

NITROGEN FIXATION BY CORONA DISCHARGE ON THE EARLY PRECAMBRIAN EARTH

DELPHINE NNA-MVONDO^{1,3,*}, RAFAEL NAVARRO-GONZÁLEZ¹,
FRANÇOIS RAULIN² and PATRICE COLL²

¹Laboratorio de Química de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares, Universidad Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-543, México Distrito Federal 04510, México; ²Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Universités Paris 12 et 7, 61 av. Général de Gaulle, 94010 Créteil Cedex, France; ³Present address: Space Science Division, NASA-Ames Research Center, Moffett Field, CA 94035-1000, U.S.A.

(* author for correspondence, e-mail: dnnamvondo@mail.arc.nasa.gov, Tel.: (+1) (650) 604-0481, Fax: (+1) (650) 604-3954)

(Received 12 November 2004; accepted in revised form 4 January 2005)

Abstract. We report the first experimental study of nitrogen fixation by corona discharge on the anoxic primitive Earth. The energy yields of nitric oxide (NO) and nitrous oxide (N₂O) were experimentally determined over a wide range of CO₂-N₂ mixtures simulating the evolution of the Earth's atmosphere during the Hadean and Archean eras (from 4.5 ba to 2.5 ba). NO, the principal form of fixed nitrogen in lightning and coronal discharge in early Earth, is produced ten times less efficiently in the latter type of electrical discharge with an estimated maximum annual production rate of the order of 10¹⁰ g yr⁻¹. For N₂O the maximum production rate was estimated to be ~10⁹ g yr⁻¹. These low rates of syntheses indicate that corona discharges as point discharges on the clouds and ground did not play a significant role in the overall pool of reactive nitrogen needed for the emergence and sustainability of life.

Keywords: corona discharge, energy yield, experimental simulation, nitric oxide, nitrogen fixation, nitrous oxide, primitive Earth

1. Introduction

The development of organisms depends on the availability of nitrogen, an essential element that is implied in the formation of many of the relevant biomolecules needed for life, such as proteins, enzymes, ribozymes, RNA, DNA, energy storage molecules, coenzymes, etc. The Earth's atmosphere is the main reservoir of this element, where it is present in the form of dinitrogen gas. However, most organisms are not able to use it directly because there is a high activation energy, 948 kJ mol⁻¹, required to dissociate the triple nitrogen bond, N≡N. As a consequence, to be available for organisms, nitrogen must be present in "fixed forms" such as ammonium (NH₄⁺) or nitrates (NO₃⁻) ions. In the contemporaneous Earth, nitrogen fixation is mainly driven by a biological process carried out by certain bacteria, representing

about 70% of the total quantity of fixed nitrogen (Bezdicsek and Kennedy, 1998). Before the advent of biological nitrogen fixation, the sources of fixed nitrogen needed for the emergence and sustainability of life were abiotical driven by energetic processes. The nature and relative abundance of the nitrogen compounds formed in the primitive terrestrial environment by the different energy sources depend on the oxidation state of the atmosphere. A chemically reducing environment, such as an atmosphere mostly composed of nitrogen and methane may drive to the formation of organic nitrogen compounds such as hydrogen cyanide and acetonitrile (Zahnle, 1986). Such an atmosphere would be very efficient in triggering a rich prebiotic chemistry leading to the formation of more complex compounds needed for the emergence and evolution of life, such as amino acids, purines, and pyrimidines. Nevertheless, according to current knowledge of the terrestrial environment, the early Earth's atmosphere was more likely neutral, composed of carbon dioxide and nitrogen, with a CO₂-rich composition during the first 2.5 billion years (Walker, 1985; Kasting, 1990; Kasting *et al.*, 2001). Under these conditions, HCN and other nitriles are not synthesized in the atmosphere (Stribling and Miller, 1987). Instead, the main form of fixed nitrogen is nitric oxide (Kasting, 1990; Navarro-González *et al.*, 1998, 2001). With a NO production rate of $\sim 10^{12}$ – 10^{13} g yr⁻¹ (Navarro-González *et al.*, 1998), volcanic lightning could have been the most important source of reactive nitrogen followed closely by post-impact plumes with $\sim 10^{12}$ g N yr⁻¹ (Kasting, 1990) and by thunderstorm lightning with $\sim 10^{11}$ g N yr⁻¹ (Navarro-González *et al.*, 2001). Reduced nitrogen in the form of ammonia could have been efficiently produced in hydrothermal systems with $\sim 10^{10}$ – 10^{12} g yr⁻¹ (Brandes *et al.*, 1998). Ammonia, hydrogen cyanide and other more complex nitrogenated organics, could have been delivered to the early Earth by exogenous sources such as interplanetary dust particles and comets with rates of delivery of $\sim 10^{10}$ and $\sim 10^6$ – 10^7 g yr⁻¹ respectively (Chyba and Sagan, 1992). Exogenous sources would have had a modest role in the overall pool of fixed nitrogen available for the origins of life (Navarro-González *et al.*, 1998), but perhaps a more important role in providing more complex organo-nitrogen compounds.

