

Article

New Estimates of Nitrogen Fixation on Early Earth

Madeline Christensen ^{1,2,*} , Danica Adams ^{3,4}, Michael L. Wong ^{4,5} , Patrick Dunn ⁶ and Yuk L. Yung ^{2,7}

¹ Bellarmine Preparatory Marine Chemistry Program, Tacoma, WA 98405, USA

² Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

³ Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA

⁴ NHFP Sagan Fellow, NASA Hubble Fellowship Program, Space Telescope Science Institute, Baltimore, MD 21218, USA

⁵ Earth and Planets Laboratory, Carnegie Institution for Science, Washington, DC 20015, USA

⁶ Space Sciences Laboratory, University of California, Berkeley, CA 94720, USA; pdunn@ssl.berkeley.edu

⁷ NASA Jet Propulsion Laboratory, Pasadena, CA 91109, USA

* Correspondence: mchrste@caltech.edu

Abstract: Fixed nitrogen species generated by the early Earth's atmosphere are thought to be critical to the emergence of life and the sustenance of early metabolisms. A previous study estimated nitrogen fixation in the Hadean Earth's N₂/CO₂-dominated atmosphere; however, that previous study only considered a limited chemical network that produces NO_x species (i.e., no HCN formation) via the thermochemical dissociation of N₂ and CO₂ in lightning flashes, followed by photochemistry. Here, we present an updated model of nitrogen fixation on Hadean Earth. We use the Chemical Equilibrium with Applications (CEA) thermochemical model to estimate lightning-induced NO and HCN formation and an updated version of KINETICS, the 1-D Caltech/JPL photochemical model, to assess the photochemical production of fixed nitrogen species that rain out into the Earth's early ocean. Our updated photochemical model contains hydrocarbon and nitrile chemistry, and we use a Geant4 simulation platform to consider nitrogen fixation stimulated by solar energetic particle deposition throughout the atmosphere. We study the impact of a novel reaction pathway for generating HCN via HCN₂, inspired by the experimental results which suggest that reactions with CH radicals (from CH₄ photolysis) may facilitate the incorporation of N into the molecular structure of aerosols. When the HCN₂ reactions are added, we find that the HCN rainout rate rises by a factor of five in our 1-bar case and is about the same in our 2- and 12-bar cases. Finally, we estimate the equilibrium concentration of fixed nitrogen species under a kinetic steady state in the Hadean ocean, considering loss by hydrothermal vent circulation, photoreduction, and hydrolysis. These results inform our understanding of environments that may have been relevant to the formation of life on Earth, as well as processes that could lead to the emergence of life elsewhere in the universe.

Keywords: astrobiology; origin of life; early Earth; photochemistry; atmospheric chemistry; nitrogen fixation; prebiotic chemistry



Citation: Christensen, M.; Adams, D.; Wong, M.L.; Dunn, P.; Yung, Y.L. New Estimates of Nitrogen Fixation on Early Earth. *Life* **2024**, *14*, 601. <https://doi.org/10.3390/life14050601>

Academic Editor: Amedeo Balbi

Received: 6 February 2024

Revised: 10 April 2024

Accepted: 12 April 2024

Published: 8 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

One of the greatest scientific mysteries is the origin of life. On Earth, life may have emerged in hydrothermal systems at the bottom of the Hadean ocean [1–4]. It is hypothesized that this nascent life would have used fixed nitrogen species as a high-potential electron acceptor to oxidize hydrogen and methane and help reduce CO₂ to organic carbon [5–7]. Early metabolisms may have continued to use nitrogen oxides (NO_x) as one source of high-potential electron acceptors [8–10]. Other hypotheses for the origin of life place a large emphasis on hydrogen cyanide (HCN) chemistry for protein and nucleotide synthesis [11].

NO_x can form abiotically on ancient Earth via production in the atmosphere by lightning, which is capable of breaking down CO₂ and N₂, followed by photochemistry

and rainout to surface waters (Figure 1) [12,13]. Lightning discharges decompose CO_2 and N_2 as follows:

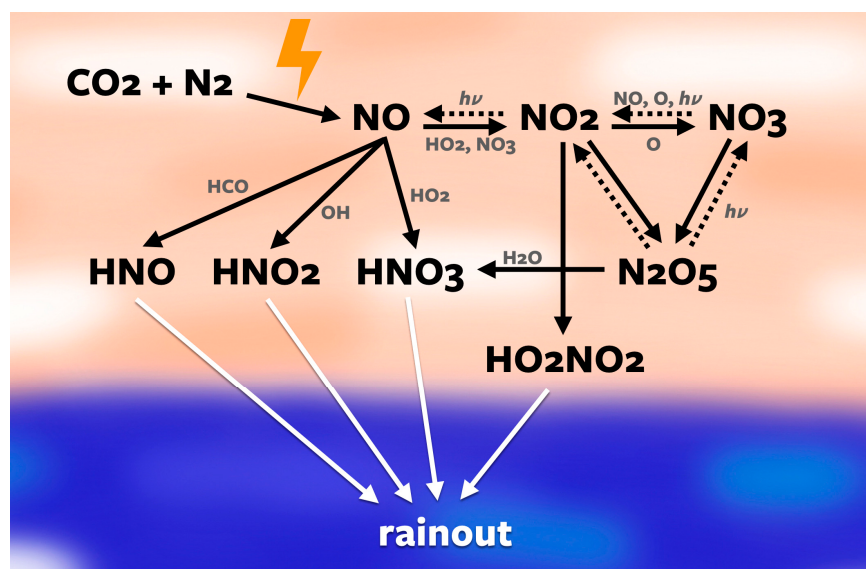
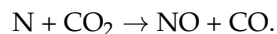
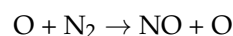
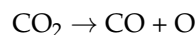


Figure 1. Diagram of the nitrogen oxide reaction pathways. As the pressure and heat of lightning strike these chemicals, it forces them to react and form nitrogen oxides which then react with other species to form nitroxyl (HNO), nitrous acid (HNO_2), or nitric acid (HNO_3), which then rain out into the atmosphere.

Because of diatomic nitrogen's strong triple bond, very few processes are able to decompose N_2 in the way lightning does. As lightning is discharged into the atmosphere, its current-carrying channel heats the air around it. The shockwave that follows, commonly referred to as thunder, carries that heat to distant particles that dissociate under the heat and pressure of the shockwave. Molecules that form via lightning discharges become kinetically frozen, unable to revert back to their original state because the atmosphere cools back to ambient temperatures in less than a second, kinetically inhibiting reverse reactions [14]. Similarly, HCN is known to form on present-day Earth through impacting solar energetic particles. These break down N_2 into N and $\text{N}(^2\text{D})$, an excited state of nitrogen, which then react with CH_3 radicals to form H_2CN , which then yields HCN [15]. These species are soluble and dissolve in condensed water, which then rains on to the surface.

