

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

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## Abstract

We quantify the amount of nitrogen oxides (NO<sub>x</sub>) 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 (NO<sub>3</sub><sup>−</sup>) and nitrite (NO<sub>2</sub><sup>−</sup>) 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 CO<sub>2</sub> and N<sub>2</sub>, will produce nitric oxide (NO) when shocked by lightning. Photochemical reactions involving NO and H<sub>2</sub>O vapor will then produce acids such as HNO, HNO<sub>2</sub>, HNO<sub>3</sub>, and HO<sub>2</sub>NO<sub>2</sub> 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 NO<sub>x</sub> to the Hadean ocean. In our 0.1-, 1-, and 10-bar pCO<sub>2</sub> models, we calculate the NO<sub>x</sub> delivery to be  $2.4 \times 10^5$ ,  $6.5 \times 10^8$ , and  $1.9 \times 10^8$  molecules cm<sup>−2</sup> s<sup>−1</sup>. After only tens of thousands to tens of millions of years, these NO<sub>x</sub> 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, 975–983.

## 1. Introduction

NITROGEN OXIDES (NO<sub>x</sub>)—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 (NO<sub>3</sub><sup>−</sup>) and nitrite (NO<sub>2</sub><sup>−</sup>) could conceivably have initiated the first metabolic pathway through the oxidation of hydrothermal CH<sub>4</sub> and the concomitant hydrogenation of CO<sub>2</sub> at ancient submarine alkaline hydrothermal vents (Ducluzau *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)<sub>2</sub>) 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<sup>II</sup><sub>4</sub>Fe<sup>III</sup><sub>2</sub>(OH)<sub>12</sub>[CO<sub>3</sub>]•3H<sub>2</sub>O) along with the iron sulfides mackinawite and greigite, dosed with nickel, cobalt, and molybdenum (Russell and Hall, 1997; Génin *et al.*, 2005, 2006; Młoszewska *et al.*, 2012; Nitschke and Russell, 2013; Russell *et al.*, 2014; White *et al.*, 2015; Tosca *et al.*, 2016; Halevy *et al.*, 2017).

Electro-geochemical gradients would have been imposed across inorganic precipitates between the mildly acidic, CO<sub>2</sub>-rich Hadean seawater and the alkaline hydrothermal fluid laden with H<sub>2</sub> and CH<sub>4</sub>, products of serpentinization and hydrothermal leaching, respectively (Russell *et al.*, 1989;

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TABLE 1. ALKALINE (E.G., LOST CITY) VERSUS ACIDIC (“BLACK SMOKER”) HYDROTHERMAL VENTS

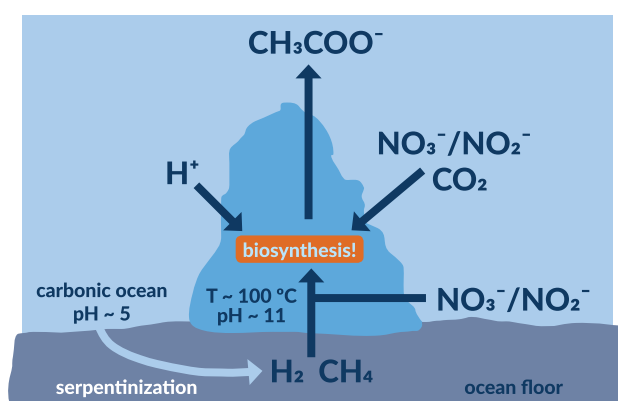
Acidic vents	Alkaline vents
Ocean ridge	Off ridge, peridotite hosted
Driven by magmatic intrusion	Driven by exothermic serpentinization
T ~ 400°C	T ~ 130°C
pH ~ 3	pH ~ 11

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-geochemical 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).

