

# Atmospheric Prebiotic Chemistry and Organic Hazes

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**Abstract:** Earth's atmospheric composition at the time of the origin of life is not known, but it has often been suggested that chemical transformation of reactive species in the atmosphere was a significant source of prebiotic organic molecules. Experimental and theoretical studies over the past half century have shown that atmospheric synthesis can yield molecules such as amino acids and nucleobases, but these processes are very sensitive to gas composition and energy source. Abiotic synthesis of organic molecules is more productive in reduced atmospheres, yet the primitive Earth may not have been as reducing as earlier workers assumed, and recent research has reflected this shift in thinking. This work provides a survey of the range of chemical products that can be produced given a set of atmospheric conditions, with a particular focus on recent reports. Intertwined with the discussion of atmospheric synthesis is the consideration of an organic haze layer, which has been suggested as a possible ultraviolet shield on the anoxic early Earth. Since such a haze layer – if formed – would serve as a reservoir for organic molecules, the chemical composition of the aerosol should be closely examined. The results highlighted here show that a variety of products can be formed in mildly reducing or even neutral atmospheres, demonstrating that contributions of atmospheric synthesis to the organic inventory on early Earth should not be discounted. This review intends to bridge current knowledge of the range of possible atmospheric conditions in the prebiotic environment and pathways for synthesis under such conditions by examining the possible products of organic chemistry in the early atmosphere.

**Keywords:** Amino acid formation, Abiotic synthesis, Chemical evolution, Early earth atmosphere, Organic haze, Prebiotic chemistry, Primitive earth.

## 1. INTRODUCTION TO “EARLY EARTH” AND ITS ATMOSPHERE

Planet Earth has gone through a lengthy evolution, from its initial formation to its present state as the only known harbor of life in the universe. Earth's current atmosphere has a surface pressure of 1 bar, and is composed of approximately 78% nitrogen (N<sub>2</sub>) and 21% oxygen (O<sub>2</sub>), with small amounts (< 1%) of other species including argon (Ar), water (H<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>). The current balance of gases in the Earth's atmosphere is heavily driven by the biosphere, as evidenced by the large abundance of O<sub>2</sub> outside of thermodynamic equilibrium. The atmospheric composition has clearly not been constant over time, and the state of the atmosphere in the first billion years of Earth's existence has significant implications for the origin and evolution of life. Several key markers can be placed along Earth's evolutionary path constraining the state of the environment during different epochs.

The planet came into being some time after the formation of the Sun approximately 4.55 billion years ago (Ga), most likely from the rapid accretion of material within the solar nebula [1], and the moon-forming impact likely occurred shortly thereafter [2]. If a primary atmosphere was accumulated from the primitive solar nebula, it was subsequently lost, and replaced by a secondary atmosphere generated by gases released from the solid planetesimals that comprised the early planet, either through volcanism or impact degassing during and after accretion of materials [for a review see ref. 3]. The secondary atmosphere hypothesis is informed by the depletion of noble gases on Earth and the other terrestrial planets relative to solar abundances [4].

Isotopically light carbon found in ancient meta-sediments suggests that life may have been present as early as 3.8 Ga [5]. This evidence, combined with the discovery of elevated  $\delta^{18}\text{O}$  in detrital zircons [6, 7] and water-lain sediments [8], indicates that there was liquid water present, and likely global oceans, as the Hadean transitioned into the Archean at approximately 3.8 Ga [9]. About 1.5 billion years later, there appears to have been a distinct rise in the amount of molecular oxygen in the atmosphere. The most convincing evidence of this is the mass-independent fractionation of sulfur isotopes observed in rocks, which indicates that prior to 2.1 Ga the atmosphere was almost completely anoxic [10]. This evidence is supported by the chemical profile of paleosols and the appearance of red beds around 2.2 Ga [11]. The period in the geologic record between the oldest known rocks and the rise in atmospheric oxygen, during which life was developing, is known as the Archean [12].

It is difficult to know what the state of the atmosphere prior to and during the early evolution of life was. One can start with the assumption that the prebiotic atmosphere and the secondary atmosphere generated by outgassing are one in the same. Yet the questions of how the secondary atmosphere was generated and what it was composed of are still controversial. Several hypotheses have been put forward, including theories that the atmosphere was outgassed volcanically from the differentiated interior and controlled by the redox state of the Earth's mantle, which appears to have been constant since 3.8 Ga [13]. Such an atmosphere would be composed mostly of H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>, and represents a possible end-member in the discussion of the redox state of the prebiotic atmosphere [14]. Alternatively, the secondary atmosphere may have been formed by the degassing of impacting materials as they were incorporated into the growing planet, with the volatile reservoir influenced more strongly by the composition of the accreting materials, a scenario that has been modeled in particular to evaluate the delivery of H<sub>2</sub>O to supply the hydrosphere [15, 16]. Recent work by Schaefer and

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Fegley [17] has shown that for ordinary chondritic material, this type of outgassed atmosphere may be significantly more reducing than previously thought and may support a substantial abundance of  $\text{CH}_4$ . Across all types of chondrites and a variety of temperature and pressure conditions, predicted atmospheric abundances fall along a range of redox states, albeit likely more reduced than modern volcanic gases [18]. The nature of the volatile inventory is then strongly influenced by the balance between early and late accretion, and a fraction of late accretion on the order of as little as 1% or more would lead to the delivery of significant amounts of reduced compounds to the atmosphere [3, 19]. Serpentinization of the ultramafic seafloor could have supported a significant flux of abiotic  $\text{CH}_4$  to the atmosphere, regardless of the bombardment flux, as in present day outgassing at mid-Atlantic ridges [20, 21], although the magnitude of this flux for the prebiotic Earth is unknown.

An additional constraint placed on the composition of the atmosphere relates to the luminosity of the early Sun and assumed surface temperature conditions. The study of G-type stars of different ages is used to inform our knowledge of how the Sun has evolved over time [22]. Stars like our Sun increase in luminosity over time due to their increasing temperature, which is a consequence of the conversion from hydrogen to helium burning in their cores [23]. It is estimated that the solar radiation reaching Earth during the Archean was approximately 75 - 80 % of the current terrestrial flux, and thus a more significant greenhouse effect may have been necessary to sustain proper surface temperatures for liquid water and resolve the so-called "Faint Young Sun Paradox" [24, 25]. Various solutions to this paradox have come in and out of favor over the years depending on the currently accepted model of the source of the secondary atmosphere and perspectives on prebiotic chemistry. Some workers have sought solutions to the Faint Young Sun Paradox that alter the albedo of the Earth as a way of controlling temperature in lieu of increased abundance of greenhouse gases [26, 27], but these solutions are controversial and not likely to eliminate the need for an enhanced greenhouse effect [28-31].

The idea of the prebiotic Earth as a roiling organic "soup" with a highly reduced atmosphere of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , methane ( $\text{CH}_4$ ), and ammonia ( $\text{NH}_3$ ) was first presented by Oparin [32]. Such an atmosphere was part of his model of chemical evolution in which reduced gases led to the production of organic molecules, providing an environment more conducive to the evolution of life. The landmark experiments by Miller and Urey, partially modeled on Oparin's hypothesis, demonstrated production of amino acids via the action of an electric discharge on a  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  gas mixture, supporting the theory of prebiotic synthesis in a reduced primitive atmosphere [33-35]. Sagan and Mullen [24] determined that moderate quantities (ppm) of  $\text{NH}_3$  would resolve the Faint Young Sun Paradox. However, since the early 1980s, it has been thought that the primitive atmosphere was more oxidized, and contained large quantities of carbon dioxide. Comparisons of the carbon reservoirs on Earth and Venus (the former being equivalent in magnitude, but sequestered largely in the crust) suggest that  $\text{CO}_2$  on the early Earth could have provided the needed warming if it was more abundant in the atmosphere [36].  $\text{NH}_3$  was shown to have a very short lifetime in the atmosphere of the early Earth due to photodissociation [37].  $\text{CO}_2$ , however, was assumed to be abundant and long-lived in the ancient atmosphere; as long as volcanic emissions were as high as those seen today and weathering was low,  $\text{CO}_2$  could have accumulated to large concentrations in the atmosphere [38]. A partial pressure of 0.20 bar  $\text{CO}_2$ , more than 500 times the present atmospheric level, would have been needed to maintain a surface temperature

above the freezing point of water [38]. Such an atmosphere may have been less favorable to the formation of organic molecules, although not necessarily prohibitive depending on ocean chemistry [39, 40]. This spurred an interest in the origin of life in specialized environments such as hot springs and mid-ocean ridge hydrothermal vents, as well as the delivery of organic compounds from space [41, 42].