The atmospheric production and oceanic concentrations of NO_x were estimated for plausible early-Earth conditions by Wong et al. [12]. This study considered lightning production and rainout fluxes to estimate the amount of nitrogen oxides raining out into the ocean, and then only used hydrothermal vent circulation to determine the loss of aqueous nitrogen oxides in the ocean. Adams et al. [16] improved upon the methods of Wong et al. [12] to estimate the concentrations of both nitrogen oxide and hydrogen cyanides on early Mars. The new reactions and processes included in Adams et al.'s [16] study showed that solar energetic particle (SEP) deposition dominates HCN formation in early terrestrial atmospheres, and that photoreduction dominates over hydrothermal circulation as a loss mechanism for aqueous NO_x , as first described by Ranjan et al. [17].

Here, we utilize the modeling framework of Adams et al. [16] and apply it to early Earth to update and expand upon the findings of Wong et al. [12]. We present state-of-the-art estimates of hydrogen cyanide and nitrogen oxides on early Earth to estimate the amount of fixed nitrogen available at the time of life's emergence and early evolution. We

also compute the abundance of carbon monoxide (CO), a molecule that could have added to conducive conditions for the formation of organic molecules and therefore life [18,19].

Additionally, this study is the first to consider the production of hydrogen cyanide on Earth through a formation pathway involving HCN_2 (Figure 2), motivated by Berry et al. [20]. These reactions were previously used in Krasnopolsky and Cruikshank [21] to model haze formation on Pluto, but to our knowledge they have never been used in a terrestrial context. To simulate a more accurate and complete atmosphere and estimate of hydrogen cyanide, we have added these reactions to improve estimates of HCN production on early habitable worlds.

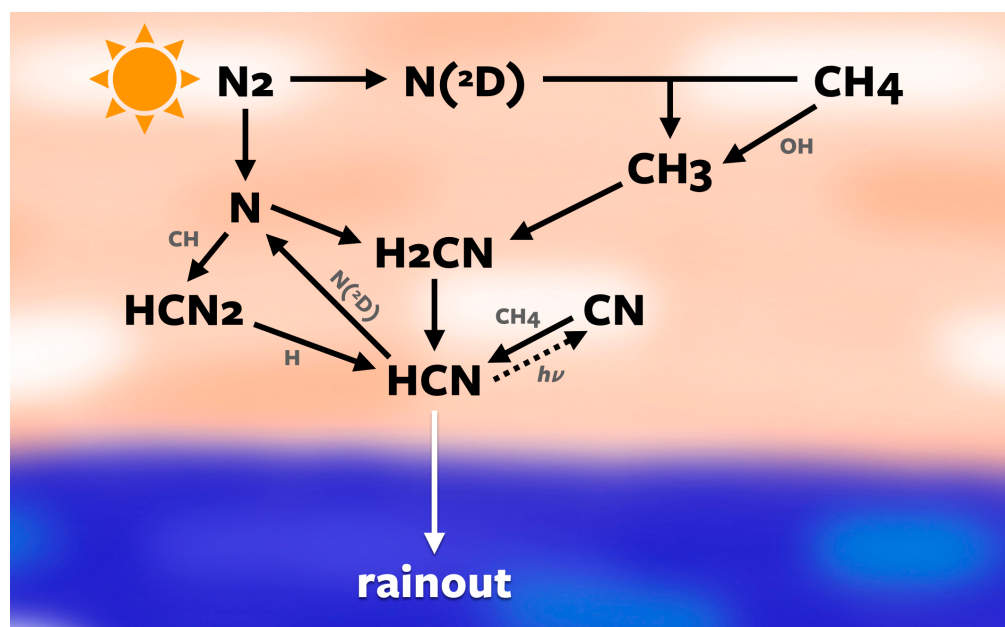


Figure 2. Diagram displaying the hydrogen cyanide pathways. Diatomic nitrogen is broken down into atomic nitrogen, which then reacts with CH_3 to form methylene amidogen (H_2CN), which then breaks down via reactions with primarily hydrogen into hydrogen cyanide, which then rains out into the ocean. The left side of the diagram shows the alternate pathway via HCN_2 added in this study. Some hydrogen photolyzes to CN, which then turns back into hydrogen cyanide through reactions with methane.

2. Methods

Due to the vast uncertainty with regard to Hadean atmospheric composition, we modelled 12 different possible Hadean Earth atmospheres. We varied the total pressure between 1 bar, 2 bars, and 12 bars, with background compositions of 90% N_2 , 10% CO_2 in the 1-bar case, 1 bar N_2 and 1 bar CO_2 in the 2-bar case, and 10 bars N_2 and 2 bars CO_2 in the 12-bar case. We varied the amounts of H_2 and CH_4 in each atmosphere, allowing the surface mixing ratio of each gas to take values of 0.1%, 0.3%, 1%, or 3%. To form HCN and NO_x in an N_2/CO_2 -dominated atmosphere, an energy source is required. We took into account three sources of energy: lightning, SEPs, and photochemistry.

2.1. Thermochemical and Energetic Particle Deposition Modeling

We used the Chemical Equilibrium with Applications (CEA) model [22] to calculate the effect of lightning and its thermal energy (3000 K) and pressure on each of the 12 atmospheric cases. Thermodynamic equilibrium at this immense heat and pressure favors the creation of HCN and NO. The CEA output for HCN and NO was used as input fluxes for the lower boundary conditions in our photochemical model.

SEPs are energetic protons and electrons streaming from the Sun that impact planetary atmospheres. They deposit their energy in the atmosphere and are energetic enough to

split the strong triple bond of N₂. We used the Geant4 simulation platform to run new energy deposition profiles for the atmosphere of early Earth in each of the cases described above. Similar to Adams et al. [16], we assumed a coronal mass ejection (CME) frequency of 1 event per day, as the early Sun would have been much more magnetically active than today, with each event having an average differential energy flux similar to that of the 29 October 2003 CME event [23]. The Geant4 simulation platform computes the flux profiles of N and N(²D) produced by SEPs deposited at each altitude layer on early Earth by considering the total SEP energy flux divided by the N₂ bond-dissociation energy and finally multiplied by the concentration of N₂ at that altitude. These profiles of reactive N atoms are then included in our photochemical model.

