Biodata of **Rafael Navarro-Gonzalez** author (with co-author Antigona Segura) of ***"The Possible Role of Volcanic Lightning in Chemical Evolution"***

**Dr Rafael Navarro-Gonzalez** is a distinguished research professor at the Laboratory of Plasma Chemistry and Planetary Studies of the Institute of Nuclear Science of the National Autonomous University of Mexico He obtained his B Sc in biology in 1983 at this University, and his Ph D in chemistry in 1989 from the University of Maryland at College Park working under the supervision of Dr Cyril Ponnamperuma His current research interest focuses on the origin and evolution of life on Earth and other planetary environments Dr Navarro-Gonzalez is also active in future space missions to Mars and Europa, and in terraforming Mars His studies on Mars brought him recently to Mars-like environments such as the Atacama Desert in Chile, one of the driest places on Earth, and Pico de Orizaba, Mexico, a volcano with the highest treeline in the world Dr Navarro-Gonzalez has been a visiting professor at the University of Maryland, The Massachusetts Institute of Technology, the Universties of Paris 7 and 12

E-mail **navarro@nuclecu unam mx**

**Dr Antigona Segura** is now a postdoctoral student at the Pennsylvania State University working with Dr James Kasting in theoretical modeling of planetary atmospheres She obtained her B Sc in physics in 1994 at the Universidad Autonoma de San Luis Potosi, in Mexico, graduating with honors as the best student in the country During her undergraduate studies she started to do research in the detection of binaries in the Hyades cluster by statistical methods under the direction of Dr Arcadio Poveda and Dr Miguel Angel Herrera She continued to do this research towards her master's degree, graduating in astronomy in 1997 Looking for a research subject related to extraterrestrial life she joined Dr Rafael Navarro-Gonzalez' research group and changed to the Earth Science graduate program, where she got her Ph D in 2001 Her research during her PhD was on the synthesis of reactive nitrogen compounds relevant for prebiotic chemistry in the volcanic plumes of early Mars

E-mail **antigona@essc psu edu**

**R Navarro-Gonzalez**

**A Segura**



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# THE POSSIBLE ROLE OF VOLCANIC LIGHTNING IN CHEMICAL EVOLUTION

**RAFAEL NAVARRO-GONZÁLEZ AND ANTIGONA SEGURA**
*Laboratorio de Química de Plasmas y Estudios Planetarios, Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México. Circuito Exterior, Ciudad Universitaria. Apartado Postal 70-543, México, D.F. 04510 MEXICO.*

## 1. Introduction

Nitrogen and phosphorus are fundamental elements for life. Nitrogen is present in structural (*e.g.,* proteins), catalytic (*e.g.,* enzymes and ribozymes), energy transfer (*e.g.,* ATP) and information storage (RNA and DNA) biomolecules. Atmospheric and planetary models suggest that nitrogen was abundant in the early atmospheres of Earth and Mars as dinitrogen ($N_2$), an inert gas under normal atmospheric conditions. To be available for prebiotic synthesis it must be converted into hydrogen cyanide, ammonia and/or nitrate, in a process referred to as nitrogen fixation. Due to the strength of the triple bond in $N_2$, nitrogen fixation, while thermodynamically favored is kinetically restricted (Navarro-González *et al.,* 2001). In a reducing atmosphere dominated by $CH_4$-$N_2$, thunderstorm lightning efficiently produces HCN and $NH_3$ (Toupance *et al.,*1975; Stribling and Miller, 1987; Chameides and Walker, 1981). Nevertheless, photochemical and geochemical constraints strongly suggest that the early atmosphere was weakly reducing, dominated by $CO_2$ and $N_2$ with traces of $CH_4$, CO, and $H_2$ (Kasting, 1993). Under these conditions, HCN is no longer synthesized in the lightning channel and instead NO is formed (Navarro-González, *et al.*, 2001 and references therein). NO has not yet been implicated in the syntheses of amino acids, purines or pyrimidines under prebiotic conditions. The lack of formation of HCN by thunderstorm lightning introduces serious barriers to the process of chemical evolution in the early Earth.

Phosphorus, on the other hand, is present in ribozymes, ATP, RNA and DNA molecules. This element occurs naturally as apatite ($Ca_5(PO_4)_3(F, Cl)$), an insoluble mineral (Glindemann *et al.*, 1999). In order to be available for prebiotic process, phosphorus must be reduced to hydrophosphites or phosphites.