Available geologic evidence, however, suggests that high  $\text{CO}_2$  levels ( $\geq 0.1$  bar) were unlikely in the Archean atmosphere [43, 44], but these data are representative of the atmosphere after the emergence of life and may not constrain the prebiotic environment. Kiehl and Dickinson [45] attempted to resolve this issue by showing that with only a small amount of  $\text{CH}_4$  in the atmosphere (100 ppm), the  $\text{CO}_2$  content could have been reduced significantly. Sagan and Chyba [25] revived the idea of an atmosphere of a  $\text{CH}_4/\text{NH}_3$  early Earth atmosphere, folding in the idea that the resulting photochemistry formed a haze which could serve as an ultraviolet shield protecting the photolabile gases, but it is unlikely that there would have been sufficient shielding of  $\text{NH}_3$  to maintain this gas at significant levels in the atmosphere [46]. In addition, the partial pressure of  $\text{NH}_3$  is dependent on the pH of the primitive oceans, and much would be dissolved as  $\text{NH}_4^+$  [47]. Tian *et al.* [48] suggested that the prebiotic atmosphere could have built up large concentrations of  $\text{H}_2$ , in combination with  $\text{CO}_2$  and small amounts of  $\text{CH}_4$ , given a reduced rate of  $\text{H}_2$  escape. Because of the combination of greenhouse warming potential and the possibility of forming larger organic molecules (as on Saturn's moon Titan), much work has gone into examining the potential abundances and influences of  $\text{CH}_4$  in the early Earth atmosphere [45, 49-51]. Explaining a significant steady-state of  $\text{CH}_4$  in the prebiotic atmosphere is problematic, though many workers have elaborated mechanisms by which  $\leq 1000$  ppm of  $\text{CH}_4$  may have been present, such as the aforementioned serpentinization [20] or due to transient impact events [3, 52, 53].

As demonstrated by the above discussion, the nature of the Earth's atmosphere at the time of the origin of life is far from certain, has been hotly debated, and will not be resolved in the present work. Concerns about the oxidation state of the atmosphere and the perceived need for there to have been liquid water arise from considerations of the limits of prebiotic chemistry and the origin of life. There have been many reviews over the years of the state of the knowledge of the earliest atmosphere and the climatic and geologic implications [see 3, 14, 19 and references therein]. These discussions touch upon chemistry in terms of whether or not the atmosphere was favorable for organic synthesis but often do not explore in detail. There have also been many reviews on the origin of life and possible chemical mechanisms provided a source of organic material is present in an aqueous environment, whether it be from atmospheric synthesis, exogenous delivery, or hydrothermal source [see 54, 55, 56, 57 and references therein]. The goal of this review is to bridge these topics by addressing the role atmospheric synthesis may play in the steps leading to the origin of life, with a focus on the different chemical products given a range of scenarios for the early Earth. Specifically this discussion will focus on recent experimental and theoretical work that has bearing on the question of atmospheric synthesis and provide new bounds on atmospheric conditions that allow for organic chemistry to take place.

### 1.1. Model Scenarios for the Prebiotic Atmosphere

For the purposes of this discussion, several model atmospheres are defined to explore the constraints placed on atmospheric synthe-

**Table 1. Model Scenarios for Early Earth Atmospheres**

Relative Abundances <sup>a</sup>	Titan-like Early Earth	High CO <sub>2</sub>	High H <sub>2</sub>	Weakly Reduced
CH <sub>4</sub>	1	1	1	—
CO <sub>2</sub>	—	10	10	0-1
H <sub>2</sub>	—	—	150 <sup>c</sup>	0
CO	—	—	—	0-1
Organic aerosol formation factor <sup>b</sup>	1	0.1	0.03	n/a

<sup>a</sup>Most studies assume a bulk atmosphere of N<sub>2</sub>, and with trace species mixing ratios at or above 100s of ppm.

<sup>b</sup>After DeWitt *et al.* [126]

<sup>c</sup>DeWitt *et al.* [126] experiments were performed with 15% H<sub>2</sub>, 1% CO<sub>2</sub>, and 0.1% CH<sub>4</sub> in N<sub>2</sub> as described in the text, but Table 1 in their manuscript misrepresents the relative abundance of H<sub>2</sub>.

sis of organics, and to examine the chemical composition of the molecules produced. (Table 1) gives the name and assumed parameters for each of the model atmospheres to be discussed in the following sections. These include a highly reduced atmosphere (early Earth as “Titan-like”), a mildly reducing atmosphere with dominant CO<sub>2</sub> but some CH<sub>4</sub>, a reduced atmosphere with significant amounts of H<sub>2</sub> accumulation as proposed by Tian *et al.* [48], and a weakly reduced atmosphere composed of mostly CO/CO<sub>2</sub> and N<sub>2</sub>. These atmospheres are defined to highlight recent results which have expanded the understanding of early Earth atmospheric synthesis, but are very simplified models. First, the proportions of gases such as NH<sub>3</sub> and CO<sub>2</sub> are not fully understood, as the atmosphere would have been sensitive to many conditions which are not well constrained: subduction and outgassing rates, the chemical equilibration following subduction, and oceanic pH to name a few. The simplified model atmospheres presented in (Table 1) do not reflect the dynamic nature of the atmosphere, which would not have been at equilibrium but rather may have existed at different steady state conditions. Second, the models in (Table 1) are framed in terms of relative abundances of gases, but for synthesis the absolute mixing ratios of reactive species is also critical. Not all of the experimental or theoretical works have identified lower limits on concentrations needed for detectable yields of material, but typically mixing ratios of at least 100 - 1000 ppm of trace species are cited. This discussion focuses on the ratios of gases to understand how the chemical composition of the products is affected by relative proportions, assuming that abundances are sufficient for appreciable yields.

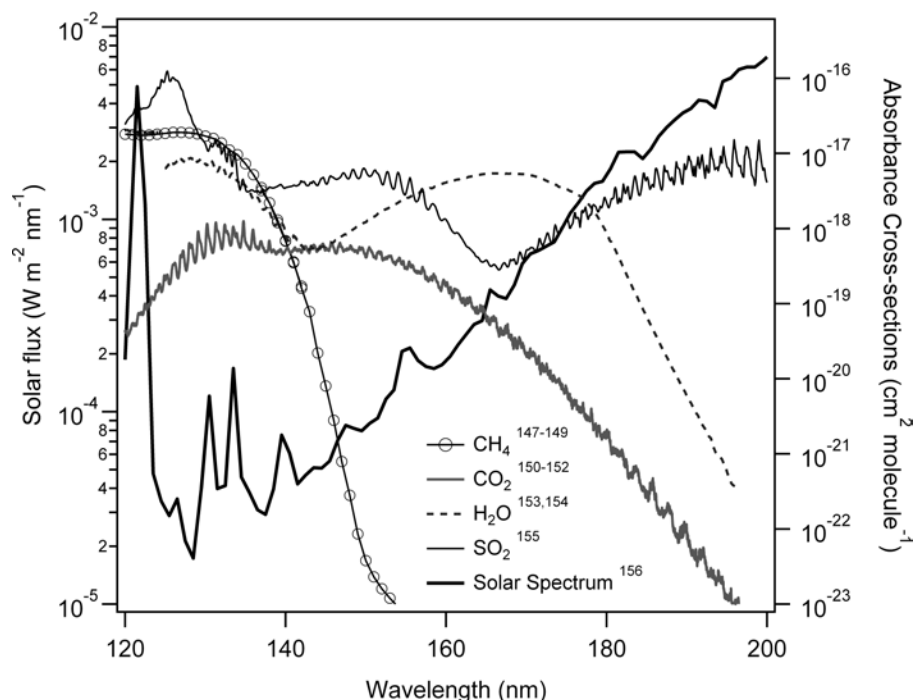
There have been several discussions in the literature on the relative importance of available energy sources (solar UV, discharges, lightning, etc.) on the prebiotic Earth with respect to the inventory of organics [41, 55-58]. As noted by Chyba and Sagan [41], the contributions of energy sources on prebiotic synthesis depends strongly on the composition of the atmosphere and cannot be decoupled. Initially laboratory work on prebiotic synthesis relied on hot plasma discharges [see summary in reference 59], meant to simulate lightning, to initiate chemical reaction. It is difficult to estimate the expected discharge (coronal processes and lightning) rates on the early Earth. Oró *et al.* [55] estimated a flux of  $\sim 10^{19}$  J yr<sup>-1</sup>, with the flux of  $\lambda < 150$  nm UV radiation  $\sim 2x$  less this value. However, the extreme and far-UV flux on the prebiotic Earth would have been several times greater than today, and other workers have estimated a flux closer to  $10^{20}$  J yr<sup>-1</sup> for far-UV [22, 41, 48]. To build upon previous reviews in the literature, this discussion will focus on recent studies which have looked at chemistry initiated by

UV photolysis, a more global and predictable energy source. In contrast to high temperature discharges or high energy particles, which are well above dissociation energies of the reactant molecules, the chemical behavior of irradiated primary atmospheric molecules is very sensitive to wavelength and absorption cross-sections. (Fig. 1) shows measured cross-sections for some of the principle atmospheric molecules discussed in this review, wavelength ranges at which the molecules photodissociate and the relative strengths of the absorbers. The solar spectrum in the figure is the current flux at the Earth's orbit (1 AU) and is expected to have a different shape billions of years ago [22].

