

# Ocean–Atmosphere Interactions in the Emergence of Complexity in Simple Chemical Systems

ELIZABETH C. GRIFFITH,<sup>†</sup> ADRIAN F. TUCK,<sup>‡</sup> AND  
VERONICA VAIDA<sup>\*,†</sup>

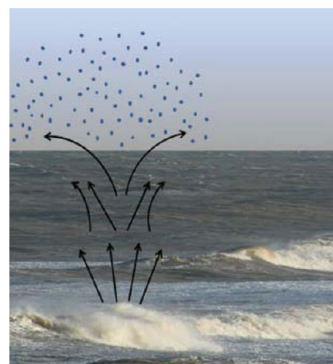
<sup>†</sup>*Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder Colorado 80309, United States, and* <sup>‡</sup>*Department of Physics, Imperial College London, SW7 2AZ, UK*

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## CONSPECTUS

The prebiotic conversion of simple organic molecules into complex biopolymers necessary for life can only have emerged on a stage set by geophysics. The transition between “prebiotic soup,” the diverse mixture of small molecules, and complex, self-replicating organisms requires passing through the bottleneck of fundamental chemistry. In this Account, we examine how water–air interfaces, namely, the surfaces of lakes, oceans, and atmospheric aerosols on ancient Earth, facilitated the emergence of complex structures necessary for life. Aerosols are liquid or solid suspensions in air with a broad, power law size distribution. Collectively, these globally distributed atmospheric particles have an enormous surface area. Organic films at the interface between water and air offer advantages for biomolecular synthesis compared with the bulk and can simultaneously participate in the folding of biopolymers into primitive enclosed structures.

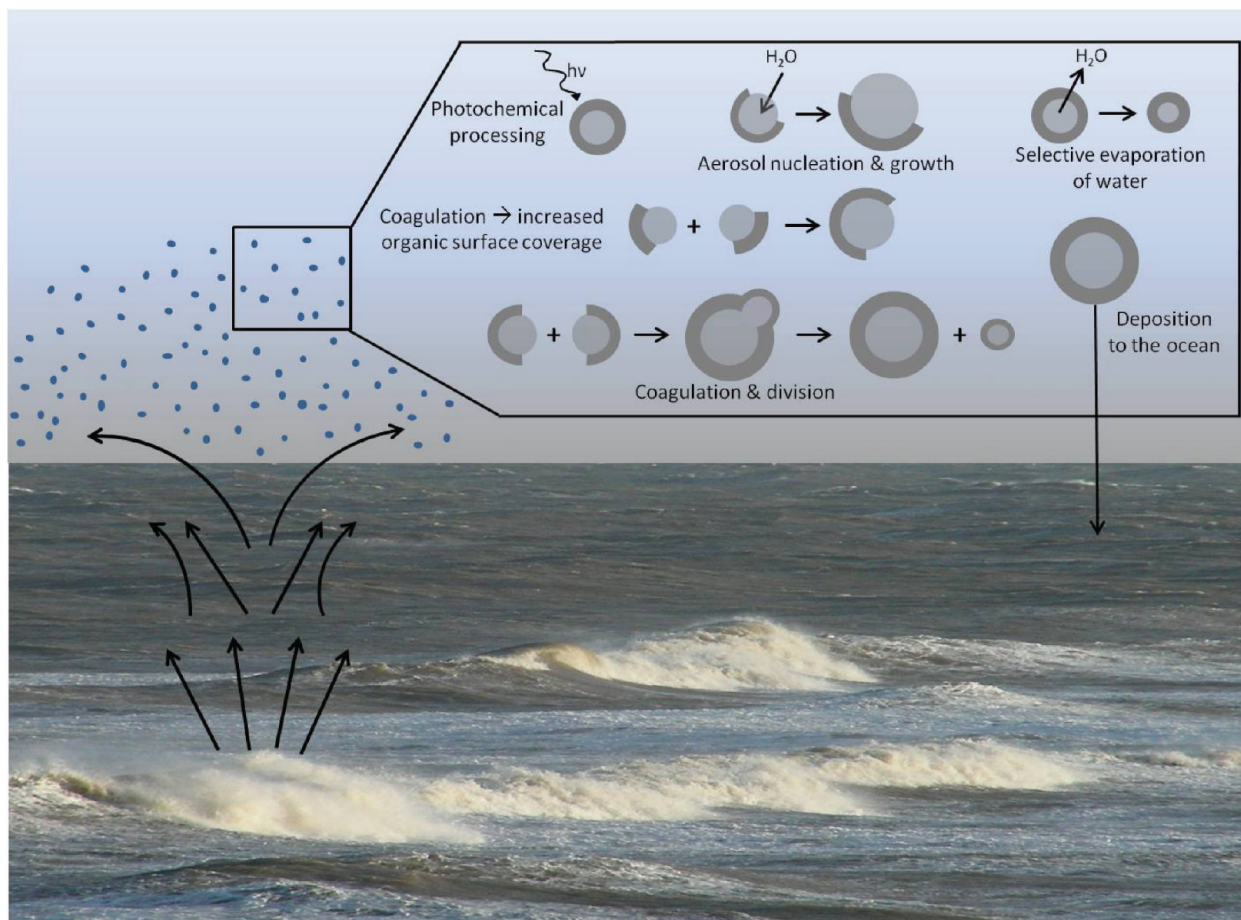
We survey the advantages of the water–air interface for prebiotic chemistry in a geophysical context from three points of view. We examine the formation of biopolymers from simple organic precursors and describe the necessity and availability of enclosures. In addition, we provide a statistical mechanical approach to natural selection and emergence of complexity that proposes a link between these molecular mechanisms and macroscopic scales. Very large aerosol populations were ubiquitous on ancient Earth, and the surfaces of lakes, oceans, and atmospheric aerosols would have provided an auspicious environment for the emergence of complex structures necessary for life. These prebiotic reactors would inevitably have incorporated the products of chemistry into their anhydrous, two-dimensional organic films in the three-dimensional fluids of the gaseous atmosphere and the liquid ocean. The untrammelled operation of natural selection on these aerosols provided the likely location where condensation reactions could form biopolymers by elimination of water. The fluctuating exposure of the large, recycling aerosol populations to radiation, pressure, temperature, and humidity over geological time allows complexity to emerge from simple molecular precursors. We propose an approach that connects chemical statistical thermodynamics and the macroscopic world of the planetary ocean and atmosphere.



