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Can rapid loss and high variability of Martian methane be explained by surface H₂O₂?

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ABSTRACT

It has been reported by several groups that methane in the Martian atmosphere is both spatially and temporally variable. Gough et al. (2010) suggested that temperature dependent, reversible physical adsorption of methane onto Martian soils could explain this variability. However, it is also useful to consider if there might be chemical destruction of methane (and compensating sources) operating on seasonal time scales. The lifetime of Martian methane due to known chemical loss processes is long (on the order of hundreds of years). However, observations constrain the lifetime to be 4 years or less, and general circulation models suggest methane destruction must occur even faster (< 1 year) to cause the reported variability and rapid disappearance. The Martian surface is known to be highly oxidizing based on the Viking Labeled Release experiments in which organic compounds were quickly oxidized by samples of the regolith. Here we test if simulated Martian soil is also oxidizing towards methane to determine if this is a relevant loss pathway for Martian methane. We find that although two of the analog surfaces studied, TiO₂·H₂O₂ and JSC-Mars-1 with H₂O₂, were able to oxidize the complex organic compounds (sugars and amino acids) used in the Viking Labeled Release experiments, these analogs were unable to oxidize methane to carbon dioxide within a 72 h experiment. Sodium and magnesium perchlorate, salts that were recently discovered at the Phoenix landing site and are potential strong oxidants, were not observed to directly oxidize either the organic solution or methane. The upper limit reaction coefficient, α , was found to be $< 4 \times 10^{-17}$ for methane loss on TiO₂·H₂O₂ and $< 2 \times 10^{-17}$ for methane loss on JSC-Mars-1 with H₂O₂. Unless the depth of soil on Mars that contains H₂O₂ is very deep (thicker than 500 m), the lifetime of methane with respect to heterogeneous oxidation by H₂O₂ is probably greater than 4 years. Therefore, reaction of methane with H₂O₂ on Martian soils does not appear to be a significant methane sink, and would not destroy methane rapidly enough to cause the reported atmospheric methane variability.

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1. Introduction

Since 2004, both ground-based and orbiter observations have indicated that there are trace amounts of methane (CH₄) in the Martian atmosphere (Formisano et al., 2004; Krasnopolsky et al., 2004; Geminale et al., 2008; Mumma et al., 2009; Fonti and Marzo, 2010). This is a difficult measurement to make due to the small amount of CH₄ on the planet and, in the case of ground-based observations, the possibility of telluric CH₄ contamination could add further uncertainty (Zahnle et al., 2010). However, the

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consistency in reported mixing ratios (~ 10 – 50 ppbv) between measurements taken with different instruments and using different absorbance features has inspired confidence in the reported CH₄ observations. The source of this CH₄ is unknown, although possible sources include hydrothermal alteration of minerals (Lyons et al., 2005; Oze and Sharma, 2005; Atreya et al., 2007), CH₄ clathrate degassing or dissociation (Max and Clifford, 2000; Prieto-Ballesteros et al., 2006; Chastain and Chevrier, 2007; Madden et al., 2007; Chassefiere, 2009), or methanogenic bacteria (Boston et al., 1992; Weiss et al., 2000; Jakosky et al., 2003; Varnes et al., 2003; Krasnopolsky et al., 2004).

The only processes known to destroy Martian CH₄ are UV photolysis and gas phase oxidation. Together, these yield a CH₄ lifetime of several hundred years, significantly longer than either the vertical or horizontal mixing time (~ 10 days and ~ 0.5 years, respectively) (Krasnopolsky et al., 2004). Methane is thus

expected to be well mixed; however, several groups have reported spatial and/or temporal variability of CH₄ in the Martian atmosphere (Formisano et al., 2004; Geminale et al., 2008; Mumma et al., 2009; Fonti and Marzo, 2010). This observed variability implies that additional processes are removing CH₄ from the atmosphere and also that strong, local CH₄ sources must be present on Mars today. Carefully constraining the Martian CH₄ sinks is important for constraining and quantifying the possible CH₄ sources.