## 2. ORGANIC AEROSOLS, HAZES, AND PREBIOTIC CHEMISTRY

A consequence of ‘significant’ amounts of CH<sub>4</sub> photolysis in the early Earth atmosphere is the possible formation of an organic haze layer like that on Titan, as first explored in detail by Sagan and Chyba [25] and revisited in many modeling studies [46, 51, 60-63]. Most of the work in the literature has been focused on the climatic impact of the haze, but there has been less focus on the chemical composition of the aerosol particles that comprise the global haze, and how they may have contributed to prebiotic chemistry. Yet the discussion of the formation of organic aerosols, and possibly a haze layer, is intertwined with the formation of organic molecules containing more than a few carbon atoms in the atmosphere of early Earth. Chemical models of Titan's atmosphere (historically a model for early Earth) assume nucleation of aerosol – defined as a particles suspended in a gas matrix as small as a few molecules [64] – occurs once hydrocarbon chemistry proceeds to C<sub>7</sub>-C<sub>8</sub> molecules [65, 66]. Nucleation of semi-volatile organics into aerosol would be dependent on the thermodynamic conditions in the region where organic molecules are synthesized, and given temperatures and abundances on early Earth as compared to Titan these nucleation rates may be much lower although models for the early Earth rarely take this into account [51].

On the modern Earth, organics contributes up to 50% of atmospheric aerosol mass, but the organic fraction is either biogenically or anthropogenically sourced [67]. However, an examination of the types of molecules that dominate aerosols can be useful for understanding the partitioning of molecules on prebiotic Earth. Today, primary organic aerosols are either emitted directly into the atmosphere or formed from the nucleation of organic molecules without any chemical alteration, and are largely sourced from combustion [68]. Secondary organic aerosol (SOA) is formed when volatile organic molecules in the atmosphere age to form com-



**Fig. (1).** Absorption cross-sections ( $\text{cm}^2 \text{molecule}^{-1}$ ) in the far ultraviolet for some atmospheric molecules suggested for the prebiotic Earth. The cross-section data were compiled using the MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules ([www.atmosphere.mpg.de/spectral-atlas-mainz](http://www.atmosphere.mpg.de/spectral-atlas-mainz)), and sourced from the indicated references [157-165]. The dissociation thresholds – wavelengths below which photodissociation will occur – for CO and  $\text{N}_2$  are 104 and 100 nm, respectively, and thus these molecules are not included on this graph. The solar spectrum represents the irradiation at the top of the current Earth atmosphere (~600 km) [166].

pounds with lower vapor pressures, which is primarily accomplished via oxidation or nitrogenation in the current atmosphere [69]. This process is a more appropriate analog for early Earth aerosol chemistry, in which photochemical or other processing of gaseous precursors leads to the formation of species with low enough vapor pressures to partition into the particle phase. The types of molecules which commonly occur in SOA are oxygenated terpenes and aromatics [70], fatty acids  $\geq \text{C}_{12}$  [71], and even sugars such as glucose and fructose [72]. Modern terrestrial aerosols are known to contain free amino acids [73], and can even be formed with molecules as small as oxalic acid ( $\text{C}_2\text{O}_4\text{H}_2$ ) [74], provided the oxygen functionality increases the polarity to a sufficient degree as is the case for carboxylic acids. Thus, the more likely a molecule is to have functionalities of interest to prebiotic chemistry, the more likely it is to exist in aerosol phases in the atmosphere. Many laboratory studies examining this chemistry have looked at the condensed phase products of atmospheric synthesis. An effective approach to explore the conditions under which organic synthesis may take place in the atmosphere is to examining the chemical and physical properties of the aerosol into which these organic products are likely to nucleate.

With sufficient nucleation of aerosols in the primitive atmosphere, a global haze would have accumulated, affecting transmission of solar radiation. The possibility of organic haze formation on the early Earth has been studied extensively because of its potential to help resolve the “Faint Young Sun Paradox”, via the formation of a UV-shield that maintains higher abundances of photolabile greenhouse gases such as  $\text{CH}_4$  and  $\text{NH}_3$  [25]. Similarly, the critiques of the existence of a haze layer are also climatic in nature, as the optical properties of the aerosol may be such that the haze layer also absorbs longer wavelength radiation and lead to an anti-greenhouse effect, thus counteracting the benefit of higher

$\text{CH}_4/\text{NH}_3$  abundances. Analysis of the anti-greenhouse effect of such a haze in the literature have understandably relied on assumptions on aerosol radiative properties that are based on Titan aerosol composition, shape, and size and are often over-simplified [46, 63]. Recently Wolf and Toon [61] looked at the formation of a haze layer on the early Earth in which spherical monomers with  $r = 50$  nm nucleate from atmospheric synthesis and then aggregate into fractal haze particles, a phenomenon observed on Titan [75]. Using a size-resolved aerosol model in a three-dimensional global climate model, they determined that the resulting fractal aggregates could be optically thick in the UV but not in the visible – thus providing the needed UV shielding without contributing to an anti-greenhouse effect. In parallel, laboratory work from Hasenkopf *et al.* [76] has shown that the refractive indices of aerosol formed from irradiation of  $\text{CH}_4/\text{CO}_2/\text{N}_2$  (Early Earth analog) are greater in the mid-visible than aerosol formed from  $\text{CH}_4/\text{N}_2$  (Titan analog), with implications of a stronger anti-greenhouse effect of the resultant haze layer. This is undoubtedly due to the differences in the aerosol composition [77], which will be explored in more detail below. These studies demonstrate that a one-size-fits-all approach to evaluating the impact of a haze layer on the early Earth is not appropriate. Thus, in addition to the chemical composition of atmospheric synthesis, this review will address the properties of organic aerosol where relevant and the predicted impact on early Earth climate.

Depending on atmospheric composition and energy flux, much of the organic synthesis may occur in the stratosphere where water vapor pressures are fairly low. Pavlov *et al.* [49] estimated stratospheric mixing ratios of  $\text{H}_2\text{O}$  to range from  $10^{-7} - 10^{-4}$ , depending on surface temperature and  $p\text{CH}_4$ . Water would have been a trace reactant in photochemical reactions. Prebiotic simulations over water reservoirs more closely resemble a localized chemical synthesis occurring via lightning near the surface. Yet following atmos-

pheric synthesis, photochemical aerosol would eventually be deposited onto the surface and into pools, lakes, or oceans that may have existed at the time. Depending on the aerosol size, the particles may have been transported to the surface with shorter timescales than gas molecules [78], and thus may be a more efficient delivery system of prebiotic reactants to the primitive ocean. Even prior to deposition, the organic molecules in aerosols can undergo further chemical processing via uptake of water [79]. In more humid regions of the atmosphere, aerosols could serve as cloud condensation nuclei (CCN). Adsorption of water could lead to the formation of aqueous aerosols, which also may enable uptake of trace gas-phase species, as in seen with enhanced partitioning of small volatile compounds (e.g. ethanol and isopropanol) on organic aerosols at high relative humidities [80]. This mechanism may provide an alternate route to linking atmospheric synthesis and prebiotic chemistry in a way that concentrates organic molecules sufficiently to lead to more extensive polymerization prior to introduction into larger water systems [59]. The idea of aqueous aerosols on the early Earth serving as prebiotic reactors has been discussed [81-83], but formation was assumed to occur via wind-driven wave action followed by bubble bursting at the ocean/atmosphere interface. Organic material deposited after atmospheric formation could provide the films suggested to serve as surfactant layers in these mechanically-generated aerosols. Alternatively, water uptake by organic haze particles formed higher in the atmosphere could also result in aqueous aerosols that serve as a prebiotic reaction medium [59]. Thus, in the case of early Earth aerosols it is important to understand the chemical composition and potential for reaction once present in an aqueous system.

