Other questions among many concern salinity difference between cells and the ocean, and the mechanism by which homochirality arose in the amino acids in proteins and in the sugars in nucleic acids.

The Inverted Micelle Model of Aerosol Structure

The structural model deduced recently (3) from single-particle laser mass spectrometric observations (2) of present atmospheric aerosols implies that much of the organic content of the particles resides at their surface. In this model the surfactants lie with their polar heads inserted into the ionic aqueous core, with their hydrophobic hydrocarbon tails exposed to the atmosphere. The ocean surface acts as a global scale concentrator, even of small organic molecules (11). This concentration could have been important in the early stages of chemical evolution. It has long been known (12, 13) that aerosols are formed by wind-driven wave action followed by bubble-bursting at the ocean surface; aerosols therefore act as separators that concentrate surfactants such as long-chain carboxylic acids at the aerosol air-water interface. There is evidence that organic molecules partition in laboratory-formed aerosols such that the more hydrophobic molecules in a mixture tend to migrate to the outside of the droplets (14). The surface organic coating can increase both by coagulation of partially covered aerosols and by selective evaporation of water vapor at relative humidities less than 100%. Consequently, those aerosols that become encapsulated by a full surfactant monolayer become inert to external chemical attack on their contents. The film coating the particle in addition slows the loss of water and other contents from the central cavity (3). It is important to note that aerosol droplets (radii 10⁻⁷ to 10⁻⁶ m) are different in crucial respects from cloud droplets (radii 10⁻⁵ to 10⁻⁴ m) and raindrops (radii ≈10⁻³ m). The fractional organic content of these larger hydrometeors is small, is minuscule for surfactants (3), and is therefore a significant handicap for their previously proposed role in the origin of life (15).

Much of the evidence from the early stages of the biosphere has been obliterated. However, fundamental similarities in physical properties and life cycles of aerosols that would have been persistent over geological times allow us to gain information from the tools of modern atmospheric observations. Recent real-time WB57F aircraft measurements of individual aerosol particles in the upper atmosphere show that, on average, organic molecules comprise roughly 50% of the mass of the upper tropospheric aerosol particles in the tropics (2), an amount difficult to account for on the basis of bulk solubility, but which is predicted by the inverted micelle model (3). These measurements (2) also show that a total of 45 elements have been detected in the atmospheric aerosol at altitudes between 5 and 19 km. All of the elements essential for present-day life are there, including much higher concentrations of carbon, nitrogen, and trace elements than are found in seawater (16). In addition, it is

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likely that small particles of minerals such as aluminosilicates will be present; such species have been implicated in some models of prebiotic chemistry (17). We note that Miller (9) recommended the examination of cloud droplets as a reaction medium in the prebiotic atmosphere, and Lovelock (18) suggested a prebiotic radiative role for an upper tropospheric layer of smog particles derived from the reactions of methane. Current aerosols tend to be acidic, and the presence of aerosols in the prebiotic atmosphere could have extended the pH range for possible chemistry from the 7–9 characteristic of seawater to lower values. Finally, the dehydration required in the formation of a peptide bond between two amino acids would be facilitated in an aerosol particle compared with the bulk ocean.

The size range of aerosol particles is determined by three fundamental properties: the surface tension of liquid water, the aerodynamics as expressed by Stokes' law, and the Earth's gravitational field. Kasten (19) gives the vertical fall velocity w of a particle of radius r and density ρ_p as

$$w = (2/9)(\rho_p - \rho)(r^2g/\eta)(1 + \{\lambda/r\}[\alpha + \beta \exp(-\chi r/\lambda)]), \quad [1]$$

where g is the acceleration caused by the Earth's gravitational field, η is the viscosity of air, λ is the mean free path, ρ_p is the density of the particle, ρ is the density of the gaseous atmosphere, and α , β , and χ are empirical constants. Application of Eq. 1 to the present standard atmosphere at different pressures (altitudes) yields a family of curves for r on a graph of atmospheric pressure (altitude) versus terminal vertical velocity; it is shown in Fig. 1A, where the density of $1.5 \text{ g}\cdot\text{cm}^{-3}$ has been assumed for ρ_p . Fig. 1B shows the time to fall 1 km at 10 km altitude as a function of r . We note that while many authors use the present surface pressure of one bar for the prebiotic atmosphere, estimates range as high as 97 bar (20). In such an atmosphere, aerosol residence time would be correspondingly longer for a given r . These values allow the range of aerosol sizes able to maintain a significant lifetime in an atmosphere on Earth to be estimated as 0.1 to $5 \mu\text{m}$. These sizes are remarkably close to those of present-day single-celled organisms (several tenths to several micrometers). We suggest that this result may offer an explanation for the general size of such organisms. One prediction of the model is that on a planet with a less dense atmosphere, the aerosol particles hence would be smaller. In this context, the only available test, however uncertain, lies in the small size of the cell-like structures claimed to exist (21) in the Martian meteorite ALH84001. The production of organic aerosols on the prebiotic Earth would have become operative as soon as oceans formed, and it would probably have been accelerated by meteor bombardment; the mechanism could thus have produced life as early as the end of the Hadean period.

