EXPERIMENTAL SIMULATION OF EARLY MARTIAN VOLCANIC LIGHTNING

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ABSTRACT

A mixture of possible Martian volcanic gases were reproduced and irradiated by a high-energy infrared laser to reproduce the effects of lightning on the production of prebiotic molecules. The analysis of products were performed by a gas chromatograph interfaced in parallel with a FTIR-detector and a quadrupole mass spectrometer equipped with an electron impact and chemical ionization modes. The main products identified were hydrocarbons and an uncharacterized yellow film deposit. Preliminary results indicate the presence of hydrogen cyanide among the resultant compounds. © 2001 COSPAR. Published by Elsevier Science Ltd. All rights reserved.

INTRODUCTION

An explosive or plinian volcanic eruption is characterized by magma that disrupts into very small fragments that become locked into an expanding gas plume rising buoyantly from the vent (Wilson and Head, 1994). This type of volcanic eruption is relevant to prebiotic chemistry due to (1) the presence of reduced magmatic gases; (2) the production of volcanic lightning activity; and (3) the fast escape of the nascent molecules from the high temperature zone at sonic speeds (Navarro-González and Basiuk, 1998). Navarro-González (1998) demonstrated that on early Earth, volcanic lightning might have been the most important source of fixed nitrogen in the troposphere.

The exploration of Mars has shown that geophysical conditions for development of life were present about 3.8 billion years ago. Since volcanism was globally distributed (Mouginis-Mark *et al.*, 1992) during its early history, volcanic plumes could have been favorable environments for the production of key molecules needed for chemical evolution and the origins of life.

EXPLOSIVE VOLCANISM ON MARS

Volcanic activity on Mars extended for a long period and volcanic surfaces cover more than half of Mars (Mouginis-Mark *et al.*, 1992). Numerical simulations imply that it may have been common for basaltic magmas to produce plinian eruptions due to the lower martian gravity and atmospheric pressure (Wilson and Head, 1983; Mouginis-Mark *et al.*, 1992).

The oldest volcanic units identified on Mars are plateau plains that were formed by fissure eruptions (Greeley and Spudis, 1981). It has been shown that basaltic fissure eruptions can produce buoyant plumes of several kilometers when interaction with water occurs (Woods, 1993). Then, because groundwater was

an important part of Mars's upper crust (Wilson and Head, 1994), plinian volcanic plumes may have been common on this planet.

A POSSIBLE MIXTURE OF EARLY MARTIAN VOLCANIC GASES

In order to infer a possible composition of martian volcanic gases, the results from the accretion model of Kuramoto and Matsui (1996) were used. The model considers a hot Earth which accreted homogeneously to calculate partitioning of H and C among fluid, silicate melt and molten metallic iron within a growing Earth at temperatures from 2000 to 2500 K and pressures from 0.2 to 5 GPa. The planetesimals accreted had the composition given by the two-component model slightly modified from Ringwood (1977) and Wänke (1981). The two-component model considers that the accreting refractory fraction of a terrestrial planet is composed of a mixture of a highly reduced, volatile free component A, and an oxidized, volatile rich component B (Kuramoto and Matsui, 1996). Kuramoto (1997) applied this model to Mars using a mixing composition of 35% for A and 65% for B. The major volcanic provinces on Mars were due to upwelling mantle plumes, similar to hot spots on Earth (Schubert *et al.*, 1992) and this kind of volcanism originated from the deepest layer of the mantle. The gas mixture formed at higher pressures, according to Kuramoto's model, was chosen because it was more probable that those gases were kept deep in the mantle and later degassed by volcanism. Nitrogen was not considered in Kuramoto's model, for the experiment it was included considering the C/N ratio= 19±5 from the magmatic component measured on Nakhlitas and Chassigny meteorites (Wright *et al.*, 1992).

