

PRODUCTION OF LOW MOLECULAR WEIGHT HYDROCARBONS BY VOLCANIC ERUPTIONS ON EARLY MARS

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Abstract. Methane and other larger hydrocarbons have been proposed as possible greenhouse gases on early Mars. In this work we explore if volcanic processes may have been a source for such molecules based on theoretical and experimental considerations. Geologic evidence and numerical simulations indicate that explosive volcanism was widely distributed throughout Mars. Volcanic lightning is typically produced in such explosive volcanism. Therefore this geologic setting was studied to determine if lightning could be a source for hydrocarbons in volcanic plumes. Volcanic lightning was simulated by focusing a high-energy infrared laser beam inside of a Pyrex reactor that contained the proposed volcanic gas mixture composed of 64% CH₄, 24% H₂, 10% H₂O and 2% N₂, according to an accretion model and the nitrogen content measured in Martian meteorites. The analysis of products was performed by gas chromatography coupled to infrared and mass spectroscopy. Eleven hydrocarbons were identified among the products, of which acetylene (C₂H₂) was the most abundant. A thermochemical model was used to determine which hydrocarbons could arise only from volcanic heat. In this case, acetylene and ethylene are formed at magmatic temperatures. Our results indicate that explosive volcanism may have injected into the atmosphere of early Mars $\sim 6 \times 10^{12}$ g yr⁻¹ of acetylene, and $\sim 2 \times 10^{12}$ g yr⁻¹ of 1,3-butadiyne, both produced by volcanic lightning, $\sim 5 \times 10^{11}$ g yr⁻¹ of ethylene produced by volcanic heat, and 10^{13} g yr⁻¹ of methane.

Keywords: explosive volcanism, hydrocarbons, lightning, magmatic gases, Mars, Martian atmosphere, volcanic activity, volcanic lightning

1. Introduction

Mars is thought to have had similar environmental conditions (e.g., liquid water, active volcanoes and a denser atmosphere) to Earth when life arose in this planet at ≤ 3.5 Ga ago (McKay and Stoker, 1989). Mars must have had a warmer atmosphere in order to sustain those conditions. Because hydrocarbons have been proposed as greenhouse gases (e.g. Sagan and Chyba, 1997), we explore the significance of early Martian volcanism in the production of these compounds. Volcanic activity was a common phenomenon in the early Mars' history and was widely distributed through-out its surface (Mouginis-Mark *et al.*, 1992). Geologic evidence

and numerical simulations indicate that Martian volcanic activity was explosive in nature (Wilson and Head, 1994). Explosive volcanism is characterized by the formation of floating plumes composed of ashes and volcanic gases that acquire electric charge during their ejection into the atmosphere producing lightning discharges of hundreds of meters in length (Navarro-González *et al.*, 1996). The explosive eruption column of a volcano is particularly an interesting locale 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 or supersonic speeds (Basiuk and Navarro-González, 1996; Navarro-González and Basiuk, 1998; Navarro-González *et al.*, 1996; Navarro-González and Segura, 2001). The purpose of this paper is to explore the significance of this microenvironment in the production of hydrocarbons by volcanic lightning and volcanic heat.

2. Composition of Early Martian Volcanic Gases

The nature of the chemical compounds formed by volcanic lightning strongly depends on the initial composition of magmatic gases, which is controlled by the oxidation state and abundance of iron in the upper mantle (Whittet, 1997 and references therein). The oxidation state of a planet is the result of its accretionary history and its later evolution. In a homogenous accreted planet, like Mars (Dreibus and Wänke, 1989) with metallic iron present in its upper mantle, the volcanic gases would have been reduced in nature (Whittet, 1997). To simulate the volcanic plume environment, a possible volcanic gas composition was derived from an accretional model of Mars developed by Kuramoto (1997). The model calculates the amount of hydrogen, oxygen and carbon that was distributed among the fluid, silicate melt and molten metallic iron during the accretion of the planet. We assume that accreting planetesimals 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 a hot homogeneously accreted Mars using a mixing composition of 35% for A and 65% for B.

In the model Kuramoto (1997), nitrogen was not considered in the volatile fraction; therefore we estimated the abundance of nitrogen in magmatic gases based on the carbon–nitrogen ratio measured in Chassigny and the nakhlitas (Segura and Navarro-González, 2000, 2001). Magmatic gases may exist in igneous rocks as fluid inclusions which are released during stepped combustion as the minerals which contain them begin to soften and melt (Wright *et al.*, 1992). Melt occurs at temperatures greater than 700 °C; therefore volatiles liberated above that temperature will give information regarding the magmatic species. Magmatic components measured in Chassigny and the nakhlitas indicate a C/N ratio of 11–28 (Wright *et al.*, 1992).