The Atmospheric Behavior of Inverted Micelles

In addition to their size, the nature of typical aerosol particles, with a concentration of organic and other molecules within a surfactant wall, has obvious parallels with simple cells. Moreover, many aerosol particles that persist in the atmosphere would experience environments under which chemical transformations can occur. Particles with $r \leq 5 \mu\text{m}$ are transported by the wind currents of the general circulation and experience large fluctuations in relative humidity as a natural process. During sunlit hours, we would expect the hydrophobic molecules in the surface layer to be attacked by atmospheric gaseous free radicals (3). In the present atmosphere these are mainly OH and HO₂, but in the reducing prebiotic atmosphere they may have been OH, NH₂, CH, CH₂, CH₃, and SH (22). However, in the absence of molecular oxygen in prebiotic times, we would not expect rapid degradation of the surfactants; some production of functionalized hydrocarbons would have occurred. In fact, if the solar

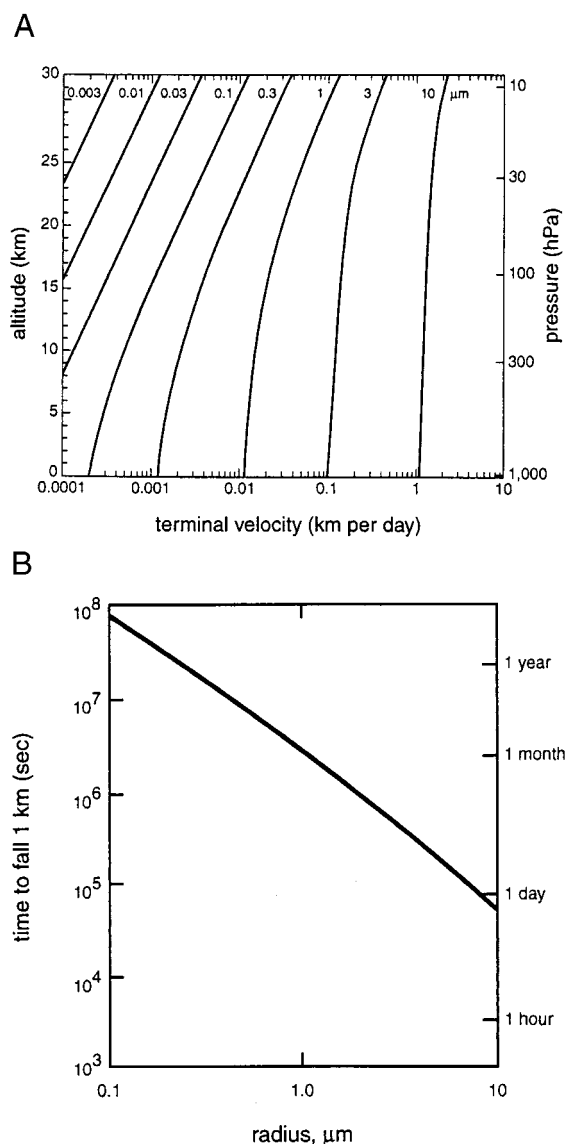


Fig. 1. (A) The terminal vertical velocity w ($\text{m}\cdot\text{s}^{-1}$) plotted on the abscissa as a function of pressure (right ordinate) and altitude (left ordinate) for a family of curves, each of which is labeled by the radius r (μm) of a spherical particle with density $1.5 \text{ g}\cdot\text{cm}^{-3}$. The data are applicable to the current Earth atmosphere; note that $1 \text{ hPa} = 1 \text{ millibar} = 0.001 \text{ atmosphere}$. (B) The time to fall 1 km at 10 km altitude for a spherical particle with density $1 \text{ g}\cdot\text{cm}^{-3}$ in the present atmosphere. Note that particles greater than about $1 \mu\text{m}$ quickly reach a terminal velocity. In the current atmosphere, the photochemistry in the presence of O₂ generates hydrophilic groups on the exterior ends of the lipids (3), probably resulting in significant removal by rainout and washout (23); this may not have been the case in the prebiotic atmosphere.