A promising environment for the synthesis of organic molecules and their rapid removal from the reaction zone is volcanic ash-gas clouds (Markhinin and Podkletnov, 1977; Podkletnov and Markhinin, 1981; Lavrentiev *et al.*, 1984; Hill, 1992), where all the gaseous (or vaporous) components necessary for the formation of prebiotic compounds are present under sharp pressure gradients. At the same time, ash particles are represented by minerals possessing large surface area and well-expressed catalytic properties. Ash-gas

clouds are also characterized by the presence of various temperatures as well as powerful electric discharges, which can serve as an efficient energy source (Schwartz and Henderson-Sellers, 1983; Hill, 1992). Recent experimental work conducted in this laboratory and elsewhere shows that the lightning formed in volcanic clouds during highly explosive eruptions may be an important source of reactive nitrogen and phosphorus. This paper reviews the available knowledge on the role of volcanic lightning in chemical evolution, the available data on this environment, and the most important chemical and physical parameters relevant to the Archean.

## 2. Volcanic Activity

As the collapse of the presolar nebula began, planetesimals coalesced into small planetary embryos. The heating produced by accretion, radioactive decay and electromagnetic induction, from a putative T Tauri phase of the early Sun, led to planetary differentiation and magmatic activity on several planetary embryos in the inner Solar System. Magmatic activity on small planetary objects has been inferred for approximately 70 parent bodies represented by igneous meteorites, such as the Angra dos Reis, the aubrites, the ureilites and the howardite-eucrite-diogenites (Hewins and Newsom, 1988), and some carbonaceous chondrites (Kurat and Kracher, 1980). Remote sensing has indicated the presence of basaltic rocks on the surface of a large asteroid, Vesta (Gaffey, 1983). As these planetary embryos continued to grow into terrestrial planets, their interiors became very hot, with temperatures essentially at the solidus.

Thermal history models of the Earth suggest that the planet cooled rapidly in the first several 100 Myr by a vigorous mantle convection system (Schubert *et al.*, 1989). During this period volcanism should have been very intense, characterized by extraordinarily explosive eruptions on account of the higher content of volatiles in the magma and the greater temperatures in the mantle.

In addition to the above classical mantle-derived volcanism, there was an additional type of volcanism during the late heavy bombardment process (4.5 to 3.8 Gyr) induced by impacts from space bodies. During this period, a large number of projectiles (20 km $\leq$ diameter $\leq$ 300 km) collided with the Earth accreting a substantial mass, estimated in the range of $1\times10^{25}$ to $4\times10^{25}$ g (Chyba *et al.*, 1994). Such catastrophic events were likely to destroy the incipient crust and trigger volcanism. Evidence for impact-triggered volcanism has been found on the Moon at the crater Tsiolkovski and on the Earth at the Sudbury Structure in Ontario, Canada, dated at about 2 Gyr old (French, 1970).

Subsequent to a few 100 Myr after the end of the heavy bombardment process, the Earth underwent a slow and gradual cooling at a rate of the order of 100 K $Gyr^{-1}$ controlled by deep convective heat transport and near-surface conductive heat transport through a mobile lithosphere (Schubert *et al.*, 1989). At this stage, volcanic activity gradually declined to its present rate. The contemporaneous global volcanic activity on Earth has been estimated at about 4 $km^3$ of lava and pyroclasts emitted yearly (Decker and Decker, 1982); this figure includes material vented by subduction zone (about 1 $km^3\ yr^{-1}$), rift (2.5 $km^3\ yr^{-1}$) and hot-spot (0.5 $km^3\ yr^{-1}$) volcanoes.

## 3. Explosive Volcanism

Volcanoes emit three types of physical products: gases, liquids, and solids; their relative importance is determined by the degree of explosivity of the eruption, which depends on (1) the viscosity of the magma, (2) its gas content, (3) the rate of emission, and (4) the environment of the vent (Decker and Decker, 1982). Gentle or effusive volcanoes discharge small amounts of fumes and airfall fragments, and large volumes of lava, which may boil out in spectacular fire fountains or simply flow from cracks or vents into streams of lava. Explosive volcanoes generate large volumes of gases and hot solid fragments that can either billows upward as a huge ash cloud or avalanche rapidly down slopes as fluidized flows. The volume of ejecta in explosive eruptions ranges from $10^6$ $m^3$ to $10^{12}$ $m^3$ and the height of the ash cloud column can vary from 1-5 km up to 25 km depending on the rate of emission of pyroclasts (Settle, 1978; Simkin *et al.*, 1981). Additionally, explosive volcanoes exhibit intense lightning activities, which makes them particularly relevant to prebiotic chemistry. There are two dominant mechanisms leading to explosive volcanism; these are: (1) the magmatic process, which involves exsolution of dissolved volatiles from the melt during the rise and decompression of magma; and (2) the hydromagmatic process, which operates during contact of melt with external water (liquid or solid) at or near the surface of the Earth. These two processes may operate simultaneously during an eruption if the magma composition and environmental factors permit. It seems likely that these mechanisms also operated in the Archean.

