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 nitrite and nitrate. 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 10^6 years.*

Nitrogen is often a limiting nutrient for life, despite its ubiquitous presence in air and water. It occurs in the atmosphere mainly as N_2, 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 NO_3^-. It is delivered to the ocean by rivers and by rain and is returned to the atmosphere (as N_2 and N_2O) 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 10^7 and 4×10^7 tons of N per year. The gas is formed by reactions

$$\begin{array}{c} O_2 \rightleftarrows O + O \\ O + N_2 \rightleftarrows NO + N \\ N + O_2 \rightleftarrows NO + O \end{array} \qquad (1)$$

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 NO_2, HNO_2, and HNO_3 by reactions such as (*5*)

$$\begin{array}{c} NO + O_3 \rightarrow NO_2 + O_2 \\ NO + HO_2 \rightarrow NO_2 + OH \\ NO + OH + M \rightarrow HNO_2 + M \\ NO_2 + OH + M \rightarrow HNO_3 + M \end{array} \qquad (2)$$

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 O_2 was presumably low in the early prebiotic atmosphere. Under such conditions, production of NO in lightning would have been dominated by reactions involving H_2O rather than O_2. At low concentrations of O_2 we must consider

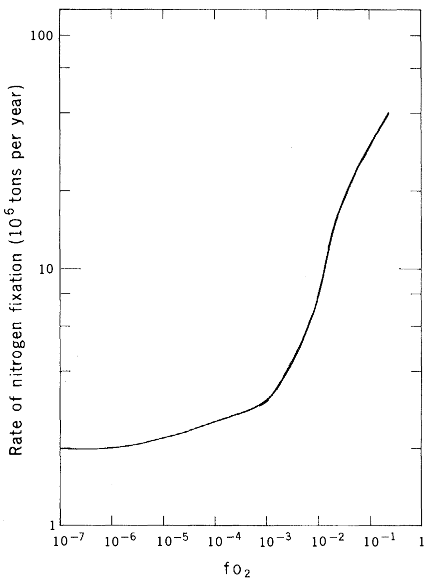

Fig. 1. Rate of nitrogen fixation in the primitive atmosphere as a function of mixing ratio of O_2. Production of NO by lightning in the contemporary atmosphere is taken as 40×10^6 tons of N per year.

$$\begin{array}{c} H_2O \rightleftarrows OH + H \\ OH + OH \rightleftarrows H_2O + O \\ O + N_2 \rightleftarrows NO + N \\ N + OH \rightleftarrows NO + H \end{array} \qquad (3)$$

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

$$\begin{array}{ll} & NO + H \rightarrow N + OH \\ \text{and} & NO + N \rightarrow N_2 + O \end{array} \qquad (4)$$

in contrast to the high-oxygen case, for which

$$\begin{array}{ll} & NO + O \rightarrow N + O_2 \\ \text{and} & NO + N \rightarrow N_2 + O \end{array} \qquad (5)$$

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 HNO_2 and HNO_3, depends on the detailed chemistry of the ambient atmosphere. A summary of more important atmospheric reactions is given in Table 1. The reaction

$$NO + h\nu \rightarrow N + O \qquad (6)$$

followed by

$$NO + N \rightarrow N_2 + O \qquad (7)$$

represents the primary atmospheric sink for fixed nitrogen; it is most important at low concentrations of O_2, where the abundance of NO is largest, reflecting inefficient conversion of NO to NO_2, HNO_2, and HNO_3. 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 H_2O and CO_2 at concentrations similar to those in the present system (*8*).

