Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars

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[1] The most comprehensive search for organics in the Martian soil was performed by the Viking Landers. Martian soil was subjected to a thermal volatilization process to vaporize and break organic molecules, and the resultant gases and volatiles were analyzed by gas chromatography-mass spectrometry. Only water at 0.1–1.0 wt% was detected, with traces of chloromethane at 15 ppb, at Viking landing site 1, and water at 0.05–1.0 wt% and carbon dioxide at 50–700 ppm, with traces of dichloromethane at 0.04–40 ppb, at Viking landing site 2. These chlorohydrocarbons were considered to be terrestrial contaminants, although they had not been detected at those levels in the blank runs. Recently, perchlorate was discovered in the Martian Arctic soil by the Phoenix Lander. Here we show that when Mars-like soils from the Atacama Desert containing 32 ± 6 ppm of organic carbon are mixed with 1 wt% magnesium perchlorate and heated, nearly all the organics present are decomposed to water and carbon dioxide, but a small amount is chlorinated, forming 1.6 ppm of chloromethane and 0.02 ppm of dichloromethane at 500°C. A chemical kinetics model was developed to predict the degree of oxidation and chlorination of organics in the Viking oven. Reinterpretation of the Viking results therefore suggests ≤0.1% perchlorate and 1.5–6.5 ppm organic carbon at landing site 1 and ≤0.1% perchlorate and 0.7–2.6 ppm organic carbon at landing site 2. The detection of organics on Mars is important to assess locations for future experiments to detect life itself.

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1. Introduction

[2] The elemental composition of the Martian soil has been measured in situ by the Viking Landers [*Clark et al.*, 1976, 1982; *Clark and van Hart*, 1981], the Mars Pathfinder Rover [*Wänke et al.*, 2001; *Brückner et al.*, 2003; *Foley et al.*, 2003], and the two Mars Exploration Rovers [*Gellert et al.*, 2004, 2006; *Rieder et al.*, 2004] with the use of X-ray fluorescence spectrometry. Chlorine (Cl) has been recognized as an important chemical component of the Martian surface. Its concentration varied from 0.1 wt% at Chryse Planitia (22.7°N, 48.2°W) to 0.9 wt% at Utopia Planitia (48.3°N, 226.0°W) as determined by Viking Landers 1 and 2, respectively [*Clark et al.*, 1976, 1982; *Clark and van Hart*, 1981]. At Ares Vallis (19.3°N, 33.6°W) the Pathfinder rover found Cl at 0.55 wt% [*Wänke et al.*, 2001; *Brückner et al.*, 2003; *Foley et al.*, 2003]. In the Southern Hemisphere, at Gusev crater (14.6°S, 175.5°E), Cl concentrations were measured in the range 0.06–0.68 wt% by Spirit [*Gellert et al.*, 2004, 2006], whereas at the equator, at Meridiani Planum (1.9°S, 354.5°E), Cl was found at much higher concentrations (0.2–2.6 wt%) by Opportunity [*Rieder et al.*, 2004]. In addition, the abundance of Cl has been determined by remote sensing using the γ-ray spectrometer on board Mars Odyssey [*Keller et al.*, 2006]. Cl is not homogeneously distributed, varying from 0.2 to 0.8 wt% from the equator to midlatitudes (±50°). However, the instruments on board these missions were able to detect the element itself but provided no information on its chemical form. Because on Earth chlorine is generally found as chloride (Cl^-), it was logically believed to be in this form in the Martian soil [*Baird et al.*, 1976]. The only chemical analysis of soluble salts in soil was recently carried out by the Phoenix Lander in the Martian Arctic (68.3°N, 127.0°W) [*Hecht et al.*, 2009]. Surprisingly, chlorine was present as perchlorate (ClO_4^-) at 0.4 to 0.6 wt%, and chloride was only a minor constituent, at 0.01 to 0.04 wt%. Additional support for the identification of perchlorate came from the thermal evolved gas analysis, which detected the release of molecular oxygen (O_2) when the soil was heated from 325° to 625°C [*Hecht et al.*, 2009]. No inorganic Cl species were observed during this analysis, presumably because Cl atoms reacted with the Ni ovens of the instrument and therefore were not evolved to

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the mass spectrometer [*Lauer et al.*, 2009]. On the basis of the abundances of dissolved cations present in the Martian soil, it is expected that perchlorate is in the form of magnesium perchlorate, $Mg(ClO_4)_2$, or calcium perchlorate, $Ca(ClO_4)_2$ [*Hecht et al.*, 2009].

[3] In perchlorate the chlorine atom is in a high oxidation state (+7) and is surrounded by four oxygen atoms in tetrahedral (T_d) symmetry. Thermodynamically speaking, perchlorate is a very strong oxidant. The standard oxidation potential for perchlorate is $E° = 1.20$ V ($ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$); however, owing to its symmetry, it has tremendous kinetic stability unless it is present in a highly acidic medium or is subjected to heat [*Parker*, 2009]. The natural occurrence of perchlorate in the Atacama Desert has been known since 1880 [*Schumacher*, 1960; *Ericksen*, 1981, 1983; *Jackson et al.*, 2006], one of the driest places on Earth with Mars-like soils [*Navarro-González et al.*, 2003], where its soil abundance is only about 0.03 wt%, in contrast to 4.6 wt% for Cl^- [*Parker*, 2009]. It has also been found recently in the dry valleys, at a soil abundance of 0.0001% [*Kounaves et al.*, 2010]. Perchlorate is thought to be formed globally on Earth by the reaction of chlorine species with atmospheric oxidants [*Michalski et al.*, 2004; *Kounaves et al.*, 2010]; however, it accumulates in the soil surface in arid environments [*Kounaves et al.*, 2010]. The discovery of soil perchlorate at one site on Mars does not by itself imply that perchlorate should be ubiquitously in the planet's surface. However, because it has been hypothesized that on Mars, perchlorate is formed in a process similar to that on Earth [*Catling et al.*, 2010], it is to be expected that perchlorate is more commonly distributed throughout the Martian surface.

[4] The discovery of perchlorate in the Martian soil has important implications for the detection of organics in past and future missions. Soil perchlorate will burn organics into carbon dioxide (CO_2) when heated in an oven, preventing their detection in the analytical instrument [*Ming et al.*, 2009].

[5] In 1976 the Viking Landers carried out a series of molecular analyses to search for the presence of organic compounds in the Martian soil [*Biemann et al.*, 1976, 1977]. Two soil samples were investigated by each Viking Lander. In these experiments soil was subjected to thermal volatilization-gas chromatography-mass spectrometry (TV-GC-MS); this assay consisted of rapid heating of the soil to vaporize small molecules and break down larger ones into smaller organic molecules, and the resultant fragments were swept away from the oven into the gas chromatograph, where they were separated and then analyzed by MS. Unexpectedly, in none of the experiments could organic material thought to be released from the soil be observed at detection limits generally of the order of parts per billion. The evolution of carbon dioxide (50–700 ppm) and water (H_2O at 0.1–1%), but not of other inorganic gases, was observed upon heating of the sample at 200°, 350°, and 500°C. Interestingly, chloromethane (CH_3Cl) was detected in soils by the Viking Lander 1 at levels of 15 ppb. In contrast, dichloromethane (CH_2Cl_2) was detected in surface soils and underneath a rock at levels of 2–40 ppb by Viking Lander 2 (see Table 1). However, these chlorohydrocarbons were not considered to be indigenous to Mars because it was not expected that they could be the major organic molecules detected on Mars or Earth. Therefore, they were considered to be terrestrial contaminants because the $^{37}Cl/^{35}Cl$ ratio in these chlorohydrocarbons was similar to the ratio in those found on Earth, although these compounds were not detected at such levels in the blank runs [*Biemann et al.*, 1976, 1977].