Barge *et al.*, 2015). Nitschke and Russell (2013) suggested that the first carbon fixation pathway operated through the process of denitrifying methanotrophic acetogenesis—a putative variant of the ancient acetyl-coenzyme A pathway still used by anaerobic microbes—in which  $H_2$  reduces  $CO_2$  to CO, and  $CH_4$  is oxidized through methanol to a methylene entity before being reduced and thiolated to give  $CH_3SH$ . The CO and  $CH_3SH$  react on an iron-nickel sulfide to produce activated acetate (Huber and Wächtershäuser, 1997). Thereafter, more complex biomolecules are formed through a series of hydrogenations, carboxylations, aminations, and condensations (Huber and Wächtershäuser, 2003; Kawamura *et al.*, 2011). The eventual waste product is acetate ( $CH_3COO^-$ ) (Russell and Martin, 2004).

However, this scheme cannot proceed unassisted;  $CH_4$  and  $CO_2$  are each notoriously unreactive molecules. The high-potential electron acceptors nitrate and/or nitrite perform two crucial roles in the earliest carbon fixation engines of life by providing the following: (1) The required extra disequilibrium to activate  $CH_4$ , which is converted into methanol as nitrate/nitrite, is re-reduced to nitric oxide (NO) (Nitschke and Russell, 2013) and (2) redox bifurcate electrons by coupling the acceptance of one of two outer shell molybdenum electrons, as the other reduces the low-potential electron acceptor  $CO_2$  to CO (Schoepp-Cothenet *et al.*, 2012; Nitschke and Russell, 2013; Helz *et al.*, 2014) (Fig. 1).

In addition, nitrate and/or nitrite represent a form of fixed nitrogen that could have been reduced to ammonium for proto-biosynthesis in the otherwise inorganic membranes surrounding compartments in the Hadean hydrothermal mound. In the interlayers of green rust, carbonate, sulfide, and chloride are stable as intercalates, but nitrate and nitrite are reduced to ammonium ( $NH_4^+$ ) in a matter of hours (Hansen *et al.*, 2001; Trolard and Bourrié, 2012). Ammonium is a key ingredient for building amino acids from  $\alpha$ -carboxylic acids in the presence of mixed ferrous-ferric hydroxides—which are critical for turning a primitive metabolic pathway into a ligand-accelerated autocatalytic system (Huber and Wächtershäuser, 2003; Milner-White and Russell, 2008; Russell *et al.*, 2014; White *et al.*, 2015). For example, pyruvate, in the presence of  $NH_4^+$ , can be aminated to alanine (Huber and Wächtershäuser, 2003). Alanine could then have condensed to a 5-mer peptide on carbonate surfaces in the mound (Ka-



**FIG. 1.** The first metabolic engines would have “burned” hydrothermal fuels  $H_2$  and  $CH_4$  with the  $NO_3^-$ ,  $NO_2^-$ , and  $CO_2$  found in early Earth’s carbonic ocean (Branscomb and Russell, 2013; Nitschke and Russell, 2013). Nitrate and/or nitrite would be necessary to reduce  $CO_2$  to CO and oxidize  $CH_4$  to a methyl group. An excess of  $H^+$  outside of the chimney produces a steep pH gradient—a natural proton motive force with the same directionality as the proton motive force driving metabolic pathways and cycles operating universally across biology to this day. Color images available online at [www.liebertpub.com/ast](http://www.liebertpub.com/ast)

wamura *et al.*, 2011). 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; Bianchi *et al.*, 2012). 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 ~14 h 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).

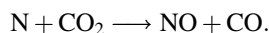
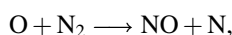
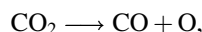
Although geochemical evidence points to an atmosphere dominated by  $CO_2$  and  $N_2$ , it is still uncertain how massive the atmosphere was. Indeed, it is likely to have varied greatly during the Hadean eon under the vagaries of bolide collisions, mantle convective overturn, and accompanying tectonics. After the magma ocean phase and the condensation of ocean, the Earth’s atmosphere was likely composed of around 50 bars of  $CO_2$ . This pressure decreased quickly with the formation of carbonates at the seafloor. Sleep *et al.* (2001) estimated that the partial pressure of  $CO_2$  ( $pCO_2$ ) 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 NO<sub>x</sub> on the early Earth, we must address a wide range of atmospheric pressures. In this study, we test CO<sub>2</sub> partial pressures of 0.1, 1, and 10 bars, complemented by 1 to 2 bars of N<sub>2</sub>.