## 4. Characteristics of Volcanic Clouds

Volcanic clouds have been proposed as a viable environment for prebiotic synthesis because volcanism was a very common phenomenon in the Archean (Fox and Harada, 1961; Harada and Fox, 1964). During these eruptive episodes, the magma and part of the volcanic system are fragmented in particles known as pyroclasts. A volcanic plume is formed by the discharge of a mixture of pyroclasts and magmatic gases into the atmosphere. Such plumes typically exhibit strong electric fields and generate copious lightning discharges of hundreds of meters in length at rates of $10\text{-}10^2$ flash $min^{-1}$ in and around the plume near the eruption site (Navarro-González *et al.*, 1996). The compounds formed in the volcanic lightning channel can escape the high temperature zone of the eruption site at sonic or supersonic speeds and be injected into the troposphere and stratosphere where they would undergo photochemical processing. These characteristics allow volcanic plumes to serve as natural chemical reactors. This environment has been recently reviewed by Basiuk and Navarro-González (1996), and Navarro-González *et al.*, 1996, and an overview is given below.

### 4.1. GAS PHASE

The composition of volcanic gases can vary considerable from volcano to volcano, and even within the same volcano that undergoes different eruptive phases. A large variety of volatiles are emitted, being the most abundant water steam, $CO_2$, $SO_2$, $N_2$, $H_2S$, $H_2$, CO,

HCl, HF, Ar, $CH_4$, $NH_3$, COS (Basiuk and Navarro-González, 1996). Large variations, within several (up to 8) orders of magnitude, are observed in the concentrations of these volatiles. Steam is on the average the most abundant and has a relatively constant content. These fluctuations are attributed to a heterogeneous mantle from which the volatiles are released, namely from the deep (less altered) and the upper (more recycled) mantles. Analyses of isotopic composition of noble gases in a suite of volcanic glasses from different sources by Allègre *et al.* (1983) indicate that the volatiles emitted by Hawaiian volcanoes are richer in nonradiogenic noble gases. This has been interpreted to imply the existence of a primordial, undegassed reservoir deep in the Earth's mantle (Allègre *et al.*, 1983, 1993). Therefore, the volatiles emitted by Hawaiian volcanoes could, perhaps, exemplify more closely the nature of gases emitted by Archean volcanoes. The typical composition of volatiles emitted by Kilauea, one of the Hawaiian volcanoes is (Gerlach, 1993): $H_2O$: 52% (±14%); $CO_2$: 31% (±13%); $SO_2$: 15 (±4%); CO: 1% (±0.4%); $H_2$: 0.8 (±0.2%); and $H_2S$: 0.2 (±0.1%).

## 4.2. ASH

Volcanic ash is a fine-grained magmatic material (Kearey *et al.*, 1993), composed of a combination of oxides of the major rock-forming elements. It is formed by disordered Si-O tetrahedra with inclusions of the ions of Mg, Fe, Ca, Na, and K. Depending on the composition, magmatic materials may be classified under the following types: (1) dacite; (2) basalt; (3) andesite; (4) rhyolite; and (5) komatiite. For the early phase of the evolution of the Earth, komatiite was the dominant type of volcanic material erupted. The typical composition of ashes from this type of volcanism is: $SiO_2$: 48.6%; $Al_2O_3$: 6.3%; FeO: 11.2%; CaO: 5.7%; $Na_2O$: 0.1%; MgO: 30.8%; $K_2O$: 0.02%; and $TiO_2$: 0.3%.