In model A we assume a closed atmosphere with negligible import and export

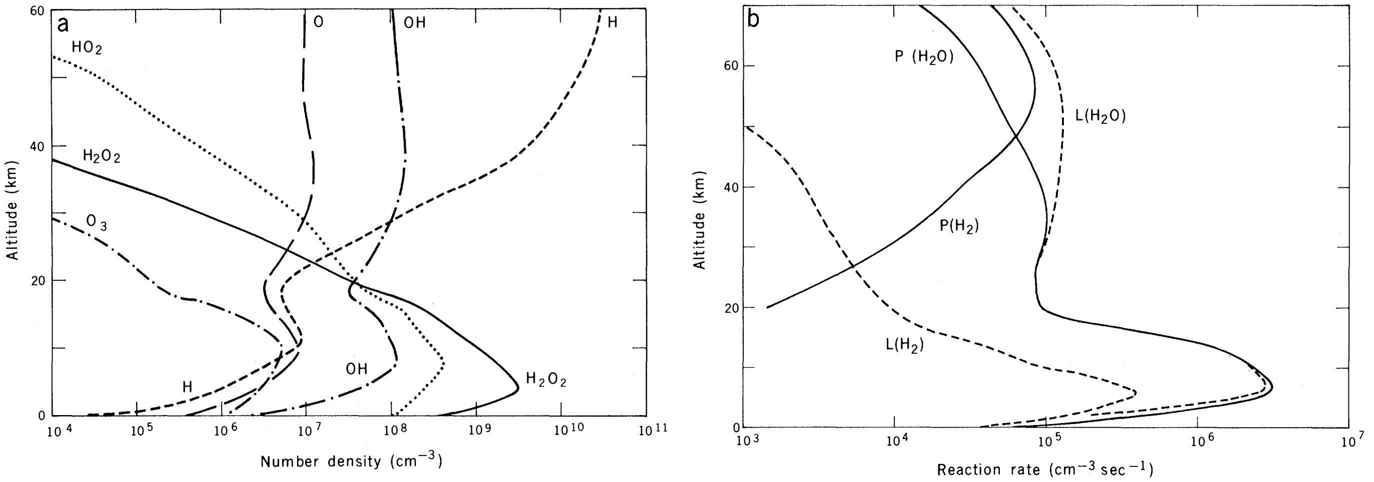

Fig. 2. (a) Concentrations of H, OH, HO_2, O, and O_3 for model A. The temperature profile and abundances of N_2, H_2O, and CO_2 are assumed to be the same as today. Mixing ratios of O_2, H_2, and CO are 5×10^{-8}, 1×10^{-7}, and 1×10^{-9}, respectively. (b) Production and loss rates of H_2O and H_2 in model A.

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

$$H_2O + h\nu \rightarrow H + OH \qquad (8)$$

Formation of H_2O proceeds primarily by

$$\begin{aligned} OH + H_2 &\rightarrow H_2O + H \\ OH + HO_2 &\rightarrow H_2O + O_2 \end{aligned} \qquad (9)$$

Molecular oxygen and hydrogen are formed by reactions such as

$$\begin{aligned} O + OH &\rightarrow O_2 + H \\ H + HO_2 &\rightarrow H_2 + O_2 \\ H + H + M &\rightarrow H_2 + M \end{aligned} \qquad (10)$$

and in steady state these gases attain mixing ratios of 5×10^{-8} and 1×10^{-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 H_2O and H_2 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 H_2 (*9*) equal to 3×10^6 ton/year (1×10^{10} 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*)

$$\begin{aligned} N_2^+ + H_2 &\rightarrow N_2H^+ + H \\ N_2H^+ + e &\rightarrow N_2 + H \end{aligned} \qquad (11)$$

Mixing ratios for H_2 and O_2 are calculated as 1×10^{-3} and 2×10^{-12}, respectively, for model B. Concentrations of OH and HO_2 are low, of order 1×10^5 cm^{-3}. The assumption of a steady state requires that the concentration of O_2 be exceedingly low in model B. Higher levels of O_2 would result in rapid conversion of H_2 to H_2O. The escape rate for hydrogen would be lowered accordingly, and water would accumulate in the ocean until the mixing ratio for O_2 was restored to its equilibrium value, 2×10^{-12}.

Model C describes a possible later phase in atmospheric evolution when the mixing ratio for O_2 has risen to 1×10^{-5}, due, for example, to the influence of photosynthesis. This model describes a quasi-steady state with the level of O_2 constrained as given. Input of H_2 at the surface is assumed to balance escape of H from the exosphere, and the level of O_2 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⁻¹, respectively. Mean dissociation rates are denoted by *J* and have units sec⁻¹; numerical values refer to the optically thin regime (*13*).