Based on these data the volcanic gas mixture used for our experiments was composed of: 64% CH₄, 24% H₂, 10% H₂O and 2% N₂. This mixture corresponds to a C/N ratio of 20.

3. Experimental Simulation of Volcanic Lightning

The gases used for the simulation of Martian volcanic lightning were of ultra-high purity (CH₄ = 99.97%, H₂ = 99.99% and N₂ = 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 cm³ min⁻¹ capacity. The experimental setting for preparing the gas mixture is presented in Figure 1. A reactor made with a 1 L Pyrex glass flask closed by a high vacuum stopcock, was connected to the manifold in order to prepare the final mixture. The reactor was evacuated to 10⁻² mbar before water was added. In order to avoid the water condensation, this compound was introduced as vapour by maintaining the system at constant temperature (19 °C). At this temperature the water vapour pressure is 23 mbar, the vapour pressure was confirmed every time a sample was prepared by the pressure controllers in the vacuum line. After the water was added, the reactor was closed to evacuate the gas line, then the anhydrous mixture was introduced into the reactor until the total pressure of the system was 230 mbar. The final composition of the gas was 64% CH₄, 24% H₂, 10% H₂O and 2% N₂.

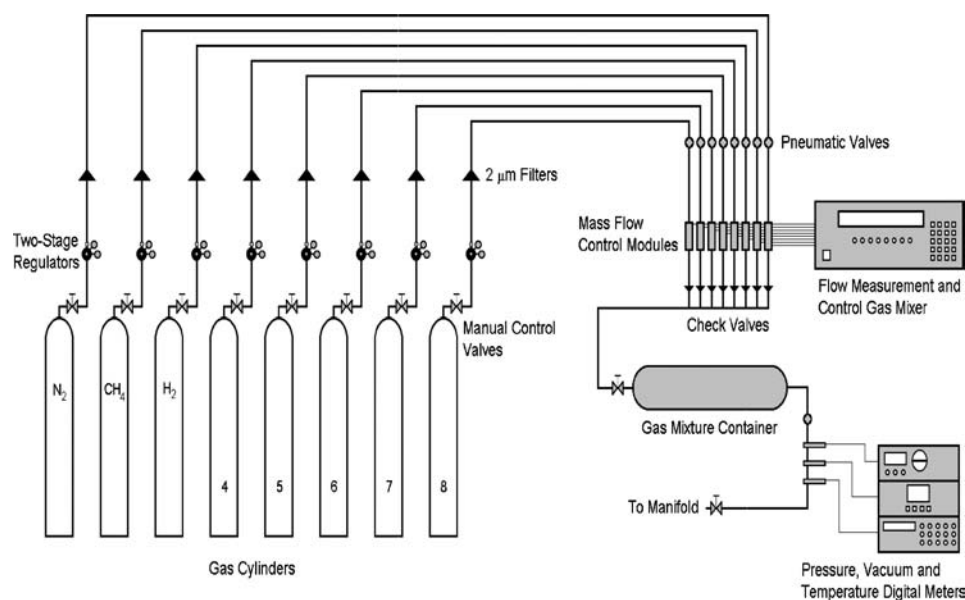


Figure 1. Gas blending system used to prepare the complex gas mixtures.

Volcanic lightning was simulated in the laboratory by focusing an infrared Nd-YAG laser which produces a laser induced plasma (LIP). This technique has shown to be the best to simulate lightning because it avoids the contamination by electrodes and allows a direct measure of the energy deposited in the plasma. The properties of LIP have been carefully evaluated with respect to its spectral properties, temperature, electron density evolution, optical emission, focal size, hydrodynamic evolution and stable products (Borucki *et al.*, 1985; Borucki and Mckay, 1987; Jebens *et al.*, 1992; Navarro-González and Villagrán-Muniz, 2001; Navarro-González *et al.*, 2001a, b; Radziemski *et al.*, 1983; Raga *et al.*, 2000; and Sobral *et al.*, 2000). The laser delivers a beam of $1.06\ \mu\text{m}$ photons with an energy of 300 mJ per pulse in 5–7 ns at 10 Hz. The beam was focused inside a reactor with a plano-convex optical glass lens coated with an anti-reflecting film and obtaining a focal spot size of $\sim 9.7\ \mu\text{m}$ (Figure 2).