## 4.3. TEMPERATURE AND PRESSURE

The initial temperatures at which the magmatic materials reaches the planetary surface depends on the melt composition. For instance, basaltic andesite magma of the 1979 eruption of Soufriere volcano was at 1000°C (Brazier *et al.*, 1982); basaltic lava of the 1980 eruption of Large Tolbachik volcano was at 980°C to 1070°C (Fedotov *et al.*, 1980); for Hawaiian basalts, 980°C to 1200°C (Peck *et al.*, 1979); lava of the Niragongo 1977 eruption, 1100°C (Tazieff, 1977). The temperature of the Mount St. Helens dacitic/andesitic melt varied from 920°C to 990°C (Casadevall *et al.*, 1983). Nisbet (1985) has pointed out that in the Archean the temperatures of primary igneous melts rising up from the mantle were probably much higher than today (1700°C or more). However, the temperature of erupted materials rapidly drops with altitude; for instance for Mount St. Helens, the plume temperature 100 m above the crater was only slightly higher than the ambient temperature (Lawrence *et al.*, 1980).

Magma and gases are compressed at very high pressures prior to eruption, *e.g.* 2200±500 bar for Mt. Pinatubo's eruption on June 15, 1991 (Rutherford, 1991). However, it is very difficult to estimate the pressures at which volcanic matter is erupted from the crater, although it is thought that they cannot exceed a few hundred atmospheres. But after the eruption, the pressure equilibrates with the atmospheric one even faster than the

temperature does. Therefore, this plume parameter is generally defined by the altitude. The densest part of the Mount St. Helens plume on May 18, 1980, was reported to reach the upper tropospheric and lower stratospheric levels, which are characterized by the pressure of about 300 and 200 mbar, respectively (Carey and Sigurdsson, 1982). Thus one may accept the pressure range for present-day volcanic ash-gas clouds to be from 200 to 1000 mbar.

## 4.4. ELECTRIC FIELD

Although there are few reports aimed at studying electric field potentials in volcanic plumes, these seem to lead to the conclusion that injection of volcanic fumes and/or ash into the atmosphere results in a cloud positively charged, both horizontally and vertically, with an abnormal electrostatic field, *i.e.* it differs from the regular fine-weather field of +100-130 V $m^{-1}$ by several orders of magnitude (Anderson *et al.*, 1965; Brook *et al.*, 1974; Cobb, 1980). Anderson *et al.* (1965) recorded electric field potentials during the formation of Surtsey volcano. The cloud had an electric potential as high as 30 kV $m^{-1}$ in the upper regions. The net charge decreased rapidly as the cloud was carried away from the crater by wind. At sea level the electric potential was recorded to be about 8 kV $m^{-1}$ and point discharge currents were measured in the microampere magnitude. Brook *et al.* (1974) detected potential gradients sometimes exceeding 7 kV $m^{-1}$ in the Westmann island of Heimaey's eruption. Kikuchi and Endoh (1982) measured 15 kV $m^{-1}$ about 5 km away from the Mount Usu volcano. Cobb (1980) measured 20 kV $m^{-1}$ at the ground whereas Hobbs and Lyons (1983) registered in an aircraft 10 kV $m^{-1}$ at 175 km from Mount St. Helens on May 18, 1980.

During the explosive phase of a volcano, the potential gradient is oscillating drastically between high and low values (Anderson *et al.*, 1965; Brook *et al.*, 1974). The drop in the potential toward the fine weather values is caused by neutralization of charges through lightning activity whereas its growth is related to new injection of positively charged particles into the atmosphere by the volcano.

The electrification process responsible for the positive charge in the high-velocity tephra eruptions of marine volcanoes might be due to interaction of lava with ocean waters (Anderson *et al.*, 1965). This is supported by the experiments of Blanchard (1964) and Pounder (1980), who found that contact of seawater with molten lava results in the production of a positively charged cloud of particles. Woodcock and Spencer (1961) have shown that these particles are composed of sea salt. Undoubtedly, other charge-separation mechanisms must play a role since land volcanoes are also electrified even though sea water is not present, such as in the eruptions of Vesuvius, Paricutin and Redoubt volcanoes, for example. Possible mechanisms include rock fracture (Fujinawa *et al.*, 1992; Takahashi, 1993), fragmentation of pyroclasts (Cheng, 1982), and grazing collisions between ash particles (Hatakeyama and Uchikawa, 1952).

## 4.5. VOLCANIC LIGHTNING

Despite several reports of volcanic lightning in the past, few researchers have been interested in studying volcanic lightning. Some possible explanations for such an apparent

lack of interest are the unpredictability of the event (though a volcano's violent eruption phase can extend to several months with a sustained lightning activity), the hazards associated to perform field studies, and the inapplicability of typical lightning remote sensing techniques (*e.g.*, visible detection by satellites of thunderstorm lightning at nighttime) to monitor volcanic lightning.