While the significance of lightning as a source of fixed nitrogen for the early Earth is largely acknowledged, the contribution of corona discharges still remains unknown. The study of electrical discharges is often restricted to the field of the effect of lightning discharges although electrical discharges appear also in the form of corona discharges from pointed objects. During the initial development of a lightning flash, charge is transferred from cloud to ground as a result of a continuing current flow between cloud and the earth (Uman, 1984). A coronal discharge from pointed objects is the dominant mechanism of charge propagation. Point discharge occurs when the tip of any sharp object acts to concentrate a local electric field, causing breakdown and an electron avalanche for sufficiently high field values (Chyba and Sagan, 1991). The chemical effects of corona discharges as pointed discharges in the contemporaneous Earth have been studied in detailed by laboratory experiments (Brandvold *et al.*, 1989; Martinez and Brandvold, 1996)

and field measurements (Brandvold *et al.*, 1996; Martinez and Brandvold, 1996). However their effects in a CO₂-N₂ early terrestrial troposphere are not known. In this work we provide an experimental simulation of the production of nitrogen oxides by point discharge in the primitive Earth's atmosphere during the Hadean and the Archean eras.

2. Experimental

Simulated atmospheres composed of CO₂ (99.99% purity) and N₂ (99.999% purity) were prepared at various mixing ratios using a Linde mass flow measuring and control gas blending console (FM4660) equipped with fast response mass flow control modules of 20 cm³ min⁻¹ capacity. The reactor was evacuated to 10⁻⁷ bar and flushed twice with the gas mixture before filled up at 1 bar total pressure. The CO₂-N₂ gas samples were then submitted to corona discharge irradiation.

The negative corona discharge was induced in a coaxial Pyrex 0.48 liter reactor composed of a central tungsten rod acting as an internal electrode surrounded internally by a grounded stainless steel cylinder acting as a ground electrode. A high vacuum stopcock in the upper part of the glass vessel permitted the connection to the manifold or to the gas chromatograph. The internal electrode was connected to a regulated high voltage DC power (maximum current of 3 mA and maximum voltage of 30 kV from Glassman High Voltage, Inc., series EH) with digital gauges to monitor the current and voltage supplied to the system (see Figure 1). The power supplied was calculated according to $P = V \times I$. For safety and to minimize electric power losses occurring on the electric circuits and electrode tips, high voltage cables with special electrically insulated connectors were used (Navarro-González *et al.*, 1998).

