Nitrogen Oxides in Early Earth’s Atmosphere as Electron Acceptors for Life’s Emergence

Michael L. Wong,1 Benjamin D. Charnay,2,3 Peter Gao,4 Yuk L. Yung,1,5 and Michael J. Russell5

Abstract

We quantify the amount of nitrogen oxides (NOx) produced through lightning and photochemical processes in the Hadean atmosphere to be available in the Hadean ocean for the emergence of life. Atmospherically generated nitrate (NO3−) and nitrite (NO2−) are the most attractive high-potential electron acceptors for pulling and enabling crucial redox reactions of autotrophic metabolic pathways at submarine alkaline hydrothermal vents. The Hadean atmosphere, dominated by CO2 and N2, will produce nitric oxide (NO) when shocked by lightning. Photochemical reactions involving NO and H2O vapor will then produce acids such as HNO, HNO2, HNO3, and HO2NO2 that rain into the ocean. There, they dissociate into or react to form nitrate and nitrite. We present new calculations based on a novel combination of early-Earth global climate model and photochemical modeling, and we predict the flux of NOx to the Hadean ocean. In our 0.1-, 1-, and 10-bar pCO2 models, we calculate the NOX delivery to be $2.4 \times 10^5$, $6.5 \times 10^8$, and $1.9 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$. After only tens of thousands to tens of millions of years, these NOx fluxes are expected to produce sufficient (micromolar) ocean concentrations of high-potential electron acceptors for the emergence of life. Key Words: Nitrogen oxides—Nitrate—Nitrite—Photochemistry—Lightning—Emergence of life. Astrobiology 17, xxx–xxx.

1. Introduction

Nitrogen oxides (NOx)—formed by lightning discharges and photochemistry in the Hadean atmosphere and rained out into the all-enveloping Hadean ocean—may have played a vital role in the emergence and early evolution of life on Earth (Mancinelli and McKay, 1988). In particular, the high-potential electron acceptors nitrate (NO3−) and nitrite (NO2−) could conceivably have initiated the first metabolic pathway through the oxidation of hydrothermal CH4 and the concomitant hydrogenation of CO2 at ancient submarine alkaline hydrothermal vents (Ducluzeau et al., 2009; Nitschke and Russell, 2013; Shibuya et al., 2016).

In contrast to the renowned magma-driven “black smoker” springs (350–400°C, pH ~ 3), Hadean alkaline hydrothermal systems would have been powered by the geothermal gradient, augmented by exothermic serpentinization of the mainly peridotitic crust (Table 1). Their effluents would have been not only moderately hot (~92°C) but also alkaline (pH ~ 11). These fluids would have reacted with the then acidic ocean to produce porous submarine hydrothermal mounds (Russell et al., 2010).

The present-day hydrothermal vents at Lost City, where fluid exhalation temperatures reach 92°C at a pH of ~11, provide a modern analogue (Kelley et al., 2001; Martin et al., 2008; Seyfried et al., 2015). Brucite (Mg[OH]2) is a major initial component of Lost City mounds, owing to the high concentration of Mg in the present-day ocean, whereas Hadean mounds would have had an iron-dominated mineralogical composition. The Hadean ocean was carbonic and rich in iron and other transition metals, so the porous precipitate mounds would have comprised amorphous to microcrystalline brucite-structured iron oxyhydroxides or green rusts (e.g., ~Fe$^{II}$Fe$^{III}$6(OH)$_{12}$(CO$_3$)$_{3}$(H$_2$O)$_{3}$) along with the iron sulfides mackinawite and greigite, dosed with nickel, cobalt, and molybdenum (Russell and Hall, 1997; Génin et al., 2005, 2006; Mloszewska et al., 2012; Nitschke and Russell, 2013; Russell et al., 2014; White et al., 2015; Tosca et al., 2016; Haley et al., 2017).