Lightning discharges of hundreds of meters in length are frequently generated during volcanic eruptions, in which both gases and tephra are emitted simultaneously into the atmosphere. They have been observed in explosive eruptions caused by magmatic (Green, 1944), hydromagmatic (Anderson *et al.*, 1965; Brook *et al.*, 1974) and glacier-pyroclastic processes (Hoblitt, 1994). Several types of lightning are produced, such as intracloud, cloud-to-ground, ground-to-cloud, and air-discharges (Anderson *et al.*, 1965; Brook *et al.*, 1974; Salanave, 1980; Hoblitt, 1994); however, there are no available statistics about their relative frequencies. Maximum flashing rates have been reported to be 10 flash $min^{-1}$ for the February 4, 1964 eruption of Surtsey (Anderson *et al.*, 1965), 11 flash $min^{-1}$ for March 18, 1980 eruption of Mt. St. Helens (Cobb, 1980), 16 flash $min^{-1}$ for the February 15, 1990 eruption of the Redoubt Volcano (Hoblitt, 1994), and >60 flash $min^{-1}$ for the April-June, 1979 eruption of the Soufriere Volcano (Shepherd *et al.*, 1979).

## 5. Energy Dissipation Rate

Volcanism is an expression of heat transfer from the mantle to the surface. The planet loses internal heat (i) by conduction from the interior to the surface and then into space, (ii) by advection where melts are generated in the interior and migrate to the surface or near the surface, and (iii) by convection involving gravity-induced turn-over by plastic flow of the mantle. The current mean surface heat flow due to conduction has been estimated to be about 56.6 mW $m^{-2}$ (Schubert, 1997; Schubert *et al.*, 1980 and 1989). Volcanism is the surface manifestation of advection and/or convection (Park, 1997). At present the volcanic flux has been estimated at about 4 $km^3$ $yr^{-1}$ (Decker and Decker, 1982); this includes material vented by subduction zone (~ 1 $km^3$ $yr^{-1}$), rift (~ 2.5 $km^3$ $yr^{-1}$) and hot-spot volcanoes (~ 0.5 $km^3$ $yr^{-1}$). Taking into account a density of ~ 2900 kg $m^{-3}$, and an enthalpy of melting ~418 J $g^{-1}$ for basalts (Yoder, 1976), the surface heat flow due to volcanism is estimated to be ~ 0.3 mW $m^{-2}$. Approximately 30% of this value is dissipated explosively by subaerial eruptions in the form of tephra (Pyle, 1995) where volcanic lightning is generated. Based on thermal evolution models, it is predicted that 4 billion years ago the surface heat flow of the Earth was ~ 400 mW $m^{-2}$ (BVSP, 1981; Schubert *et al.*, 1980; 1989). If we assume that the surface heat loss due to conduction through the lithosphere and hydrosphere has remained constant over time, the surface heat flux due to volcanic activity is derived to be about 340 mW $m^{-2}$. This value is somewhat of an upper limit since the heat flow by conduction may have varied with time. This implies that approximately $4.6 \times 10^3$ $km^3$ of basalt erupted annually. Eruption rates of this magnitude are consistent with major flood basalt episodes of the recent geologic past (250 to 14 Myr ago) (Richards *et al.*, 1989; Longhi, 1997). Observations suggest that about 10 wt% of the basaltic magma is fragmented into fine ash and entrained into volcanic plumes above flood eruptions (Stothers *et al.*,

1986; Woods, 1993a,b). The mass flux of tephra ( $MF$ ) injected to the atmosphere is therefore calculated to be ~ $1.3 \times 10^{15}$ kg $yr^{-1}$. Measurements of the electrical charge on ash particles from explosive volcanic eruptions indicate that the particles are nearly saturated with charge. The charge-to-mass ratio ($Q / m$) averages ~ $8 \times 10^{-4}$ C $kg^{-1}$ for both positive and negative charges (Gilbert and Lane, 1994). Injection of these electrically charged tephra particles into the atmosphere leads to the generation of strong electric fields within the volcanic plume. The plume typically exhibits a dipole structure with negatively charged particles in its lower region close to the vent site and positively charged particles in its upper portion. The electric field potential ($V$ ) between these two regions has been recorded in a number of volcanic plumes and ranges from 10 to 30 kV $m^{-1}$ (Navarro-González *et al.*, 1996). Electric breakdown within volcanic plumes leads to the generation of lightning discharges with a typical length ($L$ ) of about 500. The maximum electric power ($P$ ) available in explosive volcanic eruptions may be readily estimated according to the following equation: $P = MF\ V\ L\ Q / m$. Considering a mean value of 20 kV $m^{-1}$ for $V$, this results in about ~ $1 \times 10^{19}$ J $yr^{-1}$ accessible for nitrogen fixation (Navarro-González *et al.*, 1998).