## I. Introduction

The prebiotic conversion of simple organic molecules into complex biopolymers necessary for life can only have emerged on a stage set by geophysics. Fundamental chemistry provides the bottleneck in the transition between the diversity of small molecules (“prebiotic soup”) and complex, self-replicating organisms. We examine in this Account the role provided by water–air interfaces, namely, the surfaces of lakes, oceans, and atmospheric aerosols on ancient

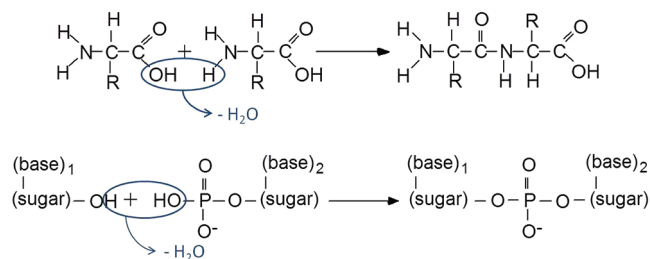
Earth, in the emergence of complex structures necessary for life. Aerosols are liquid or solid suspensions in air with a broad, power law size distribution. Collectively, these globally distributed atmospheric particles have an enormous surface area. Organic films at the interface between water and air have unique properties, not yet fully explored, offering advantages for biomolecular synthesis compared with the bulk, and can simultaneously participate in the folding of biopolymers into primitive enclosed structures.



**FIGURE 1.** Ocean–atmosphere interaction by atmospheric aerosol (dark gray areas represent surface-active organics, and lighter gray represents the aqueous core of the particle). Highlighted are some of the processes affecting aerosols during their atmospheric lifetime.