EXPERIMENTAL

The gases used for volcanic lightning simulations were ultra-high purity (CH_4 =99.97%, H_2=99.99% and N_2=99.99%), supplied by Praxair, Inc. The volcanic gas mixture chosen was the following mole fraction: 0.64 CH_4, 0.24 H_2, 0.10 H_2O, 0.02 N_2 at 194 mbar. The anhydrous mixture was prepared using a Linde mass flow measuring and control gas blending console (FM4660) equipped with fast response mass flow control modules (FRC) of 20 cm^3 min^{-1} capacity. Water was added later as vapor to avoid condensation.
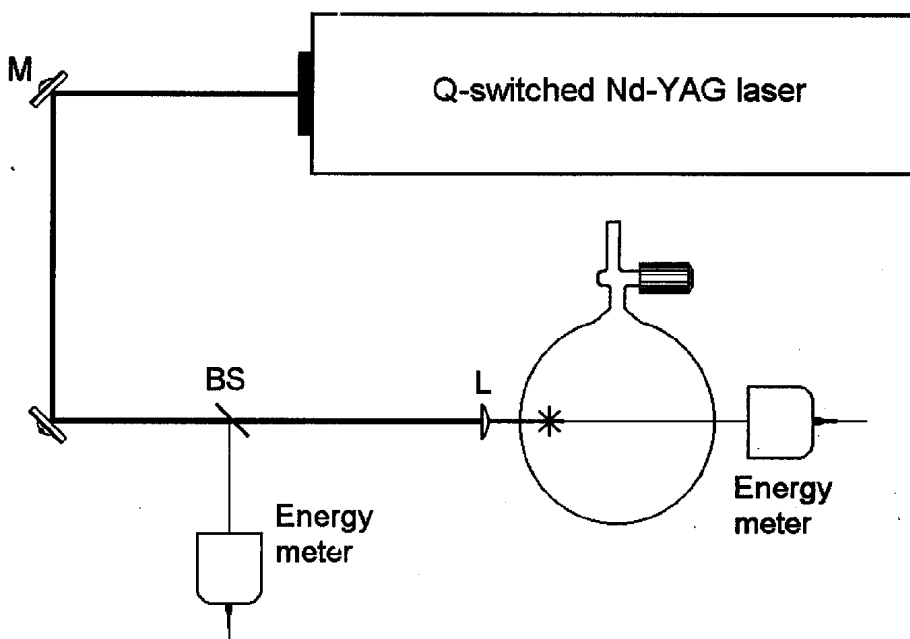

Fig. 1. Experimental design for simulating volcanic lightning. M= Mirror, BS= Beam Splitter, L= Lens

Volcanic lightning was simulated in the laboratory by focusing an infrared Nd-YAG laser that produces a laser induced plasma (LIP). The laser delivers a beam of 1.06 µm photons with an energy of 480 mJ per pulse in 5-7 ns at 10 Hz. The beam was focused inside a closed Pyrex flask with a plano-convex optical glass lens coated with an anti-reflecting film and obtaining a focal spot size of ~9.7 µm. The energy deposited into the system was determined by the difference between the input laser energy and that transmitted by the LIP, and quantified with a power and energy measurement system. About 60% of the input laser energy was transmitted by the LIP. Figure 1 shows the experimental design for the irradiation of volcanic gases. The samples were irradiated in the interval from 2.5 to 30 minutes to determine the energy yields of lightning products. Each experiment was repeated three times in order to calculate error bars.

RESULTS AND DISCUSSION

The products were analyzed using a Hewlett Packard (HP) gas chromatograph 5890 series interfaced in parallel with a HP FTIR-detector (model 5965) and a HP quadrupole mass spectrometer (5989B) equipped with an electron impact and chemical ionization modes. Figure 2 shows the mass chromatogram of the products after the irradiation. Table 1 presents peaks identification and the relative abundances (compared to acetylene) of the products. As an example of identification techniques used Figure 3 shows the absorption pattern for hydrogen cyanide and its mass spectrogram. The main products have been identified as hydrocarbons and an uncharacterized yellow film deposit. It is especially relevant the presence of hydrogen cyanide (HCN) among the resultant compounds. Other N-containing products such as ammonia and acetonitrile were not detected.