## 6. Nitrogen Fixation

The principal reservoir of nitrogen is molecular dinitrogen in the atmosphere. However to be available for chemical evolution it must be in the form of ammonia or nitrate, forms known as fixed nitrogen. Due to the strength of the triple bond in $N_2$, nitrogen fixation, while thermodynamically favored is kinetically restricted. Navarro-González *et al.* (1998) examined the effect of volcanic lightning as a mechanism to fix nitrogen on early Earth. For their experiment, it was assumed that the chemical composition of Archean volcanic gases was similar to that of Hawaiian volcanoes. Volcanic gases generally undergo rapid mixing with underground or ground water or with the surrounding atmosphere present outside the volcanic vent environment. Consequently, the effects of dilution of volcanic gases with water and the atmosphere were investigated, assuming that early Earth's atmosphere was composed by 80% carbon dioxide and 20% molecular nitrogen (Kasting, 1990).

The magmatic gases gas mixture was excited by flowing into a microwave discharge cavity, and the products were analyzed in a flow system coupled to chemical ionization mass spectroscopy. Figure 1 shows the mass spectrograms for the various gas mixtures examined. A quantitative study of the experimental production efficiency of nitric oxide (NO) is given in Figure 2 as a function of dilution of the volcanic gas mixture with water and atmospheric gases. In addition, this figure also includes the predicted trends for NO and other minor species expected to form in the cooling channel of volcanic lightning. The experimental and predicted trends for NO agree quite well under most conditions except at high dilutions of water vapor ($\geq$ 60%). This discrepancy is attributed to the injection of excess water in the form of aerosols when a high helium flow passes through the water bubbler. The predicted NO energy yield is estimated to be ~ $1 \times 10^{16}$ molecule

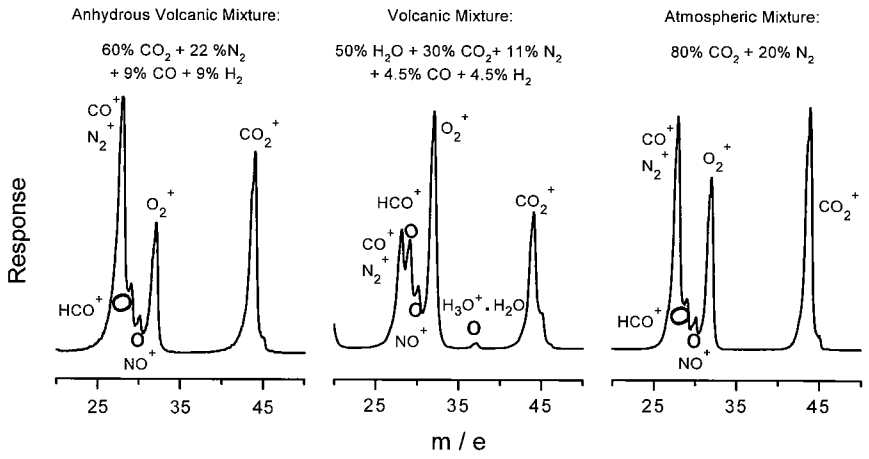


**Figure 1.** Chemical ionization mass spectrograms of effluents from different types of volcanic gas mixtures subjected to a microwave discharge.