## 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<sup>8</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>. In the anoxic early atmosphere, electrical discharges would have heated air temperatures to tens of thousands of kelvin and incited the normally unreactive molecules CO<sub>2</sub> and N<sub>2</sub> to react. Electrical-discharge events shatter the robust covalent double bonds of CO<sub>2</sub>, splitting CO<sub>2</sub> into CO and O. The highly reactive O radical breaks N<sub>2</sub>'s triple bond, producing NO and N. The N radical then goes on to react with another CO<sub>2</sub> molecule, creating CO and even more NO (Nna Mvondo *et al.*, 2001; Ducluzeau *et al.*, 2009). The process can be summarized as follows:



This lightning-induced NO is the fundamental source of all higher-order NO<sub>x</sub> generated by photochemistry.

To estimate the amount of lightning-induced NO in the Hadean, we must first estimate the amount of lightning in the Hadean. Roms *et al.* (2014) derived the most accurate 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<sup>-2</sup> s<sup>-1</sup>),  $P$  is the precipitation rate (kg m<sup>-2</sup> s<sup>-1</sup>), 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<sup>-1</sup>. 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<sup>-2</sup> year<sup>-1</sup>) 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

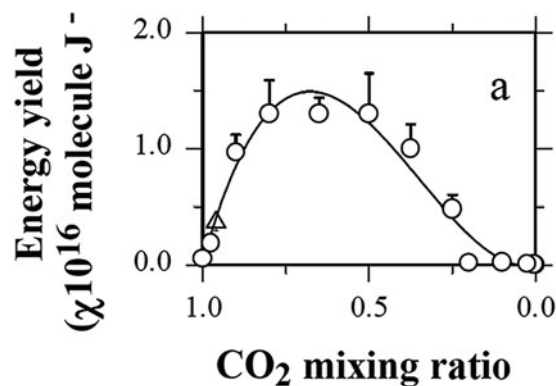
lower atmosphere, volatile condensation in the atmosphere and surface, a 2-layer dynamic ocean, and surface and subsurface thermal balance. It has been used to great effect in studies of other planetary scenarios, including Archean Earth (Charnay *et al.*, 2013), early Mars (Forget *et al.*, 2013), and even terrestrial-mass exoplanets (Wordsworth *et al.*, 2011).

The computed lightning flash rates are 0.41, 9.3, and 3.1 flashes km<sup>-2</sup> year<sup>-1</sup> for the 0.1-, 1-, and 10-bar pCO<sub>2</sub> 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 (Roms *et al.*, 2014). As expected, our model produces a higher lightning flash rate for the 1-bar pCO<sub>2</sub> case (mean surface temperature of 332.8 K) than for the 0.1-bar pCO<sub>2</sub> case (280.4 K). Surprisingly, the 10-bar pCO<sub>2</sub> (388.1 K) case has a lower flash rate than the 1-bar pCO<sub>2</sub> case. The 10-bar pCO<sub>2</sub> case features the warmest troposphere. Hence, the lower atmosphere is rich in water vapor, making it extremely opaque (only 7 W/m<sup>2</sup> 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 CO<sub>2</sub>/N<sub>2</sub> mixtures (Nna Mvondo *et al.*, 2001) (reproduced in Fig. 2), and  $E \sim 5 \times 10^9$  J flash<sup>-1</sup>, we are able to calculate a lightning-induced NO flux for each pCO<sub>2</sub> (Tables 2 and 3).

## 3. Photochemical Production of NO<sub>x</sub>

To evaluate the production of NO<sub>x</sub> species in the Hadean atmosphere, we adapt the 1D Caltech/JPL chemical transport model (Allen *et al.*, 1981) to simulate the Hadean Earth.



**FIG. 2.** A reproduction of Figure 1a from Nna Mvondo *et al.* (2001) showing the NO yield per J of lightning for various mixtures of CO<sub>2</sub> and N<sub>2</sub>. The circles are Nna Mvondo's data points; the triangle is an experimental result from Venusian lightning (Levine *et al.*, 1982) for comparison. After calculating lightning flash rates for our 0.1-, 1-, and 10-bar pCO<sub>2</sub> cases, we use this plot to evaluate the lightning-generated NO flux in the troposphere for each case. Although we take this data as ground truth for our study, we hope that future work (either experimental or theoretical) will confirm, or otherwise, the results in this plot.