spectrum in prebiotic times was cut off by CO₂, photoionization of species such as water, methane, ammonia, and hydrogen sulfide would not have occurred, but solar photons down to about 174-nm wavelength (7 eV , $160 \text{ kcal}\cdot\text{mol}^{-1}$) would have been available to induce reactions on both the interior and the exterior of the aerosols.

Coagulation of aerosol particles is a well-known phenomenon (23). In the case of an inverted micelle, even with partial surfactant monolayer coverage, the fission of the larger aerosol formed by the coagulation of two average-sized particles would result in the formation of a somewhat larger aerosol particle together with a much smaller one, which could end up inside or outside the larger

one. Both resulting particles would have a complete monolayer. Because of the surface-to-volume ratio of a sphere ($3/r$), the result is thus a bimodal size distribution, a frequently observed condition (23) for current-day aerosols. Organic aerosols may thus both coagulate and divide, with the latter process being enabled by the need to minimize free energy. Free energy minimization will occur in the course of maximizing coverage by surfactant monolayers (24). It is interesting to note that the size estimates for vesicles arrived at by Tanford (24) on the basis of molecular dynamics and diffusively driven formation in aqueous solution are tens of nanometers, or two to three orders of magnitude smaller than both atmospheric aerosols and single-celled organisms. Laboratory work on self-reproducing vesicles in organic solutions (25) and a mathematical treatment of their dynamics (26) using the Becker–Döring equations are consistent with Tanford’s estimates, producing a size distribution peaked at 30 nm. Vesicles produced in bulk liquid thus appear to be too small to have been direct precursors to single-celled organisms. As noted earlier, hydrometeors (cloud drops and precipitation) are too large, being dilute and settling rapidly under gravity. Aerosol particles, the natural resultant of the interplay of gravity and aerodynamics, are the right size to have significant atmospheric lifetimes; we consider later the implications of size for the ability to sustain a sufficiently diverse chemistry.

The general circulation of the atmosphere transports some aerosol particles to much higher and colder regions, which in general might be expected to have more intense light fields at shorter, UV wavelengths. Although there was no ozone layer in the prebiotic atmosphere, there would have been water clouds and a high cold tropopause as the result of there being liquid water at the surface (27). The tropopause is a location where incoming meteoritic aerosols from space will encounter upwelling aerosols from the Earth’s surface; in the tropics it is cold enough to freeze aerosol particles. We do not know how such different temperature and radiation fields might have affected reactions of the organic molecules, whether these were surfactants on the exterior or smaller more soluble species on the interior. It is important to note that the range of typical aerosol sizes, their enormous populations, and the variety of their exposure times afforded by the general circulation to any particular wavelength interval of the solar spectrum would have permitted any requisite actinic flux necessary on some fraction of the aerosol population. Such a flux would have been enough to induce polymerization while at the same time avoiding destruction of the products or the production of tars. It is therefore likely that with the abundance of potentially reactive species in the primitive atmosphere, a wide range of molecular species, including the precursors for macromolecular synthesis, could have been formed and retained in organic aerosols. After such synthetic processes, fuelled by the absorption of light from the sun, some of the particles would enter clouds, and those with any hydrophilicity on their exteriors would act as cloud condensation nuclei and so return to the surface in rainfall. Other such aerosols would be carried by the winds back to the surfactant-covered ocean surface without experiencing rainout, a time in the current atmosphere believed to be of order 10 days (23). There would have been an enormous number of repetitions of the cycles where aerosol particles, with lifetimes of days to months, returned to the ocean, whose surface was continually producing fresh populations of aerosols. Over tens to hundreds of million years, we suggest that this cycling would have led to an atmospheric population of aerosols with an enriched carbonaceous chemistry and having the same size as single-celled organisms, and which thus could have been their precursors.