### 3. EARLY EARTH AS "TITAN-LIKE"

Titan has long fascinated scientists who look to Saturn's moon as a possible model of the prebiotic Earth that has been literally frozen in time [84-87]. Irradiation of CH<sub>4</sub> – ranging from 5.6% at the surface [88] to 1.5% in the stratosphere [88-90] to 2.2 - 2.7% in the outermost atmosphere [91, 92] – in the N<sub>2</sub>-dominated atmosphere initiates prolific organic chemistry resulting in the formation of many gas-phase hydrocarbon and nitrile species [88-93] in addition to the aforementioned organic aerosols, which comprise the haze layer. The reaction schemes for the formation of gas-phase products, and some theoretical exploration of aerosol production, have been modeled extensively in the literature [65, 66, 94-97] and will not be discussed in detail here.

If the early Earth had a CH<sub>4</sub>-dominant atmosphere, photochemical products may have resembled those known to occur on Titan, although with some key differences that will be addressed later in this section. This is then a relatively straightforward thought exercise; unlike the early Earth, there are direct observations of the chemical products in Titan's atmosphere. *In situ* measurements by the Ion Neutral Mass Spectrometer (INMS) and Cassini Plasma Spectrometer (CAPS) in the very upper atmosphere (> 900 km) of Titan have found evidence for C1 – C8 hydrocarbon chains and benzene, and indirect evidence for polycyclic aromatic hydrocarbons (PAHs) and other such compounds with molecular masses up to hundreds of Daltons [91-98]. Spectroscopic observations of the haze layer show various carbon-carbon and carbon-nitrile bonds [99], and recent work in the far-IR suggests stratospheric aerosols exhibit low frequency lattice vibrations, potentially the result of multi-ring PAHs [100].

Laboratory studies simulating the formation of Titan aerosols have found similar compounds [for a comprehensive review of

laboratory results, see ref. 101]. Depending on the energy source, pressure, and temperature conditions, condensed-phase products have been found to have C/N ratios varying from 11 to 2 [102-105].

Two recent analyses using high-resolution mass spectrometry to generate van Krevelen diagrams of aerosol products reveal strong participation of HCN, HCCN, and CH<sub>2</sub>-HCN as 'formula units' [105, 106], although it is important to remember that the aerosol analog is more complex than a simple repeating polymer [107]. The relevance of these results to prebiotic chemistry is that the action of extreme ultraviolet (EUV,  $\lambda < 100$  nm) radiation in a cold plasma leads to significant conversion of free atmospheric nitrogen into compounds which are then available for chemical synthesis [108]. On the present Earth this occurs via the biological conversion of nitrogen into NH<sub>3</sub> or nitrate (NO<sub>3</sub><sup>-</sup>), and is an essential process for life. A similar process would be needed on the prebiotic Earth to incorporate nitrogen into organic molecules for availability to biosynthesis. It is thought that on the prebiotic Earth this process may occur via the formation of NO<sub>x</sub> with energy supplied by lightning [109], but in an anoxic atmosphere it would certainly be a limiting nutrient [110]. Instead, the formation of nitriles within organic molecules generated from CH<sub>4</sub> photolysis may provide the needed N were the atmosphere reducing like Titan's. For example, estimates by Kasting and Walker [110] for the "reducing" atmosphere show delivery rates of NO<sub>3</sub><sup>-</sup> to the oceans on the order of  $4 \times 10^{-17}$  g N cm<sup>-2</sup> s<sup>-1</sup>. Given the estimates of Imanaka and Smith [105], HCCN inclusion into aerosol could be as high as  $4 \times 10^{-16}$  g N cm<sup>-2</sup> s<sup>-1</sup> in Titan's upper atmosphere, and similar processes may be competitive for nitrogen fixation on the early Earth depending on the energy input and CH<sub>4</sub> abundance. Recent work by Trainer *et al.* [111] shows that even at longer wavelengths ( $\lambda > 120$  nm) CH<sub>4</sub>/N<sub>2</sub> photochemistry can produce aerosol analogs with up to 16% N by mass, which given Titan aerosol production rates would yield approximately  $2 \times 10^{-15}$  g N cm<sup>-2</sup> s<sup>-1</sup> [77]. Similar experimental results for a more moderately reducing atmosphere will be discussed in the following section.

Titan only has trace amounts of oxygen in its atmosphere, possibly derived from water ice emitted by the nearby plumes of Enceladus [112], and stored in CO and CO<sub>2</sub> [113]. The formation of hydrocarbon and nitrile species in Titan's atmosphere is far less compelling as a prebiotic chemical cycle [85]. However, recent work has suggested that the contribution of CO to synthesis in Titan's upper atmosphere may lead to oxygen incorporation in the organic molecules formed. Experiments by Horst *et al.* [114] have shown that when the energetic conditions of the upper atmosphere of Titan were simulated in a plasma laboratory setup (> 10eV, similar to EUV [115]), percentage levels of CO irradiated in N<sub>2</sub>/CH<sub>4</sub> mixtures led to the formation of oxygenated organics, including products identified as amino acids and nucleotide bases. This is the first time such molecules have been shown to form in an atmospheric synthesis without a hydrolysis step, and the first to indicate that Titan's upper atmosphere could yield compounds of interest to prebiotic chemistry, although it should be noted that pCO was enhanced ~400 fold in the experiment relative to Titan.

Following atmospheric synthesis on Titan, even if only CHN compounds are formed, the aerosols ultimately deposit on the surface of Titan, which could contain transient liquid water and ammonia mixtures as a result of impacts [116] or cryovolcanism [117]. Neish *et al.* [118] found that Titan aerosol analog produced in simulated CH<sub>4</sub>/N<sub>2</sub> atmospheres hydrolyze in low temperature water/ammonia solutions to form amino acids. At Titan cryolava tem-

peratures (~176 K), the hydrolysis occurs with a half-life between  $10^0 - 10^4$  years [119], and the rates are slower for hydrolysis in pure water [120].

Though the past climate of the Earth is uncertain, it was likely to have been far warmer than present-day Titan, where the current surface temperature is approximately 94 K [121]. By definition, the early Earth's surface water temperatures would have been at or above 273 K, and experimental evidence shows that the hydrolysis of Titan-like  $C_xH_yN_z$  solids incorporate oxygen with time scales on the order of days [120]. The early Earth would have been humid near the surface, and the processing of organic molecules into potential biological precursors could have even occurred in water droplets in the troposphere. In this scenario, organic synthesis in a reduced atmosphere without a significant oxygen source (assuming a tropopause-like cold trap for  $H_2O$ ) would form CHN compounds, but these could be processed into prebiotically-relevant molecules in the lower atmosphere. Although all of these materials will ultimately deposit in the oceans for eventual hydrolysis, the concentrated environment of a droplet is advantageous to promote reaction of the organics and possible polymerization into larger structures prior to dilution in the larger hydrosphere.

In Neish *et al.* [120] several possible reaction schemes were presented to explain these results, including imine hydrolysis, amine substitution, and nitrile hydrolysis. Although not favored energetically, the response to higher pH [119] and the tentative identification of products such as asparagine ( $C_4H_8N_2O_3$ ) and glutamine ( $C_5H_{10}N_2O_3$ ) [118] suggest that at least partial nitrile hydrolysis may play a role. If so this places increased importance on the formation of HCN and nitrile production via photochemistry in the atmosphere, since it is the inclusion of the heteroatom of nitrogen in the hydrocarbon which confers reactivity on the molecule. Regardless, the reactions responsible for the formation of biomolecules from Titan-like  $C_xH_yN_z$  compounds need to be studied further, particularly if high  $CH_4$  abundances were possible on the early Earth, whether before or after the origin of life.