Electro-geochemical gradients would have been imposed across inorganic precipitates between the mildly acidic, CO2-rich Hadean seawater and the alkaline hydrothermal fluid laden with H$_2$ and CH$_4$, products of serpentinization and hydrothermal leaching, respectively (Russell et al., 1989;
Acidic vents are believed to be too hot and acidic for the emergence of life, but alkaline mounds offer a promising milieu for the first metabolic pathways. In addition to their innate electro-geochemo-plastic gradients imposed across their margins, submarine alkaline hydrothermal vents provide the fuels H$_2$ and CH$_4$, ambient electron acceptors in the form of nitrate, nitrite, and ferric iron, and a powerful suite of mineral catalysts that resemble the Fe/Ni clusters in enzymes that promote metabolism in life today (Proskurowski et al., 2006; Martin et al., 2008; Seyfried et al., 2015).

In the interlayers of green rust, carbonate, sulfide, and chloride are critical for turning a primitive metabolic pathway into a universally applicable one. Alanine could then have condensed on an iron-nickel sulfide to produce a 5-mer peptide on carbonate surfaces in the mound (Kawamura et al., 2003). Such peptides have the potential to render iron-nickel sulfides and pyrophosphate clusters that are more stable and catalytically active, thus quickening the reactions along the pathway that had previously relied on the unadorned inorganic clusters themselves (Milner-White and Russell, 2011). Such a positive feedback would lock this cycle in as the foundation for an autocatalytic pathway at the emergence of life (e.g., Mielke et al., 2011).

Given the important role that nitrogen oxides might have played at life’s emergence—both as vital high-potential electron acceptors and as the main source of fixed nitrogen to emerging biosynthesis—it behooves us to ascertain whether the production of NOX in the Hadean atmosphere would produce sufficient concentrations of nitrate and nitrite in the Hadean ocean to meet model requirements.

The Hadean, which spans the first half billion years of Earth’s history, was a tumultuous time. The planet was bombarded by bolides and singed by the young Sun’s intense ultraviolet radiation. Days were only ~14h long, massive tides were induced by a closer Moon, and continents did not exist. The ocean was twice its present volume, and the atmosphere was suffused with the products of ubiquitous volcanism (Russell et al., 2014, and references therein).

Although geochemical evidence points to an atmosphere dominated by CO$_2$ and N$_2$, it is still uncertain how massive the atmosphere was. Indeed, it is likely to have varied greatly during the Hadean eon under the vagaries of bolide collisions, mantle convective overturn, and accompanying tectonics. After the magma ocean phase and the condensation of ocean, the atmosphere was. Indeed, it is likely to have varied greatly during the first 1–20 Myr. Afterward, pCO$_2$ was 5–20 bars during the first 1–20 Myr. Afterward, pCO$_2$ decreased to an equilibrium value that is still unknown. Ongoing work coupling global climate models (GCMs) to carbon cycling models results in a Hadean pCO$_2$ between 0.1 and 0.5 bar.
depending on the continental cover and the recycling in the subduction (Charnay et al., 2017).

To determine the abundance of NOx on the early Earth, we must address a wide range of atmospheric pressures. In this study, we test CO2 partial pressures of 0.1, 1, and 10 bars, complemented by 1 to 2 bars of N2.

2. Estimates of Lightning and Lightning-Induced NO

Along with the contribution from volcanic activity (Martin et al., 2007), lightning is the main source of nitrogen oxides (Schumann and Huntrieser, 2007) generated in the lower atmosphere. For simplicity, we ignore nitrogen fixation caused by coronal mass ejection events from the Sun (Airapetian et al., 2016). On the oxygen-rich present-day Earth, ~300 moles of NO are generated per lightning flash (Choi et al., 2009), corresponding to a lightning-induced NO flux of ~6×10^8 molecules cm^{-2} s^{-1}. In the anoxic early atmosphere, electrical discharges would have heated air temperatures to tens of thousands of kelvin and incited the normally unsociable molecules CO2 and N2 to react. Electrical-discharge events shatter the robust covalent double bonds of CO2, splitting CO into CO and O. The highly reactive O radical breaks N2’s triple bond, producing NO and N. The N radical then goes on to react with another CO2 molecule, creating NO and even more NO (Nna Mvondo et al., 2001; Duchuzeau et al., 2009). The process can be summarized as follows:

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + \text{O}, \\
\text{O} + \text{N}_2 & \rightarrow \text{NO} + \text{N}, \\
\text{N} + \text{CO}_2 & \rightarrow \text{NO} + \text{CO}.
\end{align*}
\]

This lightning-induced NO is the fundamental source of all higher-order NOx species generated by photochemistry.