The energy deposited into the system was determined by the difference between the input laser energy and that transmitted by the LIP, and was determined with energy meters (LabMaster Ultima with crystalline pyroelectric sensor LM-P10i from Coherent). About 90% of the input laser energy was deposited into the LIP at 230 mbar of 64% CH_4 , 24% H_2 , 10% H_2O , 2% N_2 . The samples were irradiated in the range from 3 to 12.5 min to determine the energy yields.

The analysis of the samples was performed using a Hewlett Packard gas chromatograph (5890 series) interfaced in parallel with a HP FT (5965) infrared spectrophotometer and a HP quadrupole mass spectrometer (5989B) operating in electron impact mode at 70 eV. The coupled system is equipped with computerized data acquisition, analysis and database search capabilities. In all cases the gas-phase products were injected, immediately after irradiation, into the gas chromatograph

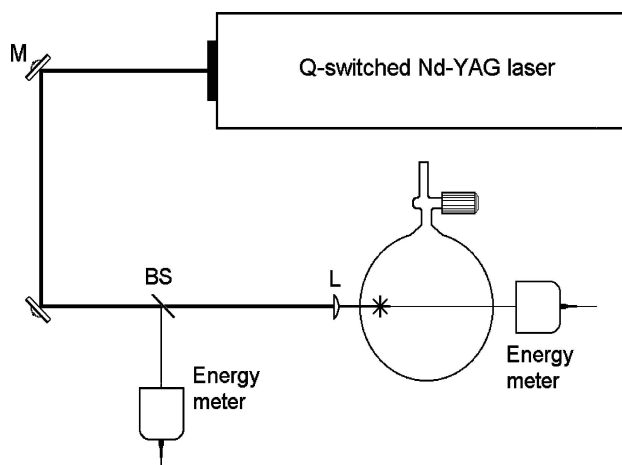


Figure 2. Experimental design for simulating volcanic lightning. M = mirror, BS = beam splitter, L = lens. See details in the text above.

by an automatic six-port gas-sampling valve with a gas loop of 2 mL. The column used was a 25 m \times 0.32 I.D. PoraPlot Q fused-silica with a 2.5 m gas particle trap. 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 5.62 min. The carrier gas was He (chromatographic grade from Praxair, Inc.) with a flow of 1.2 mL min⁻¹. The temperature at the GC-MS-FTIR interfaces was at 250 °C. Mass and infrared spectral database matches were confirmed by visual inspection. Once the chemical identity of the compounds synthesized by the different energy sources was established, a selective ion monitoring method was used to increase the analytical sensitivity of the products. The ions used were 26, 27, 39, 40, 41, 50, 52, 54, 66, and 78 m/e. The peak areas measured using the mass spectrometer as detector allowed the estimation of the number of molecules of each compound because the peak area is proportional to the abundance of the compound. Calibration curves were done using C₂H₂ and C₂H₆. To estimate the yields of the rest of the hydrocarbons, it was assumed that their responses were similar to those of C₂H₆ and C₂H₂. Acetylene and ethylene were resolved in one chromatographic peak. Their abundance was estimated by infrared spectroscopy.

4. Thermochemical Modeling of Magmatic Gases

Thermochemical data (NIST SRDB 69) were used to determine the main stable chemical species produced by volcanic heat at equilibrium temperatures between 1000 and 5000 K. The equilibrium concentrations as a function of temperature were computed using the program ACUCHEM which numerically solves the differential equations of the reaction mechanism (Braun *et al.*, 1988). The following chemical species were included in the model: H, H₂, OH, H₂O, H₂O₂, O, O₂, O₃, C_g, CO, CO₂, CHO, CH, CH₂, CH₃, CH₄, C₂H₆, C₂H₅, C₂H₄, C₂H₃, C₂H₂, C₂H, C₂, HCHO, HCO₂H, CH₃OH, N, N₂, N₂O, NO, NO₂, CN, HCN, HOCN, NH, NH₂, NH₃, N₂H₄, CH₃NH₂, CH₃CN, CH₃CHO, C₂H₅CHO, C₂H₅CN, CH₂CHCN, HC₃N, C₃H₈, C₃H₆, C₃H₄, C₂H₅NH₂, C₂N₂, and C₂H₅OH.