Ground-based observations constrain the CH₄ lifetime to be less than 4 years (Mumma et al., 2009). However, recent theoretical work by Lefevre and Forget (2009) finds that the unknown loss must occur even more rapidly, on a timescale of ~200 days, in order to explain the observations of Mumma et al. (2009). If this is the case, the CH₄ loss is occurring about 600 times faster than gas phase oxidation by ·OH and O(¹D) or UV photolysis and would require a much stronger source than previously believed. Although there may be a rapid CH₄ sink on Mars, the mechanism of CH₄ loss, the exact removal rate, and the geographic location (or spatial homogeneity) of the removal process are still unknown.

One proposed CH₄ loss pathway is the dissociation of CH₄ by large-scale electric fields that result from convective dust activity (Farrell et al., 2006). However, it has recently been suggested that electric discharges may not occur during Martian dust saltation and therefore CH₄ dissociation is perhaps less significant than previously thought (Kok and Renno, 2009).

Alternatively, Gough et al. (2010) proposed that seasonal cycles of physical adsorption and desorption by the regolith, which is a reversible phenomena, could account for the observed CH₄ variability. However, theoretical work by Meslin et al. (this issue) suggests that the effect of this mechanism is likely to be small. Reasonable values for regolith albedo, thermal inertia, and specific surface area only result in atmospheric CH₄ variability on the order of a few %, although high surface area minerals such as zeolites can increase atmospheric CH₄ variability to greater than 5%. However, it is likely that there are more rapid processes removing CH₄ from the Martian atmosphere.

Heterogeneous oxidation of CH₄ by the Martian surface is a possible loss pathway that has been frequently proposed (Atreya et al., 2006; Lefevre and Forget, 2009; Mumma et al., 2009), but not yet experimentally investigated. It has been known since the Viking mission in the 1970s that the Martian regolith has the ability to oxidize organic compounds. The Labeled Release (LR) experiment onboard both Viking landers investigated the ability of the soil to oxidize a solution of ¹³C-labeled organic molecules into ¹³CO₂. Prior to launch, oxidation of the organic solution was a criteria for the discovery of life. However, it is now widely believed that a strong oxidant associated with the mineral grains, or perhaps the soil itself, was chemically reactive.

The species most frequently proposed to be the Martian soil oxidant is hydrogen peroxide (H₂O₂) (Huguenin et al., 1979; Hunten, 1979; Levin and Straat, 1981; Bullock et al., 1994; Zent and McKay, 1994). H₂O₂ could have arrived in the soil via a number of different processes or mechanisms. Following photochemical (Krasnopolsky, 1993) or electrostatic (Atreya et al., 2006; Delory et al., 2006) formation in the atmosphere, the H₂O₂ could diffuse through the subsurface where it could be protected from UV photolysis (Bullock et al., 1994). Alternatively, H₂O₂ could be formed in the soil by interaction of water (H₂O) with pyrite (Davila et al., 2008), olivine (Huguenin et al., 1979), or mechanically ground basaltic minerals (Hurowitz et al., 2007).

Several studies have shown that H₂O₂ is able to closely mimic the Viking LR results, especially when the molecule is complexed with or in the presence of a mineral surface. For example, Levin and Straat (1981) found that a 0.1 M H₂O₂ solution was able to oxidize

organic compounds with the approximate kinetics measured by Viking. However, when a γ-Fe₂O₃/silica sand mixture is present, a much lower H₂O₂ concentration (10⁻³–10⁻² M) was able to recreate the LR results. Quinn and Zent (1999) reported that H₂O₂ chemisorbed onto titanium dioxide (TiO₂·H₂O₂) also has the ability to oxidize the organic compounds used in the LR experiment. TiO₂·H₂O₂ was found to possess similar reactivity and thermal stability as the Martian soil studied by Viking.

Although H₂O₂ complexed with Martian soil may be able to rapidly oxidize organic compounds such as sugars and amino acids, it is unclear over what time scale oxidation of gas phase CH₄ could occur. In this work, we have experimentally studied the reaction of CH₄ with several oxidizing analogs. The analog materials studied were peroxide-modified titanium dioxide (TiO₂·H₂O₂), JSC-Mars-1 with H₂O₂, and perchlorate salts (Na⁺ and Mg²⁺).

As mentioned above, Quinn and Zent (1999) discovered that H₂O₂ complexed with the anatase polymorph of TiO₂ was able to oxidize the Viking organic compounds to CO₂. It is also estimated that the regolith contains about 1% TiO₂ (Clark et al., 1977). As it is a suitable chemical analog of the putative soil oxidant on Mars, we chose to study the reactivity of TiO₂·H₂O₂ toward CH₄.