To estimate the amount of lightning-induced NO in the Hadean, we must first estimate the lightning flash rate, which is a predictor of lightning flash rate to date:

\[
F = \frac{\eta}{E} \times P \times \text{CAPE},
\]

where \(F\) is the lightning flash rate per area (flashes m^{-2} s^{-1}), \(P\) is the precipitation rate (kg m^{-2} s^{-1}), and CAPE is the convective available potential energy. This formula is valid in GCMs where \(P\) and CAPE are derived in a cell where there is a convective cloud. We assume the constant of proportionality, \(\eta/E\), which contains the efficiency \(\eta\) (the ratio of power per area dissipated by lightning to the CAPE per area per time available to condensates) and the energy discharge per flash \(E\) (joules), to be the same as today. We assume the present-day average lightning discharge energy \(E \sim 5 \times 10^9\) J flash^{-1}. Thus,

\[
F \propto P \times \text{CAPE}.
\]

We run the Generic LMDZ 3D GCM to compute \(P\) and CAPE for early Earth, which allows us to scale the present-day average lightning flash rate (1.1 flashes km^{-2} year^{-1}) to that of an early-Earth atmosphere. The Generic LMDZ 3D GCM has a universal dynamic core, a correlated-k radiative transfer code, universal turbulence and robust convection schemes in the lower atmosphere, volatile condensation in the atmosphere and surface, a 2-layer dynamic ocean, and surface and subsurface thermal balance. It has been used to great effect in studies of other planetary scenarios, including Archean Earth (Charnay et al., 2013), early Mars (Forget et al., 2013), and even terrestrial-mass exoplanets (Wordsworth et al., 2011).

The computed lightning flash rates are 0.41, 9.3, and 3.1 flashes km^{-2} year^{-1} for the 0.1-, 1-, and 10-bar pCO2 cases, respectively. An increase in the global mean surface temperature should enhance the frequency and power of convective storms and thus enhance the lightning flash rate (Romps et al., 2014). As expected, our model produces a higher lightning flash rate for the 1-bar pCO2 case (mean surface temperature of 332.8 K) than for the 0.1-bar pCO2 case (280.4 K). Surprisingly, the 10-bar pCO2 (388.1 K) case has a lower flash rate than the 1-bar pCO2 case. The 10-bar pCO2 case features the warmest troposphere. Hence, the lower atmosphere is rich in water vapor, making it extremely opaque (only 7 W/m^2 of sunlight reaches the surface). The absorption of solar radiation in the atmosphere and a strong thermal inversion above the surface, as expected for very warm and moist climates (Pierrehumbert, 2010, p. 418), stabilize the atmosphere against moist convection. Though the precipitation rate in the 10-bar case (5.1 mm/day) is comparable to that of the 1-bar case (5.8 mm/day), there are few convective clouds and the CAPE is low, effectively suppressing the lightning flash rate by a factor of 3.

Using empirical data for NO yield with respect to different CO2/N2 mixtures (Nna Mvondo et al., 2001) (reproduced in Fig. 2), and \(E \sim 5 \times 10^9\) J flash^{-1}, we are able to calculate a lightning-induced NO flux for each pCO2 (Tables 2 and 3).

3. Photochemical Production of NOx

To evaluate the production of NOx species in the Hadean atmosphere, we adapt the 1D Caltech/JPL chemical transport model (Allen et al., 1981) to simulate the Hadean Earth.
Other versions of this model have been well tested on numerous planetary bodies, including Jupiter, Titan, and Pluto (see, e.g., Wong et al., 2015). In our early-Earth model, we simulate 28 chemical species and 156 chemical reactions. The model calculates the chemical production and loss rates at each altitude as well as the diffusive flux between each altitude grid by solving the 1D continuity equation:

\[
\frac{dn_i}{dt} = P_i - L_i - \frac{\partial \phi_i}{\partial z},
\]