#### 4. EARLY EARTH WITH 'HIGH' $CO_2$

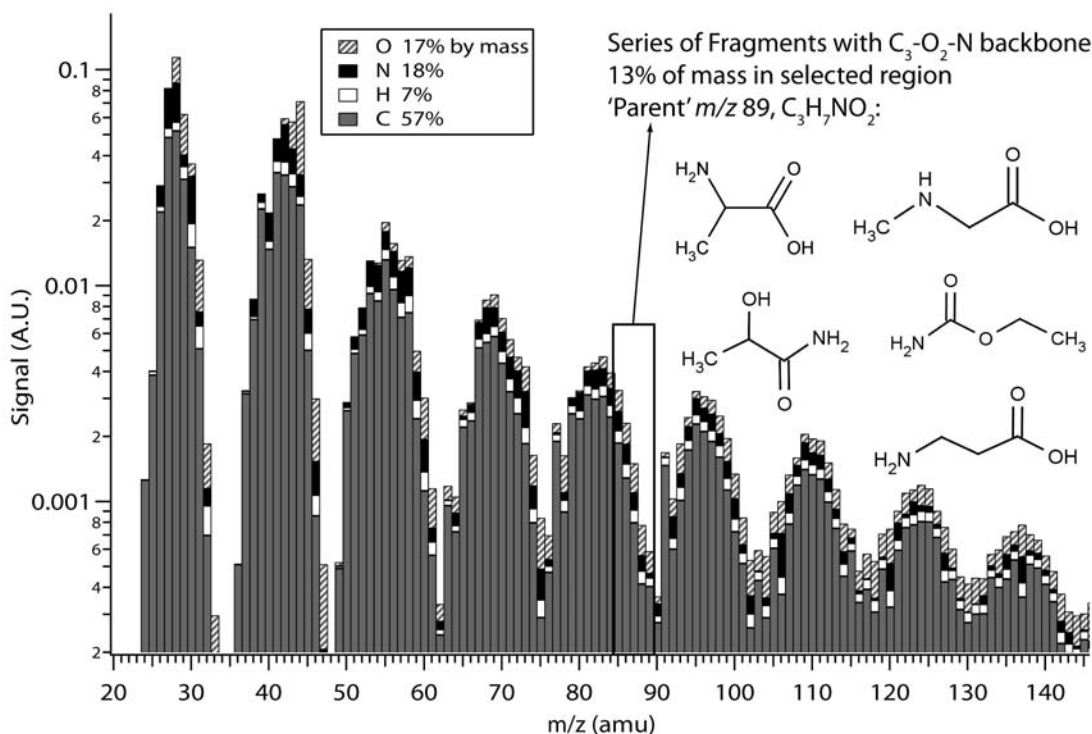
There are several problems with the "Early Earth as Titan" model. Despite some of the promising results discussed in the previous section, on the whole the formation of large hydrocarbons such as long chain alkanes or PAHs as in Titan's atmosphere does not necessarily lead to significant synthesis of proto-biomolecules that may be needed to initiate replication in an aqueous solution, as many expect for the first steps in the origin of life [54, 56]. Also, the atmosphere of the early Earth is not likely to be as reduced as Titan and would have contained some significant amount of  $CO_2$  [38]. Thus it is expected that both the rate of production and the chemical composition of organic molecules and/or aerosol would be affected by the oxidation state of the atmosphere. Previous analyses have looked at the balance of  $CH_4$  and  $CO_2$  to understand the type of reactions generated by photochemistry [122, 123]. The early models had conjectured that with minimum  $CH_4$  mixing ratios of 100 ppm, at C/O ratios exceeding unity the  $CH_4$  successfully polymerizes to form higher order hydrocarbons, and this idea was propagated through other works [46, 60]. It was thought that for  $CO_2 > CH_4$  oxidation from dissociated  $CO_2$  would become the dominant chemical process, and hydrocarbon chains would be terminated with O atoms which might inhibit the formation of aerosol. Thus, at C/O ratios below unity, oxidation of  $CH_4$  would inhibit polymerization. In this case  $CH_4$  would primarily be diverted into

smaller molecular products such as CO and  $H_2CO$ . Other models have cited a C/O ratio of ~0.6, or  $CH_4/CO_2 \geq 0.1$ , as a transition point between polymerization and oxidation [61, 62, 124].

However, experimental studies did not support this model, and organic aerosol formation was shown to be more robust to the C/O ratio. Using far-UV radiation ( $> 100$  nm), which was likely incident on the early Earth's atmosphere at altitudes over ~60 km [125], Trainer *et al.* [77] showed that with  $CH_4/CO_2$  of unity the production of organic particulates exceeded that of  $CH_4/N_2$  photolysis alone. In this work, aerosol formation was observed at  $CH_4/CO_2$  ratios as low as 0.2, and subsequent research by DeWitt *et al.* [126] observed aerosol formation down to  $CH_4/CO_2$  ratios of 0.1. To this author's knowledge, there have not been further experiments identifying the limits of aerosol formation as a function of  $CH_4/CO_2$  ratios.

Experimental work characterizing the aerosol composition using real-time techniques such as an Aerosol Mass Spectrometer (AMS) has allowed for the chemical analysis of primary condensed-phase products of photochemistry without collection or sample preparation [77]. The additional steps typically used in other experiments introduce increased possibilities for contamination or unintended chemical processing, and probe a different product than the nascent atmospheric particle. From the real-time measurements it is clear that the composition of the organic aerosol formed in simulated atmospheres where  $CH_4/CO_2 \leq 1$  differs greatly from the organic species formed in a Titan-like atmosphere. Instead of limiting the formation of organic molecules as predicted, the O atoms released from  $CO_2$  photolysis are incorporated into the molecular structure of the organic aerosols, changing the nature of the material sufficiently to distinguish a hazy early Earth from modern-day Titan. The formation of aromatic molecules is diminished in the presence of  $CO_2$ , as are the long aliphatic chains. The mass spectrum of aerosol formed with  $CH_4/CO_2$  of 0.1 shows major fragment peaks consistent with the formation of carbonyl and carboxyl groups. Spectral comparison suggests the formation of organic acids such as succinic acid ( $C_4H_6O_4$ ) [126]. Organic acids have low absorption coefficients at wavelengths greater than ~300 nm [127], and once formed they should be relatively stable to further photolysis in the lower atmosphere.

This chemistry gets considerably more compelling when one considers the coexistence of both oxygen and nitrogen heteroatoms in aerosol organics. Recent unpublished work by the author has revisited the experiments described in Trainer *et al.* [77] but with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) that provides more definitive information on the elemental composition of organic fragment ions and reveals N/C and O/C ratios of the aerosol product [128-130]. These results, shown in (Fig. 2), bring to light a significant new result regarding the activation of nitrogen and its inclusion in oxygenated organics, thus providing a new and quantifiable source for these elements into the prebiotic chemical cycle. The HR-ToF-AMS provides resolution  $m/\Delta m$  of 3000 to 4300 over the mass range shown and allows for the distinction of different chemical formula of detected ions, but does not directly indicate structural information. (Fig. 2) highlights one region of the spectrum in which a family of ions with the  $C_3-O_2-N$  backbone contributes a substantial mass fraction to the aerosol material in this mass range, and some possible structures for the parent molecule are suggested. These findings are notable in that previous simulations showing the formation of amino acids or similar compounds have included large partial pressures of  $H_2O$  and



**Fig. (2).** Recent assessment of organic aerosol produced from Far-UV irradiation of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> atmospheres using high resolution aerosol mass spectrometry shows that the aerosol is comprised of molecules containing N- and O-heteroatoms. This mass spectrum shows the elemental analysis of the photochemical aerosol produced from 1:1 CH<sub>4</sub> and CO<sub>2</sub> mixture, originally presented as Figure 5b in Trainer *et al.* [77]. Mass ratios indicated in the legend, and atomic ratios O/C and N/C are 0.23 and 0.27, respectively. Previously published fluxes for organic matter produced via this pathway [77] indicate that the aerosol could be a significant source of fixed nitrogen to the environment. Structural information cannot be determined from the mass spectrum, only chemical formulae. As an example, the region around *m/z* 89 has been highlighted as containing a series of ions with coincident O- and N-functionalities. A few possible structures are suggested, but cannot be distinguished.

hydrolysis steps [131-134] or have used higher energy sources [114], or both.