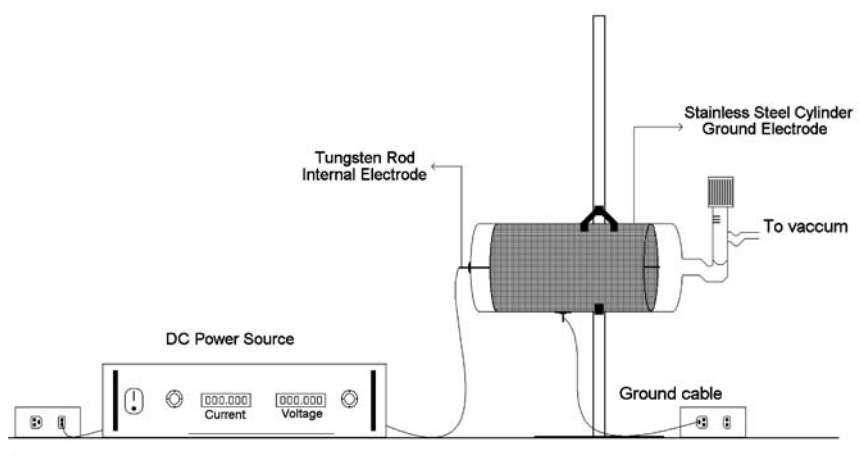


Figure 1. Experimental device used for simulating coronal discharges in CO₂ – N₂ primitive atmospheres.

The samples were irradiated in a closed-system at 298K from 8 min to 2 hours. After irradiation, the gas mixtures were immediately analyzed using a Hewlett Packard (HP) gas chromatograph (model 5890 series II) interfaced in parallel with a HP FTIR-detector (model 5965B) and a HP quadrupole mass spectrometer (model 5989B) equipped with electron impact and chemical ionization modes. The gases were injected into the gas chromatograph by an automatic six-port gas-sampling loop of 2 ml. For the separation of the products, the chromatographic column used was a capillary PoraPLOT Q fused-silica (25 m \times 0.32 mm I.D.). The temperatures at the GC-MS and GC-FTIR interfaces and in the FTIR flow cell were 260 °C. The column program temperature was isothermal at 30 °C for 4 min, and then a rate of 13 °C min⁻¹ up to 240 °C, and finally isothermal for 6 min. The carrier gas used was helium with a flow of 2 ml min⁻¹.

3. Results and Discussion

NO and N₂O were detected as the main products of the reactions occurring during the irradiation by corona discharge which is a cold plasma, e.g., the electrons and ions are at high temperature due to excitation and ionization but the neutral molecules are at room temperature. This plasma is not at thermochemical equilibrium. The energy yields (molecules J⁻¹) of the products were derived from the slopes of curves where the production (in molecules) of a given product is plotted versus the electric energy deposited (in joules) in a particular simulated atmosphere, as shown in Figure 2. The production rates of NO and N₂O were investigated as a function of the mixing ratio of carbon dioxide (see Figure 3). The production of NO (*PNO*) and N₂O (*PN₂O*) does not depend on the carbon dioxide mixing ratio, χ CO₂, between 0.2 and 0.8; however below and above these values, *PNO* and *PN₂O* rapidly decrease. A possible chemical reaction scheme leading to the

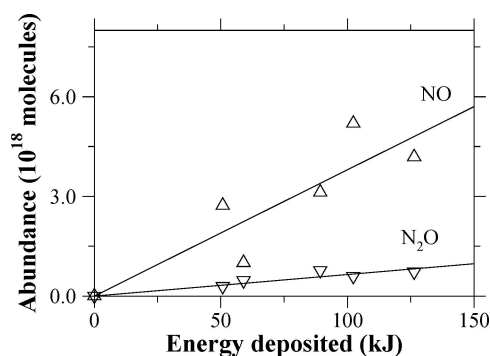


Figure 2. Formation of nitrogen oxides as a function of energy deposited by corona discharge irradiation of a 20%CO₂ – 80%N₂ simulated atmosphere at 1 bar total pressure and 298 K.

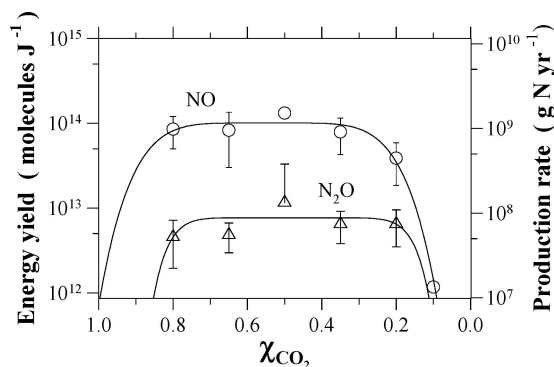


Figure 3. Production rate of nitrogen oxides as a function of the CO_2 mixing ratio in corona discharge irradiation of $\text{CO}_2 - \text{N}_2$ primitive atmospheres at 1 bar total pressure and 298 K. The energy yields were determined in experiments where electric energy deposited varied from 10 to 130 kJ.

observed products and that can explain the variation of P_{NO} and $P_{\text{N}_2\text{O}}$ with χ_{CO_2} is described by reactions 1 through 10.