[6] We report here results of the TV characterization of major gases and volatiles released for Mars-like soils from the Atacama Desert, which were enriched with 1 wt% magnesium perchlorate and processed using the Viking Lander heating protocol but with an extended temperature range, 200°–1000°C, by GC-MS. Soil samples were collected from the arid core region of the Atacama Desert in Yungay, Chile, which contains Mars-like soils in the surface. These soils show extremely low levels of culturable bacteria, low organic concentrations, and the presence of a non–chirally specific oxidant [*Navarro-González et al.*, 2003]. The search for organics in this soil sample has been thoroughly investigated using the Viking [*Navarro-González et al.*, 2006] and Phoenix [*Navarro-González et al.*, 2009] Lander protocols. We decided to use a natural soil sample rather than synthetic soil because it has been found that adding traces of organics to synthetic soils results in physicochemical properties of the sample that are different from those of native organics [*Kotler et al.*, 2009].

2. Methods

2.1. Reagents

[7] All chemicals were of the highest purity commercially available and were obtained from Sigma-Aldrich and Merck Chemicals. Magnesium perchlorate was prepared from a 3 N $HClO_4$ aqueous solution (70%–72%) that was neutralized with $Mg(OH)_2$ (95%). Finally, the solution was freeze-dried and the crystals were finely ground in an agate mortar mill. The purity of magnesium perchlorate was confirmed by powder X-ray diffraction spectroscopy using a Siemens D5000 X-ray diffractometer.

2.2. Soil Samples

[8] Approximately 500 g, representing a composite of six nearby sites (~2 m in radius) of the upper 10 cm soil layer from the upper eastern hills of the Yungay Valley (AT02-03A: 24°4′9.6″S, 69°51′58.8″W) were collected in October 2002 using sterile polyethylene scoops and stored in sterile polyethylene (Whirlpak) bags [*Navarro-González et al.*, 2003] (see Figure 1). Soil samples were freeze-dried and then were finely ground and homogenized with an agate mortar mill. Samples were kept at ambient temperature until analyses.

2.3. Soil Inorganic and Organic Carbon

[9] Inorganic carbon present as carbonates and organic carbon were quantified as carbon dioxide by GC-MS after acidification or oxidation, respectively. One gram of soil was placed in a glass flow reactor connected with two gas traps. The air trapped in the system was pumped down. Then liquid nitrogen was added into the second gas trap and 10 ml of 30% sulfuric acid was added to convert any carbonate soil into carbon dioxide. The reactor was kept under vacuum for 15 min and any CO_2 released was frozen into the liquid nitrogen trap. This trap was detached from the system, and liquid nitrogen was added to the first gas trap. Then 10 ml of a 0.001 M $KMnO_4$ solution was added to oxidize the organic matter to carbon dioxide. The solution

Table 1. Detection of Chlorohydrocarbons in Martian Soils by the Viking TV-GC-MS[a]

Sample	T (°C)	Injection Mode[b]	Compound	Abundance (ppb)
VL-1				
Blank	500	CO_2	CH_3Cl	ND
Sample 1	200	CO_2	CH_3Cl	15
	500	CO_2	CH_3Cl	ND
Sample 2	200	CO_2	CH_3Cl	ND
	350	CO_2	CH_3Cl	ND
	500	CO_2	CH_3Cl	ND
VL-2				
Blank	500	CO_2	CH_2Cl_2	ND
Sample 1	200	H_2	CH_2Cl_2	ND
	350	H_2	CH_2Cl_2	6–14
	500	H_2	CH_2Cl_2	6–14
	500	CO_2	CH_2Cl_2	2–6
Sample 2	50	H_2	CH_2Cl_2	ND
	200	H_2	CH_2Cl_2	0.04–0.08
	350	H_2	CH_2Cl_2	10–20
	500	H_2	CH_2Cl_2	<4
	500	CO_2	CH_2Cl_2	20–40

[a]From *Biemann et al.* [1977]. GC, gas chromatography; MS, mass spectrometry; ND, not determined; TV, thermal volatilization; VL-1 and VL-2, Viking Landers 1 and 2, respectively.

[b]Gases and volatiles released by TV are swept away from the oven into the gas chromatograph by a stream of either $^{13}CO_2$ or H_2.

was kept at 70°C to accelerate the reaction. CO_2 released was frozen into the liquid nitrogen trap. Both traps were then analyzed by GC-MS. The GC column used was a Varian CP-PoraBOND Q, made of fused silica, measuring 50 m long × 0.32 mm in ID. The column program temperature was initially 35°C for 10 min. The carrier gas used was helium, at a flow rate of 1.2 ml/min. The gas chromatography was interfaced in parallel to an HP 5989B quadrupole mass spectrometer operating in electron impact mode at 70 eV. Temperatures at the interfaces were 250°C. The mass analyzer was scanned from m/z 12 to m/z 100 at a scan rate of 4.4 scans/s. The electron impact chamber and the quadrupole were maintained at 250° and 100°C, respectively. CO_2 was determined quantitatively using a calibration curve for the gas at various concentrations. The CO_2 (Praxair; 99.998% purity) was mixed with nitrogen (Praxair; 99.998% purity) at various concentrations (0.002%–4%) using a Linde FM4660 mass flow measuring and control gas blending console equipped with fast response mass flow control modules.

2.4. Thermal Volatilization-Gas Chromatography-Mass Spectrometry

[10] A portion of the soil powder (10–40 mg) was loaded into a capillary quartz tube and held in place using small plugs of quartz wool. The quartz tube containing the sample was introduced inside the platinum coil wire of the pyrolyzer probe (Pyroprobe 2000; CDS Analytical, Inc.), then the pyrolyzer probe was inserted into the injection port interface of the pyrolyzer. Atmospheric air was removed from the pyrolysis cavity by flushing a stream of helium (99.9999%) at 413,700 Pa for 3 min. The sample was subjected to a thermal treatment from 30° to 200°, 350°, 500°, 750°, and 1000°C, at a heating rate of 60°C/s, with the final temperature held for 30 s. One minute after the sample reached the maximum temperature, all gases and volatiles released were transferred by a helium stream with a six-port gas-sampling valve into the injection port of an HP 5890 series gas chromatograph kept at 250°C. The gas chromatograph was equipped with a Varian CP-PoraBOND Q, fused silica, 50 m long × 0.32 mm ID column. The column program temperature was initially isothermal, at 30°C, for 7 min, then was increased to 250°C, at a heating rate of 10°C/min, and, finally, was isothermal for 3 min. The carrier gas used was helium, at a flow rate of 1.2 ml/min. The gas chromatograph was interfaced at 250°C to an HP 5989B quadrupole mass spectrometer operating in electron impact mode at 70 eV with a resolution of 1 m/z. The mass analyzer was scanned from m/z 10 to m/z 150 at a rate of 4.9 scans per second. The electron impact chamber and the quadrupole were maintained at 250° and 100°C, respectively.