2.2. Photochemical Modeling

After computing the lightning-induced fluxes for NO and HCN using CEA and the N and N(²D) profiles produced by SEP deposition, we modelled how these species react to produce HNO_x and HCN. To do this, we used the Caltech–JPL photochemistry–transport model KINETICS [24], which solves the continuity equation:

$$\frac{dn_i}{dt} = P_i - L_i - \frac{\partial \varphi_i}{\partial z},$$

where n_i is the number density of species i , φ is the vertical flux, P_i is the chemical production rate, and L_i is the chemical loss rate evaluated at time t and altitude z . The vertical flux is given by the following:

$$\varphi_i = -\frac{dn_i}{dt} (D_i + K_{zz}) - n_i \left(\frac{D_i}{H_i} + \frac{K_{zz}}{H_{atm}} \right) - n_i \frac{\partial T}{\partial z} \left[\frac{(1 + \alpha_i)D_i + K_{zz}}{dT} \right],$$

where D_i is the species' molecular diffusion coefficient, H_i is the species' scale height, H_{atm} is the atmospheric scale height, α_i is the thermal diffusion coefficient, K_{zz} is the vertical eddy diffusion coefficient, and T is the temperature [25].

Our model considers 495 chemical reactions. We varied the H₂ and CH₄ content of the atmosphere, and for each case, the lightning-induced fluxes of the reduced gases computed by CEA were used as lower boundary conditions for NO and HCN in KINETICS. The complete list of boundary conditions in our model is presented in Table 1.

KINETICS then computes the change of species concentration over time, considering both chemical production/loss terms and transport. The model runs for upwards of 10⁸ simulated years to ensure the concentrations converge to a steady state. The outputs of the chemical reactions over time were graphed for analysis (see Section 3).

Table 1. The boundary conditions used in this study. If a range is shown, that value varies between atmospheric cases. If the number is in bold, it represents a deposition velocity (cm s^{−1}); standard text, a fixed flux (molecules cm^{−2} s^{−1}); and italicized, a fixed mixing ratio. The HCN and NO_x ranges displayed are referenced from Figure 3.

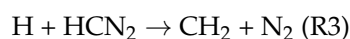
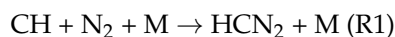
Species	Lower Boundary	Upper Boundary
O	0	0
O ₂	−1.00 × 10^{−6}	0
O ₃	−1.00 × 10^{−2}	0
H ₂	<i>1.00 × 10^{−3}– 3.00 × 10^{−2}</i>	0
HO _x	0	0

Table 1. Cont.

Species	Lower Boundary	Upper Boundary
N_xH_y	-1.00×10^{-2}	0
HNO_x	-1.00×10^{-2}	0
N_xO_y	0	0
CH_x ($x \neq 4$)	0	0
CH_4	1.00×10^{-3} – 3.00×10^{-2}	0
CO	-1.00×10^{-6}	0
N	0	-1.60×10^9
H_xC_yO	-1.00×10^{-2}	0
NO	1.07×10^8 – 1.49×10^8	0
HCN	3.43×10^0 – 6.67×10^0	0
C_xH_y ($y = \text{even}$)	-1.00×10^{-3}	0
C_xH_y ($y = \text{odd}$)	0	0
CN	-1.00×10^{-2}	0
C_xN	-1.00×10^{-2}	0
$H_xC_yN_z$	-1.00×10^{-2}	0

2.3. New Reactions Involving HCN_2

To create a more realistic and holistic atmospheric reaction network, three reactions were added to the KINETICS database:

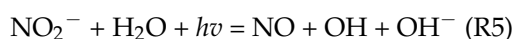


with $k_1 = 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, $k_2 = 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_3 = 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, and where M denotes background molecules that remove energy from the system. From the lab work of Berry et al. [20] and Trainer et al. [26], it was hypothesized that these reactions would increase the production of HCN in the Hadean Earth's atmosphere. In this work, we added them to our chemical network and quantified their effect on HCN production (see Section 3.3).

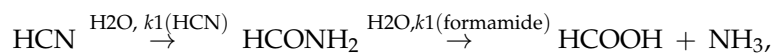
2.4. Oceanic Concentrations

As the motivation behind this study is to understand how early life may have formed on Earth, we used the rainout rates of NO_x and HCN, calculated by KINETICS, to estimate oceanic concentrations of NO_x and HCN during the Hadean period. We computed equilibrium concentrations by balancing delivery from the atmosphere with loss due to photoreduction, hydrolysis, and hydrothermal vents, with an assumed Hadean ocean depth of $5.33 \times 10^5 \text{ km}$ [27].

Two photoreduction reactions for NO_x were considered:



with rate constants of $k_4 = 2.3 \times 10^{-8} \text{ s}^{-1}$ and $k_5 = 1.2 \times 10^{-6} \text{ s}^{-1}$, respectively. These reactions were chosen because they are well constrained and are good representations of the reaction pathway in the ocean [17]. Additionally, when considering loss of HCN within hydrothermal vents, we assumed a water mass of flux through high-temperature vents of $7.2 \times 10^{12} \text{ kg yr}^{-1}$. We also considered the loss of HCN through hydrolysis, as discussed by Miyakawa et al. [28]. Specifically, the reaction:



where $k_1(\text{HCN})$ and $k_1(\text{formamide})$ are derived from the laboratory hydrolysis rates from the study by Miyakawa et al. [28], which, when fit to an Arrhenius equation, finds a hydrolysis kinetic rate of $2.265 \times 10^{-12} \text{ molecules/cm}^2/\text{s}$, corresponding to a temperature of 273 K. These loss processes for NO_x and HCN, combined with our production rates calculated via KINETICS, allowed us to solve for the equilibrium concentrations of these species in the Hadean ocean.

3. Results

3.1. Lightning-Induced HCN and NO

After running the CEA thermochemical model to calculate the creation of NO (the precursor to NO_x species) and HCN by lightning under different background atmospheric compositions, it was clear that NO and HCN respond inversely to increases in background H_2 and CH_4 surface mixing ratios (Figure 3). (Note that NO and HCN are on massively different scales of concentration within the atmosphere.) HCN increases as CH_4 increases, which is to be expected as HCN forms via reactions with CH_3 , a photochemical product of CH_4 . NO decreases as both CH_4 and H_2 increase, as both CH_4 and H_2 make the environment more chemically reduced, while NO is thermodynamically more favorable in more oxidized environments.