Inverted Micelles as Chemical Reactors

Particles returning to the ocean by such a mechanism would have the possibility of a number of transformations. Among the most interesting of these is the possibility that a particle settling on to

an aqueous surface containing surfactants could lead to the formation of a complete bilayer around the particle, followed by incorporation into the bulk ocean; see Fig. 2. Such a mechanism could result in the formation of a double layer of surfactants around the aqueous interior, with the hydrocarbon chains tail-to-tail much as in biological membranes. The size of this double-walled vesicle in the ocean would, however, have been determined in the atmosphere, as embodied in Eq. 1. Once in the bulk ocean surrounded by a bilayer, the molecular species on the interior would experience a milder environment with less short-wave UV light. Reactions, such as polymerization, that would be inhibited in the bulk ocean because of the high dilution of chemical species would perhaps be favorable in the crowded interior of an airborne aerosol droplet and its oceanic successor. A wide range of reactions has been found to be possible in simple vesicles, including the synthesis and organization of molecular structures (28). If a template was required, the regular pattern of charge density centers at the spherical interface between the aqueous interior and the monolayer of surfactants could potentially provide one. The regular pattern would occur as a result of the self-assembling characteristic of the surfactant in the spherical surface film. The interaction between atmospheric particles and the ocean surface is one of many feedback processes, acting on large populations over many cycles, that could have resulted in a richer chemistry in the aerosols that are generated continually from the oceans. Indeed, it is abundantly clear that the composition of present-day atmospheric aerosols reflects the existence of chemical species in the biosphere (3). We note that fluid mechanical mixing is even more effective than diffusion at dispersing monomers, and at length scales larger than about a millimeter there would be little chance of producing biopolymers without a container. The need for a container has been seen in numerical simulations of chemical evolution (29). Two characteristics of present single-celled organisms would occur naturally by the aerosol mechanism—chemical heterogeneity in the surface layer of the ocean would make the outer lipid layer different from the inner one, and the fluctuations in relative humidity would allow a different salinity than seawater.

For specific chemical reactions to take place under milder conditions than the atmosphere, such as would have existed if vesicular structures were to have formed, catalysts need to be present. Metal ions and their complexes are able to catalyze a wide range of reactions in both inorganic and living systems (16). As we have noted earlier, a very wide range of elements, including many transition metals, notably iron and copper, are present in atmospheric aerosols (2). Because at least some of these are of extraterrestrial origin, they would have undoubtedly been present in the prebiotic atmosphere.

There have been attempts to estimate the variety and concentration of molecules necessary to develop macromolecules capable of replication. Dyson (30) used an elegant mathematical model to estimate the need for a minimum of nine different monomers to be present, in an ensemble of at least 10^{10} coacervate droplets in the ocean each containing 2,000 to 20,000 monomers. Joyce and Orgel (31) estimated that about 1 kg of monomers would be necessary to produce a 40-unit RNA. The present-day troposphere contains several hundred aerosol particles per cubic centimeter, each containing 10^8 to 10^{10} molecules. The molecular content of individual organic aerosol particles therefore fulfills Dyson’s conditions in the atmosphere rather than in the ocean: the number of aerosol particles needed to contain 1 kg of monomers, however, would be rapidly dissipated by fluid mechanical mixing, even assuming it could be assembled in the first place. Nor would aerosol–aerosol collision rates allow free encounters among all of the monomer molecules in the 1-kg mass. Because proteins contain up to 20 amino acids, whereas nucleic acids contain only 4 purines or pyrimidines, our mechanism in conjunction with Dyson’s model would imply the