2.5. Chemical Evolution Code

[11] We have developed a code for integrating a set of chemical rate equations, following the ideas developed by *Mott et al.* [1998] and *Mott and Oran* [2001] for their CHEMEQ2 code. The reactions can be written in the general form

$$\sum_{i=1}^{N_R} R_i \rightarrow \sum_{j=1}^{N_P} m_j P_j,$$

where R_i denotes the reactant species and P_j denotes the products. The number of reactants N_R and the number of

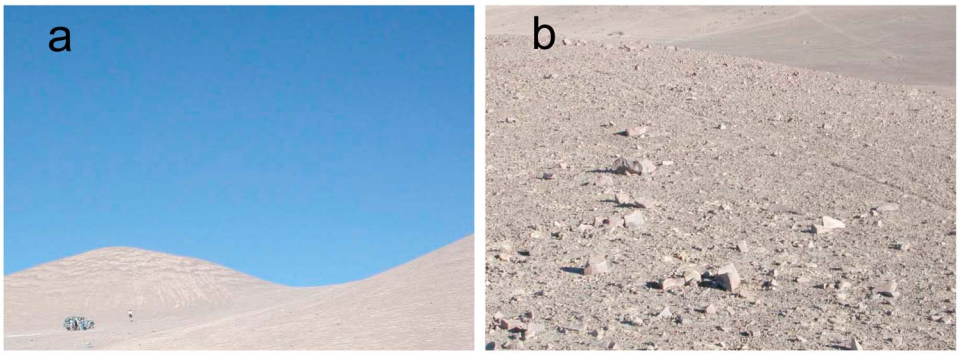

Figure 1. (a) General and (b) closeup views of site AT02-03A on the top hills of the Yungay area in the Atacama Desert.

different products N_P can have values N_R, N_P = 1, 2, or 3 (although the code can easily be generalized to higher numbers of reactants or products). The m_j factors represent the number of molecules of species P_j that are produced in the reaction.

[12] Depending on the number of reactants, the reaction rates r are given by

$$N_R = 1\text{: } r = n_R q(T),$$

$$N_R = 2\text{: } r = n_{R_1} n_{R_2} q(T),$$

$$N_R = 3\text{: } r = n_{R_1} n_{R_2} n_{R_3} q(T),$$

where n_R values are the number densities of the reactants, and $q(T)$ coefficients give the rate per reactant as a function of the temperature (these can be given, e.g., in the form of Arrhenius interpolations).

[13] Following the general suggestion of *Mott and Oran* [2001], we compute rates averaged over a time step Δt considering equations of the following forms. For N_R = 1,

$$\frac{dn_R}{dt} = -n_R q(T),$$

$$\frac{dn_R}{dt} = n_R q(T) \rightarrow \langle r \rangle = \frac{n_R}{\Delta t}\left[1 - e^{-q(T)\Delta t}\right].$$

For N_R = 2,

$$\frac{dn_{R_1}}{dt} = -n_{R_1} n_{R_2} q(T),\ I = 1, 2,$$

$$\rightarrow \langle r \rangle_1 = \frac{n_{R_1}}{\Delta t}\left[1 - e^{-n_{R_2} q(T)\Delta t}\right],$$

$$\rightarrow \langle r \rangle_2 = \frac{n_{R_2}}{\Delta t}\left[1 - e^{-n_{R_1} q(T)\Delta t}\right].$$

For N_R = 3,

$$\frac{dn_{R_1}}{dt} = -n_{R_1} n_{R_2} n_{R_3} q(T),\ I = 1, 2, 3,$$

$$\rightarrow \langle r \rangle_1 = \frac{n_{R_1}}{\Delta t}\left[1 - e^{-n_{R_2} n_{R_3} q(T)\Delta t}\right],$$

$$\rightarrow \langle r \rangle_2 = \frac{n_{R_2}}{\Delta t}\left[1 - e^{-n_{R_1} n_{R_3} q(T)\Delta t}\right],$$

$$\rightarrow \langle r \rangle_3 = \frac{n_{R_3}}{\Delta t}\left[1 - e^{-n_{R_1} n_{R_2} q(T)\Delta t}\right].$$

[14] The average reaction rates are calculated by integrating the differential equations over Δt, assuming that the temperature T (and therefore the q coefficient) is constant over the time step. For N_R = 2 and 3, we also assume that the reactants not present in the time derivative are constant over Δt and, therefore, obtain two possible expressions of the average rate for N_R = 2 and three for N_R = 3. We then set $\langle r \rangle = \min[\langle r \rangle_1, \langle r \rangle_2]$ for N_R = 2 and $\langle r \rangle = \min[\langle r \rangle_1, \langle r \rangle_2 \langle r \rangle_3]$ for the N_R = 3 case.

[15] The equation governing the time evolution of the densities of chemical species a has the general form

$$\frac{dn_a}{dt} = \sum_j (m_a c_a)_j - \sum_j (D_a)_j,$$

where the C_a terms correspond to the rates of reactions creating a number of m_a molecules of species a (i.e., reactions with species a as a product), and the D_a terms correspond to rates of reactions that destroy species a (i.e., reactions in which a participates as a reactant). The sums over j represent all of the reactions involving species a.

[16] To carry out a full time step from a time t to a time $t + \Delta t$, we compute a sequence of 2^k sub–time steps $\Delta t_k = \Delta t/2^k$ (with k = 0, 1, 2,…) of the form

$$n_a(t_l) = n_a(t_{l-1}) + \Delta t_k \left[\sum_j (m_a \langle C_a \rangle)_j - \sum_j (\langle D_a \rangle)_j\right],$$

where $t_l = t + l\Delta t_k$, starting from l = 1 and ending with $l = 2^k$, and the time-averaged rates are calculated as described above.

[17] Through these 2^k sub–time steps, we compute predictions $n_{a,k}(t + \Delta t)$ for k = 1, 2, 3,…, until the condition

$$\min\left[\frac{|n_{a,k}(t + \Delta t) - n_{a,k-1}(t + \Delta t)|}{n_{a,k}(t + \Delta t)}\right] < \epsilon$$

is satisfied, where the minimum is taken over all species a, and ϵ is the chosen error estimate for the time integration (in the present work, we have set ϵ = 0.1). When we reach a value of k for which this condition is satisfied, we finalize the time step Δt by setting $n_a(t + \Delta t) = n_{a,k}(t + \Delta t)$.

[18] The concentration of gaseous species released by the TV process are given by volume, while the concentration of nonvolatile species is given by weight.