JSC-Mars-1 is a palagonite, or weathered basalt, that is mineralogically amorphous although possibly microcrystalline (Murakami et al., 1989). The major elemental composition of JSC-Mars-1 as determined by X-ray fluorescence is as follows: 43.5% SiO₂, 23.3% Al₂O₃, 15.6% Fe₂O₃, 6.2% CaO, 3.4% MgO, 3.8% TiO₂, and 2.4% Na₂O (Allen et al., 1998). The exact mineralogies present, along with the nature of the active mineral surface, are not known; however, it is a common chemical and spectral analog for the Martian soil (Morris et al., 2003) and frequently used in laboratory studies of the Martian surface (Singer, 1982; Orenberg and Handy, 1992; Quinn and Orenberg, 1993). Therefore, we chose to study the ability of JSC-Mars-1 to oxidize CH₄ both in the presence and absence of H₂O₂.

Perchlorate salts were recently discovered at the Phoenix landing site at a concentration of ~0.5% (Hecht et al., 2009). The salt was detected in three samples originating from both the surface and shallow subsurface of the north polar landing site. The relevance of this measurement to the general planetary composition is not yet known, but the detection is potentially of interest to the global CH₄ cycle as perchlorate is often reported to be a strong oxidant. Although some have suggested that perchlorate would be fairly unreactive at cold Martian temperatures due to high energetic barriers (Hecht et al., 2009; Catling et al., 2010), the ability of perchlorate salts to oxidize CH₄ has not been investigated. Therefore, we studied the ability of sodium and magnesium perchlorate salts to directly oxidize CH₄. These specific cations (Na⁺ and Mg²⁺) are thought to be the dominant cations at the Phoenix landing site (Hecht et al., 2009).

In addition to the CH₄ studies, a separate series of experiments was performed in which the Viking organic compounds (alanine, glycine, formic acid, glycolic acid, and lactic acid) were added to each oxidizing analog. These experiments were performed in order to compare the results of the Viking LR experiment and therefore allowing us to compare the reactivity of each analog to the reactivity of the Martian surface.

To detect oxidation of the carbon species (organic solution or CH₄), gas phase CO₂ production was monitored over a 72 h time period. CO₂ is the complete oxidation product of all organic species, including CH₄, and the quantification of CH₄ oxidation by measurement of evolved CO₂ has commonly been performed (Kiyosu and Krouse, 1989; Kiyosu and Imaizumi, 1996). However, it is possible that other gas-phase oxidation products were formed in the headspace. Therefore, formaldehyde (CH₂O), an intermediate oxidation product of CH₄, was also monitored in selected experiments to determine if there was any incomplete oxidation occurring.

2. Experimental methods

2.1. Sample preparation

TiO₂ (anatase) was synthesized and complexed with H₂O₂ as described in Quinn and Zent (1999). Carefully synthesizing TiO₂, rather than purchasing the material or using natural samples, allowed the chemical state and reactivity of the surface to be carefully controlled and also guaranteed the sample was free of microbial, organic, or other chemical contaminants. It was determined by Quinn and Zent (1999) that calcination for 4 h at 250 °C results in the removal of molecular H₂O from the sample but leaves the majority of surface hydroxyl groups intact. They found this fully hydroxylated sample was able to mimic the Viking LR results better than a partially dehydroxylated sample (a result of higher temperature calcination).

Peroxide was complexed with the TiO₂ mineral surface by suspending samples of calcined TiO₂ in freshly prepared 1% H₂O₂ solution for 30 min. There was a sudden and dramatic color change from white to yellow, which indicated the formation of the TiO₂·H₂O₂ complex (Munuera et al., 1980). The samples were then rinsed with distilled H₂O and filtered to remove excess, unbound H₂O₂ from the mineral complex (Quinn and Zent, 1999). As we followed the same experimental procedure outlined by Quinn and Zent (1999), we assume the TiO₂·H₂O₂ sample we synthesized has similar properties as they report, namely, the Brunauer–Emmett–Teller (BET) specific surface area (SSA_{BET}) and H₂O₂ coverage of this material are $2.08 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ and $7.2 \times 10^{17} \text{ molecules m}^{-2}$, respectively. Using scanning electron microscopy (SEM), particle sizes were found to range from ~1 to 10 μm, with an average particle diameter of ~5 μm. After synthesis, the TiO₂·H₂O₂ was immediately transferred to a N₂-filled glove bag. After a brief drying period to remove most adsorbed H₂O, 0.1 g portions of the sample were placed into 8.5 cm³ vials that had been sterilized using an autoclave.