Measurements of the composition of aerosols in the Earth's contemporary atmosphere at different altitudes and locations have revealed that aerosols consist of rich mixtures.<sup>1</sup> An important finding of these measurements is the large organic content of atmospheric aerosols.<sup>1,2</sup> While the detailed physical and chemical environment 3–4 billion years ago is obviously uncertain, some general statements can be made. Then as now, the planet was rotating about a tilted axis with the resulting thermal and pressure gradients producing winds above a liquid ocean. The resulting whitecaps provided aerosol-producing mechanisms at the air–water interface (Figure 1), which would have offered numerous opportunities for natural selection to operate on a vast recycling population of aerosol reaction vessels. Through this mechanism, aerosols are formed having entrained hydrophobic organic material from the ocean surface. Aerosols encapsulated in organic films would have possessed many advantages in providing the sites at which the earliest assemblages of molecules emerged that eventually became life: a role for the ocean surface, aerosols and

bubbles having been suggested.<sup>3–10</sup> The distribution of sizes of nascent aerosols is determined on Earth by the competition between their coagulation and possible division and the gravitational deposition of the larger particles, leading to a median aerosol diameter of a few micrometers. The analogy between the size and structure of atmospheric aerosols and single cell bacteria has been pointed out by Dobson et al.<sup>5</sup> The air–sea interface would have acted as a two-dimensional concentrator and integrator of the three-dimensional chemistry of the atmosphere and ocean, the meteoric infall and the output from hydrothermal vents on the sea floor, in addition to being the primary generator and recycler of the aerosols and their chemical content. Emerging biomolecules would have found these vast populations of micrometer and submicrometer sized particles to be ready-made, adventitious containers. As a result, organic molecules would have been exposed to a widely varying and fluctuating set of conditions of solar irradiation, temperature, pressure, and humidity during the host aerosol's atmospheric cycle, far from equilibrium.



**FIGURE 2.** Condensation reactions responsible for the formation of (a) peptide bonds and (b) phosphodiester bonds.

Concentration, alignment, and orientation at the surface of water of organic molecules are possible in these environments. Models of the origin of life assume that the chemical monomeric precursors (amino acids, lipids, sugars, purine and pyrimidine bases, phosphates) for biopolymers existed on Earth. These could be chemically synthesized endogenously<sup>11–16</sup> or generated exogenously<sup>17–20</sup> and transported to Earth. Increased efficiency of production of protein-forming amino acids as well as purines and dihydroxy compounds in a Urey-Miller experiment has been demonstrated when aerosols were present.<sup>21,22</sup> Note that endogenous, chemical synthesis of biomolecules could not have avoided a role for aerosols generated at the Earth's sea surface from the very start.

It has been appreciated that the simultaneous generation of enclosures is necessary in any model that attempts to form protocells.<sup>23,24</sup> Lipids and other amphiphilic molecules have been postulated as intermediates in prebiotic evolution.<sup>25–27</sup> They could have been available on early Earth through prebiotic synthesis,<sup>28</sup> gas phase chemistry in the atmosphere,<sup>6</sup> or they could have been delivered to Earth through meteoric and cometary infall.<sup>17–20</sup> In this Account, we focus attention on properties of surfaces of aqueous solutions, such as the atmospheric aerosols and the atmosphere–ocean interface.

## II. Chemistry at the Water–Air Interface

The progression from simple chemical monomers to complex biomolecules is an essential step in the origin of life. The synthesis of such necessary biomolecules involves numerous condensation reactions,<sup>29</sup> two examples are given in Figure 2, resulting in both thermodynamic and kinetic challenges in the absence of enzymes in a bulk aqueous environment.<sup>5</sup> Concentrated, aqueous solutions are the preferred reaction media for current biology, but on early Earth the bulk ocean would have been the dilute, aqueous environment holding relevant monomers. In such dilute aqueous solutions, condensation reactions, such as the reactions between amino acids to form peptides and

