Fixation of Nitrogen in the Prebiotic Atmosphere

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Reports

Fixation of Nitrogen in the Prebiotic Atmosphere

Abstract. Reactions between nitrogen and water in the air surrounding lightning discharges can provide an important source of nitric oxide even under conditions where oxygen is a minor atmospheric constituent. Estimates are given for the associated source of soluble nitrate and nitrite. It is shown that lightning and subsequent atmospheric chemistry can provide a source of nitrate for the primitive ocean as large as 10^6 tons of nitrogen per year, sufficient to fill the ocean to its present level of nitrate in less than 10^5 years.

Nitrogen is often a limiting nutrient for life, despite its ubiquitous presence in air and water. It occurs in the atmosphere mainly as N₂, an inert gas that must be fixed or dissociated before it can be incorporated in living organisms. Fixation is to a large extent biologically mediated, with important contributions due to symbiotic bacteria and blue-green algae (1). Most of Earth's fixed nitrogen resides in the ocean as NO₃⁻. It is delivered to the ocean by rivers and by rain and is returned to the atmosphere (as N₄ and N₂O) in a variety of biologically mediated reactions. Biological reactions serve as both source and sink for fixed nitrogen in the present system.

In this report we attempt to identify processes that may have influenced fixation of nitrogen in the early prebiotic environment. We consider in particular the role of lightning. In the present atmosphere lightning is a source for NO (1-3) amounting to between 10^15 and 4 x 10^17 tons of N per year. The gas is formed by reactions

\[
\begin{align*}
O_3 &\rightarrow O + O_2 \\
O + N_2 &\rightarrow NO + N \\
N + O_3 &\rightarrow NO + O
\end{align*}
\]

(1)

that take place in the volume of high-temperature air near the lightning discharge. Temperatures are raised initially to values in excess of 30,000 K, but decrease rapidly due to expansion, radiation, and other means of heat exchange with the surrounding medium. The concentration of NO at temperatures above about 2000 K (3, 4) may be estimated from considerations of thermodynamic equilibrium. At lower temperatures the chemical time constant is long compared with the time required for the air parcel to cool toward ambient conditions, and NO is frozen in at an effective temperature of about 2000 K. Nitric oxide formed in lightning is converted photochemically in the ambient atmosphere to NO₂, HNO₂, and HNO₃ by reactions such as (5)

\[
\begin{align*}
NO + O_3 &\rightarrow NO_2 + O_2 \\
NO + HO_2 &\rightarrow NO_2 + OH \\
NO + OH + M &\rightarrow HNO_2 + M \\
NO_2 + OH + M &\rightarrow HNO_3 + M
\end{align*}
\]

(2)

These reactions are followed by dry and wet deposition of products, contributing ultimately to the fixed nitrogen pool of the hydrosphere and soil.

The abundance of O₃ was presumably low in the early prebiotic atmosphere.

Under such conditions, production of NO in lightning would have been dominated by reactions involving H₂O rather than O₃. At low concentrations of O₂ we must consider

\[
\begin{align*}
H_2O &\rightarrow OH + H \\
OH + OH &\rightarrow H_2O + O \\
O + N_2 &\rightarrow NO + N \\
N + OH &\rightarrow NO + H
\end{align*}
\]

(3)

in addition to reactions 1. As before, the concentration of NO tends to be frozen in at a temperature of about 2000 K (6). The concentration of NO decreases as the shock-heated air mass cools down, with a chemical time constant set mainly by

\[
\begin{align*}
NO + H &\rightarrow N + OH \\
NO + N &\rightarrow N_2 + O
\end{align*}
\]

(4)

in contrast to the high-oxygen case, for which

\[
\begin{align*}
NO + O &\rightarrow N + O_2 \\
NO + N &\rightarrow N_2 + O
\end{align*}
\]

(5)

play a determinative role (4). Figure 1 shows the source strength for NO that might be expected to arise as a function of the assumed oxygen concentration if the frequency of lightning in the low-oxygen atmosphere was similar to that observed today.

The ultimate yield of precipitable products, mainly HNO₂ and HNO₃, depends on the detailed chemistry of the ambient atmosphere. A summary of more important atmospheric reactions is given in Table 1. The reaction

\[
\begin{align*}
NO + hν &\rightarrow N + O
\end{align*}
\]

(6)

followed by

\[
\begin{align*}
NO + N &\rightarrow N_2 + O
\end{align*}
\]

(7)

represents the primary atmospheric sink for fixed nitrogen; it is most important at low concentrations of O₂, where the abundance of NO is largest, reflecting inefficient conversion of NO to NO₂, HNO₂, and HNO₃. However, absorption by water vapor molecules effectively shields NO from dissociation below the tropopause (7).