As mentioned in the previous section, 'fixed' nitrogen may have been a limiting ingredient on the early Earth. The formation rates of HCN in the atmosphere and deposition flux to the surface have been studied [123] and revisited [125] as a function of pCH<sub>4</sub>. The analysis presented by Tian *et al.* [125] makes the case for up to 30 Tg yr<sup>-1</sup> of HCN deposited in the ocean given a CH<sub>4</sub>/CO<sub>2</sub> ratio of 0.1, but the authors suggested that this CH<sub>4</sub> flux would likely need to be supported by methanogenesis. One reason HCN is of interest is due to its relative resistance to chemical reaction and photolysis in the atmosphere, being on the order of 10 times longer-lived than NH<sub>3</sub>. Once in oceans, ponds, or other aqueous systems, HCN can react with aldehydes to form amino acids via the Strecker synthesis, and likely the process responsible for generating amino acids in the original Miller experiments and its subsequent variations [33-35, 131, 132, 134, 135]. It is important to note that the Strecker synthesis is sensitive to NH<sub>3</sub>. Similarly, reaction of HCN in an aqueous environment can also generate the nucleobase adenine via the Oró-Orgel synthesis [136, 137]. In addition to the formation of HCN gas, Tian *et al.* [125] propose that N-bearing molecules in aerosols may be an additional source of nitrogen for the oceans, and the recent high resolution analysis presented in (Fig. 2) suggests that this may be the case. The nitrogen mass fraction in aerosol formed with lower CH<sub>4</sub>/CO<sub>2</sub> ratios needs to be investigated to understand the limits of this source for activated nitrogen.

The mass production rates measured in the laboratory can be extrapolated to a planetary rate for the early Earth, using compari-

sons to Titan aerosol production and appropriate corrections for the solar flux on the Archean Earth. For concurrent, approximately equal abundances of CH<sub>4</sub> and CO<sub>2</sub>, the observed enhancement in aerosol nucleation suggests a high flux of organics to the early Earth environment, on the order of ~10<sup>14</sup> g C year<sup>-1</sup>, equivalent to the current carbon burial rate [77]. This could mean an early Earth that was as hazy as Titan, which would have significant climate implications. An optically thick haze layer would provide an anti-greenhouse effect, shielding the surface from radiation and counteracting the effects of having warming gases such as CH<sub>4</sub> and CO<sub>2</sub> in the first place. McKay *et al.* [63] visited this topic, first looking at the anti-greenhouse effect on Titan and then repeating the calculation for the early Earth. If the haze production rates and optical properties are taken from observations of the Titan haze layer, then the estimated antigreenhouse effect on the early Earth is significant enough to drive the surface temperature back below the freezing point of water. A reanalysis by DeWitt *et al.* [126] attempted to factor in the differences between Titan production rates and those expected on the early Earth given the presence of CO<sub>2</sub> and H<sub>2</sub> (more on H<sub>2</sub> follows in the next section). The organic production rate relative to Titan is useful for comparing various scenarios of atmospheric synthesis on the early Earth (Table 1). When this haze formation factor is used to repeat the antigreenhouse calculations it is shown that with CH<sub>4</sub>/CO<sub>2</sub> ratio of 0.1, the production rate of aerosol is low enough to prevent catastrophic cooling at the surface.

More has also been learned about the effect CO<sub>2</sub> has on the optical properties of this type of aerosol. Laboratory measurements of aerosol extinction in the mid-visible (532 nm) observed darker

aerosol resulting from CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> mixtures as compared to “Titan-like” CH<sub>4</sub>/N<sub>2</sub>-only particles [76]. This means that even with a lower particle density a haze layer on the early Earth would have a high optical depth and greatly reduce the transmission of light to the surface in this wavelength range, an important one for life on the current Earth. However, the effective extinction of the aerosol layer is very dependent on the shape and size of the individual particles. Wolf and Toon [61] showed through 3D simulations that if the particles coagulate into larger fractal aggregates as predicted in microphysical models, the haze layer may indeed serve as a UV-shield while transmitting enough visible and infrared radiation to maintain a light and wet surface. These recent studies improve our understanding of the limits of aerosol formation in a range of possible early Earth atmospheres, and the implications for the prebiotic environment. For the hazy early Earth scenario to be plausible, the organic production rate must be balanced such that there is sufficient chemical synthesis, but the haze layer formed is still transparent in the visible and infrared. The need for this optimal production rate is a concept from the discussion of a possible early Earth haze layer in Sagan and Chyba [25], but as we learn more the location of the balancing point will be constantly reevaluated.

A property of aerosol that has not been widely considered for its impact on chemistry and climate on the early Earth is the potential to serve as CCN. Using the same measurement technique as for determining optical constants, Hasenkopf *et al.* [79] examined the water uptake and cloud nucleating ability of photochemical aerosols formed in simulated CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> atmospheres. In the absence of the global sulfate aerosol population (the majority of which is of anthropo- and biogenic origin [64]) that provides current-day CCN on Earth, a global organic haze layer would be the primary source of cloud nucleation surfaces and would strongly influence cloud cover and thus albedo. The effect of clouds on the radiative properties of the early Earth's atmosphere has been touched upon in the literature, but remains poorly understood [26, 28, 138]. The water uptake experiments show that the analog aerosol is hygroscopic enough to absorb water at relative humidities less than 100%, and the growth factors were extrapolated to show that the haze could serve as CCN even at low supersaturation values. The hygroscopicity parameter of the simulated aerosol is about 4x lower than that of ammonium sulfate, but is comparable to many of the secondary organic aerosol molecules studied in the current atmosphere [79]. As expected, the oxidized early Earth aerosol analog shows higher water activity than the hydrocarbon Titan-like analog, a observable fact also noted for organic aerosol in the Earth's atmosphere [67].

The water uptake was demonstrated for the same aerosol analog that is discussed in (Fig. 2), which is known to be comprised of molecules with O- and N-functional groups. This mechanism may provide an alternate route to linking atmospheric synthesis and prebiotic chemistry in a way that concentrates the organic molecules sufficiently to lead to more extensive chemical processing and polymerization prior to introduction into larger water systems. A proposal of marine-sourced atmospheric aerosol as has been put forth as the origin of cell-like “prebiotic reactors” with the ability to divide and propagate [81-83, 139]. The mass spectrum of the CO<sub>2</sub>/CH<sub>4</sub> aerosol analog indicates the presence of carboxylic acids [77], molecules that on the modern Earth are known to coat aqueous aerosol and form the walls of an inverted micelle, similar to those proposed for the sea-spray aerosol [81]. Thus it may be possible that similar aqueous reactors are formed higher in the atmosphere when water is taken up on haze particles, resulting in longer

atmospheric lifetimes prior to deposition during which chemical alteration could progress.

## 5. EARLY EARTH WITH HIGH H<sub>2</sub>

Work by Tian *et al.* [48] showed that in an anoxic atmosphere the escape rate of H<sub>2</sub> may have been up to two orders magnitude slower than assumed due to low exobase temperatures. Lower escape rates would allow for the accumulation of this gas. The resulting abundance of H<sub>2</sub> in the atmosphere would be dependent upon volcanic outgassing of H<sub>2</sub>, which they assumed to be five times the current rate. The exobase temperature calculation driving the escape rate is dependent on efficient radiation of an atmosphere with a significant amount of CO<sub>2</sub>, but in the model the temperature is set at 250K and the assumed CO<sub>2</sub> abundance is not specified [48]. A photochemical model was used to show that the production of hydrocarbons could reach levels of 10<sup>10</sup> kg year<sup>-1</sup> with H<sub>2</sub> abundances around 30%. By necessity this calculation assumes several factors, one of which is that the increased abundance of H<sub>2</sub> (and therefore high H<sub>2</sub>/C) would allow for organic formation and a haze layer even when CO<sub>2</sub> >> CH<sub>4</sub>. This assumption was based on results showing enhanced H<sub>2</sub>CO and amino acid formation in electric discharges with H<sub>2</sub>/C = 4 [131, 134], discussed in more detail below. However, there were no experimental results supporting haze formation with high hydrogen concentrations. On Jupiter and Saturn where H<sub>2</sub> is the dominant atmospheric constituent, chemical models have demonstrated that hydrogen mitigates the formation of higher order hydrocarbons by ‘quenching’ reactions with H-atoms formed from H<sub>2</sub> dissociation [140, 141]. As discussed in the previous section, the cut-off for aerosol formation at CH<sub>4</sub>/CO<sub>2</sub> = 1 was not borne out in experimental studies, and further work has shown that the same may be true for the assumption that H<sub>2</sub> enhances organic formation on early Earth.