JSC-Mars-1 was obtained from Dr. Carlton Allen of Lockheed Martin Space Mission Systems & Services (Houston, TX). The sample was the sub-mm size fraction of a palagonitic tephra collected from the saddle between Mauna Loa and Mauna Kea volcanoes on the island of Hawaii (Allen et al., 1998). The material was mechanically ground with a mortar and pestle in order to increase the homogeneity of the sample and decrease the average particle size to be more representative of the fine-grained, mechanically weathered dust on the Martian surface. Using SEM, particle sizes were found to range from ~1 to 10 μm with an average particle diameter of ~5 μm and the SSA_{BET} was measured to be $1.00 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ (measurement by Material Synergy, Oxnard, CA). The JSC-Mars-1 sample was weighed into 0.5 g portions and placed into sterilized 8.5 cm³ vials. Hydrogen peroxide (30% by volume, 0.5 mL) was added to the appropriate vials.

Sodium perchlorate (NaClO₄, Sigma Aldrich, > 98%) and magnesium perchlorate hexahydrate (Mg(ClO₄)₂·6 H₂O, Sigma Aldrich, 99%) were used without modification. A given perchlorate salt was weighed into 0.5 g portions which were added to 8.5 cm³ vials.

After the reagents were added, the vials were immediately transferred to a N₂-filled glove bag. The vials were sealed with screw-topped caps with rubber septa while inside the N₂-filled glove bag in order to minimize atmospheric CO₂ contamination. The vials were stored in the dark at 3 °C for 48 h prior to the initial measurement and also between analyses.

2.2. Headspace analysis

An initial headspace analysis prior to addition of the organic solution or CH₄ was performed to verify that no atmospheric

contamination or sample outgassing had occurred. Analysis of CO₂ in the vial headspace was performed by gas chromatography (GC). A 1.0 cm³ sample of the headspace was extracted using a gas-tight syringe and injected into an 8610C SRI Gas Chromatograph equipped with a PORAPAK Q 6 ft × 0.085 in. ID column. A thermal conductivity detector (TCD) was used to detect CO₂ and helium was used as the carrier gas. A four level CO₂ calibration was done using 1.0% and 5.0% CO₂ gas standards (Alltech). Analysis of CO₂ in the vial headspace was performed 24, 48, and 72 h after the addition of the organic solution or CH₄. Two measurements were taken of each vial at each analysis and averaged, and error was calculated as the standard deviation of the two measurements. The data were corrected for the CO₂ removed from the vial during the previous headspace measurements. The same chromatography column and procedure was also used to monitor formaldehyde in select experiments.

2.3. Addition of organic compounds or CH₄

Immediately after the initial measurement at time (t)=0 h, either 1.0 cm³ of 630 Torr 99.99% CH₄ (Alltech) or 0.5 mL of an equimolar solution of DL-alanine (Sigma, 99% purity), glycine (Sigma, > 99% purity), formic acid (Sigma, > 97% purity), glycolic acid (Aldrich, 99% purity), and lactic acid (Sigma, 85–90% purity) was added to the vial with a gas-tight syringe. The total molarity of the organic solution was 0.25 M and the pH was adjusted to 8.0 with KOH before the solution was added to the appropriate vials. This aqueous solution of five organic species is similar to the solution used in the Viking LR experiment and will subsequently be referred to as the “organic solution”.

2.4. Experimental controls

The contents of all vials including controls are listed in Table 1. One series of vials (A, E, J, M) contained both the oxidizing analog (TiO₂·H₂O₂, JSC-Mars-1+H₂O₂, or perchlorate salt) and a carbon source (either organic solution or CH₄). A series of control vials (B, F, K, N) contained the oxidizing analog but no organic solution or CH₄. Instead, H₂O was added in place of the organic solution and N₂ gas was injected in place of CH₄. These controls were performed in order to determine if atmospheric CO₂ was contaminating the headspace or if there was any organic

Table 1

Description of the contents of all vials used in the experiments. In the text, the subscript “org” or “meth” is used to denote if the vial series contained the organic solution (or corresponding control) or CH₄ (or corresponding control).