TABLE 2. ADDITIONAL REACTIONS INVOLVING HNO AND HNO<sub>3</sub>, AND THEIR CORRESPONDING RATE COEFFICIENTS, TO THE NAIR *ET AL.* (1994) MODEL

Reaction	Rate constant <i>k</i>	Reference
H + NO + M → HNO + M	$2.1 \times 10^{-32} e^{300/T}$	Hampson and Garvin (1977)
H + HNO → H <sub>2</sub> + NO	$7 \times 10^{-12}$	Hampson and Garvin (1977)
OH + HNO → H <sub>2</sub> O + NO	$8 \times 10^{-11} e^{-500/T}$	Tsang and Herron (1991)
HO <sub>2</sub> + NO + M → HNO <sub>3</sub> + M	$3.5 \times 10^{-14} e^{250/T}$	Butkovskaya <i>et al.</i> (2007)

The units for two-body and three-body reactions are cm<sup>3</sup> s<sup>-1</sup> and cm<sup>6</sup> s<sup>-1</sup>, respectively.

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

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

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

TABLE 3. UPDATED NAIR *ET AL.* (1994) PHOTOLYSIS RATE COEFFICIENTS AT THE TOP OF THE ATMOSPHERE

Reaction	Photolysis rate coefficient at 100 km (s <sup>-1</sup> )
O <sub>2</sub> + <i>hν</i> → O + O	$2.71 \times 10^{-6}$
O <sub>2</sub> + <i>hν</i> → O + O( <sup>1</sup> D)	$1.10 \times 10^{-5}$
O <sub>3</sub> + <i>hν</i> → O <sub>2</sub> + O	$3.68 \times 10^{-4}$
O <sub>3</sub> + <i>hν</i> → O <sub>2</sub> + O( <sup>1</sup> D)	$9.16 \times 10^{-7}$
H <sub>2</sub> O + <i>hν</i> → H + OH	$3.03 \times 10^{-5}$
NO + <i>hν</i> → N + O	$3.50 \times 10^{-6}$
NO <sub>2</sub> + <i>hν</i> → NO + O	$2.74 \times 10^{-3}$
NO <sub>3</sub> + <i>hν</i> → NO <sub>2</sub> + O	$5.26 \times 10^{-2}$
NO <sub>3</sub> + <i>hν</i> → NO + O <sub>2</sub>	$7.63 \times 10^{-3}$
N <sub>2</sub> O + <i>hν</i> → N <sub>2</sub> + O( <sup>1</sup> D)	$1.33 \times 10^{-5}$
HNO + <i>hν</i> → H + NO	$1.70 \times 10^{-3}$
HNO <sub>2</sub> + <i>hν</i> → OH + NO	$6.04 \times 10^{-4}$
HNO <sub>3</sub> + <i>hν</i> → OH + NO <sub>2</sub>	$5.72 \times 10^{-5}$
HO <sub>2</sub> NO <sub>2</sub> + <i>hν</i> → HO <sub>2</sub> + NO <sub>2</sub>	$9.59 \times 10^{-5}$
CO <sub>2</sub> + <i>hν</i> → CO + O	$3.31 \times 10^{-7}$
CO <sub>2</sub> + <i>hν</i> → CO + O( <sup>1</sup> D)	$5.68 \times 10^{-7}$

Other than the rate coefficient for HNO + *hν* → 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.

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<sub>2</sub> mixing ratio of  $1 \times 10^{-3}$ , corresponding to a volcanically active, weakly reduced early Earth (Kasting, 1993).