between nucleotides to form nucleic acids, are extremely unfavorable. Accordingly, attempts to synthesize such biopolymers under prebiotic conditions (in the absence of an enzyme) have only been successful when the reaction is conducted in anhydrous environments.<sup>30</sup> These thermodynamic constraints could be alleviated if reaction occurs at an aqueous environmental surface where a water poor environment exists. These reactions also face kinetic constraints in a dilute aqueous environment like the early ocean. Molecules at the surface are known to be less ionized than those in the bulk,<sup>31,32</sup> thereby minimizing unfavorable zwitterion formation of biomolecular monomers. Adam and Delbrück<sup>33</sup> have demonstrated the ability of surfaces to accelerate reactions in a molecular population in a biochemical context. Environmental interfaces like the surface of the ocean and atmospheric aerosols have the ability to align and concentrate these monomers, helping to alleviate both the kinetic and thermodynamic constraints facing polymerization reactions.

As an example of the ability of the air–water interface to facilitate such condensation reactions, we will survey the work done on peptide bond formation at the surface of water. As early as 1948, it was known that long-chain amino acid esters spontaneously condense at the water–air interface forming peptides.<sup>34</sup> Many have since confirmed that the water–air interface provides a favorable environment.<sup>35–37</sup> Oliver and co-workers have shown, using proton NMR, that amide bond formation occurs preferentially at the interface with kinetic enhancement through surface compression.<sup>36,38</sup> Using octadecyl esters of amino acids, Fukuda et al. have also shown with infrared spectra of collected films that polycondensation may be achieved at the air–water interface.<sup>39</sup> Through shifts in the amide I band, they were able to further identify the secondary structure of the polypeptide formed ( $\beta$ -sheet,  $\alpha$ -helical, random coil).<sup>40</sup> In addition, Fukuda et al. showed kinetic enhancement of the polycondensation with the presence of a metal cation ( $\text{Cu}^{2+}$ ) in the solution beneath the film.<sup>41</sup> However, Eliash et al. contradict the work of Fukuda et al.<sup>42</sup> Fukuda et al. claim there is evidence of secondary structure in their infrared spectra, suggesting that polypeptide chains of at least eight monomers were formed.<sup>40</sup> Eliash et al., using grazing incidence X-ray diffraction (GIXD) and MALDI-TOF mass spectrometry, claim that although condensation does occur at the water–air interface, only dipeptides may be formed.<sup>42</sup> Regardless of the length of the peptide formed, it is clear that the air–water interface provides a favorable environment for condensation reactions, a crucial step on the way to biomolecular complexity.

Although the work described above has demonstrated the possibility of peptide bond synthesis at an interface, the techniques used to identify the products formed are not ideal. In all of these studies, the products formed at the surface were collected from the surface and dried out to allow for analysis and characterization: the process of drying amino acid solutions onto a substrate could have prompted the formation of peptide bonds. Without an *in situ* technique, it is impossible to know how much of the polycondensation actually occurred at the interface. Also, there is some question as to the prebiotic relevance of the long chain amino acid esters used in these experiments. They are complex synthetic molecules not found in modern biochemistry, and are not likely to have been abundant on early Earth. The use of more simple, naturally occurring monomeric precursors are necessary to test a plausible origin of life scenario where an interface prompts the emergence of complex biomolecules.

In an attempt to utilize naturally occurring amino acids and to facilitate some selection in the products produced, Luisi and co-workers have combined another necessary component in the origin of life with polymerization: an enclosure. The hydrophobic interaction between the amino acids (or small peptides) and a lipid membrane results not only in polycondensation, but depending on the type of lipid used (strictly hydrophobic, negatively charged, etc.), different amino acids can be attracted and selectively polymerized.<sup>43–45</sup> The water-restricting environment provided by the membrane thus promotes the condensation reaction needed in the formation of the peptide bonds and allows for some selection among the many possibilities of random products. It has further been proposed that there is a selection for longer peptides within such membranes (thereby increasing the complexity of the system as a whole).<sup>46</sup> Sutherland and Powner have also acknowledged the need to couple membranes with biomolecular synthesis on early Earth, and have sought to find prebiotic chemical routes in which both long chain alkyl phosphates and ribonucleotides may be synthesized.<sup>47</sup> Condensation reactions like those described above are necessary precursors for genome formation: the coupling of a self-replicating genome<sup>48,49</sup> with an enclosure is an essential step in the understanding of how life arose on Earth.