where \(n_i\) is the number density of species \(i\), \(\phi_i\) is the vertical flux, \(P_i\) is the chemical production rate, and \(L_i\) is the chemical loss rate, all evaluated at time \(t\) and altitude \(z\). The vertical flux is given by

\[
\phi_i = -\frac{\partial n_i}{\partial z} (D_i + K_{zz}) - n_i \left( \frac{D_i}{H_i} + \frac{K_{zz}}{H_{atm}} \right)
- \frac{\partial n_i}{\partial z} \left[ T (1 + \alpha_i) D_i + K_{zz} \right] \frac{T}{T_{atm}},
\]

where \(D_i\) is the species’ molecular diffusion coefficient, \(H_i\) is the species’ scale height, \(H_{atm}\) is the atmospheric scale height, \(\alpha_i\) is the thermal diffusion coefficient, \(K_{zz}\) is the vertical eddy diffusion coefficient, and \(T\) is the temperature (Yung and DeMore, 1999).

The atmospheric temperature profiles for our photochemical runs are based on those obtained from the GCM’s output. The temperature decreases with altitude, following a wet adiabat from the surface to the mesosphere, where it becomes isothermal. We calculate the eddy diffusion coefficient profile by using the formulation in the work of Ackerman and Marley (2001). Figure 3 shows the temperature and eddy diffusion coefficient profiles of all three cases.

In the lowest atmospheric level, which extends from 0 to 1.4 km, we inject an NO flux corresponding to our calculations for lightning-induced NO production. We assume a surface \(H_2\) mixing ratio of \(1 \times 10^{-3}\), corresponding to a volcanically active, weakly reduced early Earth (Kasting, 1993).

The bulk of our photochemical scheme is based on the Nair et al. (1994) model for Mars’ \(CO_2\)-\(N_2\) atmosphere, updated to include HNO and a new formation pathway for HNO$_3$ (discussed later in this section). The additional reactions are listed in Table 2. Unlike the Nair et al. (1994) model, our model atmospheres are irradiated by the faint young Sun (Claire et al., 2012), and the updated photolysis rates at the top of the atmosphere (100 km) are calculated and catalogued in Table 3.

Our model calculates and outputs chemical abundances for each species at every level. The vertical profiles of photochemically derived \(O_3\), \(NO_x\), and \(N_2O\) in the 1-bar pCO$_2$ case are presented in Figure 4.

The rainout rates for various electron acceptors are summarized in Figure 5 and Table 4. Among the NO$_x$ species, in all three cases, the flux of HNO rain is the highest, followed by HNO$_3$, HNO$_2$NO$_2$, and HNO$_2$. Across all species, the highest rainout rate is produced in the 1-bar pCO$_2$ case. The total amount of NO$_x$ rained out into the Hadean ocean is \(2.4 \times 10^7, 6.5 \times 10^8,\) and \(1.9 \times 10^9\) molecules cm$^{-2}$s$^{-1}$ for the 0.1-, 1-, and 10-bar pCO$_2$ cases, respectively.

The rainout rate of H$_2$O$_2$, another effective electron acceptor that is generated on early Earth, is quoted for comparison. In the 0.1-bar pCO$_2$ case, H$_2$O$_2$ makes up only 2% of the electron acceptors delivered from the atmosphere to the ocean. This fraction drops to 0.02% and 0.0001% in the 1-bar and 10-bar cases, respectively, which is to be expected as the amount of CO$_2$ increases but the surface mixing ratio of H$_2$ remains constant. Although H$_2$O$_2$ should be considered a possible electron acceptor for early metabolisms, it was by no means the dominantly available species.