Reaction	Rate constant
$O_2 + h\nu \rightarrow O + O$	$J_1 = 1.3 \times 10^{-6}$
$O_3 + h\nu \rightarrow O_2 + O$	$J_2 = 4.8 \times 10^{-3}$
$H_2O + h\nu \rightarrow OH + H$	$J_3 = 3.7 \times 10^{-6}$
$H_2O_2 + h\nu \rightarrow OH + OH$	$J_4 = 5.7 \times 10^{-5}$
$CO_2 + h\nu \rightarrow CO + O$	$J_5 = 4.7 \times 10^{-7}$
$NO + h\nu \rightarrow N + O$	$J_6 = 2.7 \times 10^{-6}$
$HNO_2 + h\nu \rightarrow OH + NO$	$J_7 = 1.0 \times 10^{-3}$
$HNO_3 + h\nu \rightarrow NO_2 + OH$	$J_8 = 6.0 \times 10^{-5}$
$NO_2 + h\nu \rightarrow NO + O$	$J_9 = 3.5 \times 10^{-3}$
$O + O_2 + M \rightarrow O_3 + M$	$k_1 = 1.1 \times 10^{-34} \exp(520/T)$
$O + O_3 \rightarrow O_2 + O_2$	$k_2 = 1.3 \times 10^{-11} \exp(-2140/T)$
$O + O + M \rightarrow O_2 + M$	$k_3 = 2.0 \times 10^{-34} \exp(710/T)$
$OH + O_3 \rightarrow HO_2 + O_2$	$k_4 = 1.3 \times 10^{-12} \exp(-956/T)$
$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	$k_5 = 1.0 \times 10^{-12} \exp(-1875/T)$
$O + OH \rightarrow O_2 + H$	$k_6 = 1.4 \times 10^{-10} \exp(-300/T)$
$O + HO_2 \rightarrow OH + O_2$	$k_7 = 8.0 \times 10^{-11} \exp(-500/T)$
$H + O_3 \rightarrow OH + O_2$	$k_8 = 2.6 \times 10^{-11}$
$H + O_2 + M \rightarrow HO_2 + M$	$k_9 = 1.8 \times 10^{-32} \exp(340/T)$
$OH + HO_2 \rightarrow H_2O + O_2$	$k_{10} = 5.0 \times 10^{-11}$
$H + HO_2 \rightarrow H_2 + O_2$	$k_{11} = 3.0 \times 10^{-11} \exp(-330/T)$
$H + HO_2 \rightarrow OH + OH$	$k_{12} = 1.0 \times 10^{-10} \exp(-330/T)$
$H + HO_2 \rightarrow H_2O + O$	$k_{13} = 8.3 \times 10^{-11} \exp(-500/T)$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{14} = 1.0 \times 10^{-11} \exp(-500/T)$
$H_2O_2 + OH \rightarrow H_2O + HO_2$	$k_{15} = 4.1 \times 10^{-13} T^{1/2} \exp(-600/T)$
$H + H + M \rightarrow H_2 + M$	$k_{16} = 1.0 \times 10^{-32}$
$OH + OH \rightarrow H_2O + O$	$k_{17} = 2.6 \times 10^{-12}$
$OH + H_2 \rightarrow H_2O + H$	$k_{18} = 1.8 \times 10^{-11} \exp(-2350/T)$
$OH + CO \rightarrow CO_2 + H$	$k_{19} = 2.1 \times 10^{-13} \exp(-115/T)$
$N + NO \rightarrow N_2 + O$	$k_{20} = 2.2 \times 10^{-11}$
$NO + OH + M \rightarrow HNO_2 + M$	k_{21}*
$NO_2 + OH + M \rightarrow HNO_3 + M$	k_{22}*
$NO + HO_2 \rightarrow NO_2 \rightarrow OH$	$k_{23} = 8.0 \times 10^{-12}$
$N + OH \rightarrow NO + H$	$k_{24} = 7.0 \times 10^{-11}$
$N + O_2 \rightarrow NO + O$	$k_{25} = 1.0 \times 10^{-16}$

*See expression in Hudson (*14*).