A thermochemical model was developed to predict if HCN could be formed in the volcanic plume due to its high temperature. The model considers the formation of chemical species with one and two atoms of carbon from the original gas mixture used in the experiment, at temperatures between 1000 and 5000 K. According to the model, HCN is formed above ~1600 K. Analysis of the orthopyroxene-silica assemblage in ALH84001, the oldest martian meteorite, indicates a magmatic temperature of ~1700 K at 40 km depth in the planet (Kring and Gleason, 1997). But models of the martian interior show that mantle temperatures are lower, 1200 K (McSween, 1994), consequently HCN may have been a characteristic product of volcanic lightning.
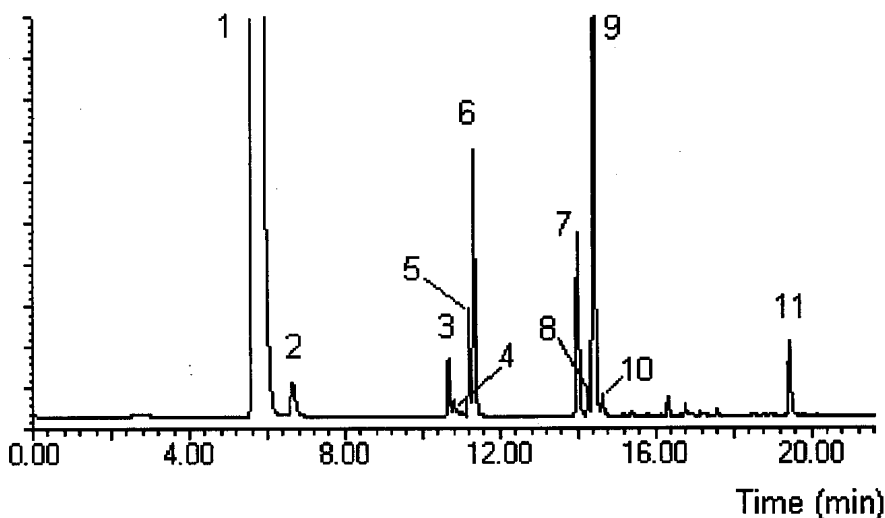

Fig. 2. SIM gas chromatogram using 26, 27, 39, 40, 41, 50, 52, 54, 66, 78 m/z, of compounds produced by 2 minutes LIP discharge irradiation of a gas mixture composed by CH_4 (64%), H_2 (24%), H_2O (10%) and N_2 (2%) For peak identification see Table 1.

Table 1. Relative Abundance of Volcanic Lightning Products

Peak number	Compound	Identification technique	Relative Abundance
1	Acetylene,	MS, IR	1
	Ethylene	MS, IR	1.0×10^{-2}
2	Ethane	MS, IR	3.5×10^{-2}
3	Propene	MS, IR	1.0×10^{-2}
4	Hydrogen cyanide	MS, IR	3.0×10^{-3}
5	1,2-propadiene	MS, IR	1.5×10^{-2}
6	Propyne	MS	4.5×10^{-2}
7	1-buten-3-yne	MS	3.0×10^{-2}
8	1-butyne	MS	5.0×10^{-3}
9	1,3-butadiyne	MS	1.0×10^{-1}
10	2-butyne	MS	5.0×10^{-3}
11	Benzene	MS, IR	1.0×10^{-2}