Previous studies quantifying the production of prebiotic compounds as a function of energy input and H<sub>2</sub>/C (where C = CH<sub>4</sub>, CO<sub>2</sub>, or CO) has shown that for electric discharge experiments over water there is a peak in organic yields (as HCN + H<sub>2</sub>CO, Strecker synthesis reactants) at H<sub>2</sub>/C ratios between 1 and 3 depending on the source of carbon [131]. Mixtures of H<sub>2</sub>/CO<sub>2</sub> had the lowest yields. Other organics were neither mentioned nor quantified in this study since the detection techniques were specific to HCN and H<sub>2</sub>CO, but it is likely that other compounds were formed during the sparking of the gas mixtures. The energy inputs by “hot” discharges like the one used by Stribling and Miller [131] and in the original Miller experiments [34], meant to simulate synthesis via lightning, are known to generate large quantities of organic products and are more efficient than UV at breaking chemical bonds and forming new compounds. Interestingly, work comparing several energy inputs by Scattergood *et al.* [58] suggests that while the discharge experiments simulate the high temperature “shock” processing of atmospheric molecules into secondary molecules such as HCN and C<sub>2</sub>H<sub>2</sub> efficiently, photochemical processing is needed in order to further react and produce larger hydrocarbon molecules.

Thus photochemical synthesis may be a more significant source for organic production than electric discharges. As discussed by Tian *et al.* [48], an increase in photochemical organic deposition with increasing H<sub>2</sub>/C is predicted, but this was based on H<sub>2</sub>CO production only, not general hydrocarbon formation. Laboratory experiments by DeWitt *et al.* [126] do not support this assumption. As the proportion of H<sub>2</sub> in a 10/1 CO<sub>2</sub>/CH<sub>4</sub> mixture was increased from 0 – 15%, the production rate of aerosol was observed to decrease by a factor of 3.3. These experiments explored a much larger range of



H<sub>2</sub>/C ratios than previous work, to better simulate organic synthesis within the H<sub>2</sub>-rich early Earth [48]. The chemical nature of the aerosol was not observed to change significantly, however, and the aerosol appeared to be composed of oxidized organics like those formed without additional H<sub>2</sub>. These results provide clues to the chemistry occurring with the addition of H<sub>2</sub>: instead of “scrubbing” oxygen produced by CO<sub>2</sub> photolysis and reducing the oxygenation of the organics (thus increasing hydrocarbon haze production), the H atoms sources from dissociated H<sub>2</sub> may be saturating methyl radicals and hydrocarbon chains in the gas-phase products as modeled for high H<sub>2</sub> atmospheres such as Saturn’s [141]. The effect of increased saturation is that a population of product molecules are prevented from reaching sufficient molecular weights to condense into aerosol, reducing the mass production of the aerosol but not the chemical character. When the haze formation factor of 0.03 (Table 1) is applied to the values calculated by Trainer *et al.* [77], this reduced amount of organic production is still on the order of 10<sup>9</sup> kg year<sup>-1</sup>. The implications are therefore beneficial to prebiotic chemistry since the addition of H<sub>2</sub> does not inhibit the formation of C-N-O compounds discussed in the previous section.

That less total organic material may be produced and deposited in the oceans in the high H<sub>2</sub> scenario may be beneficial from the perspective of the climate and surface temperature. The haze formation factor for the high H<sub>2</sub> case relative to the Titan-like early atmosphere implies a less hazy environment where more light reaches the surface even with increased levels of infrared absorbing gases [126]. In addition, the saturation of hydrocarbon radicals in the gas phase may enhance the production of molecules such as ethane (C<sub>2</sub>H<sub>6</sub>), which would contribute to the greenhouse warming of the atmosphere [51]. These effects should be studied to understand the impact on predicted UV-shielding particularly when fractal particles are considered, as in Wolf and Toon [61].

## 6. WEAKLY REDUCED ATMOSPHERE

Some might argue that there was unlikely any (or sub-ppm at the most) CH<sub>4</sub> available in the prebiotic terrestrial atmosphere and that the amount of organic molecules produced endogenously in a weakly reduced atmosphere would be negligible in comparison to exogenous delivery or processing at hydrothermal vents [41, 142]. Recent work has sought to address this assumption, and there are promising results which suggest that the production of prebiotic molecules may still occur in atmospheres lacking CH<sub>4</sub>, NH<sub>3</sub>, or H<sub>2</sub>. Cleaves *et al.* [39] repeated experiments performed by Schlesinger and Miller [134] to show that the yields of amino acids formed from sparking CO<sub>2</sub>/N<sub>2</sub> mixtures over water were 2-15 times those previously reported when the pH of the collecting solution was buffered to maintain a value close to 7. In more acidic solution, the Strecker synthesis from nitrile and aldehyde precursors is inhibited; thus the ultimate contribution of amino acids to the prebiotic ocean may be highly dependent on ocean pH as controlled by the presence of carbonic, nitric, nitrous acids, and mineral surface buffering.

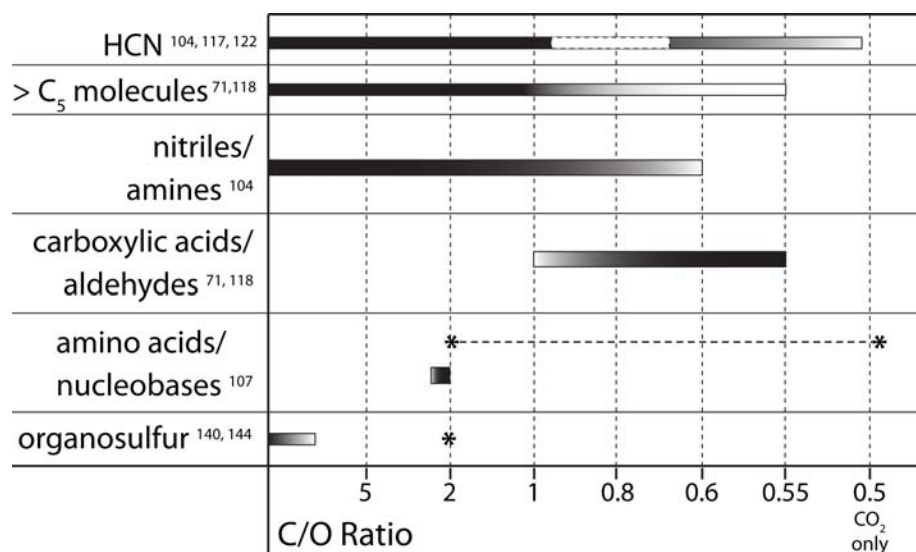
Miyakawa *et al.* [132] also performed experiments exploring amino acid formation from atmospheres with CO and/or CO<sub>2</sub> as the only carbon source, using high energy protons (~3 MeV) as the energy source. Again, amino acids were detected and with comparable yields to Cleaves *et al.* [143]. In this study, it was observed that amino acid yields increased markedly as the CO/CO<sub>2</sub> increased, and in experiments where CO is the only carbon source the yields were observed to be comparable to irradiation of CH<sub>4</sub>/N<sub>2</sub>/H<sub>2</sub>O mixtures with the same energy source, meant to simulate the flux of cosmic rays into the atmosphere. What these studies

and their predecessors have in common are high energy sources and large concentrations (> 3%) of H<sub>2</sub>O vapor. Thus the simulations are most analogous to localized environments where lightning discharges and high partial pressures of water drive chemistry, as opposed to the global source of organics resulting from photochemical processes. Estimated fluxes for cosmic rays to the early Earth atmosphere are 2 x 10<sup>17</sup> J yr<sup>-1</sup> [144]. Though orders of magnitude below the UV fluxes cited earlier, it may be that in a weakly reduced atmosphere cosmic rays and corona discharges are the primary drivers of atmospheric organic synthesis. For example Bar-Nun and Chang [145] reported that when a mixture of CO and H<sub>2</sub>O are irradiated at 185 nm, significant formation of organic molecules such as hydrocarbons, alcohols and aldehydes is observed, but that no hydrocarbons or nitrogen-bearing organic compounds are formed when either CO<sub>2</sub> or N<sub>2</sub> are substituted for CO. This is because the chemistry in the cell is initiated by the photolysis of water in this wavelength range to form OH radicals (see Fig. 1). While CO + ·OH is a favorable reaction (and major chemical sink for CO in the modern Earth atmosphere), reaction of ·OH with CO<sub>2</sub> and N<sub>2</sub> is not. Similar gas mixtures have not been studied in the far-UV, and this wavelength of light may not reach the regions of the atmosphere where high partial pressures of water are likely.