mixing ratio for H_2 equal to 1×10^{-8}, with an escape rate for H equal to 1×10^8 atom/cm²-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^{15} g/year, which could in principle be supplied by photosynthesis followed by burial of organic material. We must note, however, that the photochemical steady 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_2 should respond immediately to changes in O_2. Concentrations of OH and HO_2 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 2×10^{-12}, approximately 10 percent of the nitrogen fixed in lightning is converted to HNO_2. 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 10^6 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_2 and HNO_3. There should be a corresponding source of reduced atmospheric species such as H_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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6. For thermodynamic calculations we used a computer code given by W. B. White, S. M. Johnson, and G. B. Dantzig [*J. Comput. Phys.* **28**, 751 (1958)]. Thermodynamic data were taken from *JANAF Thermodynamic Tables 1965* (PB-168370, 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, 1.5×10^{-3}; H_2, 3.4×10^{-3}; H_2O, 1.7×10^{-2}; N, 2.8×10^{-7}; NO, 1.7×10^{-3}; O, 4.2×10^{-4}; O_2, 8.4×10^{-4}; OH, 1.6×10^{-3}; CO, 1.9×10^{-4}; and CO_2, 1.5×10^{-4}.
7. Dissociation of NO occurs primarily in three bands around 1700 to 1900 Å. The diurnally averaged dissociation rates at zero optical depth for the $\delta(0,0)$, $\delta(1,0)$, and $\epsilon(2,0)$ bands are, respectively, 9.8×10^{-7}, 1.4×10^{-6}, and 3.1×10^{-7} sec^{-1}, adding up to a total dissociation rate of $J_6 = 2.7 \times 10^{-6}$ sec^{-1} [D. F. Strobel, *J. Geophys. Res.* **76**, 8384 (1971); private communication]. In calculating the effective yields of HNO_2 and HNO_3, we used the rain-out rates given by S. C. Wofsy, M. B. McElroy, and Y. L. Yung [*Geophys. Res. Lett.* **2**, 215 (1975)]. The results for models A, B, and C are, respectively, 100, 99.7, and 10 percent for removal of NO as HNO_2 and HNO_3.
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. Conclusions are relatively insensitive to the choice of temperature profile and would be similar if we had used the profiles given by M. H. Hart [*Icarus* **33**, 23 (1978)]. 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 models described here ranges from 10^8 to 10^{10} atom/cm²-sec. This spread should adequately account for deficiencies in our understanding of thermal structure in the early atmosphere.
9. Note that the input of H_2 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_2, as discussed in (*2*).
10. These reactions take place preferentially under conditions where the concentration of H_2 is high relative to that of O. The reaction $N_2^+ + e \rightarrow N + N$ competes with reactions 11 when the mixing ratio for H_2 falls below 1×10^{-3}. The reaction $N_2^+ + O \rightarrow NO^+ + N$ dominates reactions 11 when $[O] \geqslant 0.1\ [H]$ (brackets denote concentration).
11. The oceans, at the current epoch, contain much less nitrate than one might anticipate on the basis of chemical equilibrium. In the absence of biological processes, lightning provides a path for the primitive atmosphere and hydrosphere to evolve toward a thermodynamically favored state. The rate of nitrate production represents a large flux of fixed nitrogen to the oceans but does not perturb the atmospheric nitrogen reservoir by more than a few percent over 10^9 years.
12. The role of nitrite and nitrate in the evolution of Precambrian organisms has been discussed by L. Margulis, J. C. G. Walker, and M. Rambler [*Nature (London)* **264**, 620 (1976)]. Influx of large quantities of HNO_2 and HNO_3 to the ocean could lower the mean *p*H and might cause an increase in the abundance of atmospheric CO_2 with possible implications for paleoclimate [L. T. Knauth and S. Epstein, *Geochim. Cosmochim. Acta* **40**, 1095 (1976)]. These matters are beyond the scope of this report. Our overall conclusions are unaffected by these complications. In particular, higher levels of CO_2 could provide additional paths for the lightning-related source of NO.
13. Rate constants are taken from Y. L. Yung and M. B. McElroy [*Icarus* **30**, 97 (1977)] and Y. L. Yung, D. F. Strobel, T. Y. Kong, and M. B. McElroy (*ibid.*, p. 26) and updated with information from Hudson (*14*).
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15. We thank S. C. Wofsy for helpful discussions. Supported by NSF contract NSF-ATM-75-22723 to Harvard University and NASA grant NSG 7376 to the California Institute of Technology. Contribution 3109 of the Division of Geological and Planetary Sciences, California Institute of Technology.

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Observations of Hydrogen at Room Temperature (25°C) and High Pressure (to 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 360 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. Many 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 into a pressure cell at cryogenic temperatures and afterward remove the cell from the assembly and