### III. Enclosures, Protocells, and Vesicles

Containment and organization are central to prebiotic formation, evolution, and division of primitive cells. Different models have been proposed for the origin of biological

systems,<sup>30,50–55</sup> all of which recognized the need for enclosures within which living systems may have originated.<sup>56,57</sup> Some studies of prebiotic synthesis yielded lipid-like amphiphilic molecules, long chain hydrocarbons, and their derivatives.<sup>11,12,28</sup> Elegant work has been performed in the literature regarding the self-assembly and functioning of primitive enclosures, and has shown that the amphiphilic monomers necessary for their self-assembly can be produced endogenously in different environments on ancient Earth<sup>13–16</sup> or transported to Earth through meteoric and cometary infall.<sup>20,58–61</sup> The organization of these primitive enclosures is driven by hydrophobic interactions among the composite amphiphiles.<sup>62,63</sup> It is important to note that the sea surface will be the place where both endogenous and exogenous fluxes of prebiotic molecules will accumulate and intermingle, and will furthermore be incorporated into the vast populations of aerosols that are produced through breaking waves (whitecaps). The amphiphiles will not only be concentrated at the sea surface, but also on the surfaces of the aerosols, which can coagulate and divide.<sup>6,7,64</sup>

Once generated, the synthetic compartments have been found to have many properties analogous to those known to be necessary for the functions of modern life.<sup>23,65,66</sup> Szostak and Zhu have shown that when a vesicle is suspended in solution and fatty acid micelles are added, the vesicles spontaneously grow and divide.<sup>67</sup> If a primitive genetic material was present in the vesicle before division, it remained encapsulated during the process.<sup>67</sup> Selective permeability is important; modern cells use pumps and channels to control diffusion across their membranes, but such machinery would not have been present prebiotically.<sup>49</sup> Without such complex machinery, the double-tailed lipids composing modern cells would not allow for transport into and out of the cell due to the rigidity and stability of the membrane formed, a significant problem for primitive cells, as such exchange is essential.<sup>68</sup> These enclosures are typically composed of single-tailed lipids like fatty acids, forming less stable but more dynamic vesicles, thereby accomplishing many of the functions of a modern cell without any of the complex machinery.<sup>49,68</sup>

In order for these enclosures to have formed in the bulk ocean, equilibrium between the lipids in solution and in the membrane is required, necessitating a very high concentration of monomer<sup>24,69</sup> (near the critical aggregate concentration), an unlikely scenario in the bulk ocean on ancient Earth. Without such a high lipid concentration, the protocells will simply disassemble.<sup>69</sup> The two-dimensional

water–air interface characteristic of oceans and the immense population of atmospheric aerosols on early Earth<sup>5,7,70</sup> has the ability to facilitate the concentration and alignment of organic monomers to promote folding into protocell-type structures, eliminating the need for high bulk concentrations. It has also been proposed that other processes like thermophoresis can alleviate this concentration problem through accumulation of relevant monomers in porous rock.<sup>71–73</sup> These processes are less versatile, however, than the cycling undergone by the vast population of atmospheric aerosols. In contrast to vesicles in the ocean, atmospheric aerosols are nonequilibrium structures generated by mechanical wind action at the ocean surface with less than monolayer surfactant coverage. This coverage can increase by a number of processes (see Figure 1) during the aerosol's atmospheric lifetime. These include selective evaporation of water in the atmosphere, coagulation of aerosols with partial organic coating, and chemistry in the aerosol phase leading to surface-active polymers. One of the distinct features of the aerosol model is the possibility of aerosol fission.<sup>64,74</sup> Although this process is thermodynamically forbidden for pure liquid droplets, it could become possible when the particle is coated with a surfactant, thereby providing a primitive mechanism for growth and division.<sup>74</sup>

