EXPERIMENTAL SIMULATION OF VOLCANIC LIGHTNING ON EARLY MARS

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Abstract

A mixture of probable volcanic gases was reproduced and irradiated by a high-energy infrared laser beam to simulate volcanic lightning on early Mars in order to determine the possible role of this phenomenon in prebiotic synthesis. Analysis of products was performed using a gas chromatograph interfaced in parallel with an infrared detector and a quadrupole mass spectrometer. Hydrogen cyanide, a key molecule for prebiotic synthesis, was detected among the products.

1. Introduction

Lightning produced in explosive volcanic eruption columns may had been the main source of fixed nitrogen and was therefore a favorable environment for prebiotic synthesis (Navarro-González, *et al.*, 1996) on early Earth (Navarro-González, *et al.*, 1998) and early Mars (Navarro-González and Basiuk, 1998).

Explosive eruption column of a volcano 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).

The exploration of Mars has shown that life may have developed 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 a favorable environment for the production of key molecules needed for chemical evolution and the origins of life.

2. 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 have shown that explosive activity would occur if magma volatile contents exceed 0.01 weight percent on Mars (Wilson and Head, 1983). An explosive or plinian volcanic eruption is

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characterized by magma that disrupts into very small fragments that become locked to an expanding gas plume rising buoyantly from the vent (Wilson and Head, 1994). Because of the lower martian gravity, nucleation of magma would occur at systematically greater depths than on Earth since volatile solubility is pressure-dependent, volatile release would likely be more efficient (Mouginis-Mark, *et al.*, 1992). More vigorous gas release and higher eruption rates in Martian magmas compared with those on Earth imply that it may have been common for basaltic magmas to produce plinian eruptions (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 is present (Woods, 1993). Then, because groundwater is an important part of Mars's upper crust (Wilson and Head, 1994) volcanic plumes may have been common on this planet.

2.1. VOLCANIC GASES ON EARLY MARS

Kuramoto and Matsui (1996) have developed a thermodynamic model considering 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). On the two-component model is considered that accreting rock of a terrestrial planet is 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 fraction of 35% for the volatile-rich component. Because nitrogen was not considered in Kuramoto's model, for the experiment it is included considering the C/N ratio from the magmatic component measured on Nakhlitas and Chassigny meteorites (Wright, *et al.*, 1992).

The major volcanic provinces on Mars are due to upwelling mantle plumes, similar to hot spots on Earth (Schubert, *et al.*, 1992), this kind of volcanism comes from the deepest layer of the mantle. We choose the mixture formed at higher pressures because it has more probability to have been kept in the mantle and later degassed by volcanism.

3. Experimental

Volcanic lightning was simulated in the laboratory by focusing an infrared Nd-YAG laser that produce 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 at 194 mbar of 0.64 CH_4, 0.24 H_2, 0.10 H_2O, 0.02 N_2. The samples were irradiated 2.5, 5, 7.5, 10, 15, 20, 25 and 30 minutes to determine the energy yields. Each experiment was repeated three times in order to calculate errors.

The gases used for LIP irradiation were ultra-high purity (CH_4 =99.97%, H_2=99.99% and N_2=99.99%), supplied by Praxair, Inc. 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.

4. Results and Discussion

Analyses of the gases were performed 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. Table 1 lists the compounds identified. 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.

TABLE 1. Relative abundance of volcanic lightning products.

Compound	Identification technique	Relative Abundance
Acetylene,	MS, IR	1
Ethylene	MS, IR	1.0×10^{-2}
Ethane	MS, IR	3.5×10^{-2}
1-propene	MS, IR	1.0×10^{-2}
Hydrogen cyanide	MS, IR	3.0×10^{-3}
1,2-propadiene	MS, IR	1.5×10^{-2}
1-propyne	MS	4.5×10^{-2}
1-buten-3-yne	MS	3.0×10^{-2}
1-butyne	MS	5.0×10^{-3}
1,3-butadiyne	MS	1.0×10^{-1}
2-butyne	MS	5.0×10^{-3}
Benzene	MS, IR	1.0×10^{-2}

In order to explore the possibility that HCN could be formed in the volcanic plume due to its high temperature, a thermochemical model was developed. 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, the 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 were lower, about 1200 K (McSween, 1994); consequently HCN may have been a characteristic product of volcanic lightning. Therefore volcanic lightning on early Mars may have formed important quantities of HCN, a key molecule for origins of life and could have been an important source of fixed nitrogen.

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