Abbreviation	Vial contents
A _{org} /A _{meth}	TiO ₂ ·H ₂ O ₂ +organic solution/CH ₄
B _{org} /B _{meth}	TiO ₂ ·H ₂ O ₂ +H ₂ O/N ₂
C _{org} /C _{meth}	TiO ₂ +organic solution/CH ₄
D _{org} /D _{meth}	Organic solution/CH ₄ only
E _{org} /E _{meth}	JSC-Mars-1+H ₂ O ₂ +organic solution/CH ₄
F _{org} /F _{meth}	JSC-Mars-1+H ₂ O ₂ +H ₂ O/N ₂
G _{org} /G _{meth}	JSC-Mars-1+organic solution/CH ₄
H _{org} /H _{meth}	H ₂ O ₂ +organic solution/CH ₄
I _{org} /I _{meth}	Organic solution/CH ₄ only
J _{org} /J _{meth}	NaClO ₄ +organic solution/CH ₄
K _{org} /K _{meth}	NaClO ₄ +H ₂ O/N ₂
L _{org} /L _{meth}	Organic solution/CH ₄ only
M _{org} /M _{meth}	Mg(ClO ₄) ₂ +organic solution/CH ₄
N _{org} /N _{meth}	Mg(ClO ₄) ₂ +H ₂ O/N ₂
O _{org} /O _{meth}	Organic solution/CH ₄ only

contamination in the sample or vial. Another series of controls (C and G) contained a mineral (TiO_2 and JSC-Mars-1, respectively) and carbon source (organic compounds or CH_4) but no added oxidant (H_2O_2). Control H contained oxidant (H_2O_2) and a carbon source (organic solution or CH_4) but no mineral. These controls were performed in order to understand the relative importance of the mineral and the oxidant in the oxidation process. Lastly, a series of controls (D, I, L, O) contained only the carbon source (organic solution or CH_4). These were used to determine if any oxidation was occurring which was unrelated to the either the mineral or oxidant; for example, due to chemical contamination, photolysis or microbial metabolism.

In the remainder of this paper, the subscript “org” will follow the vial letters given in Table 1 if the vial series being discussed contained organic solution (or corresponding controls) and the subscript “meth” will follow the letter if CH_4 was added (or corresponding control) (e.g., A_{meth} represents a vial that contains $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and CH_4 , whereas O_{org} is a control containing organic solution only, etc.).

3. Results

3.1. $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ experiments

At $t=0$ h, prior to the addition of the organic solution, there was very little CO_2 in all vials A_{org} , B_{org} , C_{org} , or D_{org} (less than 50 nmol). When the organic solution was added to the $0.1 \text{ g TiO}_2 \cdot \text{H}_2\text{O}_2$ (vial A_{org}), CO_2 was produced at a rate of a few hundred nanomoles per day for the first few days, with the CO_2 production rate leveling off after 48 h (Fig. 1a). None of the controls (B_{org} , C_{org} , and D_{org}) contained appreciable amounts of CO_2 even after 72 h, confirming that little chemical, biological, or atmospheric contamination was occurring and also that the $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ complex, not just the TiO_2 mineral, was responsible for the observed oxidation.

The amount of CO_2 produced per gram of $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ sample upon addition of the organic solution is very similar to previous studies (Quinn and Zent, 1999). In our study, 4×10^2 nmol of CO_2 had been produced by oxidation of the organic molecules after 72 h. Quinn and Zent measured 4.5×10^2 nmol CO_2 released from the same sample mass after 72 h, suggesting that our sample probably has similar BET surface area and peroxide coverage.