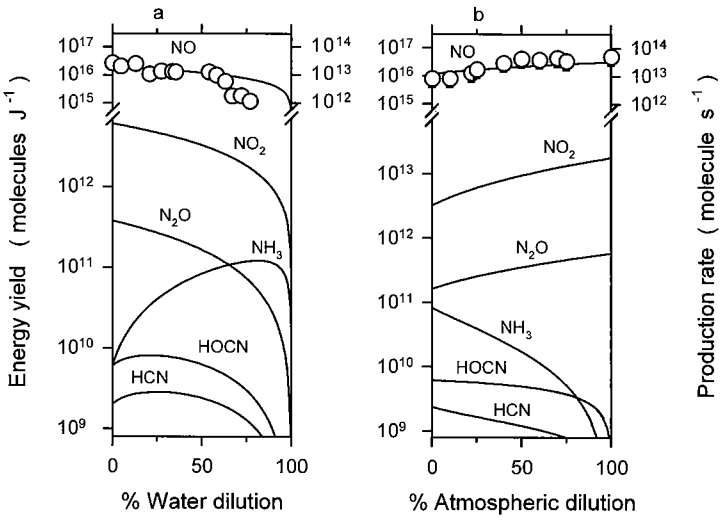


**Figure 2.** Production yields for several volcanic lightning products as a function of dilution of volcanic gases with (a) water and (b) the surrounding atmosphere. Lines are predicted trends from the thermochemical-hydrodynamic model whereas symbols are the experimental values derived in a microwave discharge.

$J^{-1}$ for volcanic lightning produced in a Hawaiian style volcanic mixture. This value can increase to ~$2\times10^{16}$ molecule $J^{-1}$ in an anhydrous volcanic mixture or to ~$3\times10^{16}$ molecule $J^{-1}$ at 97.5% dilution of the magmatic gases with the surrounding atmosphere.

If the magmatic gases are significantly diluted with water, this value can decrease down to ~$2\times10^{15}$ molecule $J^{-1}$ at 97.5% dilution. Other minor products predicted (see Fig. 2) were not detected experimentally on account of their extremely low product energy yields. A detailed analysis of volcanic lightning compared with other endogenous and exogenous sources showed that this source was the most important to fix nitrogen in early Earth (Navarro-González *et al.*, 2000).

Segura and Navarro-González (2000) examined the effect of volcanic lightning in a more reducing atmosphere from a simulated Martian volcanic plume. The chemical composition of the gas mixture used in these experiments was derived from the accretion model developed by Kuramoto and Matsui (1996) that was applied to Mars by Kuramoto (1997). The composition of volcanic gases was 64% $CH_4$, 24% $H_2$, 10% $H_2O$, 2% $N_2$. This was irradiated by focusing a high-energy infrared laser beam to simulate lightning, and the resulting products were analyzed by gas chromatography coupled to infrared and mass spectrometry. Figure 3 shows a gas chromatogram of the irradiation products. It has found that HCN was the most important form of fixed nitrogen with an energy yield of ~$6\times10^{14}$ molecules $J^{-1}$. HCN is considered a key intermediate in chemical evolution since it can lead to the formation of amino acids, purines and pyrimidines (Ferris and Hagan, 1984).

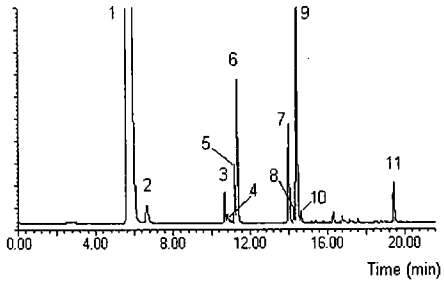


**Figure 3.** Gas chromatogram of compounds produced by lightning in a simulated Martian volcanic plume. Peak identification: 1. Acetylene + ethylene; 2. Ethane; 3. Propene; 4. Hydrogen cyanide; 5. 1,2-propadiene; 6. Propyne; 7. 1-buten-3-yne; 8. 1-butyne; 9. 1,3-butadiyne; 10. 2-butyne; 11. Benzene.

## 7. Phosphate Reduction

Glindemann *et al.* (1999) and de Graaf and Schwartz (2000) studied the reduction of phosphate by volcanic lightning using a spark discharge which was generated by applying a microwave field between the ends of a quartz tube containing the sample. In a first set of experiments, Glindemann *et al.* (1999) used samples as solution of $Na_2HPO_4$ or as pastes (mixtures of fluorapatite with montmorillonite) in water-saturated with a nitrogen atmosphere containing 1-10% $CH_4$. A spark discharge was generated in the device using a domestic microwave oven. The products were analyzed

by gas chromatography-mass spectrometry and the results are summarized in Table 1. In 10%

TABLE 1. Formation of phosphite by reduction of orthophosphate in $CH_4 + N_2$ mixtures.