3. Results and Discussion

3.1. Atacama Experiments

[19] Analysis of Atacama soil samples without added perchlorate revealed that the major gases and volatiles released by the TV step are H_2O, CO_2, O_2, nitric oxide (NO), and nitrous oxide (N_2O), with traces of benzene (C_6H_6) and toluene (C_6H_5–CH_3). Figure 2a shows a reconstructed gas chromatogram of the organic fraction detected by TV treatment of Atacama soils using selective ion monitoring. Figures 3a and 3b show the mass spectra of organic compounds detected. H_2O is the main product whose abundance increases with temperature, reaching a maximum value at 1000°C. It originates from the dehydration processes of soil minerals by adsorption and coordination forces; a small fraction originates from the oxidation of organic matter. CO_2 is the second most abundant gas product (Figure 4); at low temperatures (200°C) its yield is low, but it increases rapidly at higher temperatures, reaching a steady high value at ≥750°C. There are three possible sources for the release of CO_2: (a) atmospheric absorption (≤200°C), (b) oxidation of organic matter at temperatures ≥200°C, and (c) thermal decomposition of carbonates at temperatures ≥450°C. O_2 is

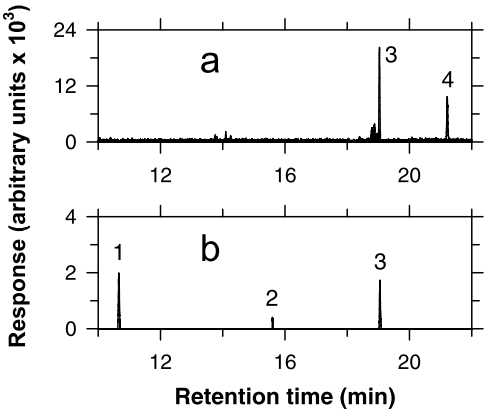

Figure 2. Reconstructed gas chromatographs of Atacama soils (a) without and (b) with added magnesium perchlorate that were thermally treated at 500°C and were acquired using selective ion monitoring of 50, 78, 84, and 91 *m/e*: (1) chloromethane; (2) dichloromethane; (3) benzene; (4) toluene.

the third most abundant gas released (Figure 4), with a maximum value at ~750°C. It originates from the dehydroxylation of clay minerals at low temperatures (≤350°C) and from the decomposition of nonmetal (C, N, O, P, S, Cl, etc.) and metal (Al, Fe, etc.) oxides at higher temperatures (≥500°C). NO evolves with a maximum yield at 750°C (Figure 4) and originates from the thermal oxidation of nitrogenated organics at low temperatures (<500°C) and from the degradation of nitrates at high temperatures (>500°C) (see Figure 4). N_2O has a maximum yield at 350°C (Figure 4) and originates from the thermal oxidation of nitrogenated organics. C_6H_6 and C_6H_5–CH_3 are the main organics detected (Figures 2a, 3a, 3b, and 4) and are formed at very low yields at 500°C, the maximum temperature investigated by the Viking mission. Their yields reach a maximum value at 750°C [*Navarro-González et al.*, 2003, 2006]. The formation of formic acid (HCO_2H), a highly oxidized organic, was reported earlier [*Navarro-González et al.*, 2003] by TV treatment of Atacama soils. This compound was not detected as a final product in this study but was found to originate in the MS ionization chamber by ion molecule reactions initiated by the electron impact ionization of the CO_2, an oxidized form of carbon, in the presence of a hydrogen source. In the presence of perchlorate, CO_2 and O_2 show formation patterns as a function of temperature similar to those found in the absence of perchlorate (Figure 4). In the presence of perchlorate the formation of NO from nitrogenated organics is completely inhibited at ≤500°C; in contrast, the formation of NO from nitrates is significantly reduced at ≥500°C. Similarly, the formation of N_2O from nitrogenated organics is completely inhibited by perchlorate at ≤500°C; however, its yield increases at higher temperatures, reaching a maximum value at 750°C (see Figure 4), and originates from the decomposition of

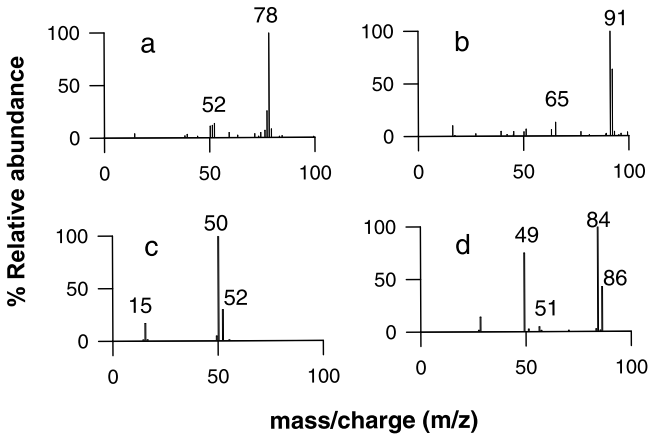

Figure 3. Mass spectra of Atacama soils with or without added magnesium perchlorate that were thermally treated at 500°C: (a) benzene; (b) toluene; (c) chloromethane; (d) dichloromethane.

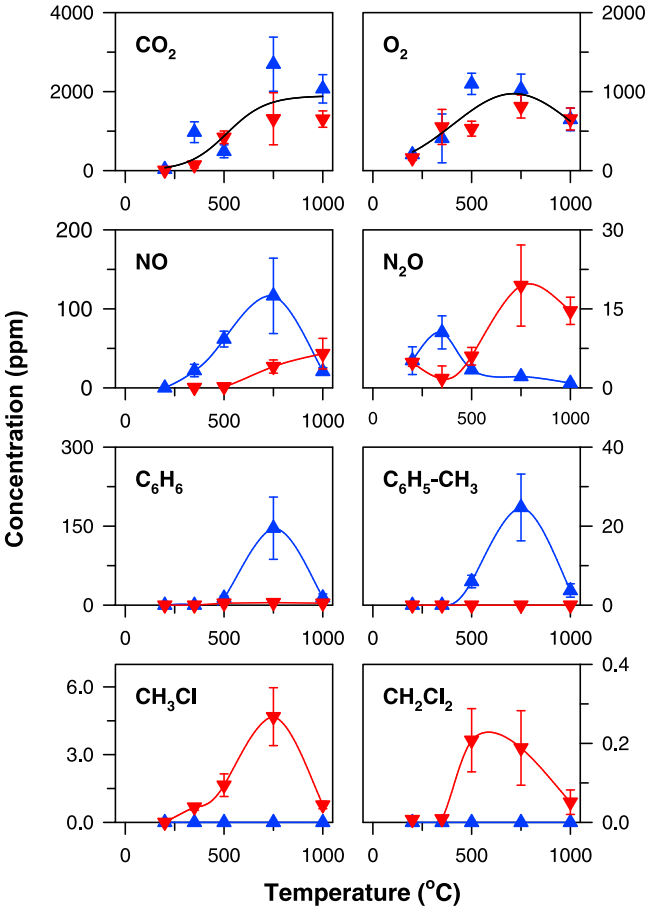

Figure 4. Production of major gases and volatiles from Atacama soils during the thermal volatilization (TV) step at various temperatures in the absence (upward (blue) triangles) or presence (downward (red) triangles) of 1 wt% magnesium perchlorate. Each data point is the average of six to eight runs and the error bars are the standard deviation of the data set. This soil sample is characterized by 32 ± 6 ppm of organic carbon, with a $\delta^{13}C$ value of −26, a C/N ratio of 8.2, and significant quantities of inorganic carbon in the form of carbonates (1414 ± 5 ppm). One part per million of organic carbon is equivalent to 3.7 ppm of carbon dioxide and 6.5 ppm of benzene.

nitrates in the presence of perchlorate. Surprisingly, C_6H_6 and C_6H_5–CH_3 are significantly destroyed (Figures 2b and 4) by combustion with oxygen atoms released from the thermal decomposition of perchlorate. Instead, the only organics detected at a very low yield are CH_3Cl and CH_2Cl_2 at temperatures above 350° and 500°C, respectively (Figures 2b, 3c, 3d, and 4). Their maximum yields occur at 750°C and 500–750°C, respectively (Figure 4). These compounds are not formed by TV in Atacama soils without perchlorate (Figures 2 and 4). It is not surprising that chlorinated organic compounds are formed by the thermal treatment of environmental samples [*Laniewski et al.*, 1998]; what is unexpected is that they could be the exclusive organic products in the presence of perchlorate.