Carbon dioxide can be dissociated by the corona electrons according to reaction 1.



O^+ can then react with molecular nitrogen to form NO^+ (reaction 2), which by neutralization with an electron leads to nitric oxide formation (reaction 3).



Reaction of NO^+ with atomic nitrogen leads to the formation of positively charged nitrous oxide (reaction 4) that can lead to neutral nitrous oxide by reaction with an electron (reaction 5).



At $\chi_{\text{CO}_2} \leq 0.2$, the productions of nitric oxide and nitrous oxide drop not only because of a lesser availability of atomic oxygen but also due to the reaction of nitric oxide with atomic nitrogen leading to the regeneration of molecular nitrogen according to reaction 6.



Similarly at $\chi CO_2 \leq 0.8$, the productions of nitric oxide and nitrous oxide drop not only because of a lesser availability of molecular nitrogen but also due to the reaction of nitric oxide with atomic oxygen leading to the formation of molecular oxygen according to reaction 7.



The above chemical scheme involves principally positively charged species with neutrals and radicals since corona discharges propagate mostly by ionization and excitation of molecules (Hill *et al.*, 1984; Bhetanabhotla *et al.*, 1985). But reactions with free radicals and stable molecules can also take part in cold plasma to form NO (reactions 8, 9, 10):



Recently, an extensive model study of nitrogen fixation by lightning in the past has been realized by experimental simulation of the Hadean and Archean Earth's atmosphere (Navarro-González *et al.*, 2001). In this work it was estimated the maximum production rate of nitric oxide, the predominant fixed nitrogen form during lightning thunderstorm in the primitive terrestrial troposphere, to be $\sim 3 \times 10^{11}$ g N yr⁻¹. Assuming that the global coronal discharge energy available on early Earth estimated by Chyba and Sagan (1991) was 5×10^{17} J yr⁻¹, our results imply that the maximum annual production rate of NO was $\sim 1 \times 10^9$ g N yr⁻¹ (see Figure 3). NO in the atmosphere would have been converted into nitrosyl hydride (HNO) by its reaction with atomic hydrogen. HNO is thought to be readily soluble in water. Therefore it dissolved very likely in rain where it dissociated into H⁺ and NO⁻. The latter anion decomposed in water according to reaction 11 (Mancinelli and McKay, 1988):



Nitrite and nitrate ions were delivered to the lithosphere and hydrosphere where they were readily available in the early Earth. Current theories for the origin of life require however the availability of reduced forms of nitrogen. Reduction of nitrite and nitrate ions to ammonia by Fe(II) has been shown to be favorable, provided that the ocean was warm (>25 °C) and weakly basic, e.g., pH \geq 7.3 (Summers and Chang, 1993). Nevertheless, nitric oxide is a highly reactive molecule which has been used effectively in the synthesis of peptides (Collet *et al.*, 1996); therefore, it may have played a more active role in the origin and early evolution of life. The estimate for the nitrogen fixation rate in a cold plasma is two orders of magnitude

lower than that obtained in hot plasma processes. Therefore, we conclude that corona discharges in the early atmosphere did not play a dominant role in the overall supply of reactive nitrogen needed for the origins of life.

The production rate of nitrous oxide is estimated to be $\sim 9 \times 10^7$ g yr⁻¹. N₂O is predicted to form preferably in cold plasma discharge than by hot plasma processes (Hill *et al.*, 1980). Our results indicate undoubtedly that point discharges on the ground might have provided a source of N₂O in the primordial atmosphere. This has been corroborated by laboratory simulation of negative point discharges in present Earth with an estimated energy yield of $\sim 8 \times 10^{13}$ molecules J⁻¹ (Brandvold *et al.*, 1989) and also by field measurements (Brandvold *et al.*, 1996). At first glance, the production of nitrous oxide by point discharge might present an interest in the supply of reactive nitrogen for the primitive organisms; however N₂O is not very soluble in water, so N₂O was not rained out from the atmosphere (Levine and Shaw, 1983). Consequently, N₂O produced in the atmosphere could not be available for the living organisms and did not contribute directly in the supply of reactive nitrogen to the terrestrial biosphere during the evolution of the Earth.