Before CH_4 was added to the second series of vials (A_{meth} , B_{meth} , C_{meth} , D_{meth}), there was less than 50 nmol of CO_2 present at $t=0$. However, after CH_4 was added, no additional CO_2 was produced during the 72 h experiment (Fig. 1b). The CO_2 present in vial A_{meth} ($\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and CH_4) after 72 h was no greater than that in any of the control vials (B_{meth} , C_{meth} , or D_{meth}), signifying that no CH_4 was oxidized to CO_2 within the detection limit of the TCD. The slight increase in control vial D_{meth} (CH_4 only) at $t=72$ h is likely due to a leak in the septum causing atmospheric CO_2 contamination and not due to oxidation of CH_4 . In Fig. 1 through 3, the horizontal dashed line at 150 nmol CO_2 represents the current concentration of CO_2 in Earth's atmosphere, confirming that the CO_2 in some control vials is approaching ambient atmospheric mixing ratios due to slow leakage, but also that significantly more CO_2 is being produced by oxidation of the organic solution than could result from atmospheric contamination.

3.2. JSC-Mars-1 + H_2O_2 experiments

Unlike the vials containing $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$, there was significant CO_2 in the headspace of the vials containing JSC-Mars-1 and H_2O_2 at $t=0$ (even before the organic solution was added). Specifically,

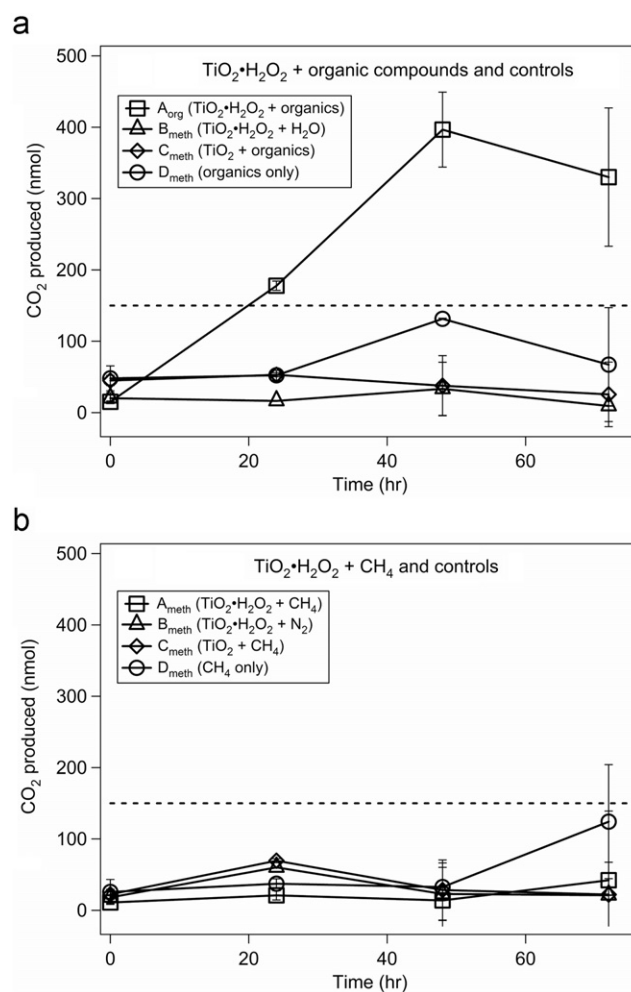


Fig. 1. The amount of CO_2 produced when the organic solution (a) or CH_4 (b) was added to a vial containing $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ (vial A, open squares). Other controls, described in Table 1, are also shown. The only vial in which any CO_2 was produced was that which contained $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and organic solution. None of the vials to which CH_4 was added produced any CO_2 during the 72 h experiment. The dashed line at 150 nmol CO_2 represents the current concentration of CO_2 in Earth's atmosphere.

as seen in Fig. 2a, vials E_{org} and F_{org} contained 4.2×10^2 nmol of CO_2 at $t=0$ h. This is most likely due to the oxidation by H_2O_2 of organic compounds inherent to the JSC-Mars-1 sample. It is not surprising that this analog soil contains organic matter, as JSC-Mars-1 is an environmental sample and was not chemically treated prior to these experiments. However, after the organic solution was added, there was much more additional CO_2 produced in vial E_{org} (JSC-Mars-1 + H_2O_2 + organic solution) than in control vial F_{org} (JSC-Mars-1 + H_2O_2 + H_2O). This suggests that the organic solution was being rapidly oxidized in addition to the organic compounds contained in JSC-Mars-1. There was also a small amount of CO_2 produced in vial H_{org} (JSC-Mars-1 + organic solution) and I_{org} (H_2O_2 + organic solution). However, when both the mineral analog (JSC-Mars-1) and the oxidant (H_2O_2) were present, more oxidation of the organic solution occurred than when only one of these species was present, suggesting that there is an interaction between the surface and H_2O_2 which enhances oxidation of the organics. These results showing that H_2O_2 is a stronger oxidant in the presence of minerals are consistent with the results of Levin and Straat (1981).