#### IV. Molecular Dynamics, Scale Invariance, and Natural Selection

An essential step in the origin of life on Earth is the emergence of natural selection. In the protocell work described in the previous section by Chen et al.,<sup>48</sup> the remarkable ability of such primitive cells to selectively grow as a result of successful RNA replication was demonstrated, thereby providing a possible early example of natural selection. The mechanisms displayed by these laboratory protocells require chemical equilibrium,<sup>24,75</sup> while modern cells and life in general are known to be far-from-equilibrium systems. The Earth's atmosphere is known to be some 30 orders of magnitude removed from chemical equilibrium<sup>76,77</sup> and far from physical equilibrium,<sup>78,79</sup> as highlighted by the observed occurrence of scale invariance.<sup>80</sup> In this environment, organic molecules on atmospheric aerosols are exposed to different temperature, photon, and relative humidity conditions. A physical framework for understanding the operation of natural selection as an inherent property of molecular populations is available from this observed occurrence of scale invariance over a large range of scales, ranging from residue (monomer) sequences in proteins and

nucleic acids, the distribution of surfactant domains in films at air–water interfaces, throughout the physics and chemistry of the atmosphere and ocean surface to the vast molecular clouds of interstellar space.<sup>81–84</sup> Of all known astrochemical chemistries, only Earth's atmosphere has the characteristics of a scale-free network, a feature it shares with metabolic biochemistry.<sup>83</sup> Such reaction networks require the existence of a few molecules among many that have many reaction partners, such as OH in the atmosphere and pyruvic acid in cell metabolism.

The pioneering numerical simulation of a thermalized population of Maxwellian hard spheres subjected to an anisotropy in the form of a flux<sup>85</sup> showed how fluid flow can emerge in such a population, characterized by a power law speed distribution, with a long tail to high velocities relative to a Maxwell–Boltzmann curve. This overpopulation of high-speed molecules interacts with the emerging “ring currents”, or vortices, in a nonlinear fashion to sustain both itself and the organized flow. The high-speed molecules pile up higher number density ahead of themselves, leaving lower number density behind. The more numerous randomly moving molecules, that have more nearly average speeds, attempt to eliminate this density gradient and in so doing create the ring current. These randomly moving molecules are also responsible for maintaining an operationally definable temperature in the nonequilibrium fluid, as they maximize dissipation and hence entropy production.<sup>80</sup> The most energetic molecules are associated with negative entropy production, that is to say they account for the organization. This simplest possible example of the emergence of organization (fluid flow) in a randomized population provides a perspective on the behavior of air molecules in the prebiotic atmosphere of Earth. The emergence of organization in the Alder-Wainwright molecular dynamics calculations can be seen to constitute an extremely simple form of natural selection, which nevertheless embodies the three essential principles: competition for a finite resource, variation, and memory. These principles are, respectively, the collisional competition for the energy of the molecules, the variation caused by the collisional redistribution of those energies, and the emergent propagation of the organized flow. Of course, real molecules have more degrees of freedom arising from rotations and vibrations than do hard spheres, and have attractive as well as repulsive forces of a quantal nature operating. This is of course even truer of our current focus on reactions at the air–water interface.<sup>86,87</sup> Nevertheless, the principle is clear, and is mediated by entropy production.

On a macroscopic scale, there is a formal correspondence between statistical thermodynamic relations in a molecular population and scale invariance,<sup>78,79</sup> buttressed by results showing the occurrence of similar scaling properties in numerical simulations by both molecular dynamics and fluid flow (Navier–Stokes) equations.<sup>88</sup> Physically, scale invariance is hypothesized to represent dissipation and hence entropy production: scale selectivity other than that arising from the boundary conditions would not maximize entropy production, because it would represent organization. Fractality is commonly observed among lipids in surface films.<sup>89,90</sup>

We note a formal equivalence involving scale invariance variables  $q$  and  $K(q)$  on one hand with statistical thermodynamic quantities temperature  $T$ , partition function  $f$ , and Gibbs free energy  $G$  on the other:

$$T \equiv 1/k_{\text{B}}q \quad (1)$$

$$f \equiv e^{-K(q)} \quad (2)$$

$$G \equiv -K(q)/q \quad (3)$$

where  $k_{\text{B}}$  is Boltzmann's constant.