N₂O, a powerful greenhouse gas, would not have accumulated in the early atmosphere because it is photolytically unstable, decomposing mostly into N₂ and atomic oxygen by UV photons <337 nm, or into NO and atomic nitrogen by UV photons <250 nm (Badr and Probert, 1993). The nitric oxide generated by this reaction represents a minor supply of reactive nitrogen to the atmosphere.

Acknowledgments

This paper describes research supported by the National Autonomous University of Mexico (DGAPA-IN102796), the National Council of Science and Technology of Mexico (CONACyT 32531-T), the French-Mexican scientific research program ECOS/CONACyT-SEP-ANNUIES (M97U01).

References

- Badr, O. and Probert, S. D.: 1993, Environmental Impacts of Atmospheric Nitrous Oxide, *Appl. Energy* **44**, 197–231.
- Bar-Nun, A. and Shaviv, A.: 1975, Dynamics of the Chemical Evolution of Earth's Primitive Atmosphere, *Icarus* **24**, 197–210.
- Bezdicsek, D. F., and Kennedy, A. C.: 1998, Microorganisms in Action, in J. M. Lynch and J. E. Hobbie (eds.), Blackwell Scientific Publications.
- Bhetanabhotla, M. N., Crowell, B. A., Coucouvinos, A., Hill, R. D. and Rinker, R. G.: 1985, Simulation of Trace Species Production by Lightning and Corona Discharge in Moist Air, *Atmos. Environ.* **19**, 1391–1397.
- Borucki, W. J. and Chameides, W. L.: 1984, Lightning: Estimates of the Rates of Energy Dissipation and Nitrogen Fixation, *Rev. Geophys. Space Phys.* **22**, 363–372.