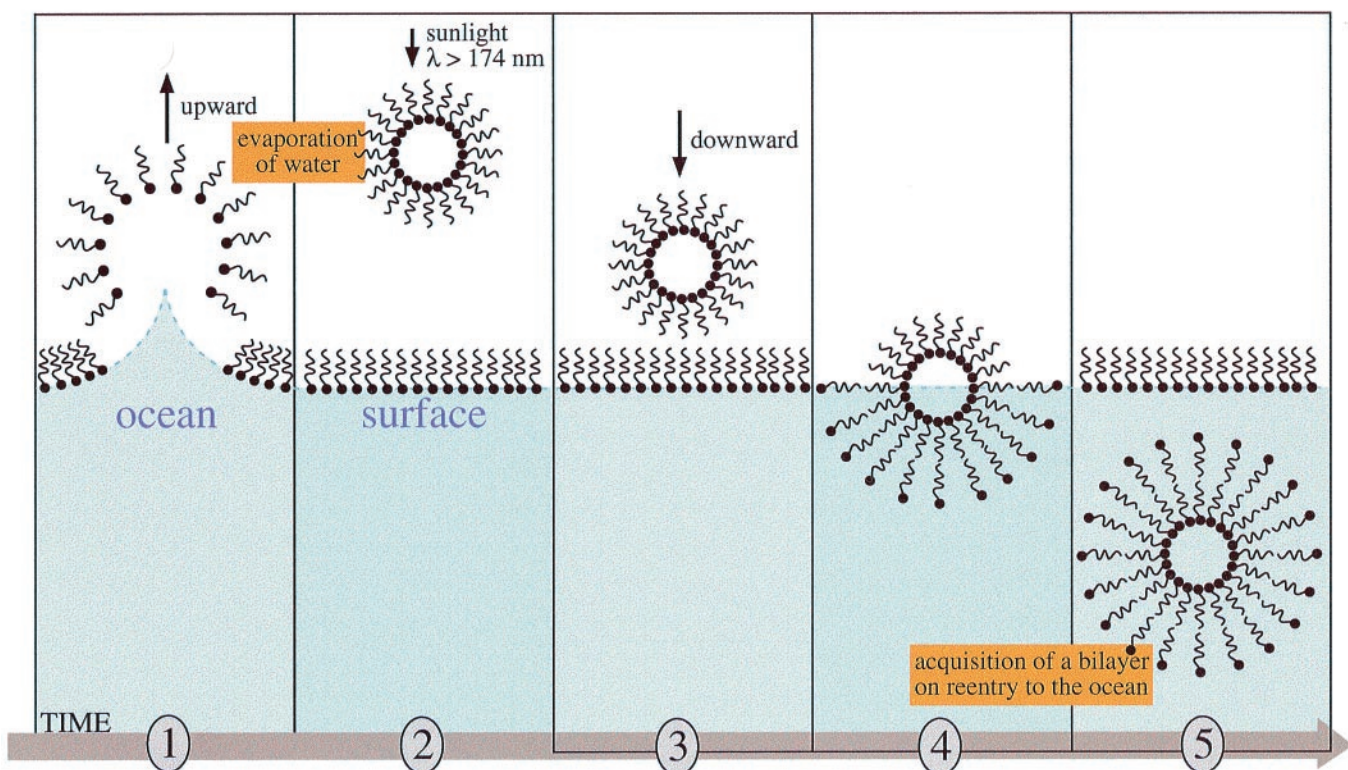
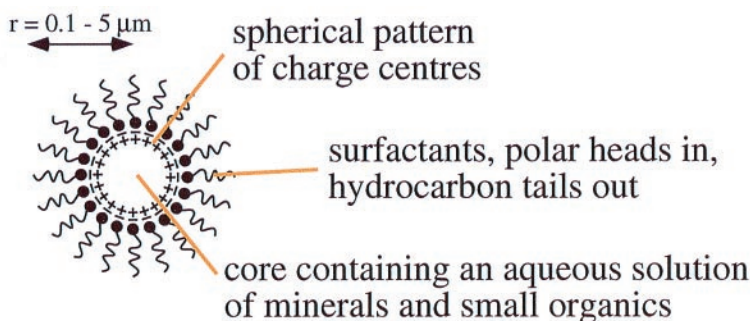


Fig. 2. A schematic representation of an organic aerosol particle (*Upper*), and a sequence of five steps representing the formation of an aerosol particle with a surfactant partial monolayer at the sea surface, its exposure to sunlight while airborne after evaporation of water from the interior produces a complete monolayer, reentry at the sea surface, and the acquisition of a second layer of surfactant that permits entry into the bulk ocean as a stable vesicle (*Lower*). The sea surface acts as a global scale concentrator of surfactants, which have their polar groups in the water and their hydrocarbon chains in the air; smaller, more soluble organics will also tend to partition to the air–water interface (11). Very large numbers of repetitions of this cycle would have occurred. The figure is not intended to be an explicit representation of the detailed mechanics at either molecular or droplet scales; cap and jet formation from bursting bubbles is involved (12, 13, 23). Note that the organic aerosol mechanism does not require the solution inside the vesicle to have the same salinity as seawater, and in general different lipids would be expected in the inner and outer layers of the vesicle. Both properties are characteristics of living cells, which would be difficult to explain by production confined to the bulk ocean. The molecules are not drawn to scale; a surfactant monolayer may be 2–3 nm deep, or of order 10^{-3} of the radius of the aerosol or vesicle.

sequence vesicles–proteins–nucleic acids. It is unlikely to be coincidence that the size of atmospheric aerosols is also the one that yields a high enough percentage of organic molecules, in large enough numbers to sustain varied chemistry. Any smaller, and the particles coagulate; any larger and they fall out rapidly. The essential point, however, is not heuristic argument but that experiments with aerosols in large reaction vessels illuminated by sunlight or simulated sunlight could be done, to see whether populations of nucleotides and amino acids can polymerize in the particle interiors, either separately or together. A reaction vessel of 100 m^3 could allow a lifetime of days for diffusion to the walls by micrometer-sized aerosols.