5. Results and Discussion

Figure 3 shows a typical chromatogram of the gases formed in our simulation of lightning in a primordial Martian volcanic plume. The main products identified by infrared and mass spectroscopy were: acetylene (HC≡CH), ethylene (CH₂=CH₂), ethane (CH₃-CH₃), propene (CH₃-CH=CH₂), hydrogen cyanide (HC≡N), propane (CH₃-CH₂-CH₃), 1,2-propadiene (CH₂=C=CH₂), propyne (HC≡C-CH₃), 1-buten-3-yne (HC≡C-C=CH₂), 1-butyne (CH₃-CH₂-C≡CH), 1,3-butadiene (HC≡C-C=CH), 2-butyne (CH₃-C≡C-CH₃), and benzene (C₆H₆). As an example of the identification of each compound formed, Figure 4 shows the infrared absorption and mass spectrometry patterns for acetylene, the main product.

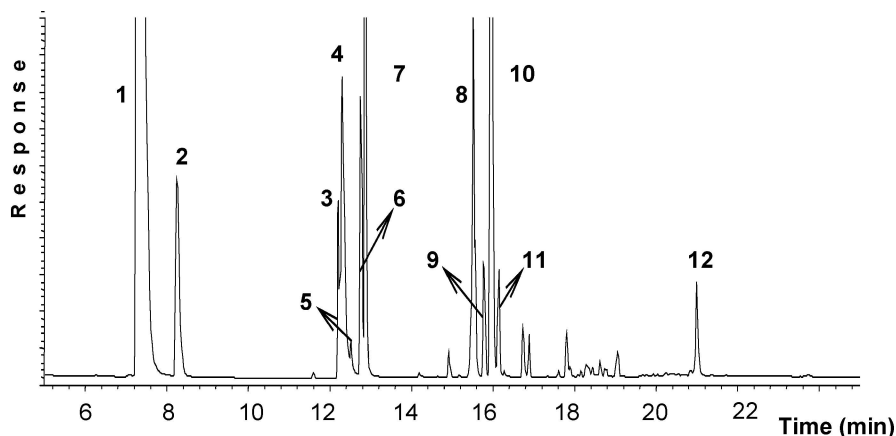


Figure 3. Selective ion monitoring gas chromatogram of compounds produced by 5 min LIP discharge irradiation of a gas mixture composed by CH_4 (64%), H_2 (24%), H_2O (10%) and N_2 (2%). Peak identifications as given in Table I.

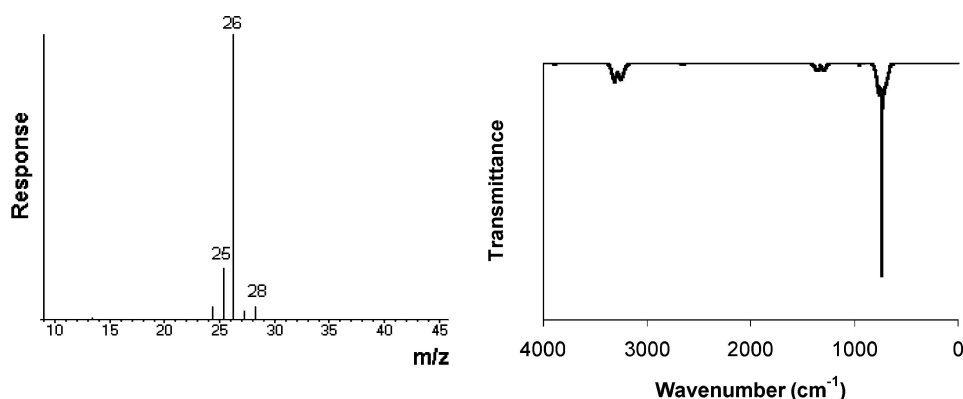


Figure 4. Electron impact (70 eV) and infrared spectra for peak no. 1 (acetylene + ethylene) in Figure 1 from 5 min LIP discharge irradiation of CH_4 (64%), H_2 (24%), H_2O (10%) and N_2 (2%) at 230 mbar. Maximum wavenumbers from IR spectra peaks correspond to acetylene. Small peak at 926.2 cm^{-1} corresponds to ethylene.

Other non-volatile hydrocarbons, not studied in this work, were deposited on the walls of the reactor as yellowish film.