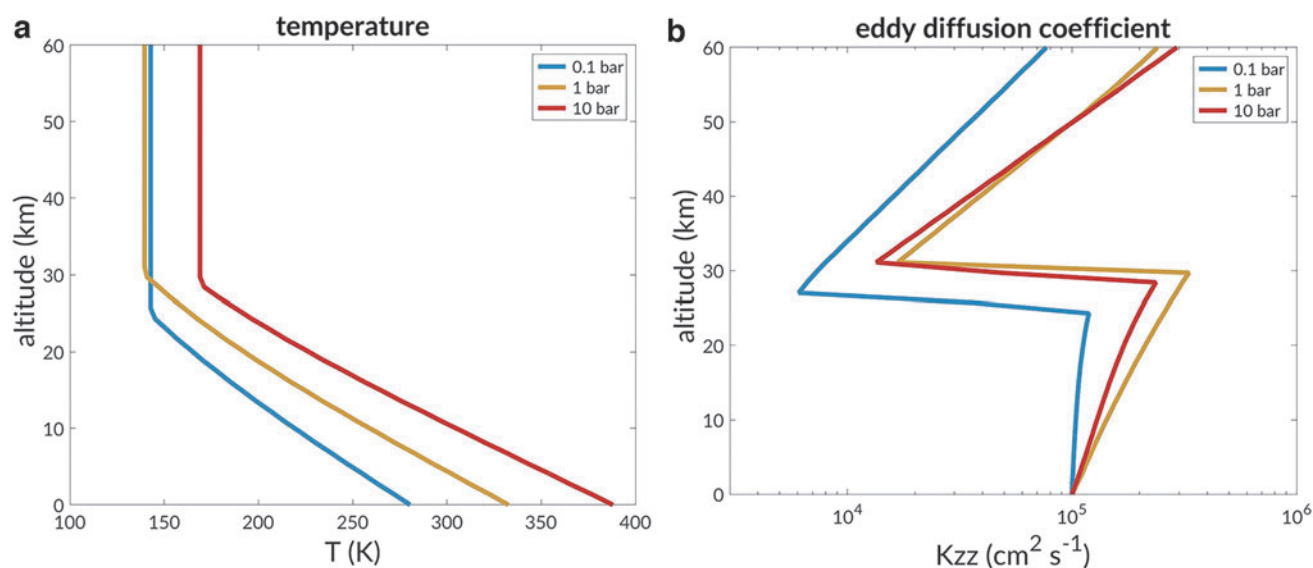
The bulk of our photochemical scheme is based on the Nair *et al.* (1994) model for Mars's CO<sub>2</sub>-N<sub>2</sub> atmosphere, updated to include HNO and a new formation pathway for HNO<sub>3</sub> (discussed later in this section). The additional reactions are listed in Table 2. Unlike the Nair *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<sub>2</sub>, NO<sub>x</sub>, and N<sub>2</sub>O in the 1-bar pCO<sub>2</sub> case are presented in Figure 4.

The rainout rates for various electron acceptors are summarized in Figure 5 and Table 4. Among the NO<sub>x</sub> species, in all three cases, the flux of HNO rain is the highest, followed by HNO<sub>3</sub>, HO<sub>2</sub>NO<sub>2</sub>, and HNO<sub>2</sub>. Across all species, the highest rainout rate is produced in the 1-bar pCO<sub>2</sub> case. The total amount of NO<sub>x</sub> rained out into the Hadean ocean is  $2.4 \times 10^5$ ,  $6.5 \times 10^8$ , and  $1.9 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup> for the 0.1-, 1-, and 10-bar pCO<sub>2</sub> cases, respectively.

The rainout rate of H<sub>2</sub>O<sub>2</sub>, another effective electron acceptor that is generated on early Earth, is quoted for comparison. In the 0.1-bar pCO<sub>2</sub> case, H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> increases but the surface mixing ratio of H<sub>2</sub> remains constant. Although H<sub>2</sub>O<sub>2</sub> should be considered a possible electron acceptor for early metabolisms, it was by no means the dominantly available species.