This links the scale invariance and power law distributions observed<sup>89,91–93</sup> in monomer sequences in proteins and nucleic acids and their distributions with lipids in membranes. It is possible that so-called junk DNA sequences represent entropy production while those having genetic function represent the emergence of organization. The folding of proteins and their binding to lipid rafts in micelles has also been observed to be fractal.<sup>90</sup> We recall that the folding, unfolding, and refolding of a small “hairpin” motif in a single RNA molecule have been observed experimentally to obey a fluctuation–dissipation theorem<sup>94,95</sup> characteristic of maximum entropy production. Aerosols obey power law size distributions. It remains however true that nonequilibrium statistical mechanics is a very difficult discipline without a rigorous mathematical foundation, in addition to which specific mechanisms must be defined,<sup>86,87</sup> a daunting prospect for a system as complex as the prebiotic Earth's fluid envelope. However, it can be seen how these principles result in natural selection as an inherent property of a molecular population in a fluctuating medium occupying a space characterized by anisotropic boundary conditions. For Earth, these are minimally the solar beam, gravitation, planetary rotation, and the surface. On long time scales, some or all of these boundary conditions will be affected by the evolving chemical composition, including biochemistry once established, with profound disequilibria arising in the atmosphere–ocean system; the nonlinearities offer great

scope for positive feedbacks and long-range correlations. The most energetic molecules express the boundary conditions and produce organization. The perspective offered is that the fittest molecular populations emerged via natural selection in this system, in which organization is the consequence after dissipation and entropy production have been maximized.

## V. Conclusions

The ocean–atmosphere interaction provides the geophysical setting for the transition from simple chemical monomers to complex biomolecules and structures implicit in the emergence of life. Water–air interfaces of Earth's ancient oceans, lakes, and the large population of atmospheric aerosols have advantages as prebiotic reactors to generate such biopolymers and enclosed structures, particularly in providing an anhydrous environment for condensation reactions. The interaction of the ocean and atmosphere, facilitated by the production, lifetime, and deposition of atmospheric aerosols, allows for the exposure to nonequilibrium conditions as illustrated by scale invariance. A physical interpretation of scale invariance can be given in a framework of nonequilibrium statistical mechanics: scale selectivity would correspond to a failure to maximize dissipation and hence entropy production; organization is what emerges after entropy production has been maximized.<sup>78,79</sup> Natural selection is an expression of the behavior of nonequilibrium populations of molecules, expressing the boundary conditions, and in the case of Earth producing self-shielding fluid populations in an environment enabling the nonlinearities to produce complexity and organization. Thus, the ocean–atmosphere interaction provides not only the favorable environment necessary for the conversion of simple monomers to complex biomolecules, but provides containment for the resulting products, and allows for a primitive form of natural selection to emerge on the way to complex life.

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## BIOGRAPHICAL INFORMATION

**Elizabeth C. Griffith** received her B.S. in chemistry from University of Maryland, Baltimore County in 2009. She is currently a graduate student at the University of Colorado, Boulder pursuing a Ph.D. in Physical Chemistry. Her research focuses on the role of organics at the air–water interface in prebiotic chemistry.

**Adrian F. Tuck** received his bachelor's degree at the University of Manchester, his Ph.D. in physical chemistry at Cambridge University, a certificate from the Meteorological Office College, and was a Fulbright Scholar at the University of California San Diego. He was a group head in Meteorological Chemistry at the Meteorological Office and at the NOAA Aeronomy Laboratory, Professeur Invité at École Nationale des Ponts-Paris Tech 2010–2011 and is Visiting Professor in Physics, Imperial College London.

**Veronica Vaida** was educated at the University of Bucharest (Romania) and Brown University where she obtained a B.S. in Chemistry. She received M.S. and Ph.D. degrees at Yale University. She started her independent career at Harvard University, and since 1984 has been on the faculty in Chemistry at the University of Colorado, Boulder.

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#### FOOTNOTES

The authors declare no competing financial interest.

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