The only vial that did not contain any CO_2 even after 72 h was control vial G_{org} (organic solution only), confirming that oxidation

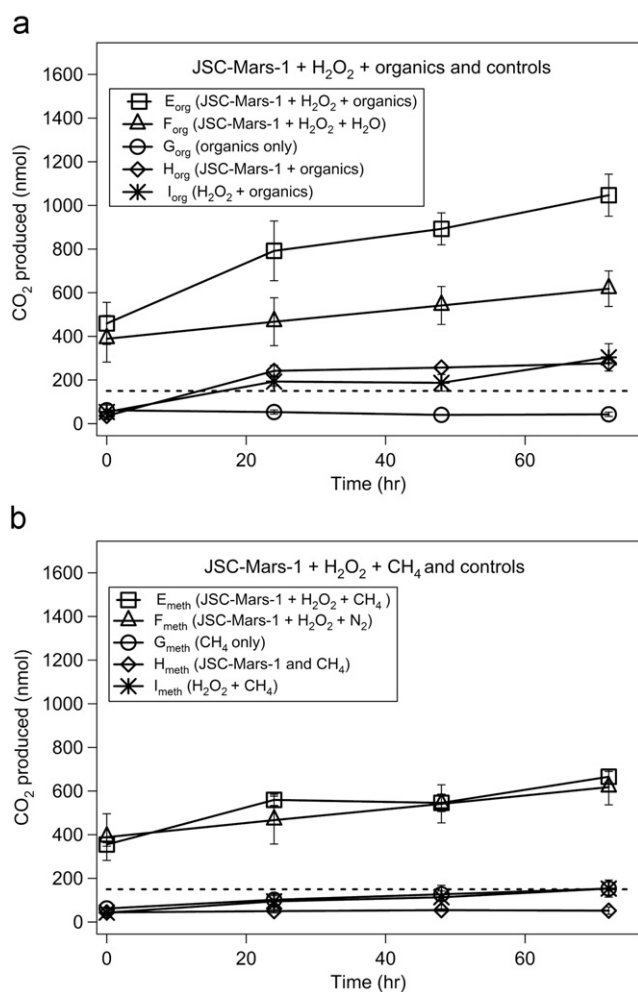


Fig. 2. The amount of CO₂ produced when the organic solution (a) or CH₄ (b) was added to a vial containing JSC-Mars-1 and H₂O₂. Other controls, described in Table 1, are also shown. The large amounts of CO₂ present at $t=0$ (before any organic solution or CH₄ was added) in vials E_{org} and F_{org} (as well as E_{meth} and F_{meth}) are due to oxidation by H₂O₂ of organic compounds contained in the JSC-Mars-1 sample. Although JSC-Mars-1 and H₂O₂ were able to oxidize the added organic solution, no CH₄ oxidation was observed. This statement is based on the fact that the E_{meth} vials (squares) contained no more evolved CO₂, within error, than the F_{meth} control vials (open triangles) to which only N₂ was added.

of the organic compounds due to chemical or biological contamination was not occurring.

As expected, there was also significant (3.7×10^2 nmol) CO₂ in both vials that contained JSC-Mars-1 and H₂O₂ (E_{meth} and F_{meth}) before CH₄ was injected ($t=0$ h) (see Fig. 2b). However, the addition of CH₄ to the JSC-Mars-1 and H₂O₂ in vial E_{meth} did not result in the production of any CO₂ beyond that produced in control F_{meth} (to which no CH₄ was added). This indicates that no CH₄ was oxidized to CO₂ within the detection limit of the TCD. The slight increase in CO₂ in several of the controls (G_{meth} and I_{meth}) is likely due to the slow leakage of atmospheric CO₂ into the vial which was discussed above.