Our models reveal that HNO$_3$ rainout is one of the primary sources of high-potential electron acceptors in the early ocean, eclipsing both HNO$_2$ and HNO$_2$NO$_2$ rainout in all three cases. The normal pathway for generating HNO$_3$,

### Table 2. Additional Reactions Involving HNO and HNO$_3$, and Their Corresponding Rate Coefficients, to the Nair et al. (1994) Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant $k$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H + NO + M \rightarrow HNO + M$</td>
<td>$2.1 \times 10^{-12}$</td>
<td>$e^{300T}$</td>
</tr>
<tr>
<td>$H + HNO \rightarrow H_2 + NO$</td>
<td>$7 \times 10^{-12}$</td>
<td>$e^{300T}$</td>
</tr>
<tr>
<td>$OH + HNO \rightarrow H_2O + NO$</td>
<td>$8 \times 10^{-11}$</td>
<td>$e^{-500T}$</td>
</tr>
<tr>
<td>$HNO_3 + NO + M \rightarrow HNO_2 + NO + M$</td>
<td>$3.5 \times 10^{-14}$</td>
<td>$e^{250T}$</td>
</tr>
</tbody>
</table>

The units for two-body and three-body reactions are cm$^{-3}$ s$^{-1}$ and cm$^{-6}$ s$^{-1}$, respectively.

### Table 3. Updated Nair et al. (1994) Photolysis Rate Coefficients at the Top of the Atmosphere

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Photolysis rate coefficient at 100 km (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + hv \rightarrow O + O$</td>
<td>$2.71 \times 10^{-6}$</td>
</tr>
<tr>
<td>$O_2 + hv \rightarrow O + O(1D)$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$O_3 + hv \rightarrow O_2 + O$</td>
<td>$3.68 \times 10^{-4}$</td>
</tr>
<tr>
<td>$O_3 + hv \rightarrow O_3 + O(1D)$</td>
<td>$9.16 \times 10^{-7}$</td>
</tr>
<tr>
<td>$H_2O + hv \rightarrow H + OH$</td>
<td>$3.03 \times 10^{-5}$</td>
</tr>
<tr>
<td>$NO + hv \rightarrow N + O$</td>
<td>$3.50 \times 10^{-6}$</td>
</tr>
<tr>
<td>$NO_2 + hv \rightarrow NO + O$</td>
<td>$2.74 \times 10^{-3}$</td>
</tr>
<tr>
<td>$NO_3 + hv \rightarrow NO_2 + O$</td>
<td>$5.26 \times 10^{-2}$</td>
</tr>
<tr>
<td>$NO_3 + hv \rightarrow NO_2 + O$</td>
<td>$7.63 \times 10^{-3}$</td>
</tr>
<tr>
<td>$N_2O + hv \rightarrow N + O(1D)$</td>
<td>$1.33 \times 10^{-5}$</td>
</tr>
<tr>
<td>$HNO + hv \rightarrow H + NO$</td>
<td>$1.70 \times 10^{-3}$</td>
</tr>
<tr>
<td>$HNO_2 + hv \rightarrow OH + NO$</td>
<td>$6.04 \times 10^{-4}$</td>
</tr>
<tr>
<td>$HNO_3 + hv \rightarrow OH + NO_2$</td>
<td>$5.72 \times 10^{-1}$</td>
</tr>
<tr>
<td>$HNO_2NO_2 + hv \rightarrow HNO_2 + NO_2$</td>
<td>$9.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>$CO_2 + hv \rightarrow CO + O$</td>
<td>$3.31 \times 10^{-7}$</td>
</tr>
<tr>
<td>$CO_2 + hv \rightarrow CO + O(1D)$</td>
<td>$5.68 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Other than the rate coefficient for $HNO + hv \rightarrow H + NO$, which was taken from Kasting and Walker (1981), these rate coefficients were computed by our model from the known photochemical cross-sections and the solar flux of the faint young Sun.
NO$_2$ + OH + M $\rightarrow$ HNO$_3$ + M, \hspace{1cm} (R1)

is stifled in the troposphere due to lack of OH. Although OH is being generated by water photolysis, it is also being consumed by the reaction

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \] \hspace{1cm} (R2)

at high rates due to the rapid photolysis of CO$_2$,

\[ \text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}. \] \hspace{1cm} (R3)

Thus, we have included the minor channel of HO$_2$ + NO (Butkovskaya et al., 2007) in our photochemical model:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \] major channel \hspace{1cm} (R4a);

\[ \text{HO}_2 + \text{NO} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \] minor channel \hspace{1cm} (R4b).

Though negligible when OH is plentiful and R1 is efficient, we find that this new pathway (R4b) dominates HNO$_3$ production on early Earth.