The energy flux delivered on Mars by volcanic lightning during its early history was calculated using the expression derived by Navarro-González $et\ al.$ (1998). The energy flux, E_F, produced by volcanic lightning is given by $E_F = MF\ V\ L\ Q/m$. The mass flux of volcanic material injected to the atmosphere, MF, is obtained from the total volcanic flux. Thermal models of Mars predict a flux that exponentially decays in the first billion years of the planet from 10 to 1 $km^3\ yr^{-1}$ (Schubert $et\ al.$, 1992), for the present work it was used, 5 $km^3\ yr^{-1}$. The analyses of the Martian meteorites indicate a density of Martian basalts of ~3200 kg m^{-3} (Wilson and Head, 1994), then, considering, as an upper limit, that all the erupted magma was injected to the atmosphere, MF ~1.6 x 10^{13} kg yr^{-1}. The electric field potential, V, of the volcanic plumes has been measured in eruptions that showed electric activity (Navarro-González $et\ al.$, 1996 and references therein), from these observations the average value of 20 kV m^{-1} was used. Other parameter measured in volcanic explosive eruptions is the charge to mass ratio (Q/m) which is about 8 x 10^{-4} C kg^{-1} (Gilbert and Lane, 1994). The typical length of the electric discharge, L, was calculated considering that: (1) volcanic lightning is exhibited during high-velocity emission of tephra (>100 m s^{-1}), (2) it is confined to the youngest part of the cloud and (3) cloud to ground discharges come from the top of the recently formed cloud (Anderson, 1965). Considering that the recently expulsed tephra ascends as a projectile launched at an initial speed v, the maximum altitude, h, reach by it will be given by $h = v/2g$, being g the acceleration due to gravity. So, a plume with $v = 100$ m s^{-1} would ascend around 500 m on
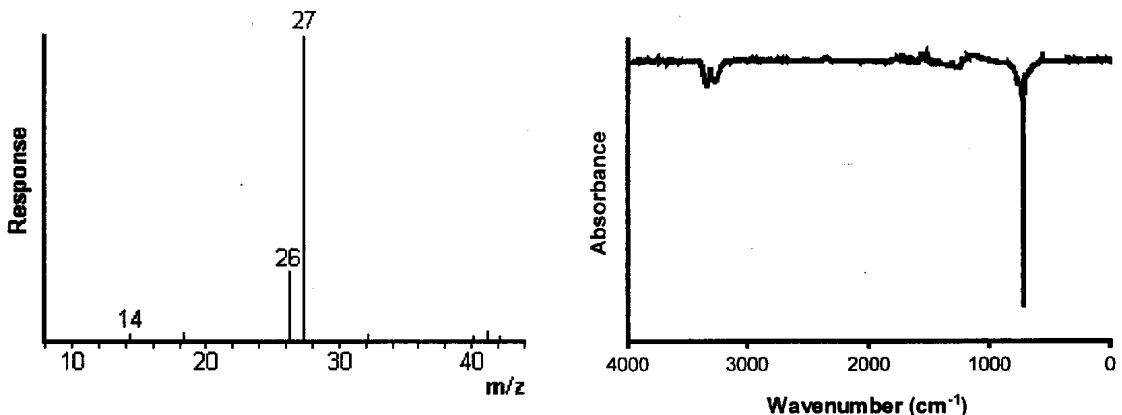

Fig. 3. Electron impact (70 eV) mass spectrum and infrared spectrum for hydrogen cyanide obtained after 2 minutes of LIP discharge irradiation of CH_4 (64%), H_2 (24%), H_2O (10%) and N_2 (2%) at 194 mbar.

Earth, which coincide with observations. On Mars, where eruption speeds will be 1.5 times larger than on Earth for the same mass eruption rates and volatile content (Wilson and Head, 1994), the altitude reached by recently formed volcanic plumes would be about 3 km. Because the rising of a volcanic cloud highly depends on its interaction with air, this value is an upper limit.

The energy flux available on early Mars in volcanic lightning was estimated to be $E_F \sim 8 \times 10^{17}$ J yr^{-1}, that represents a surface flux density of $\sim 5 \times 10^3$ J yr^{-1} km^{-2}, on early Earth this flux density was $\sim 2 \times 10^4$ J yr^{-1} km^{-2} (Navarro-González et al., 1998). Currently, we are calculating the possible contributions of fixed nitrogen by other endogenous as well as exogenous sources in order to determine the potential role of volcanic lightning on nitrogen fixation in early Mars.

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