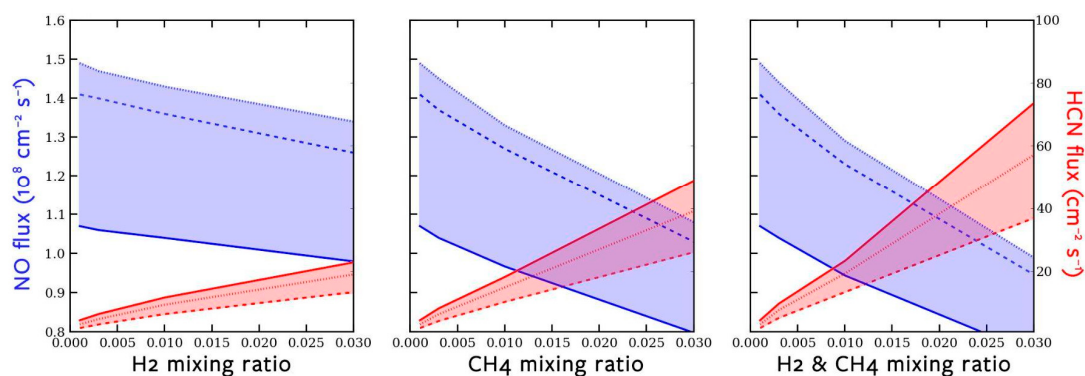


Figure 3. Graph of the CEA results, showing NO and HCN flux over different concentrations of atmospheric composition. Solid, dashed, and dotted lines refer to our 12-bar, 2-bar, and 1-bar cases, respectively. On the left side, H_2 is the only chemical that increases in concentration, as CH_4 stays constant at 0.1%, and the same is true for CH_4 in the middle. On the right, H_2 and CH_4 increase together. There is an inverse relationship present between NO and HCN, even though NO is almost six orders of magnitude more prevalent than HCN.

3.2. Photochemistry

As the photochemical model, KINETICS, runs to a steady state (for over a hundred million simulated years), it computes the amount of each species present in the atmosphere and as a function of altitude. In our 1-bar, 2-bar, and 12-bar atmospheres, we assumed surface temperatures of 280 K, 332 K, and 388 K, respectively, in accordance with the Hadean Earth general circulation model results of Wong et al. [12]. The lower atmospheric temperature profile follows the moist adiabatic lapse rate. Upon reaching a stratospheric temperature of 142.8 K, 139.6 K, or 169 K (again, corresponding to the 1-bar, 2-bar, and

12-bar cases), we set the temperature profile to an isotherm. The eddy diffusion parameter K_{zz} describes vertical transport within the atmosphere and is computed following the methods of Ackerman and Marley [29]. The H_2O profile is fixed to the saturation vapor pressure (Figure 4). The common occurrence of carbon monoxide buildup was also seen in this atmosphere (see Section 4.2).

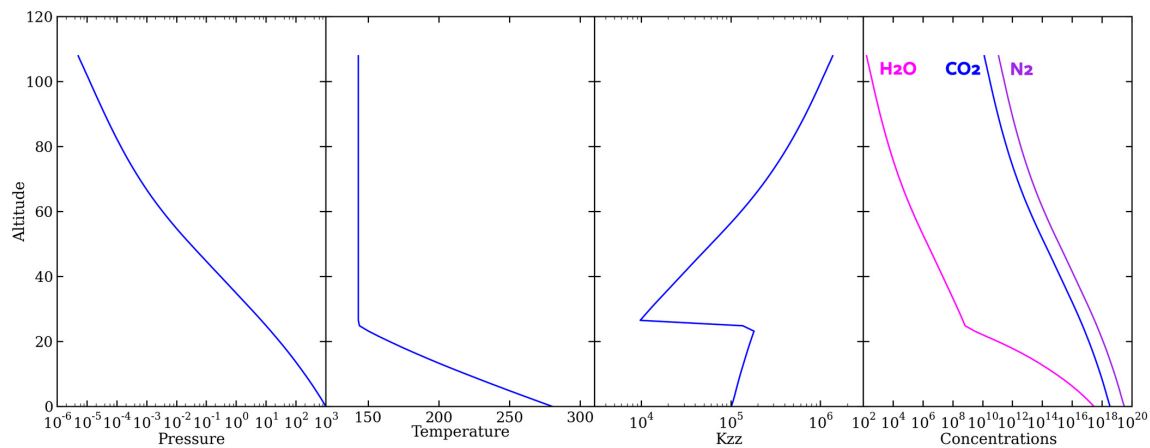


Figure 4. The boundary conditions of KINETICS based on altitude (km) of our 1-bar atmosphere: pressure (mbar); temperature (K); K_{zz} or eddy diffusion ($\text{cm}^2 \text{s}^{-1}$); and the species concentrations for N_2 , CO_2 , and H_2O (cm^{-3}).

To effectively compute the concentrations of HCN and NO_x , seven species are the focus throughout the discussion of the results: HCN , NO , HNO , HNO_2 , HNO_3 , N , and $\text{N}^{(2)\text{D}}$ (Figure 5). All of the NO_x and HNO_x species react with and affect the concentrations of each other (Figures 1 and 2). Throughout the atmosphere, the concentrations of HNO , HNO_2 , and HNO_3 are all similar, with HNO_3 having slightly lower concentrations than the other two. These species all dissolve in water droplets to rain out on to surface waters, and the equilibrium oceanic concentrations are directly proportional to the rainout rates. N and $\text{N}^{(2)\text{D}}$ vary slightly depending on the atmospheric pressure but are within a consistent range for all starting concentrations.

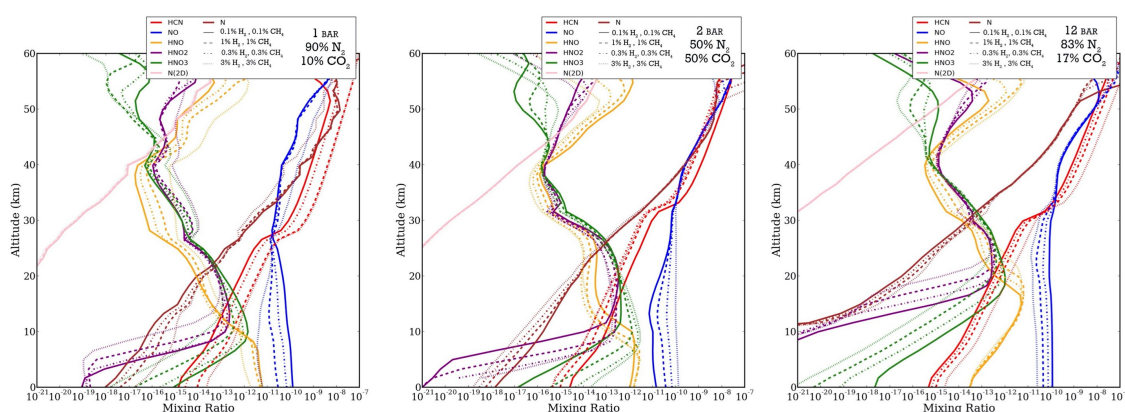


Figure 5. Mixing ratios of NO_x , HCN , HNO , HNO_2 , HNO_3 , N , and $\text{N}^{(2)\text{D}}$ vs. altitude for the (left) 1-bar atmosphere, (middle) 2-bar atmosphere, and (right) 12-bar atmosphere. A different line style presented for each assumed atmospheric concentration. HNO , HNO_2 , and HNO_3 all tend to mirror each other, and both HCN and NO_x are in relation with their original CEA values.