3.2. Viking Results

[20] The TV-GC-MS instrument on board Viking 1 was tested during its cruise to Mars [*Biemann et al.*, 1976]. One of the most important tests consisted of a complete blank experiment during which one of the sample ovens was heated to 500°C (see Table 1). The results showed the presence of a few homologous oligomers of fluoropropyleneoxide (Freon E type) in addition to residual absorbed water [*Biemann et al.*, 1976]. These were considered to be terrestrial contaminants and were present at levels low enough not to interfere with the analysis of organics in the Martian soil. After landing, a soil sample collected on sol 8 (sample 1) was analyzed by GC-MS after TV treatment at 200°C, and a sharp, well-resolved peak was identified as CH_3Cl at 15 ppb levels (see Table 1) [*Biemann et al.*, 1976]. This sample heated at higher temperatures did not show the presence of CH_3Cl. A second sample, collected on sol 31, did not show the presence of CH_3Cl or perfluoroether contaminants at 200°, 350°, and 500°C [*Biemann et al.*, 1976]. CH_3Cl is a gas under standard conditions of temperature and pressure (boiling point = −23.8 °C). *Biemann et al.* [1977] considered that CH_3Cl, or part of it, could conceivably be indigenous to Mars. However, those authors expected that other related compounds, such as ethyl chloride and methyl bromide, would also have formed, but none were detected. The abundance ratio of the mass fragments *m*/*e* 50 to *m*/*e* 52 was 3:1, corresponding to the terrestrial $^{37}Cl/^{35}Cl$ isotopic ratio of 0.319; however, this does not necessarily confirm its origin, because there was no reason to predict a different isotopic ratio for Martian chlorine [*Biemann et al.*, 1977]. Considering these facts, the authors tended to believe that all the chloromethane was from a terrestrial source that formed in the TV oven from heating of chlorinated solvents or from adsorbed traces of methanol and HC1 [*Biemann et al.*, 1977]. We have explored this possibility experimentally and have subjected a 0.4% HCl solution in methanol to TV treatment. CH_3Cl is indeed produced at ≥350°C but CH_2Cl_2 and C_6H_6 are produced at equal or higher concentrations (Figure 5). Since none of these compounds were detected at the same levels by the Viking Lander 1 instrument, it is unlikely that this was the source of CH_3Cl.

[21] At present the isotopic distribution of chlorine on Mars is still unknown. Martian meteorites do contain chlorine atoms [*Bogard et al.*, 2010], but their abundance is so low that it is not easy to derive a reliable $^{37}Cl/^{35}Cl$ isotopic ratio yet. Recent progress has been made in the development of a new technique to determine the $^{37}Cl/^{35}Cl$ isotopic ratio by thermal ionization MS [*Nakamura et al.*, 2009]. Therefore in the near-future it will be possible to obtain the $^{37}Cl/^{35}Cl$ isotopic ratio in Martian meteorites. The Mars Science Laboratory, which is scheduled to be launched by the fall of 2011, will not be capable of directly determining the $^{37}Cl/^{35}Cl$ ratio in the soil. However, studies on Earth indicate that there is no isotopic fractionation of chlorine in the mantle or crust, despite the fact that it is significantly depleted on the planet compared to the solar abundances [*Sharp et al.*, 2007]. The $^{37}Cl/^{35}Cl$ isotopic ratio in carbonaceous chondrites is similar to the Earth's value, which suggests that the terrestrial planets, including Mars, were all formed from a similar reservoir of chlorine species in the presolar nebulae and that there was no further isotopic fractionation during the Earth's differentiation or late accretion of volatiles [*Sharp et al.*, 2007]. Consequently, the $^{37}Cl/^{35}Cl$ ratio should be the same on Mars as on the Earth.

[22] The TV-GC-MS instrument on board the Viking 2 spacecraft was also tested during its cruise to Mars. A blank experiment was run during which a sample oven was heated to 500°C. The mass spectrometer displayed a much lower background than that on Viking 1, but the subsystem involved in the soil analysis, namely, the sample ovens and the tubing and valves prior to and possibly after the gas chromatographic column, were not as clean [*Biemann et al.*, 1977]. However, no chlorinated hydrocarbons were detected in the blank run (see Table 1). After landing, two soil samples were analyzed by GC-MS after TV treatment at various temperatures and using different gases to transfer the gases and volatiles released from the oven to the gas chromatograph (see Table 1). Surprisingly, CH_3Cl was not detected; instead, CH_2Cl_2 was found in the two soil samples at 350° and 500°C [*Biemann et al.*, 1977]. Its concentration varied from 6 to 40 ppb, depending on the sample (Table 1). CH_2Cl_2 was detected at 200°C at a very low abundance (0.04–0.08 ppb) in sample 2 but was not found in sample 1. CH_2Cl_2 was also not seen in sample 2 at 50°C (see Table 1). No information was provided on the $^{37}Cl/^{35}Cl$ isotopic ratio found in CH_2Cl_2 [*Biemann et al.*, 1977]. Since CH_2Cl_2 ias a common laboratory solvent, which had been used in the cleaning of the oven/gas chromatograph subsystem, it was considered a terrestrial contaminant, although it had not been detected at those levels in the blank run [*Biemann et al.*, 1977].

[23] A puzzling result was the detection of different chlorohydrocarbons by the Viking Landers at each site investigated: CH_3Cl at Chryse Planitia by Viking Lander 1 [*Biemann et al.*, 1976] and CH_2Cl_2 at Utopia Planitia by Viking Lander 2 [*Biemann et al.*, 1977]. The inorganic chemical analyses of soils at both sites indicated that they were remarkably similar. Both sites show high iron; moderate magnesium, calcium, and sulfur; low aluminum; and, apparently, very low alkalis and trace elements [*Baird et al.*, 1976]. The only difference between these sites is the abundance of chlorine, which differs by almost an order of magnitude: 0.1 wt% at Chryse Planitia and 0.9 wt% at Utopia Planitia [*Clark et al.*, 1976, 1982; *Clark and van Hart*, 1981].