The measurements of the rate coefficient of reaction R4b (Butkovskaya et al. 2005, 2007, 2009) have not been reproduced by other groups. In their evaluations, Sander et al. (2003) declined to make a recommendation for a preferred
4. Oceanic Concentration of NOx

After raining out, HNO will yield nitrate and nitrite via the following aqueous reactions (Summers and Khare, 2007):

\[ \text{HNO} \rightarrow \text{H}^+ + \text{NO}^- \]
\[ \text{NO}^- + \text{NO} \rightarrow \text{N}_2\text{O}_2^- \]
\[ \text{N}_2\text{O}_2^- + \text{NO} \rightarrow \text{N}_3\text{O}_3^- \]
\[ \text{N}_4\text{O}_8^- \rightarrow \text{NO}_3^- + \text{NO}_2^- + \text{N}_2\text{O}. \]

HNO and HNO₂ simply dissociate into H⁺ and NO₃⁻ or NO₂⁻, respectively. H₂O₂NO₂ will deoxygenate rapidly, producing nitrite:

\[ \text{HOONO}_2 \rightarrow \text{HOO}^+ + \text{NO}_2^- \rightarrow \text{H}^+ + \text{O}_2 + \text{NO}_2^- . \]

If the ocean reservoir has no sink for nitrate or nitrite, and assuming that every dissolved HNO molecule eventually contributes a nitrate or nitrite, it would take 48, 0.017, and 0.058 Myr in the 0.1-, 1-, and 10-bar pCO₂ cases, respectively, to build up to \( \mu M \) concentrations in the Hadean ocean (taking the Hadean ocean volume to be \( 3 \times 10^{18} \) m³ in volume). The timescales for the 1- and 10-bar cases—merely blinks of an eye geologically speaking—reveal that a thick, CO₂-dominated Hadean atmosphere was quite efficient at pumping nitrogen oxides into the ocean. Even the rainout in the 0.1-bar case is not insignificant. However, to better address the possibility that nitrate played an important role as an electron acceptor for denitrifying methanotrophic acetogenesis, we should consider other nitrate loss mechanisms (aside from those directly involved in this metabolic pathway), and we should solve for the equilibrium concentration of nitrate in the Hadean ocean.

\[ \text{NO}_3^- \] is a primary nutrient for life in today’s oceans; it is consumed as a source of nitrogen by some organisms and respired (denitrified to N₂) by others. However, these powerful biological sinks were, of course, completely absent before the emergence of life. Instead, we must examine abiotic processes to characterize the most effective nitrate sinks.

The Hadean ocean is expected to have had dissolved Fe²⁺, which is known to originate at hydrothermal systems, and which can be oxidized to Fe⁴⁺. However, we consider Fe⁴⁺ to be inefficient at reducing nitrate or nitrite, because on present-day Earth, where there is an abundance of nitrate and nitrite, dissolved ferrous iron is able to traverse thousands of kilometers from its origin at hydrothermal vent sites to scientific sampling stations without trouble (Fitzsimmons et al., 2014).

Summers (2005) showed experimentally that FeS suspensions can reduce nitrite to ammonium in Hadean ocean environments. Nitrate can also be reduced to ammonium, but at a significantly lower yield. Summers (2005) could not reduce nitrate to ammonium at pH > 6.9, indicating that nitrate is probably not reduced by iron sulfide in great amounts by this process at alkaline hydrothermal vents. Further, nitrate is not readily reduced to ammonium in the presence of other species such as Cl⁻ and SO₄²⁻. We expect such anions to be dissolved in the Hadean ocean, making nitrate reduction by FeS insignificant.

Aqueous photochemistry at the ocean surface is capable of converting nitrate into nitrite and vice versa (Mack and Bolton, 1999), but because both species can serve as electron acceptors, this would not present a problem for the emergence of life. Because this photochemistry only affects a tiny fraction of the ocean, the nitrate lost to nitrite in this manner, which can then be reduced by FeS, is negligible in the present context.