We consider three models, chosen to represent Earth at various stages of evolution. The gross composition of all three atmospheres is similar to what one might expect for the present atmosphere in the absence of biological perturbation. Nitrogen is the major constituent, followed by H₂O and CO₂ at concentrations similar to those in the present system (8).

In model A we assume a closed atmosphere with negligible import and export
Fig. 2. (a) Concentrations of H, OH, HO₂, O, and O₃ for model A. The temperature profile and abundances of N₂, H₂O, and CO are 5 x 10⁻⁶, 1 x 10⁻⁷, and 1 x 10⁻⁷, respectively. (b) Production and loss rates of H₂O and H₂ in model A.

of material through lower and upper boundaries. Water vapor is readily dissociated by sunlight shortward of 2400 Å

H₂O + hv → H + OH

(8)

Formation of H₂O proceeds primarily by

OH + H₂ → H₂O + H
OH + HO₂ → H₂O + O₂

(9)

Molecular oxygen and hydrogen are formed by reactions such as

O + OH → O₂ + H
H + HO₂ → H₂ + O₂
H + H + M → H₂ + M

(10)

and in steady state these gases attain mixing ratios of 5 x 10⁻⁸ and 1 x 10⁻⁷, respectively. Equilibrium is reached in less than 1 year, and mean concentrations of the more abundant radical species are shown in Fig. 2a. Production and loss rates for the major hydrogenic species H₂O and H₂ are given in Fig. 2b.

Model B describes a possible earlier phase of evolution in which degassing from a relatively reduced crust is taken to provide a surface input of H₂ (9) equal to 3 x 10⁶ ton/year (1 x 10⁶ atom/cm² sec). Hydrogen atoms escape from the exosphere at a rate exactly equal to the surface input, with escaping atoms supplied mainly by (10)

N₅⁺ + H₂ → N₅H⁺ + H
N₅H⁺ + e → N₅ + H

(11)

Mixing ratios for H₂ and O₂ are calculated as 1 x 10⁻⁵ and 2 x 10⁻¹², respectively, for model B. Concentrations of OH and HO₂ are low, of order 1 x 10⁸ cm⁻³. The assumption of a steady state requires that the concentration of O₂ be exceedingly low in model B. Higher levels of O₂ would result in rapid conversion of H₂ to H₂O. The escape rate for hydrogen would be lowered accordingly, and water would accumulate in the ocean until the mixing ratio for O₂ was restored to its equilibrium value, 2 x 10⁻⁷.

Model C describes a possible later phase in atmospheric evolution when the mixing ratio for O₂ has risen to 1 x 10⁻⁷.

due, for example, to the influence of photosynthesis. This model describes a quasi-steady state with the level of O₂ constrained as given. Input of H₂ at the surface is assumed to balance escape of H from the exosphere, and the level of O₂ is maintained solely by atmospheric photochemistry. This model yields a