3.3. Computer Modeling and Predictions of Organics and Perchlorate in the Martian Surface

[24] To understand the distribution of CH_3Cl and CH_2Cl_2 and to attempt to estimate the concentration of organics and

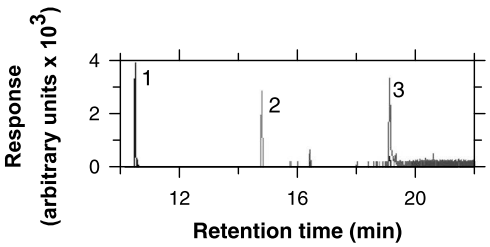

Figure 5. Reconstructed gas chromatograph of a 0.4% HCl solution in methanol that was thermally treated at 500°C and was acquired using selective ion monitoring of 50, 78, 84, and 91 *m*/*e*: (1) chloromethane; (2) dichloromethane; (3) benzene.

perchlorate in Martian soil, a simplified chemical kinetics model was implemented to predict the combustion and chlorination of organics in Viking's oven when Martian soil is heated under different initial conditions. For simplicity it was considered that only methane (CH_4) was released by the TV treatment of soil organics. Table 2 reports the chemical kinetics model used for the combustion and chlorination of methane in the gas phase; it consists of 19 chemical species and 48 reactions. These reactions and their rate expressions were compiled from the comprehensive National Institute of Standards and Technology chemical kinetics database [*Manion et al.*, 2008]. The chemical reactions listed in Table 2 were translated into a set of coupled differential equations that were integrated using a numerical code developed following the ideas of *Mott et al.* [1998] and *Mott and Oran* [2001]. The accuracy of this code in successfully predicting the behavior of a set of chemical reactions was confirmed by comparison of the results with those of other chemical kinetics codes using deterministic [*Braun et al.*, 1988] or stochastic [*Houle and Hinsberg*, 2006] simulation methods. The numerical code developed is significantly more efficient in computations when handling a complex set of chemical reactions such as those in Table 2.

[25] In computer simulations it was assumed that Martian soil contains 0.5% of absorbed water and 0.5% of hydroxyl groups present in the mineral surfaces that are released as hydroxyl radicals (OH) during the heating process at temperatures ≥200°C. Freshly ground basaltic minerals produce sufficient quantities of hydrogen peroxide (H_2O_2) when immersed in liquid water [*Hurowitz et al.*, 2007] or hydroxyl radicals when heated [*Iñiguez et al.*, 2009], to explain the oxidizing characteristics of Martian soil samples collected by the Viking Landers. Reaction of two hydroxyl radicals leads to the formation of water and molecular oxygen according to reactions 9 and 7 in Table 2. The total amount of water desorbed or chemically generated during the heating of Martian soil in the computer simulations is ≤1%, which is consistent with the values determined by the Viking Landers [*Biemann et al.*, 1977]. The abundance of magnesium perchlorate in Martian soil was varied from 0.01% to 1% in the computations. Decomposition of metal perchlorate results in the formation of oxides and/or chlorides of the corresponding metal, and the final product distribution is determined by their enthalpy of formation [*Manelis et al.*, 2003]. For the case of magnesium the standard enthalpies of formation of its oxide and its chloride in the solid state are practically identical: −601.6 and −641.6 kJ/mol, respectively [*Linstrom and Mallard*, 2010]. Consequently, magnesium perchlorate decomposes according to the following reaction [*Manelis et al.*, 2003]:

$$2Mg(ClO_4)_2 \rightarrow MgO + MgCl_2 + 7O + 2Cl.$$

When magnesium perchlorate is heated slowly (20°C/min), it decomposes at 418°–442°C in vacuum [*Acheson and Jacobs*, 1970] or at 435–525°C under 275 mbar [*Lauer et al.*, 2009]. However, when it is flash-heated (~60°C/s) at lower temperatures (≥200°C), a portion of the magnesium perchlorate decomposes, as demonstrated by the formation of CH_3Cl and CH_2Cl_2 in Figure 4. In the computer simulations it was assumed that all magnesium perchlorate was decomposed at temperatures ≥200°C. The presence of different cations in the soil, including iron species, can also result in a decrease in the decomposition temperature of perchlorates [*Hall and Marvin*, 1945].

[26] The chemically stable carbon-containing molecules produced by our chemical kinetics model (see Table 2) are methane, formaldehyde, carbon monoxide, carbon dioxide, chloromethane, and dichloromethane. Figure 6 shows their computed concentrations as a function of reaction time for a simulated Martian soil that contains ~40 ppb organic carbon, assuming that all initial reagents are instantaneously released when the soil is heated (CH_4, H_2O, OH, O, and Cl). Combustion and chlorination of methane occur rapidly in the TV oven, reaching chemical equilibrium at times ≥10 μs.

[27] Figure 7 shows the computed production of chloromethane and dichloromethane by the TV process at 200°, 350°, and 500°C under various concentrations of organic carbon and perchlorate in simulated Martian soils. A higher concentration of organic carbon or perchlorate in the soil results in higher yields of chlorohydrocarbons but does not change the distribution of chloromethane and dichloromethane. Chloromethane and dichloromethane are formed at nearly similar rates at 200°C, but as the oven temperature is raised, dichloromethane becomes the dominant product.

[28] The detection of chloromethane at 15 ppb in sample 1 (Table 1) when it was heated to 200°C by Viking Lander 1 suggests that the soil contained high levels of organic carbon, ranging from 1.5 ppm in the presence of 0.1% perchlorate to 6.5 ppm in the presence of 0.01% perchlorate (Figure 4). Combustion of this soil organic carbon leads to 1–2 ppm of carbon dioxide; however, the Viking Lander did not measure the abundance of CO_2 released by the TV step [*Biemann et al.*, 1977]. The lack of detection of chloromethane when sample 1 was heated at higher temperatures or when sample 2 was analyzed from 200° to 500°C was a puzzling result.

[29] Viking 2 detected low levels (0.04–0.08 ppb) of dichloromethane at 200°C (Table 1). The predicted concentration of soil organic carbon required to produce this amount of dichloromethane is in the range of 1–10 ppb for perchlorate concentrations ≤1% (Figure 7). Combustion of the organic carbon would lead to 0.9–8.9 ppb of carbon dioxide, which would represent a small fraction of the amount detected (50–500 ppm) at 200°C [*Biemann et al.*, 1977]. At 350°C the concentration of dichloromethane detected is 6–20 ppb (Table 1). The computed concentration of soil organic carbon necessary to generate this amount of CH_2Cl_2 and the minimum concentration of CH_3Cl is from

Table 2. Gas-Phase Reactions Used to Model the Combustion and Chlorination of Methane During the TV Step of Soil Organics in the Presence of Perchlorate