| Phosphate source | Matrix | $\%CH_4$ (in $N_2$) | %Yield |
|---|---|---|---|
| $Na_2HPO_4$ | - | 10 | 11 |
| $Na_2HPO_4$ | - | 1 | 4 |
| $Na_2HPO_4$ | - | 0 | 0.1 |
| Hydroxyapatite | Montmorillonite | 10 | 6 |
| Fluorapatite | Montmorillonite | 10 | 7 |
| Fluorapatite | Montmorillonite | 1 | 4 |
| Fluorapatite | Montmorillonite | 0 | 0.5 |
| - | Montmorillonite | 10 | - |

methane an average yield of 11% phosphite was obtained using $Na_2HPO_4$ as the source of phosphorus. As the content of methane in the atmospheric mixture decreased, the production efficiency of phosphite dropped to 4% in 1% $CH_4$ and to 0.1% in pure $N_2$. In order to extend these results to a geophysical more plausible model, Glindemann *et al.* (1999) examined the reduction of fluorapatite, the most important phosphate mineral in igneous rocks. In these experiments, a yield of 7% phosphite was obtained in the presence of 10% methane. As with the experiments of $Na_2HPO_4$, the yield of phosphite decreased but was still substantial. Small amounts of methylphosphonic acid could also be detected in small quantities in these experiments.

As was proposed by Segura and Navarro-González (2000, 2001), these reduced compositions may be geologically relevant for Mars, where phosphorus is an abundant element. Accretion models predicted concentrations exceeding those on Earth for volatile and moderatlely volatile elements (Dreibus and Wänke, 1985). Martian meteorites analyses (Banin *et al.*, 1992) and Mars Pathfinder mission results (Dreibus *et al.*, 2000) have verified the high phosphorus content on Mars. Apatite grains have been detected in the Martian meteorites (Leshin, *et al.*, 1996, Watson, *et al.*, 1994); therefore this was an available source of phosphates on Mars.

De Graaf and Schwartz (2000) extended the research using gas mixtures contained 60% $CO_2$, 22-40% $N_2$ and variable concentrations of $H_2$ and CO. These mixtures are based on a volcanic outgassing model studied by Navarro-González *et al.* (1998, 2000). For these experiments, fluorapatite was mixed in a clay mineral matrix in order to have a more representative composition of igneous rocks. Samples undergo the same experimental and analysis processes that in the experiment developed by Glindemann *et al.* (1999). Their results demonstrated that several percent reduction of apatite occurs even in the presence of as little as 1% $H_2$ and $CO_2$ in the gas mixture. In addition, they demonstrated the formation of polyphosphate production (see Table 2) as a result of heating the mineral apatite in the presence of other minerals by the lightning discharge under various atmospheric chemical compositions.

TABLE 2. Analysis for orthophosphate (Pi), pyrophosphate (PPi) and tripolyphosphate (PPPi) in water extracts after exposure to electric discharge.

| Matrix | Conditions | Pi | PPi | PPPi | % Recovery |
|---|---|---|---|---|---|
| Montmorillonite | 60% $CO_2$ + 40% $N_2$ + $H_2O_{vapor}$ | 36±8 | 10±3 | 1.7±0.8 | 48 |
| Montmorillonite | Same as above | 39±1 | 13±2 | 1.7±0.5 | 54 |
| Bentonite | Same as above | 30±2 | 10±1 | 1.7±0.8 | 42 |
| Montmorillonite | Same as above | 12±3 | 4±1 | - | 16 |
| Montmorillonite | Same as above but - water vapor | 5±1 | 5±1 | - | 10 |
| Montmorillonite | 100% $N_2$ + $H_2O_{vapor}$ | 35±5 | 12±3 | - | 47 |

## 8. Concluding Remarks

The experiments presented above demonstrate that nitrogen fixation is an efficient process in volcanic lightning. Nitric oxide and hydrogen cyanide are the major volcanic lightning products expected for early Earth and Mars, respectively. In the case of phosphite, it is produced in high yields even in neutral atmospheres. Therefore electrical discharges associated with volcanic eruptions supplied a pathway by which nitrogen and phosphorus atoms were incorporated into prebiotic molecules needed for the emergence and sustainability of life. We hope that the work described in this review may motivate additional research on volcanic lightning. For instance, it is essential a thorough characterization of intracloud, cloud-to-ground, ground-to-cloud and air discharges in terms of frequency, mode of propagation, number of return strokes, discharge length, peak current, energy dissipation and lightning spectra. In addition, good laboratory simulations have to be designed to evaluate the possible contributions of volcanic lightning to the origins of life on Earth; particularly exploring the effects of high water vapor content and the presence of catalytically active surfaces from tephra. These studies should be complemented with field work, analyzing the contemporaneous chemical effects induced by volcanic lightning in the atmosphere.

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