- Brandvold, D. K., Martinez, P. and Dogruel, D.: 1989, Polarity Dependence of N₂O Formation from Corona Discharge, *Atmos. Environ.* **23**, 1881–1883.
- Brandvold, D. K., Martinez, P. and Hipsh, R.: 1996, Field Measurements of O₃ and N₂O produced from Corona Discharge, *Atmos. Environ.* **30**, 973–976.
- Brandes, J. A., Boctor, N. Z., Cody, G. D., Cooper, B. A., Hazen, R. M. and Yoder, H. S., Jr.: 1998, Abiotic Nitrogen Reduction on the Early Earth, *Nature* **395**, 365–367.
- Chyba, C. and Sagan, C.: 1991, Electrical Energy Sources for Organic Synthesis on the Early Earth, *Origins Life* **21**, 3–17.
- Chyba, C. and Sagan, C.: 1992, Endogenous Production, Exogenous Delivery and Impact-shock Synthesis of Organic Molecules: An Inventory for the Origins of Life, *Nature* **305**, 125–132.
- Collet, H., Bied, C., Mion, L., Taillades, J. and Commeyras, A.: 1996, A New Simple and Quantitative Synthesis of (-Aminoacid-N-carboxyanhydrides (Oxazolidines-2,5-dione), *Tetrahedr. Lett.* **37**, 9043–9046.
- Coppens, F., Berton, R., Bondiou-Clergenie, A. and Gallimberti, I.: 1998, Theoretical Estimate of NO_x Production in Lightning Corona, *J. Geophys. Res.* **103**, 10.769–10.785.
- Ferris, J. J. and Nicodem, D. E.: 1972, Ammonia Photolysis and the Role of Ammonia in Chemical Evolution, *Nature* **238**, 268–269.
- Ferris, J. P. and Chen, C. T.: 1975, Chemical Evolution. XXVI. Photochemistry of Methane, Nitrogen, and Water Mixture as a Model for the Atmosphere of the Primitive Earth, *J. Am. Chem. Soc.* **97**(11), 2962–2967.
- Hill, R. D., Rinker, R. G. and Wilson, H. D.: 1980, Atmospheric Nitrogen Fixation by Lightning, *J. Atmos. Sci.* **37**, 179–193.
- Hill, R. D., Rinker, R. G. and Coucouvinos, A.: 1984, Nitrous Oxide Production by Lightning, *J. Geophys. Res.* **89**, 1411–1421.
- Hill, R. D., Rahmin, I. and Rinker, R. G.: 1988, Experimental Study of the Production of NO, N₂O, and O₃ in a Simulated Atmospheric Corona, *Ind. Eng. Chem. Res.* **27**, 1264–1269.
- Kasting, J. F.: 1990, Bolide Impacts and the Oxidation State of Carbon in the Earth's Early Atmosphere, *Origins Life Evol. Biosp.* **20**, 199–231.
- Kasting, J. F., Pavlov, A. A. and Siefert, J. L.: 2001, A Coupled Ecosystem-Climate Model for Predicting the Methane Concentration in the Archean Atmosphere, *Origins Life Evol. Biosph.* **31**, 271–285.
- Kuhn, W. R. and Kasting, J. F.: 1983, Effects of Increased CO₂ Concentrations on Surface Temperature of the Early Earth, *Nature* **301**, 53–55.
- Levine, J. S. and Shaw, E. F., Jr.: 1983, *In Situ* Aircraft Measurements of Enhanced levels of N₂O Associated with Thunderstorm Lightning, *Nature* **303**, 312–314.
- Mancinelli, R. L. and McKay, C. P.: 1998, The Evolution of Nitrogen Cycle, *Origins Life Evol. Biosphere* **18**, 311–325.
- Martinez, P. and Brandvold, D. K.: 1996, Laboratory and Field Measurements of NO_x Produced From Corona Discharge, *Atmos. Environ.* **30**, 4177–4182.
- Navarro-González, R., Romero, A. and Honda, Y.: 1998, Power Measurements of Spark Discharge Experiments, *Origins Life Evol. Biosphere* **28**, 131–153.
- Navarro-González, R., Molina, M. J. and Molina, L. T.: 1998, Nitrogen Fixation by Volcanic Lightning in the Early Earth, *Geophys. Res. Lett.* **25**, 3123–3126.
- Navarro-González, R., McKay, C. P. and Nna Mvondo, D.: 2001, A Possible Nitrogen Crisis for Archaean Life Due to Reduced Nitrogen Fixation by Lightning, *Nature* **412**, 61–64.
- Owen, T., Cess, R. D. and Ramanathan, V.: 1979, Enhanced CO₂ Greenhouse to Compensate for Reduced Solar Luminosity on Early Earth, *Nature* **277**, 640–642.
- Stribling, R. and Miller, S. L.: 1987, Energy Yields for Hydrogen Cyanide of Formaldehyde Synthesis: The HCN and Amino Acid Concentrations in the Primitive Ocean, *Origins Life Evol. Biosphere* **17**, 261–273.

- Summers, D. P. and Chang, S.: 1993, Prebiotic Ammonia from Reduction of Nitrite by Iron(II) on the Early Earth, *Nature* **365**, 630–633.
- Uman, M. A.: 1984, *Lightning*, Dover, Mineola, p. 298.
- Walker, J. C. G.: 1976, *Implications for Atmospheric Evolution of the Inhomogeneous Accretion Model of the Origin of the Earth, the Early History of the Earth*, Wiley, Windley, B.F., pp 537–547.
- Walker, J. C. G.: 1985, Carbon Dioxide on the Early Earth, *Origins Life* **16**, 117–127.
- Wang, Y., DeSilva, A. W., Goldenbaum, G. C. and Dickerson, R. R.: 1998, Nitric Oxide Production by Simulated Lightning: Dependence on Current, Energy, and Pressure, *J. Geophys. Res.* **103**, 19149–19159.
- Zahnle, K. J.: 1986, Photochemistry of Methane and the Formation of Hydrocyanic Acid (HCN) in the Earth's Early Atmosphere, *J. Geophys. Res.* **91**, D2, 2819–2834.