Table 1. Reactions and rate constants for the primitive terrestrial atmosphere. Rate constants for two-body and three-body reactions are denoted by k and have units cm³ sec⁻¹ and cm⁶ sec⁻³, respectively. Mean dissociation rates are denoted by J and have units sec⁻¹; numerical values refer to the optically thin regime (13).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + hv → O + O</td>
<td>J₁ = 1.3 x 10⁻⁶</td>
</tr>
<tr>
<td>O₃ + hv → O₂ + O</td>
<td>J₂ = 4.8 x 10⁻⁶</td>
</tr>
<tr>
<td>H₂O + hv → OH + H</td>
<td>J₃ = 3.2 x 10⁻⁶</td>
</tr>
<tr>
<td>H₂O + hv → OH + OH</td>
<td>J₄ = 5.7 x 10⁻⁶</td>
</tr>
<tr>
<td>H₂O + hv → CO + O</td>
<td>J₅ = 4.7 x 10⁻⁷</td>
</tr>
<tr>
<td>NO + hv → N + O</td>
<td>J₆ = 2.7 x 10⁻⁷</td>
</tr>
<tr>
<td>HNO₃ + hv → OH + NO</td>
<td>J₇ = 1.0 x 10⁻⁷</td>
</tr>
<tr>
<td>HNO₂ + hv → NO₂ + OH</td>
<td>J₈ = 6.0 x 10⁻⁷</td>
</tr>
<tr>
<td>NO₂ + hv → NO + O</td>
<td>J₉ = 3.5 x 10⁻⁷</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁ = 1.1 x 10⁻₃ exp (520/T)</td>
</tr>
<tr>
<td>O + O₂ + M → O₂ + M</td>
<td>k₂ = 1.5 x 10⁻⁴ exp (-210/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₃ = 2.0 x 10⁻⁴ exp (710/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₄ = 1.3 x 10⁻⁴ exp (-956/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₅ = 1.3 x 10⁻⁴ exp (-1875/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₆ = 1.4 x 10⁻⁴ exp (-300/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₇ = 8.0 x 10⁻⁴ exp (-500/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₈ = 2.6 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₉ = 1.8 x 10⁻⁴ exp (340/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₀ = 5.0 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₁ = 3.0 x 10⁻⁴ exp (-330/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₂ = 1.0 x 10⁻⁴ exp (-330/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₃ = 8.3 x 10⁻⁴ exp (-500/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₄ = 1.0 x 10⁻⁴ exp (-500/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₅ = 4.1 x 10⁻⁴ exp (-600/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₆ = 1.1 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₇ = 2.6 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₈ = 1.8 x 10⁻⁴ exp (-2350/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₁₉ = 2.1 x 10⁻⁴ exp (-115/T)</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₂₀ = 2.2 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₂₁ = 8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₂₂ = 7.0 x 10⁻⁴</td>
</tr>
<tr>
<td>O + O₂ → O₃ + M</td>
<td>k₂₃ = 1.0 x 10⁻⁴</td>
</tr>
</tbody>
</table>

*See expression in Hudson (4).
mixing ratio for $H_2$ equal to $1 \times 10^{-5}$, with an escape rate for $H_2$ equal to $1 \times 10^{-5}$ atom/cm$^2$-sec. Higher concentrations of $O_2$ would imply net conversion of $H_2$ and $O_2$ to $H_2O$ and would require an additional source for $O_2$ of order $10^{10}$ g/year, which could in principle be supplied by photosynthesis followed by burial of organic material. We must note, however, that the photosynthetic chemical state represented by model C is established exceedingly rapidly, on a time scale of less than 1 year. Photosynthesis with associated burial of organic carbon would cause a relatively slow rise in $O_2$. Model C indicates that the concentration of atmospheric $H_2O$ should respond immediately to changes in $O_2$. Concentrations of $OH$ and $H_2O$ are large, of order $10^8$ and $10^9$ cm$^{-3}$, respectively.

Nitrogen fixed by lightning in models A and C is rapidly converted to $HNO_3$ and is removed from the atmosphere by both dry and wet deposition, contributing ultimately to the reservoir of oceanic $NO_3^-$. The composition of fixed nitrogen in rain is dominated by $HNO_3$ as long as the mixing ratio for $O_2$ exceeds $10^{-11}$. In model B, with the mixing ratio for $O_2$ equal to $2 \times 10^{-11}$, approximately 10 percent of the nitrogen fixed in lightning is converted to $HNO_3$. Even under these relatively extreme conditions, nitrate should be a significant end product. Indeed, source rates for nitrate as estimated here would imply that the primitive ocean could acquire an abundance of $NO_3^-$ similar to that observed today on a time scale as short as 100 years (11). Under these circumstances one would not expect availability of fixed nitrogen to pose any serious limitation for the evolution of life on Earth (12).

The chemical processes discussed here suggest that the combination of lightning and subsequent photochemistry could result in steady removal from the atmosphere of soluble oxidized gases such as $HNO_3$ and $HNO_2$. There should be a corresponding source of reduced atmospheric species such as $N_2$. The almost inevitable segregation of reduced and oxidized compounds between atmosphere and ocean could have implications for the emergence of primitive biology and should be considered in more complete models for atmospheric evolution.

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Observations of Hydrogen at Room Temperature (25°C) and High Pressure (500 Kilobars)

Abstract. Hydrogen becomes a solid at 25°C when subjected to a pressure of 57 kilobars. The high-pressure phase appears as a transparent crystalline mass. The refractive index of the high-pressure phase increases sharply with pressure, indicating a density increase of similar magnitude. At 350 kilobars the calculated density of the high-pressure phase is 0.6 to 0.7 grams per cubic centimeter.