The energy yields of products, expressed in molecules J^{-1} , were calculated from the slopes of the linear trend of curves where the abundance of a given product was plotted as a function of the energy deposited in the plasma (Figure 5). The energy yields for the main volcanic products are summarized in Table I. These values can then be used to estimate the rate of production of hydrocarbons by volcanic lightning in early Mars by multiplying the energy yield times the energy deposited by lightning. The energy dissipated by volcanic lightning was calculated using the

TABLE I
Rate of compounds produced by volcanism on early Mars according to this model

Peak No.	Compound	Volcanic lightning		Volcanic heat
		Energy yield (molecules J ⁻¹)	Rate (g yr ⁻¹)	Rate (g yr ⁻¹)
1	Acetylene	2×10^{17}	6×10^{12}	5×10^{11}
	Ethylene	2×10^{15}	6×10^{10}	5×10^{11}
2	Ethane	8×10^{15}	3×10^{11}	None
3	Propene	3×10^{15}	2×10^{11}	None
4	Hydrogen cyanide	5×10^{15}	2×10^{11}	None
5	Propane	7×10^{14}	4×10^{10}	None
6	1,2-propadiene	7×10^{15}	4×10^{11}	None
7	Propyne	2×10^{16}	9×10^{11}	None
8	1-buten-3-yne	1×10^{16}	9×10^{11}	None
9	1-butyne	3×10^{15}	2×10^{11}	None
10	1,3-butadiyne	4×10^{16}	2×10^{12}	None
11	2-butyne	2×10^{15}	2×10^{11}	None
12	Benzene	5×10^{15}	5×10^{11}	None

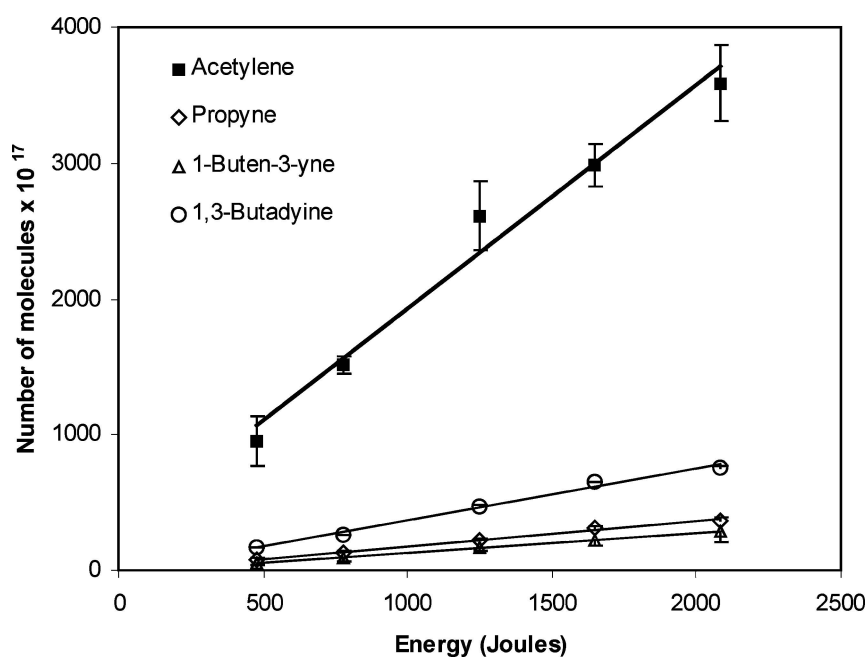


Figure 5. Abundance of some LIP products as a function of energy deposited in the plasma. Lines are the least square fit of the data. The slopes of the fitted lines are the energy yields.

expression derived by Navarro-González *et al.* (1998, 2000) for the early Earth and later adapted by Segura and Navarro-González (2001) for early Mars. The energy flux, P , produced by volcanic lightning is given by $P = MFVLQ/m$. The mass flux of tephra 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 km³ yr⁻¹ (Schubert *et al.*, 1992), for the present work, 5 km³ yr⁻¹ was used. The analysis of 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 into the atmosphere, $MF \sim 1.6 \times 10^{13}$ 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. Another parameter measured in volcanic explosive eruptions is the charge to mass ratio (Q/m) which is about 8×10^{-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 *et al.*, 1965). The recently expelled 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 Earth, which coincides 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 available on early Mars in volcanic lightning was estimated to be $P \sim 7.7 \times 10^{17}$ J yr⁻¹, that represents a surface flux of $\sim 5 \times 10^3$ J yr⁻¹ km⁻². Taking into account this value for the dissipation of volcanic lightning, we derived the rates of production of hydrocarbons in grams per year for early Mars (see Table I). The two most important hydrocarbons from volcanic lightning are acetylene and 1,3 butadiyne.