## 7. SULFUR CHEMISTRY ON EARLY EARTH

Sulfur and its isotopes have been a major focus of the discussion of the early Earth atmosphere for many years as a marker for the transition to an oxic atmosphere some 2.4 Ga [10, 146]. Before the rise of oxygen the photolysis of SO<sub>2</sub> by far-UV ( $\lambda < 200$  nm) would have been a dominant process, resulting in mass-independent fractionation (MIF) of the <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S isotopes into product reservoirs, which are well-preserved given the absence of oxidation of reduced sulfur into sulfates [147]. After the rise of atmospheric O<sub>2</sub>, and subsequent generation of a UV-shielding ozone layer, the photochemical engine at these low wavelengths is shut down. Photolysis at greater wavelengths and increased oxidative weathering combined to remove the mass-independent signal from the sedimentary rock record [148]. However, as pointed out by Farquhar *et al.* [149], the sulfur isotope record does not represent an “on” or “off” of MIF, but rather there are periods of time where the MIF signal is attenuated but not absent. These data suggest variations in atmospheric chemistry or transmission of UV through the atmosphere, both of which are influenced by variations in trace gas species. Domagal-Goldman *et al.* [62] hypothesized that an organic haze layer, sensitive to the CH<sub>4</sub>/CO<sub>2</sub> ratio of the atmosphere, could drive fluctuations in the sulfur cycle as reflected in the observed MIF signal. Although a large focus of their analysis assumes a biosphere which is driving the flux of CH<sub>4</sub> into the atmosphere, the discussion highlights the interplay of contemporaneous processing of sulfur and carbon in the atmosphere. Thus it is important to explore the effect that sulfur chemistry may have had on prebiotic chemistry.

Sulfur is one of the elements (“CHNOPS”) most commonly found in biomolecules and considered essential for life. For a period in the ‘60s and ‘70s there was interest in synthesizing S-bearing amino acids using H<sub>2</sub>S in reduced gas mixtures [see discussion in 150]. The formation of methionine (C<sub>5</sub>H<sub>11</sub>SNO<sub>2</sub>) was reported by Van Trump and Miller [151], and their observations indicated that the methionine formation was dependent on CH<sub>3</sub>SH, which was generated in the gas phase but then dissolved into the water for further reaction into methionine. Another set of simulations done by Miller in the 1950’s but not analyzed until recently sought to under-



**Fig. (3).** Summary of observed chemical products from simulations of atmospheric prebiotic chemistry. The C/O ratio is used as an approximate marker for the reduced/oxidized state of the gas mixtures studied, assuming N<sub>2</sub> or NH<sub>3</sub> contributions, with more details presented in the text or cited works. Note the scale on the horizontal axis is arbitrary. The shading in the bars indicates the direction of increasing production (lighter – darker). Note the lower limit on C/O of 0.5 represents the ratio where CO<sub>2</sub> is the only carbon source. Although amino acid and nucleobase synthesis has been extensively reported for samples collected over water baths and/or with subsequent hydrolysis [131-134, 152] (marked on graph with \*), the results indicated by bars on this graph are for direct atmospheric synthesis of amino acids. Sulfur compounds are given for irradiated atmospheres with either SO<sub>2</sub> or H<sub>2</sub>S with CH<sub>4</sub>.

stand prebiotic chemistry in volcanic plumes, which contain increased amounts of lightning, steam, and concentrated reduced gases [152]. These included experiments performed with H<sub>2</sub>S, CH<sub>4</sub>, NH<sub>3</sub>, and CO<sub>2</sub> over water, and the recent analysis detected at least 7 S-bearing organic molecules, including methionine with yields ~ 0.1% of the glycine yield, the most abundantly formed amino acid [150]. Thus in a volcanic plume, which could be more reducing and contain higher proportions of sulfur gases, there could be localized production of important S-bearing prebiotic molecules even if the global atmosphere were weakly reduced or oxidized.

Globally, sulfur photolysis may also play a role in prebiotic chemistry, but is expected to be sensitive to the oxidation state of atmosphere [153]. The disproportionation of SO<sub>2</sub> into sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sulfur allotropes (denoted S<sub>8</sub>), and organosulfur compounds (C<sub>x</sub>H<sub>y</sub>S<sub>x</sub>O<sub>z</sub>) in the anoxic atmosphere will be controlled by the amount of reduced gases present. If all sulfur was ultimately shuttled into sulfate species which then dissolve into the ocean, there would be no preserved MIF signal [147]. DeWitt *et al.* [154] explored the conditions under which S<sub>8</sub> and organosulfur compounds would form from SO<sub>2</sub> photolysis. In SO<sub>2</sub>/N<sub>2</sub> atmospheres with trace amounts of water (< 1%) the formation of sulfuric acid particles dominates until SO<sub>2</sub> concentrations reach 2%. This is many orders of magnitude greater than the predicted SO<sub>2</sub> mixing ratio on early Earth, even when considering high outgassing rates [153]. When CH<sub>4</sub> is added, however, S<sub>8</sub> aerosol forms with an order of magnitude less SO<sub>2</sub>, and organosulfur compounds are observed with only 2 ppmv SO<sub>2</sub>. Relatively high concentrations of CH<sub>4</sub> were used in this study, but the dependence on [CH<sub>4</sub>] was not explored and similar results may be achievable with lower CH<sub>4</sub> partial pressures [154]. The detection of organosulfur aerosol suggests both another chemical pathway for prebiotic processing as well as a new reservoir for S-MIF. The isotopic fractionation of sulfur in the organic aerosol has not yet been studied but may also provide insight into the Archean MIF signal.

The formation of organosulfur aerosol would also have an impact on cloud formation and therefore climate. Sulfate aerosol in the

Earth's atmosphere is known to be a significant source of CCN, and organosulfur compounds have been identified as a major portion of organic matter in rain droplets [155]. The organosulfur compounds may show a higher affinity for water vapor than some of the organic aerosol already identified as potential CCN [79], thus strongly influencing cloud formation on early Earth. Once present in an aqueous phase with other organic species, further chemical processing could lead to similar products as those identified in the Miller amino acid studies [150, 151].

## 8. CONCLUSION

Although not all of the conditions that have been studied and summarized in this work are exact replicas of the early Earth's atmosphere, the results contribute greatly to our knowledge of the environmental limits of prebiotic chemical processes. A summary of the range of organic molecules formed from atmospheric synthesis is shown in (Fig. 3) as a function of the C/O ratio of the gas system under study. This ratio is used in part for historical reasons as an assessment of how reduced or oxidized the atmospheric carbon is and therefore whether organic synthesis is plausible. This graphic shows that the range of production of prebiotic molecules may not be as constrained as previously thought, and there is much overlap in the types of compounds that can be generated within one 'type' of atmosphere. Many other considerations such as H<sub>2</sub> and H<sub>2</sub>O concentrations, pressure, and energy source are not captured in this representation, but still the message is clear that recent studies have expanded our understanding of the diversity of situations under which atmospheric chemistry may contribute essential organic compounds to the planet's evolving environment.

Exploring the boundary conditions under which prebiotic chemistry can occur in the Earth's primitive atmosphere is an exercise that is beneficial not only to understanding the appearance of life on our own planet, but also to providing insight on the types of exoplanets which may support prebiotic chemical cycles. The remote detection of atmospheric gases is one of the observations through which we can understand the character of an exoplanet

[156], and how we determine the potential habitability through this lens will be strongly influenced by the same assumptions that have gone into evaluating the early Earth. Thus the empirical data generated in the name of understanding evolution of life on Earth will prove invaluable as we continue to discover new alien worlds.

### CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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### ABBREVIATIONS

Ga	=	Billion Years Ago
AU	=	Astronomical Unit
ppm	=	Parts Per Million
SOA	=	Secondary Organic Aerosol
CCN	=	Cloud Condensation Nuclei
INMS	=	Ion Neutral Mass Spectrometer (Cassini)
CAPS	=	Cassini Plasma Spectrometer (Cassini)
PAH	=	Polycyclic Aromatic Hydrocarbon
EUV	=	Extreme Ultraviolet
AMS	=	Aerosol Mass Spectrometer
HR-ToF-AMS	=	High-Resolution Time-of-Flight Aerosol Mass Spectrometer
UV	=	Ultraviolet
MIF	=	Mass-Independent Fractionation

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