3.3. The Effect of Adding HCN_2 Reactions

We ran all atmospheric cases with and without the new HCN_2 reactions to compare the rainout rate of HCN between the atmospheres with and without these reactions and

assess the importance of including HCN_2 pathways in photochemical modeling relevant to the origins of life.

Figure 6 displays the rainout rates, without and with the new reactions, for both NO_x (magenta) and HCN (green) per each pressure case. Interestingly, the HCN rainout rate rose by a factor of five in the 1-bar case and is about the same in the 2- and 12-bar cases when the HCN_2 reactions were added.

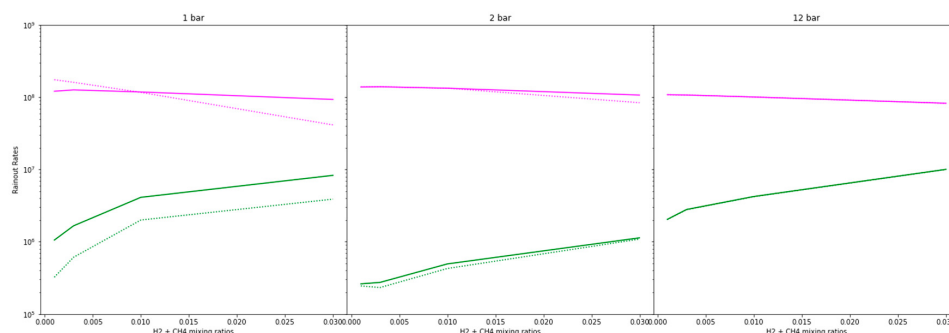


Figure 6. Rainout rates of NO_x (magenta) and HCN (green) for the various atmospheric compositions tested in this study, both with (bold) and without (dashed) the HCN_2 pathway. The HCN rainout rate rose by a factor of five in the 1-bar case and is about the same in the 2- and 12-bar cases when the HCN_2 reactions were added. These results present more accurate estimates of how much fixed nitrogen may have been available to early life.

3.4. Oceanic Concentrations

Once NO_x species and HCN reach the Hadean ocean, they are subject to a number of loss processes. We determined their equilibrium concentrations via the procedure outlined in Section 2.4, and these are shown in Figure 7. An atmosphere with more H_2 and CH_4 results in a higher oceanic concentration HCN and a lower ocean concentration of NO_x . This is because $\text{N}(^2\text{D})$ attacking methane acts as a bottleneck for HCN formation: CH_4 is the source of CH_3 radicals, which are essential for making H_2CN and eventually HCN (Figure 2). Additionally, CH_3 radicals will react with HO_x species, removing HO_x species needed to make NO_x (Figure 1). Therefore, more CH_4 results in less HO_x and less NO_x . Our sensitivity studies showed that increasing H_2 alone, on the other hand, does not contribute to CH_3 radicals, and thus is less impactful on the HCN and NO_x concentrations.

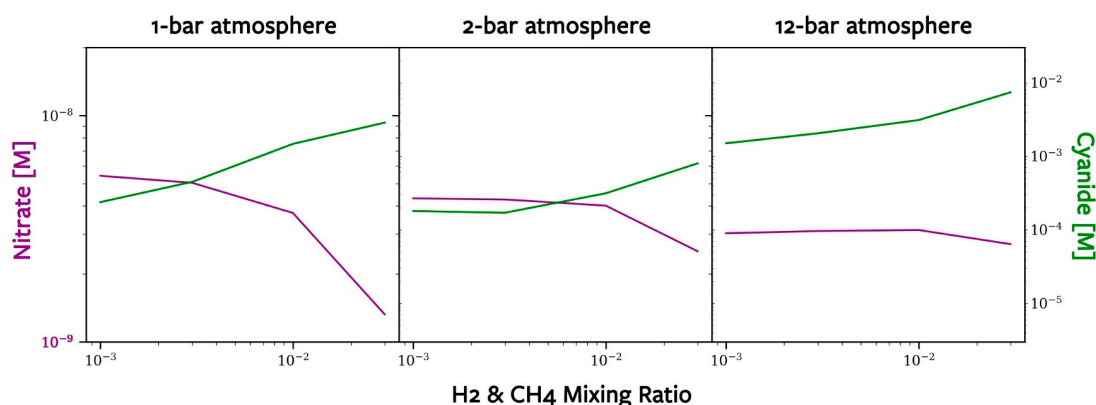


Figure 7. The oceanic concentrations of both NO_3^- , in purple, and HCN, in green, in relation to the original atmospheric concentrations of H_2 and CH_4 . Similar to the original CEA graph (Figure 3), NO_3^- and HCN are in an inverse relationship. Note that the magnitude at which these chemicals are present is completely different, as NO_3^- is $<10^{-8}$ M, whereas HCN is $>10^{-5}$ M.

4. Discussion

4.1. The Relevance of NO_x and HCN

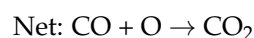
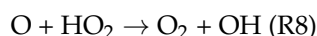
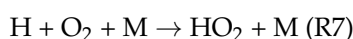
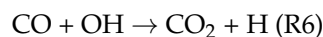
We presented updated estimates of NO_x and new estimates of photochemically derived oceanic HCN on early Earth, including the effects of SEP events on both NO_x and HCN and the photoreduction of NO_x in aqueous solution. Additionally, the new HCN_2 reactions increase the overall amount of HCN in the atmosphere, and hence the HCN rainout into the early Earth's ocean. This was expected, as these reactions provide an additional pathway of HCN formation, increasing the rainout rate of HCN by a factor of five in the 1-bar case. These results provide an update to the previous results of Wong et al. [12] and Adams et al. [16], and they are compatible with the current scientific narrative of HCN and NO_x being created in the troposphere before raining out and being accessible to any potential life in the ocean.