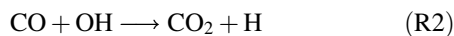
Our models reveal that HNO<sub>3</sub> rainout is one of the primary sources of high-potential electron acceptors in the early ocean, eclipsing both HNO<sub>2</sub> and HO<sub>2</sub>NO<sub>2</sub> rainout in all three cases. The normal pathway for generating HNO<sub>3</sub>,



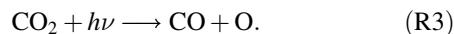
**FIG. 3.** (a) The atmospheric temperature profiles of the 0.1-, 1-, and 10-bar pCO<sub>2</sub> cases. (b) The eddy diffusion coefficient profiles of the 0.1-, 1-, and 10-bar pCO<sub>2</sub> cases, calculated by using Eq. 5 of Ackerman and Marley (2001), starting from an assumed surface value of  $1 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ . The inversion feature exhibited by all three cases corresponds to the location of the tropopause, as defined by the temperature profile. Color images available online at [www.liebertpub.com/ast](http://www.liebertpub.com/ast)



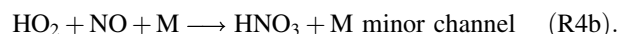
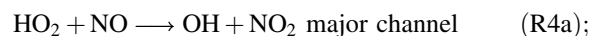
is stifled in the troposphere due to lack of OH. Although OH is being generated by water photolysis, it is also being consumed by the reaction



at high rates due to the rapid photolysis of CO<sub>2</sub>,

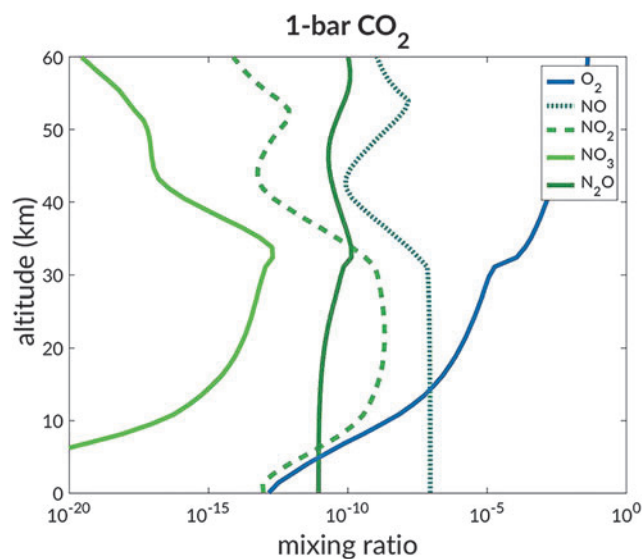


Thus, we have included the minor channel of HO<sub>2</sub> + NO (Butkovskaya *et al.*, 2007) in our photochemical model:

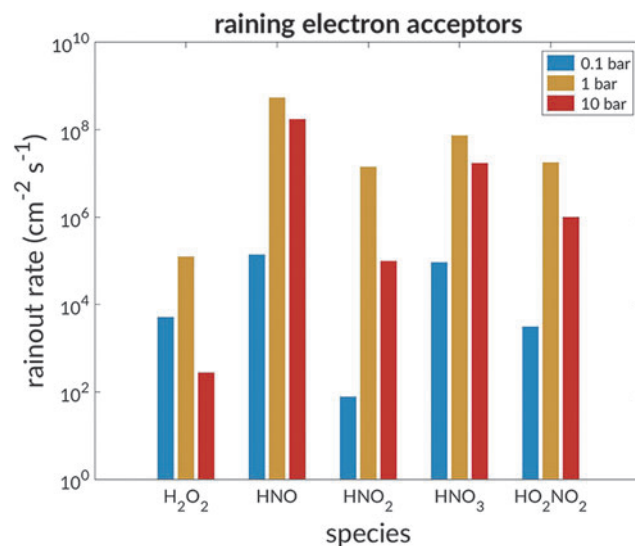


Though negligible when OH is plentiful and R1 is efficient, we find that this new pathway (R4b) dominates HNO<sub>3</sub> production on early Earth.

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



**FIG. 4.** The mixing ratio profiles of O<sub>2</sub>, NO<sub>x</sub>, and N<sub>2</sub>O for the 1-bar pCO<sub>2</sub> case. Color images available online at [www.liebertpub.com/ast](http://www.liebertpub.com/ast)



**FIG. 5.** The rainout rates of prospective electron acceptors for the emergence of life across all three atmospheric models. In every atmosphere tested, HNO is the dominant precipitate. For all species, the 1-bar pCO<sub>2</sub> case returns the maximum rainout rate. Color images available online at [www.liebertpub.com/ast](http://www.liebertpub.com/ast)