When sufficient pressure is exerted on nitrogen or argon a liquid and then a solid appears even at room temperature. Thus, at some pressure one might expect hydrogen to solidify at room temperature. Furthermore, it has been suggested that all matter would become metallic under extreme pressure. Is it possible to make metallic hydrogen? Some theoretical studies (1) answer this question affirmatively. However, experimental difficulties must be overcome before observations can be made to test this hypothesis. First, there is the problem of containing a sufficient volume of hydrogen that must ultimately be brought to what, for hydrogen, is a relatively high density. Then one must be able to exert on the hydrogen enormous pressures that are accurately known. Finally, one must be able to observe the pressure effects directly or indirectly. In the present study, experiments were designed to seal liquefied hydrogen in a precision cell at cryogenic temperatures and afterward remove the cell from the assembly and

References and Notes
4. For thermodynamic calculations we used a computer code given by W. B. White, S. M. Johnston, and G. B. Dantzig (J. Comput. Phys. 26, 751 (1983)). Thermodynamic data were taken from JANAF Thermodynamic Tables 1969 (B. G. 168376, Dow Chemical Co., Midland, Mich., 1965). In a typical calculation, we assumed a volume of air composed mainly of $N_2$, with about 2 percent $H_2O$ and 0.03 percent $CO_2$. The equilibrium composition at 2500 K, in terms of mixing ratios is calculated as: $H_2 = 1.5 \times 10^{-6}$; $H_2O = 1.7 \times 10^{-6}$; $N_2 = 2.8 \times 10^{-6}$; $CO_2 = 4.3 \times 10^{-6}$; $NO = 1.7 \times 10^{-6}$; $HNO_3 = 9.3 \times 10^{-6}$; $H_2O = 6.9 \times 10^{-6}$; $OH = 1.6 \times 10^{-6}$; $CO = 1.9 \times 10^{-6}$; and $CO_2 = 1.5 \times 10^{-6}$.
5. Dissociation of NO occurs primarily in three bands around 1700 to 1900 A. The diurnally averaged dissociation rates at zero optical depth for the $600,0,0$ (I,0,0), and $602,0,0$ bands are, respectively, $9 \times 10^{-10}$, $6 \times 10^{-11}$, and $3 \times 10^{-12}$ sec$^{-1}$, adding up to a total dissociation rate of $J = 2 \times 10^{-11}$ sec$^{-1}$.
7. The results for models A, B, and C were present, respectively, 100, 99, and 7 percent for removal of NO as $HNO_3$ and $HNO_2$.
8. We assume a thermal profile similar to that which applies today, except for the absence of an inversion in the stratosphere. The mixing ratio of $H_2O$ is taken as 10 parts per million. Continuity equations are solved for all major species and we allow for transport of long-lived species such as $H_2$, $CO_2$, and $H_2O$. Calculations are relatively insensitive to the choice of temperature profile and would be similar if we had used the profiles given by M. B. Hart (J. Atmos. Sci. 23, 978 (1976)). A change in the temperature of the equatorial tropopause could alter the quantity of $H_2O$ admitted to the upper atmosphere and might affect the rate of escape of hydrogen. The rate of hydrogen escape in our models decreases here ranges from $10^{10}$ to $10^{11}$ atom/cm$^2$-sec. This spread should adequately account for differences in our understanding of the behavior of hydrogen in the early atmosphere.
9. Note that the input of H may be taken, for present purposes, as a measure of the net supply of reduced material. Other reduced gases, in particular $CO$, will be rapidly oxidized in the atmosphere with associated production of $H_2O$, as described in (C).
10. These reactions take place preferentially under conditions where the concentration of $H_2$ is high relative to that of $H_2$ in the reaction $N_2 + e \rightarrow N + N$ competes with reactions 11 when the mixing ratio for $H_2$ falls below $1 \times 10^{-6}$. The reaction $N_2 + e \rightarrow NO + N$ dominates reactions 11 when $[O] > 0.1$ (H) brackets are used to indicate concentration.
11. The oceans, at the current epoch, contain much less nitrate than in the past. The present day oceanic inventory of $HNO_3$ and $HNO_2$ includes a large flux of fixed nitrogen to the oceans but does not perturb the atmospheric reservoir by more than a few percent per 100 years.
12. The role of nitrate and nitrate in the evolution of Precambrian organisms has been discussed by L. Margulis, J. C. G. Walker, and M. Rambler (Nature [London] 264, 628 (1976)).
13. Note that the ratios of organic molecules and of organic molecules to inorganic species are not necessarily the same. A large number of large molecules may be present.
15. We thank S. C. Wofsy for helpful discussions, supported by NSF contract NSF-ATM 75-2273 to Harvard University and NASA grant NG 7376 to the California Institute of Technology, Contribution 330 of the Division of Geological and Planetary Sciences, California Institute of Technology.
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