Our model considered a CO_2 - and N_2 -dominated Hadean atmosphere. Other studies have investigated the nature of the Hadean atmosphere post-giant impact, which causes the atmosphere to take on a much more reduced state. In this post-impact state, Wogan et al. [30] found a slower deposition rate ($<1 \times 10^5 \text{ HCN/cm}^2/\text{s}$) than our results for low- CH_4 ($<10\%$) cases, and Wogan et al. [30] and Pearce et al. [31] found the in high- CH_4 cases, the HCN production and deposition rates were much larger.

Oceanic concentrations of HCN and NO_x are of astrobiological interest because they are possible sources of fixed nitrogen—a necessity for the formation, maintenance, and evolution of early life. For HCN to be helpful in protein synthesis, local concentrations of at least 0.01 M are required [32]. Our estimated concentrations of NO_x and HCN on early Earth may be helpful to future lab work to determine the habitability, genesis, and durability of the Hadean environment [33,34].

4.2. CO Runaway

Our models reproduce the previously observed [35] “carbon monoxide (CO) runaway” (Figure 8). Because of the relatively large amount of carbon dioxide present in the Hadean atmosphere, ultraviolet light can photolyze the carbon dioxide, forming atomic oxygen and carbon monoxide. If very little to no water is present at the relevant altitudes, then HO_x , the main family of compounds that reacts with carbon monoxide to cycle it back to carbon dioxide, is unable to react with enough CO to eliminate the runaway via the following process:



As a result, carbon monoxide can accumulate in the atmosphere over time and dominate the composition of the atmosphere. However, after analyzing the model output, it became clear that the lower layer of the atmosphere was not nearly as dominated by CO as the top. This is expected, as the bottom of the atmosphere, where rain forms, has much more water vapor than at the top of the atmosphere.

Based on our modeling, it was possible that an upper-atmosphere CO runaway would be present during the Hadean eon. Although CO does not necessarily build up to a “runaway” state in the lower atmosphere, a significant fraction (over 10%) of the atmosphere is CO in the photochemical steady state across all of our atmospheric cases (Figure 8). This could have profound implications on the creation of organic compounds via CO-related species and pathways [18,19]. Our results motivate further investigation of organic synthesis under high-CO conditions.

We acknowledge that the photolysis rate of water (i.e., production rate of HO_x) is not well constrained (e.g., two largely conflicting rates are presented in Ranjan et al. [36] and Burkholder et al. [37]). Future laboratory work could re-examine H_2O photolysis rates and

compare their results and photolysis rates in practice, allowing the photolysis rates to be more constrained.

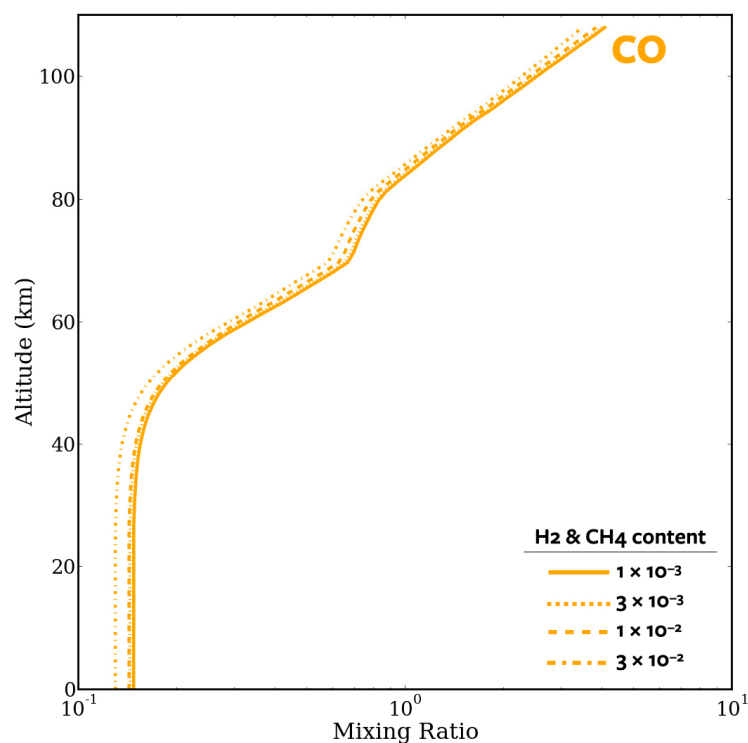


Figure 8. The mixing ratio of carbon monoxide vs. altitude for a 1 bar atmospheric case, where H_2 and CH_4 content match. CO is a photochemical product, and the total density is computed from the ideal gas law. While physically a mixing ratio cannot exceed 1, numerically this results in our code due to CO buildup. Since CO_2 is fixed, whenever CO_2 is lost to $\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}$ (and this CO_2 is not replenished via $\text{CO} + \text{HO}_x$), an infinite source of CO_2 replenishes the profile (numerically). This photolysis therefore occurs over time and CO builds until eventually CO exceeds the total density predicted by the ideal gas law. Again, while we predict the CO buildup is real, its mixing ratio exceeding unity is completely a numerical effect due to fixing CO_2 .

4.3. Other Considerations

In the future, adding HCN reactions with iron in surface waters, as a loss mechanism to HCN, would add more accuracy to the survival rates and thereby equilibrium concentrations of HCN. Additionally, lab work performed on the NO_x reaction rates with iron would also add immensely to the accuracy of the survival rates of NO_x , as those rates are currently poorly constrained [17].

Further research can build upon the biological context for these new estimates by adding more to our understanding of metabolisms involving nitrate. It is likely that NO_x is important for microbiological metabolisms and the origin of life, but it is unknown how much NO_x is needed for this to be important. Recent work [38] has shown that the precursor molecules pyruvate and nitrate can be converted into the amino acid glutamine via reductive amination on ferroan brucite, a common mineral in hydrothermal vent systems, but these system effects have not been analyzed as a full system. Clarification of these reactions and processes would help determine the potential for the emergence of life in these oceanic environments.

In conclusion, the additional HCN_2 reactions (R1–R3) and updated atmospheric processes added here improve upon HCN and NO_x rainout estimates from that of past research. The common “problem” of a CO runaway is present in our model, but only dominates the upper, thinner part of the atmosphere. A high-CO lower atmosphere may be of interest to future work on prebiotic chemistry. Further lab work on this as well as

widening information on chemical networks and microbial metabolisms could help us eventually reach the goal of understanding the roots of life on early Earth and, potentially, early Mars and Earth-like exoplanets.