No.	Reaction[a]	Rate Expression[b]
1	$H + H + M \rightarrow H_2 + M$	4.3×10^{-33} exp(1.4 kJ/RT)
2	$H + O + M \rightarrow OH + M$	6.5×10^{-33} exp(5.3 kJ/RT)
3	$H + OH \rightarrow H_2 + O$	2.2×10^{-11} exp(−33.3 kJ/RT)
4	$H + OH + M \rightarrow H_2O + M$	1.4×10^{-32} exp(10.9 kJ/RT)
5	$H_2 + M \rightarrow H + H + M$	6.1×10^{-9} exp(−426.0 kJ/RT)
6	$H_2O + M \rightarrow OH + H + M$	5.8×10^{-9} exp(−440.0 kJ/RT)
7	$O + O + M \rightarrow O_2 + M$	5.2×10^{-35} exp(7.5 kJ/RT)
8	$O + H_2O \rightarrow OH + OH$	9.9×10^{-11} exp(−75.6 kJ/RT)
9	$OH + OH \rightarrow H_2O + O$	1.3×10^{-11} exp(−4.2 kJ/RT)
10	$O_2 + M \rightarrow O + O + M$	1.5×10^{-9} exp(−489.0 kJ/RT)
11	$O_2 + H \rightarrow OH + O$	1.6×10^{-10} exp(−62.1 kJ/RT)
12	$CH_4 \rightarrow CH_3 + H$	3.5×10^{15} exp(−434.0 kJ/RT)
13	$CH_4 + H \rightarrow CH_3 + H_2$	1.9×10^{-10} exp(−51.1 kJ/RT)
14	$CH_4 + O \rightarrow CH_3 + OH$	1.4×10^{-10} exp(−43.2 kJ/RT)
15	$CH_4 + OH \rightarrow CH_3 + H_2O$	1.2×10^{-11} exp(−18.1 kJ/RT)
16	$CH_3 + O \rightarrow CH_2O + H$	1.4×10^{-10}
17	$CH_3 + O_2 \rightarrow CH_2O + OH$	3.1×10^{-13} exp(−41.2 kJ/RT)
18	$CH_2O + H \rightarrow HCO + H_2$	4.2×10^{-11} exp(−16.7 kJ/RT)
19	$CH_2O + OH \rightarrow HCO + H_2O$	5.0×10^{-11} exp(−5.0 kJ/RT)
20	$CH_2O + O \rightarrow HCO + OH$	3.0×10^{-11} exp(−12.8 kJ/RT)
21	$HCO + M \rightarrow CO + H + M$	6.0×10^{-11} exp(−64.2 kJ/RT)
22	$HCO + O \rightarrow CO + OH$	5.0×10^{-11}
23	$HCO + O \rightarrow CO_2 + H$	5.0×10^{-11}
24	$CO + O + M \rightarrow CO_2 + M$	1.7×10^{-33} exp(−12.6 kJ/RT)
25	$CO + OH \rightarrow CO_2 + H$	5.2×10^{-13} exp(−2.5 kJ/RT)
26	$CO + O_2 \rightarrow CO_2 + O$	4.2×10^{-12} exp(−200 kJ/RT)
27	$Cl + Cl + M \rightarrow Cl_2 + M$	3.5×10^{-33} exp(6.8 kJ/RT)
28	$Cl + OH \rightarrow HCl + O$	9.8×10^{-12} exp(−23.8 kJ/RT)
29	$Cl + CH_4 \rightarrow CH_3 + HCl$	2.5×10^{-11} exp(−13.0 kJ/RT)
30	$Cl + CH_3 \rightarrow CH_3Cl$	2.6×10^{-10}
31	$Cl + CH_2O \rightarrow HCO + HCl$	8.2×10^{-11} exp(−0.3 kJ/RT)
32	$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.4×10^{-11} exp(−10.5 kJ/RT)
33	$Cl_2 + M \rightarrow Cl + Cl + M$	7.1×10^{-10} exp(−224.0 kJ/RT)
34	$Cl_2 + CH_3 \rightarrow Cl + CH_3Cl$	3.6×10^{-13}
35	$HCl + CH_3 \rightarrow Cl + CH_4$	3.9×10^{-13} exp(−9.6 kJ/RT)
36	$HCl + CH_3 \rightarrow H + CH_3Cl$	2.1×10^{-14} exp(−124.0 kJ/RT)
37	$CH_3Cl + M \rightarrow CH_3 + Cl + M$	6.0×10^{-9} exp(−247.0 kJ/RT)
38	$CH_3Cl + O \rightarrow OH + CH_2Cl$	1.7×10^{-11} exp(−28.7 kJ/RT)
39	$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$	2.2×10^{-11} exp(−15.6 kJ/RT)
40	$CH_2Cl + H_2 \rightarrow CH_3Cl + H$	3.0×10^{-12} exp(−63.5 kJ/RT)
41	$CH_2Cl + OH \rightarrow CH_2O + HCl$	2.2×10^{-11} exp(−15.6 kJ/RT)[c]
42	$CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl$	7.6×10^{-13} exp(−23.6 kJ/RT)
43	$CH_2Cl + HCl \rightarrow CH_2Cl_2 + H$	5.1×10^{-13} exp(−134.0 kJ/RT)
44	$CH_2Cl + HCl \rightarrow CH_3Cl + Cl$	1.3×10^{-12} exp(−1.1/RT)[d]
45	$CH_2Cl + Cl \rightarrow CH_2Cl_2$	2.6×10^{-10}[e]
46	$CH_2Cl_2 + M \rightarrow CH_2Cl + Cl + M$	6.6×10^{-9} exp(−236.0 kJ/RT)
47	$CH_2Cl_2 + H \rightarrow CH_2Cl + HCl$	1.1×10^{-10} exp(−34.3 kJ/RT)
48	$CH_2Cl_2 + Cl \rightarrow CH_2Cl + Cl_2$	1.1×10^{-11} exp(−121.0 kJ/RT)

[a]M is any molecule or radical of those present in the chemical model.
[b]Units are cm^3 $molecule^{-1}$ s^{-1} and cm^6 $molecule^{-2}$ s^{-1} for second- and third-order reactions, respectively.
[c]Assumed to be similar to reaction 39.
[d]Assumed to be similar to the reaction $CH_2Cl + HI \rightarrow CH_3Cl + I$.
[e]Assumed to be similar to reaction 30.

0.07 to 2.6 ppm for perchlorate concentrations ≤0.1% (Figure 7). Combustion of organic carbon would lead to 0.2–1.35 ppm of carbon dioxide, which represents a small fraction of the amount detected (40–500 ppm) at 350°C [*Biemann et al.*, 1977]. At 500°C the concentration of dichloromethane detected is 2–40 ppb (Table 1). The concentration of soil organics needed to produce exclusively CH_2Cl_2 is 0.01 to 1.0 ppm and the concentration of perchlorate could be in the range of from 0.01% to 1% (Figure 7). Combustion of the organic carbon would lead to 0.2–1.0 ppm of carbon dioxide, which represents a small fraction of the amount detected (70–700 ppm) at 500°C [*Biemann et al.*, 1977]. The predicted concentration of soil organic carbon is within a similar range at 350° and 500°C but constrains the concentration of soil perchlorate to be ≤0.1%. At 200°C the predicted concentration of soil organic is underestimated by 1–2 orders of magnitude, probably because the release of oxidizing species (OH, O, and Cl) varies with temperature, and for simplicity we assumed in our chemical kinetics model that they were all released at temperatures ≥200°C.

[30] An intriguing question regarding the Viking GC-MS analysis is why inorganic chlorine species (e.g., hydrochloric acid, chlorine) were not detected in the analysis if perchlorate was indeed present in the Martian soil. The Viking GC column was filled with a liquid modified organic adsorbent consisting of 60 to 80 mesh Tenax-GC (2,6-diphenyl-para-phenylene oxide) coated with polymetaphenoxylene [*Novotny et al.*, 1975]. Tenax has been found to react readily with oxidizing agents (e.g., hydroxyl radicals, oxygen, ozone, nitrogen oxides, sulfur dioxides, and chlorine) [*Jones*, 1994; *Klenø et al.*, 2002]. Nitrogen and sulfur oxides react with moisture, producing nitric and sulfuric acids, respectively. These acids also react irreversible with Tenax [*Jones*, 1994; *Klenø et al.*, 2002]. No information was found in the literature on the reactivity of hydrochloric acid with Tenax, but based on its reactivity with other acids, it is likely that it decomposed in the column. In our GC-MS analysis we do not detect any inorganic chlorine species released by TV of Atacama soils with added perchlorate but we do detect HCl by TV-MS. Therefore, it is concluded that any inorganic chlorine was undetectable by the Viking mass spectrometer owing to its destruction in the GC column.