TABLE 4. A SUMMARY OF THE RESULTS OF THE THREE CASES: 0.1, 1, AND 10 BARS OF CO<sub>2</sub>

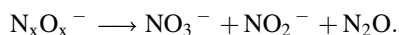
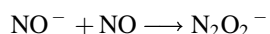
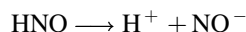
$p\text{CO}_2$ (bar)	0.1	1	10
$T_{\text{surf}}$ (K)	280.4	332.8	388.1
Lightning flash rate (flashes $\text{km}^{-2} \text{ year}^{-1}$ )	0.41	9.3	3.1
NO flux (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$6.5 \times 10^6$	$1.7 \times 10^9$	$5.6 \times 10^8$
H <sub>2</sub> O <sub>2</sub> rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$5.1 \times 10^3$	$1.3 \times 10^5$	$2.8 \times 10^2$
HNO rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$1.4 \times 10^5$	$5.5 \times 10^8$	$1.8 \times 10^8$
HNO <sub>2</sub> rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$7.8 \times 10^1$	$1.4 \times 10^7$	$9.9 \times 10^4$
HNO <sub>3</sub> rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$9.3 \times 10^4$	$7.4 \times 10^7$	$1.7 \times 10^7$
HO <sub>2</sub> NO <sub>2</sub> rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$3.1 \times 10^3$	$1.8 \times 10^7$	$1.0 \times 10^6$
Total NO <sub>x</sub> rain (molecules $\text{cm}^{-2} \text{ s}^{-1}$ )	$2.4 \times 10^5$	$6.5 \times 10^8$	$1.9 \times 10^8$
Time (Myr) to $\mu\text{M}$ concentrations of NO <sub>x</sub> if no sinks	48	0.017	0.058
Equilibrium concentration ( $\mu\text{M}$ ) of NO <sub>x</sub> assuming present-day hydrothermal circulation	8.7	$2.4 \times 10^4$	$7.2 \times 10^3$

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.

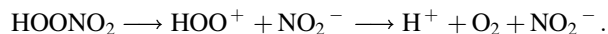
value. Recent experiments (Okumura, 2016, private communication) have indicated that the upper limit for the rate coefficient could be 2.5 times smaller than that reported in the previous work. Until further laboratory measurements are available, we warn that the production rate of HNO<sub>3</sub> in our models could be overestimated by a factor of  $\sim 3$ .

#### 4. Oceanic Concentration of NO<sub>x</sub>

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



HNO<sub>3</sub> and HNO<sub>2</sub> simply dissociate into H<sup>+</sup> and NO<sub>3</sub><sup>−</sup> or NO<sub>2</sub><sup>−</sup>, respectively. HO<sub>2</sub>NO<sub>2</sub> will deoxygenate rapidly, producing nitrite:



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 pCO<sub>2</sub> cases, respectively, to build up to  $\mu\text{M}$  concentrations in the Hadean ocean (taking the Hadean ocean volume to be  $3 \times 10^{18} \text{ m}^3$  in volume). The timescales for the 1- and 10-bar cases—merely blinks of an eye geologically speaking—reveal that a thick, CO<sub>2</sub>-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.

NO<sub>3</sub><sup>−</sup> 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 N<sub>2</sub>) 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.

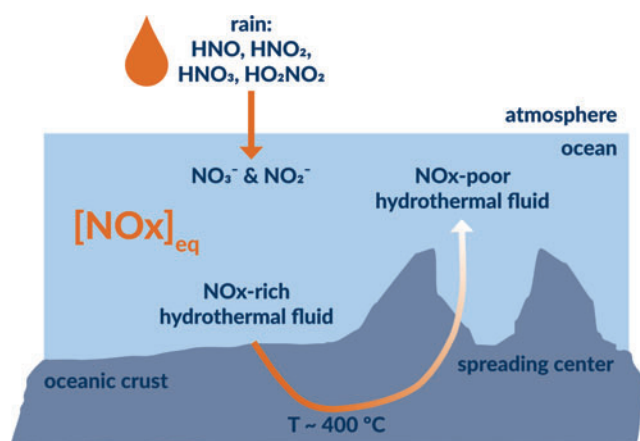
The Hadean ocean is expected to have had dissolved Fe<sup>2+</sup>, which is known to originate at hydrothermal systems, and which can be oxidized to Fe<sup>3+</sup>. However, we consider Fe<sup>2+</sup> to be inefficient at reducing nitrate or nitrite, because on present-day Earth, where there is an 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<sup>−</sup> and SO<sub>4</sub><sup>2−</sup>. 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 NO<sub>x</sub> loss mechanism to be extreme heating ( $\sim 400^\circ\text{C}$ ) as ocean water cycles through acidic hydrothermal vents. At such high temperatures, nitrate and nitrite would be reduced back to N<sub>2</sub> by iron minerals within the crust. There may also be some reduction of nitrate in the water cycling by moderate-temperature, serpentinization-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).