5. Conclusions

Understanding the processes of nitrogen fixation remains one of the keys to understanding the emergence of life on Earth and other planets. We estimated Hadean NO and HCN lightning-induced fluxes of approximately 10^8 and a few to $\sim 70 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, by computing the thermochemical equilibrium with the CEA model. We computed Hadean N and $\text{N}(^2\text{D})$ flux profiles based on solar energetic particle events using the Geant4 simulation platform. These were used as inputs for our photochemical model, the Caltech–JPL model KINETICS, which we used to derive the Hadean precipitation rates of HNO_x and HCN (on the order of 10^8 molecules/ cm^2/s and 3×10^5 – 1×10^7 molecules/ cm^2/s , respectively). With the assumed losses to photodestruction and hydrothermal vent circulation, we found concentrations of nitrate of about 1×10^{-9} – 6×10^{-9} M and hydrogen cyanide of about 1×10^{-2} – 1×10^{-4} M. We suggest more laboratory research to fully understand the astrobiological implications of these concentrations.

Author Contributions: Conceptualization, D.A. and M.L.W.; Methodology, M.C., D.A. and M.L.W.; Software, M.C., D.A., M.L.W., P.D. and Y.L.Y.; Validation, D.A. and M.L.W.; Formal analysis, M.C., D.A., M.L.W. and P.D.; Investigation, M.C.; Data curation, M.C. and P.D.; Writing—original draft, M.C.; Writing—review & editing, M.C., D.A., M.L.W., P.D. and Y.L.Y.; Visualization, M.C.; Supervision, D.A. and M.L.W.; Project administration, Y.L.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported in part by Caltech GPS Discovery Grant P2639826. This research was supported in part by a JPL RTD grant, “ASSESSING ORIGIN OF LIFE (OOL) SCENARIOS FOR EXOPLANET STUDIES.” M.L.W. and D.A. are funded by NASA through the NASA Hubble Fellowship awarded by the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy, Inc., for NASA, under contract NAS5-26555.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This study was a theoretical study and the models we used are appropriately referenced.

Acknowledgments: We thank our three anonymous peer reviewers for constructive comments on our paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sojo, V.; Herschy, B.; Whicher, A.; Camprubi, E.; Lane, N. The Origin of Life in Alkaline Hydrothermal Vents. *Astrobiology* **2016**, *16*, 1–17. [[CrossRef](#)] [[PubMed](#)]
2. Weiss, M.C.; Sousa, F.L.; Mrnjavac, N.; Neukirchen, S.; Roettger, M.; Nelson-Sathi, S.; Martin, W.F. The physiology and habitat of the last universal common ancestor. *Nat. Microbiol.* **2016**, *1*, 16116. [[CrossRef](#)] [[PubMed](#)]
3. Martin, W.; Baross, J.; Kelley, D.; Russell, M.J. Hydrothermal vents and the origin of life. *Nat. Rev. Microbiol.* **2008**, *6*, 805–814. [[CrossRef](#)] [[PubMed](#)]
4. Baross, J.A.; Hoffman, S.E. Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life. *Orig. Life Evol. Biosph.* **1985**, *15*, 327–345. [[CrossRef](#)]
5. Nitschke, W.; Schoepp-Cothenet, B.; Duval, S.; Zuchan, K.; Farr, O.; Baymann, F.; Panico, F.; Minguzzi, A.; Branscomb, E.; Russell, M.J. Aqueous electrochemistry: The toolbox for life’s emergence from redox disequilibria. *Electrochem. Sci. Adv.* **2022**, *3*, e2100192. [[CrossRef](#)]
6. Nitschke, W.; Russell, M.J. Beating the acetyl coenzyme A-pathway to the origin of life. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **2013**, *368*, 20120258. [[CrossRef](#)] [[PubMed](#)]
7. Russell, M.J.; Barge, L.M.; Bhartia, R.; Bocanegra, D.; Bracher, P.J.; Branscomb, E.; Kidd, R.; McGlynn, S.; Meier, D.H.; Nitschke, W.; et al. The Drive to Life on Wet and Icy Worlds. *Astrobiology* **2014**, *14*, 308–343. [[CrossRef](#)] [[PubMed](#)]