Thus, we consider the dominant NOx loss mechanism to be extreme heating (~400°C) as ocean water cycles through acidic hydrothermal vents. At such high temperatures, nitrate and nitrite would be reduced back to N₂ by iron minerals within the crust. There may also be some reduction of nitrate in the water cycling by moderate-temperature, serpentinitization-driven alkaline springs, though the product in this case is likely to be ammonia, thus merely adding to that entity at alkaline vents (Gordon et al., 2013).

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**Table 4. A Summary of the Results of the Three Cases: 0.1, 1, and 10 Bars of CO₂**

<table>
<thead>
<tr>
<th>( p\text{CO}_2 ) (bar)</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{surf}} ) (K)</td>
<td>280.4</td>
<td>332.8</td>
<td>388.1</td>
</tr>
<tr>
<td>Lightning flash rate (flashes km⁻² year⁻¹)</td>
<td>0.41</td>
<td>9.3</td>
<td>3.1</td>
</tr>
<tr>
<td>NO flux (molecules cm⁻² s⁻¹)</td>
<td>( 6.5 \times 10^6 )</td>
<td>( 1.7 \times 10^9 )</td>
<td>( 5.6 \times 10^8 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 ) rain (molecules cm⁻² s⁻¹)</td>
<td>( 5.1 \times 10^2 )</td>
<td>( 2.8 \times 10^5 )</td>
<td>( 6.5 \times 10^2 )</td>
</tr>
<tr>
<td>HNO rain (molecules cm⁻² s⁻¹)</td>
<td>( 1.4 \times 10^5 )</td>
<td>( 2.8 \times 10^5 )</td>
<td>( 9.9 \times 10^4 )</td>
</tr>
<tr>
<td>HNO₂ rain (molecules cm⁻² s⁻¹)</td>
<td>( 7.8 \times 10^5 )</td>
<td>( 9.3 \times 10^4 )</td>
<td>( 1.7 \times 10^5 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_3 )NO rain (molecules cm⁻² s⁻¹)</td>
<td>( 3.1 \times 10^4 )</td>
<td>( 1.8 \times 10^4 )</td>
<td>( 1.0 \times 10^4 )</td>
</tr>
<tr>
<td>Total NOx rain (molecules cm⁻² s⁻¹)</td>
<td>( 2.4 \times 10^5 )</td>
<td>( 2.4 \times 10^6 )</td>
<td>( 1.9 \times 10^6 )</td>
</tr>
<tr>
<td>Time (Myr) to ( \mu M ) concentrations of NOx if no sinks</td>
<td>48</td>
<td>0.017</td>
<td>0.058</td>
</tr>
<tr>
<td>Equilibrium concentration (( \mu M )) of NOx assuming present-day hydrothermal circulation</td>
<td>8.7</td>
<td>( 2.4 \times 10^4 )</td>
<td>( 7.2 \times 10^3 )</td>
</tr>
</tbody>
</table>

Surface temperatures and the lightning flash rates were calculated by using the Generic LMDZ 3D global climate model for early Earth. The NO fluxes were evaluated by using data presented in Figure 2. The rainout fluxes were calculated by using the Caltech/JPL 1D photochemical model. The equilibrium concentration was calculated by using the simple box model discussed in the text and represented in Figure 6.
NOx in Early Earth’s Atmosphere

The primary source of acid rain from high-temperature vents is 7.2 cm3 atmosphere for a large range of pCO2. That there was a prevalence of NOx produced in the Hadean is uncertain and likely varied widely. We have demonstrated, using atmospheric models supported by data, that there was a prevalence of NOx produced in the Hadean atmosphere for a large range of pCO2. This NOx rained out into the Hadean ocean primarily as HNO3, which reacted to form nitrate and nitrite in solution. Although the 10-bar pCO2 case probably only applies to the first few 10 s Myr of Earth’s history, it still produced significant amounts of NOx. As the pCO2 settled around the 0.1–1 bar for the long term, copious NOx was also being delivered to the Hadean ocean. If the water flux through high-temperature hydrothermal vents was not more than thousands of times what it is today, the steady-state nitrate concentration would be micromolar, supplying onsite electron acceptors and a potential amino source at the emergence of life.

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**Abbreviations Used**

GCM = global climate models

NOx = nitrogen oxide