An additional perspective can be offered on how proteins may have been involved in prebiotic chemistry. The polypeptide chains

of proteins are formed by simple dehydration reactions of amino acids, at least some of which are thought to have been present in prebiotic milieu. Such chains, which contain many hydrophobic groups with hydrogen bond donors and acceptors, have an inherent tendency to aggregate to form high molecular weight assemblies (32, 33). Polypeptide aggregates can be amorphous or highly ordered, and some forms of these aggregates, even in disordered structures, have the ability to catalyze simple reactions (34). Even aggregates formed from random couplings of amino acids could therefore perhaps have acted as primitive templates and catalysts for chemical processes taking place within a closed environment. Through evolutionary processes specific sequences of polypeptides have emerged that are able to avoid their inherent tendency to

aggregate by folding into structures that bury the aggregation-prone main chain and hydrophobic side chains within a stable core (33). These characteristics result in solubility, which may thus have been the property of proteins, rather than function, resulting in natural selection during the precursor period before the emergence of living systems.

Although our model does not address at this stage the details of the chemistry involved, we believe the examination of the first steps in the chemical processes possible in atmospheric and simulated prebiotic environments will be a fruitful field of exploration from the point of view of molecular evolution. For example, the calculation that homochiral domains of enantiomers will emerge in surfactant films (35) is of particular relevance in the context of the origin of chirality; the light transmitted to the interior of an aerosol particle through such a domain could be circularly polarized. Subsequent coagulation or division need not result in a 50–50 racemate. Another possibility for separating racemic mixtures is freezing, which could occur at the very cold temperatures at the tropical tropopause or the winter pole. The 0.5% circular polarization observed for sunlight multiply scattered by aerosols in the atmosphere at low solar angles (36) (dawn and dusk) could have been effective in the polar regions, where such conditions prevail for long periods. The emergence of stereospecificity was crucial for the development of life, as it restricts the otherwise massive configurational diversity of the compounds of carbon (37). Finally, we note that the enormous atmospheric populations of aerosols, reflecting in their chemical composition the surface heterogeneity of the planet, would allow any favored chemical population to evolve by natural selection. Complete homogeneity could not be maintained over the entire population of atmospheric aerosols; the global atmospheric mixing time (months to a year) is much longer than the aerosol residence time of days. The coagulation and division of organic aerosols may have been early forms of reproduction and replication; the particles offer a macroscopic means by which the successful chemical populations within them could evolve.

Summary

Atmospheric aerosols coated with organic surfactant films appear to offer a number of attractive features as versatile chemical reactors in the prebiotic production of polymeric molecular

species. These include their mobility through a wide range of temperature and radiation fields, their frequent, widespread, and continual formation, their natural ability to concentrate aqueous solutions, and their ability to coagulate and divide, so sharing contents and information. Atmospheric dispersion by fluid motion allied to diffusion would ensure that not all aerosols would share any evolved advantage, so natural selection would not be inhibited. Their natural tendency, through the forces of gravity, aerodynamic drag, and surface tension is to be of the same size as terrestrial single-cell organisms. We believe that our model addresses several key issues in the development of prebiotic chemistry and its conversion to biochemistry (37). At least the first steps of the evolution of monomers in aerosols are testable by experiment, particularly under light of shorter wavelengths than is cut off by ozone in the present atmosphere.

Organic aerosols offer more than freedom from the tyranny of the tidal pool or Darwin's "warm little pond" (38); they offer a possible mechanism for the precursory production and the subsequent evolution of populations of cells and the selection of macromolecular sequences able to carry out specific chemical reactions within them. The model we offer also suggests a set of characteristics that life might possess on other planets similar to but not identical to Earth. Although much of the proposed model is uncertain, and much of the detailed chemistry remains to be established, our scheme offers many opportunities for experimental tests of the separate steps and hence the refinement of the model.

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