8. Weber, K.A.; Pollock, J.; Cole, K.A.; O'Connor, S.M.; Achenbach, L.A.; Coates, J.D. Anaerobic Nitrate-Dependent Iron(II) Bio-Oxidation by a Novel Lithoautotrophic Betaproteobacterium, Strain 2002. *Appl. Env. Microbiol.* **2006**, *72*, 686–694. [[CrossRef](#)] [[PubMed](#)]
9. Bryce, C.; Blackwell, N.; Schmidt, C.; Otte, J.; Huang, Y.M.; Kleindienst, S.; Tomaszewski, E.; Schad, M.; Warter, V.; Peng, C.; et al. Microbial anaerobic Fe(II) oxidation—Ecology, mechanisms and environmental implications. *Environ. Microbiol.* **2018**, *20*, 3462–3483. [[CrossRef](#)]
10. Price, A.; Pearson, V.K.; Schwenzer, S.P.; Miot, J.; Olsson-Francis, K. Nitrate-Dependent Iron Oxidation: A Potential Mars Metabolism. *Front. Microbiol.* **2018**, *9*, 513. [[CrossRef](#)]
11. Xu, J.; Ritson, D.J.; Ranjan, S.; Todd, Z.R.; Sassellov, D.D.; Sutherland, J.D. Photochemical reductive homologation of hydrogen cyanide using sulfite and ferrocyanide. *Chem. Commun.* **2018**, *54*, 5566–5569. [[CrossRef](#)] [[PubMed](#)]
12. Wong, M.L.; Charnay, B.D.; Gao, P.; Yung, Y.L.; Russell, M.J. Nitrogen Oxides in Early Earth's Atmosphere as Electron Acceptors for Life's Emergence. *Astrobiology* **2017**, *17*, 1–9. [[CrossRef](#)] [[PubMed](#)]
13. Mvondo, D.N.; Navarro-Gonzalez, R.; McKay, C.P.; Coll, P.; Raulin, F. Production of nitrogen oxides by lightning and coronae discharges in simulated early Earth, Venus and Mars environments. *Adv. Space Res.* **2001**, *27*, 217–223. [[CrossRef](#)] [[PubMed](#)]
14. Desch, S.J.; Borucki, W.J.; Russell, C.T.; Bar-Nun, A. Progress in planetary lightning. *Rep. Progress. Phys.* **2002**, *65*, 202. [[CrossRef](#)]
15. Pearce, B.K.D.; Ayers, P.W.; Pudritz, R.E. A Consistent Reduced Network for HCN Chemistry in Early Earth and Titan Atmospheres: Quantum Calculations of Reaction Rate Coefficients. *J. Phys. Chem. A* **2019**, *123*, 1861–1873. [[CrossRef](#)] [[PubMed](#)]
16. Adams, D.; Luo, Y.; Wong, M.L.; Dunn, P.; Christensen, M.; Dong, C.; Hu, R.; Yung, Y. Nitrogen Fixation at Early Mars. *Astrobiology* **2021**, *21*, 968–980. [[CrossRef](#)] [[PubMed](#)]
17. Ranjan, S.; Todd, Z.R.; Rimmer, P.B.; Sassellov, D.D.; Babbin, A.R. Nitrogen Oxide Concentrations in Natural Waters on Early Earth. *Geochim. Geophys. Geosystems* **2019**, *20*, 2021–2039. [[CrossRef](#)]
18. Isoda, K.; Zang, X.; Ueno, Y. Glyoxylate from CO atmosphere via UV photochemistry. In Proceedings of the Japan Geoscience Union Meeting 2019, Chiba, Japan, 26–30 May 2019.
19. Eugene, A.J.; Xia, S.S.; Guzman, M.I. Aqueous Photochemistry of Glyoxylic Acid. *J. Phys. Chem. A* **2016**, *120*, 3817–3826. [[CrossRef](#)]
20. Berry, J.L.; Ugelow, M.S.; Tolbert, M.A.; Browne, E.C. The Influence of Gas-phase Chemistry on Organic Haze Formation. *Astrophys. J. Lett.* **2019**, *885*, L6. [[CrossRef](#)]
21. Krasnopolsky, V.A.; Cruikshank, D.P. Photochemistry of Pluto's atmosphere and ionosphere near perihelion. *J. Geophys. Res. Planets* **1999**, *104*, 21979–21996. [[CrossRef](#)]
22. McBride, B.J.; Gordon, S. *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications*; NASA Lewis Research Center: Cleveland, OH, USA, 1996.
23. Mewaldt, R.A.; Looper, M.D.; Cohen, C.M.S.; Haggerty, D.K.; Labrador, A.W.; Leske, R.A.; Mason, G.M.; Mazur, J.E.; von Rosenvinge, T.T. Energy Spectra, Composition, and Other Properties of Ground-Level Events During Solar Cycle 23. *Space Sci. Rev.* **2012**, *171*, 97–120. [[CrossRef](#)]
24. Allen, M.; Yung, Y.L.; Waters, J.W. Vertical Transport and Photochemistry in the Terrestrial Mesosphere and Lower Thermosphere (50–120 km). *J. Geophys. Res.* **1981**, *86*, 3617–3627. [[CrossRef](#)]
25. Yung, Y.L.; DeMore, W.B. *Photochemistry of Planetary Atmospheres*; Oxford University Press: Oxford, UK, 1999.
26. Trainer, M.G.; Jimenez, J.L.; Yung, Y.L.; Toon, O.B.; Tolbert, M.A. Nitrogen Incorporation in CH₄-N₂ Photochemical Aerosol Produced by Far Ultraviolet Irradiation. *Astrobiology* **2012**, *12*, 315–326. [[CrossRef](#)]
27. Korenaga, J.; Planavsky, N.J.; Evans, D.A.D. Global water cycle and the coevolution of the Earth's interior and surface environment. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2017**, *375*, 20150393. [[CrossRef](#)] [[PubMed](#)]
28. Miyakawa, S.; Cleaves, H.J.; Miller, S.L. The Cold Origin of Life: A. Implications Based On The Hydrolytic Stabilities Of Hydrogen Cyanide And Formamide. *Orig. Life Evol. Biosph.* **2002**, *32*, 195–208. [[CrossRef](#)]
29. Ackerman, A.S.; Marley, M.S. Precipitating Condensation Clouds in Substellar Atmospheres. *Astrophys. J.* **2001**, *556*, 872–884. [[CrossRef](#)]
30. Wogan, N.F.; Catling, D.C.; Zahnle, K.J.; Lupu, R. Origin-of-life Molecules in the Atmosphere after Big Impacts on the Early Earth. *Planet. Sci. J.* **2023**, *4*, 169. [[CrossRef](#)]
31. Pearce, B.K.D.; He, C.; Hörst, S.M. An experimental and theoretical investigation of HCN production in the Hadean Earth atmosphere. 2022. Available online: <https://doi.org/10.1021/acsearthspacechem.2c00138> (accessed on 5 February 2024).
32. Holm, N.G.; Neubeck, A. Reduction of nitrogen compounds in oceanic basement and its implications for HCN formation and abiotic organic synthesis. *Geochim. Trans.* **2009**, *10*, 9. [[CrossRef](#)] [[PubMed](#)]
33. Deamer, D.; Cary, F.; Damer, B. Urability: A Property of Planetary Bodies That Can Support an Origin of Life. *Astrobiology* **2022**, *22*, 889–900. [[CrossRef](#)]
34. Wong, M.L.; Bartlett, S.; Chen, S.; Tierney, L. Searching for Life, Mindful of Lyfe's Possibilities. *Life* **2022**, *12*, 783. [[CrossRef](#)]
35. Zahnle, K.; Haberle, R.M.; Catling, D.C.; Kasting, J.F. Photochemical instability of the ancient Martian atmosphere. *J. Geophys. Res. Planets* **2008**, *113*, E11004. [[CrossRef](#)]
36. Ranjan, S.; Schwieterman, E.W.; Harman, C.; Fateev, A.; Sousa-Silva, C.; Seager, S.; Hu, R. Photochemistry of Anoxic Abiotic Habitable Planet Atmospheres: Impact of New H₂O Cross Sections. *Astrophys. J.* **2020**, *896*, 148. [[CrossRef](#)]

37. Burkholder, J.B.; Sander, S.P.; Abbatt, J.P.D.; Barker, J.R.; Huie, R.E.; Kolb, C.E.; Kurylo, M.J.; Orkin, V.L.; Wilmouth, D.M.; Wine, P.H. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies—Evaluation Number 18*; Jet Propulsion Laboratory, National Aeronautics and Space Administration: Pasadena, CA, USA, 2015.
38. Chimiak, L.M. *Prebiotic Fingerprints*; California Institute of Technology: Pasadena, CA, USA, 2021.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.