**FIG. 6.** A simple box model for calculating the equilibrium concentration of nitrate and nitrite in the Hadean ocean. We assume that the primary source is acid rain from the atmosphere and that the dominant sink is removal by extreme heating at high-temperature hydrothermal sites. Color images available online at [www.liebertpub.com/ast](http://www.liebertpub.com/ast)

We construct a simple box model to ascertain the equilibrium nitrate concentration (Fig. 6). Assuming 100% destruction of NO<sub>x</sub> at black-smoker temperatures, the equilibrium number concentration of NO<sub>x</sub> is

$$C_{\text{NO}_x} = \frac{f_{\text{atm}} A_{\oplus} \tau_{\text{HTV}}}{V_{\text{ocean}}},$$

where  $f_{\text{atm}}$  is the NO<sub>x</sub> flux from the atmosphere (molecules  $\text{cm}^{-2} \text{s}^{-1}$ ),  $A_{\oplus}$  is the surface area of the Earth ( $5.1 \times 10^{18} \text{ cm}^2$ ),  $\tau_{\text{HTV}}$  is the timescale for cycling through high-temperature vents, and  $V_{\text{ocean}}$  is the volume of the Hadean ocean ( $\sim 3 \times 10^{18} \text{ m}^3$ ). Because  $\tau_{\text{HTV}} = V_{\text{ocean}}/F_{\text{HTV}}$ , where  $F_{\text{HTV}}$  is the mass flux of water through high-temperature hydrothermal vents,

$$C_{\text{NO}_x} = \frac{f_{\text{atm}} A_{\oplus}}{F_{\text{HTV}}}.$$

According to Nielsen *et al.* (2006), the current water mass flux from high-temperature vents is  $7.2 \times 10^{12} \text{ kg year}^{-1}$ . Using this present-day value and  $f_{\text{atm}} \sim 6.5 \times 10^8 \text{ molecules cm}^{-2} \text{s}^{-1}$  (as in the 1-bar case), then  $C_{\text{NO}_x} = 24 \text{ mM}$ . Acidic vents were more prevalent in the Hadean, though by what degree is still unknown. However, unless the water flux through high-temperature vents was thousands of times as great as today, the equilibrium nitrate concentration would still exceed  $1 \mu\text{M}$ .

## 5. Conclusion

NO<sub>x</sub> are believed to be needed as high-potential electron acceptors for the emergence of metabolism at submarine alkaline hydrothermal vents. NO<sub>x</sub> are created in early Earth's CO<sub>2</sub>-N<sub>2</sub> atmosphere, but the atmospheric pressure during the Hadean is uncertain and likely varied widely. We have demonstrated, using atmospheric models supported by data, that there was a prevalence of NO<sub>x</sub> produced in the Hadean atmosphere for a large range of pCO<sub>2</sub>. This NO<sub>x</sub> rained out into the Hadean ocean primarily as HNO, which reacted to form nitrate and nitrite in solution. Although the 10-bar pCO<sub>2</sub>

case probably only applies to the first few 10 s Myr of Earth's history, it still produced significant amounts of NO<sub>x</sub>. As the pCO<sub>2</sub> settled around the 0.1–1 bar for the long term, copious NO<sub>x</sub> 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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## Author Disclosure Statement

No competing financial interests exist.

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#### Abbreviations Used

GCM = global climate models

NO<sub>x</sub> = nitrogen oxide