Models of the Martian interior show that upper mantle temperatures were lower than 1600 K (McSween, 1994), which will be an upper limit for the magma temperature. Because methane outgassed by volcanic eruptions at such temperatures could potentially dissociate and lead to the formation of other hydrocarbons, we investigated this contribution using a thermochemical model. The results are shown in Figure 6. Volcanic heat may produce acetylene and ethylene. At 1500 K, the mixing ratio of acetylene is 3.58×10^2 and the one for ethylene is 2.94×10^{-2} . Total amount of acetylene and ethylene produced by volcanic heat was calculated by multiplying the mass rate of magma erupted times the mass fraction of gas contained in the magma times the mixing ratio of the two compounds derived from the thermochemical model. Mass erupted from Martian volcanoes was $\sim 1.6 \times 10^{16}$ g yr⁻¹, according to the calculations presented before. The amount of gas typically diluted

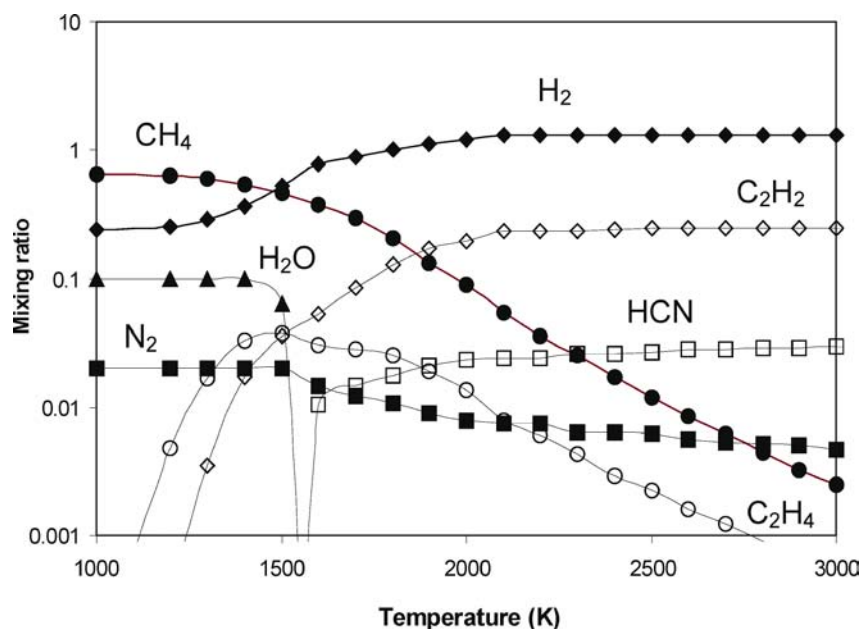


Figure 6. Mixing ratio as a function of temperature for the most abundant species obtained in a thermochemical model. The original composition of the mixture was: 64% CH₄, 24% H₂, 10% H₂O and 2% N₂.

in magma is about 0.1% wt, then about 5×10^{11} g yr⁻¹ of acetylene and the same amount of ethylene may be produced by volcanic heat in early Mars (Table I). Considering that the mixing ratio for methane in our proposed volcanic gas mixture is 0.64, about 10^{13} g yr⁻¹ of this compound may be injected into Martian atmosphere during the first billion years.

Methane injected into the Martian atmosphere may be an average of $\sim 10^{13}$ g yr⁻¹ during the first billion years, which translates into a mixing ratio of $\sim 3 \times 10^{-5}$, for an atmosphere with 1 bar of pressure in hydrostatic equilibrium ($M_{\text{atmosphere}} = 3.87 \times 10^{21}$ g) and considering a lifetime of methane of 10^4 yr. Methane polymerizes and photolyzes in an atmosphere of CO₂ (Pavlov *et al.*, 2001); such polymers may deposit in the surface or form a haze layer. Detailed photochemical models for early terrestrial atmosphere indicate that a hydrocarbon haze layer may not provide a significant UV shielding for greenhouse gases resulting from methane (Pavlov *et al.*, 2001). However, volcanic lightning is expected to have injected $\sim 6 \times 10^{12}$ g yr⁻¹ of acetylene and $\sim 2 \times 10^{12}$ g yr⁻¹ of 1,3-butadiyne, whereas volcanic heat is thought to have outgassed $\sim 5 \times 10^{11}$ g yr⁻¹ of acetylene and ethylene, in plumes of primitive Mars volcanoes. These unsaturated hydrocarbons would readily have polymerized by UV radiation in the atmosphere. Therefore, future work should address their possible impact in chemistry and meteorology of the early Martian atmosphere.

Acknowledgements

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