[31] The calculations presented in this section are obviously an oversimplification of the natural process and should be taken as a first-order approximation. The assumption that methane was the only organic product released by the TV treatment of soil organics was chosen to significantly reduce the number of chemical reactions required to model

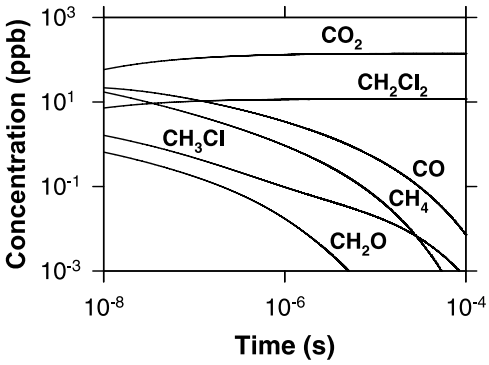

Figure 6. Predicted production of methane (CH_4), formaldehyde (CH_2O), carbon monoxide (CO), carbon dioxide (CO_2), chloromethane (CH_3Cl), and dichloromethane (CH_2Cl_2) as a function of time during the TV step at 500°C for a Martian soil containing 40 ppb organic carbon, 0.5% wt water, 0.5% of hydroxyl groups, and 1% wt magnesium peroxide. One part per billion organic carbon is equivalent to 3.7 ppb CH_4, 2.5 ppb CH_2O, 2.3 ppb CO, 3.7 ppb CO_2, 4.2 ppb CH_3Cl, and 7.1 ppb CH_2Cl_2.

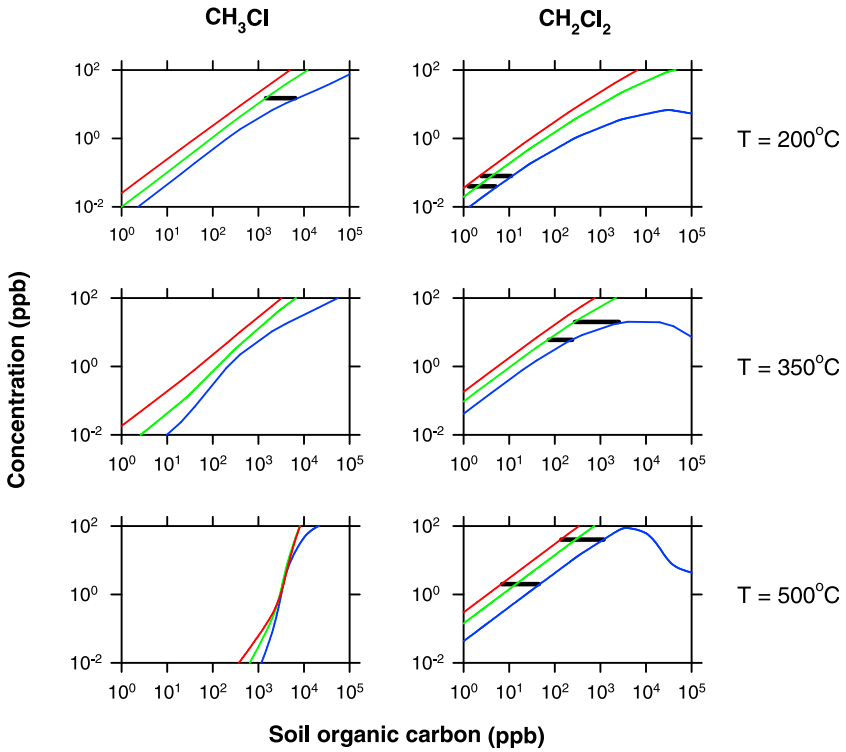

Figure 7. Predicted production of chlorohydrocarbons as a function of organic carbon and perchlorate at different oven temperatures (200°, 350°, and 500°C) from a Martian soil containing 0.5% wt water and 0.5% hydroxyl groups. Concentrations were derived after the system achieved chemical equilibrium at 100 μm. The concentration of perchlorate was varied from 0.01% (blue line), to 0.1% (green line), and, finally, to 1.0% (red line). Bold black lines indicate the concentration range detected for chlorohydrocarbons by the Viking Landers.

the process. Clearly, as one includes more organic products with increasing numbers of carbon atoms, the number of chemical reactions needed for the calculations increases exponentially, and in some cases, their rate coefficients are not known. Furthermore, we have oversimplified the system in such a way that only gas-phase reactions were considered. This is clearly not the case in nature, as we have previously demonstrated that the chemical composition of the soil does alter the outcome of the gases and volatiles released by TV-GC-MS [*Navarro-González et al.*, 2006]. However, these computer calculations do demonstrate that (1) perchlorates lead to significant combustion of the soil organics, resulting in the formation of carbon dioxide, and (2) the presence of chlorine atoms produced by the destruction of perchlorates freezes out a trace amount of the organics by forming chlorohydrocarbons. Further studies that incorporate more complex chemical processes in the computations are needed. These new studies are not expected to quantitatively change the results found in this study. Finally, it is not clearly understood why Viking Lander 1 detected exclusively CH_3Cl, whereas Viking Lander 2 instead found only CH_2Cl_2. Obviously, additional studies with different Mars-like soils from locations other than the Atacama Desert will provide more clues in this inquiry.

4. Conclusions

[32] Motivated by the discovery of perchlorate in the soil of Mars by the Phoenix Lander, we have reanalyzed the results of the Viking GC-MS search for organics. On the basis of experimental studies of Atacama Desert soils to which 1% magnesium perchlorate has been added and chemical kinetic simulations, we draw the following conclusions: (1) the detection of chloromethane and dichloromethane by Viking Lander 1 and Viking Lander 2, respectively, was due to the combined presence of perchlorate and organics in the soil sample during heating; (2) at both Viking sites a significant fraction of the Cl present is in the form of perchlorate, namely, up to ≤100% for the Viking Lander 1 site at 23°N and up to ≤10% for the Viking Lander 2 site at 48°N; and (3) the inferred organic content of Martian soil at midlatitudes is ~1 ppm.

[33] Our results demonstrate important limitations for the search of organics on Mars using the TV step to release soil organics. It is important to think of the detection of organics by TV in a soil matrix as a two-step process. The first step is the release of gases and volatile organics from the mineral soil and the second step is their detection and characterization by an analytical instrument [*Navarro-González et al.*, 2009]. Clearly, either step can limit the overall sensitivity of the experiment. Indeed, if the sensitivity of the analytical instrumentation is reasonably good, the release of organics from the soil matrix typically limits the overall sensitivity. It is evident that combustion of soil organics to CO_2 by perchlorate salts in the TV oven severely limits their detection. However, it is important to emphasize that the second step, namely, the GC-MS analyses operated as

designed in both the Viking Landers. Future missions will have to incorporate additional analytical methods to avoid the oxidation of Martian soil by TV due to iron oxides [*Navarro-González et al.*, 2006, 2009; *Iñiguez et al.*, 2009] and perchlorate. Considering that the Viking Landers did detect the presence of organics in the soil, we suggest that an *in situ* life detection mission to Mars is essential in the near-future.

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