When the headspace of vial E_{meth} (JSC-Mars-1+H₂O₂+CH₄) was sampled, the observation time was extended past the elution of the CO₂ peak to allow for detection of formaldehyde (H₂CO). We chose to monitor for H₂CO in this particular experiment type as the most total CO₂ was produced during this experiment. However, no H₂CO was detected in the headspace within the limit of detection of the GC instrument. This suggests that there was no complete or incomplete oxidation of CH₄ occurring in the vial.

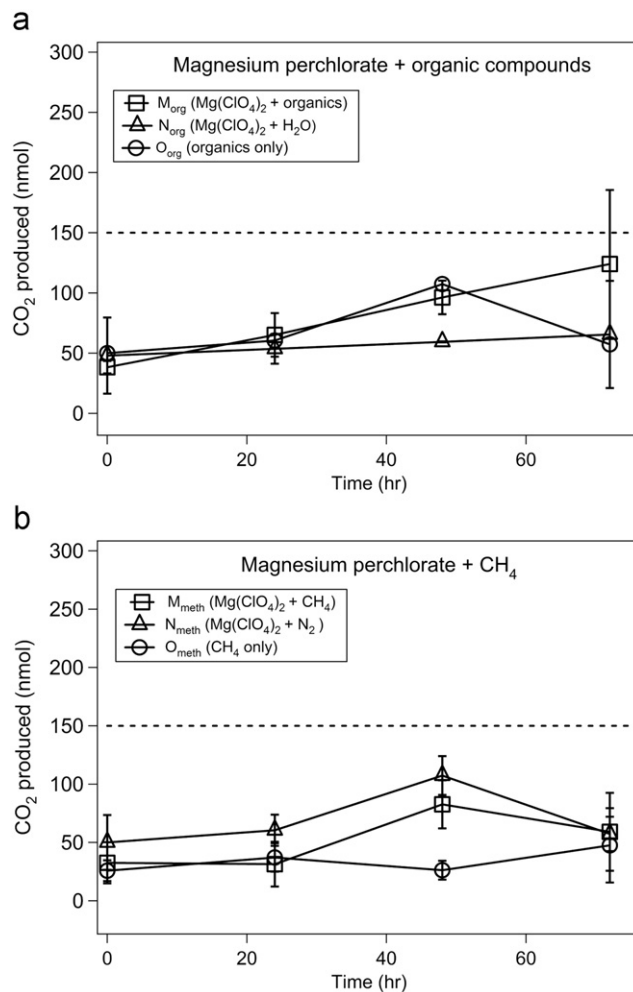


Fig. 3. CO₂ produced when the organic solution (a) or CH₄ (b) was added to Mg(ClO₄)₂. Neither the organic solution nor CH₄ were oxidized to CO₂ to any measurable extent (open squares).

3.3. Perchlorate experiments

As seen in Fig. 3a and b, when either the organic solution or CH₄ were added to Mg(ClO₄)₂ no more CO₂ was produced in the vials than when only H₂O or N₂ were injected. Although some vials appeared to have a slight leak to the atmosphere, comparison with the control vials indicates that no CO₂ was produced within the detection limit of the TCD. NaClO₄ behaved similarly; no detectable CO₂ was observed after the addition of the organic solution or CH₄ (not shown). To the best of our knowledge, the oxidation of CH₄ by perchlorate salts has not been previously studied. The oxidation of a wide range of organic compounds by perchloric acid (HClO₄) was studied by Martinie and Schilt (1976). Even under elevated reaction temperatures (200 °C), several organic molecules, including the amino acids glycine and alanine, were able to partially survive oxidation by HClO₄. It is therefore not surprising that the organic solution of amino acids and sugars was not directly oxidized by perchlorate salts in these low temperature studies. It is even less surprising that CH₄, a low reactivity molecule, was not oxidized by perchlorate salts.

4. Discussion

To compare the reactivity of the samples used in this study to the reactivity of the Martian surface, we first normalize CO₂

production with respect to soil mass. As only $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1+ H_2O_2 oxidized the organic solution, only these two analogs are considered in this comparison. The Viking LR experiment utilized 0.5 cm^3 of soil, corresponding to a mass of 0.83 g assuming a soil density (ρ_{soil}) of 1650 kg m^{-3} (Feldman et al., 2004). In our experiments and presumably in the Viking LR experiments the oxidant (H_2O_2) was the stoichiometric limiting reagent (Levin and Straat, 1981), enabling a reasonable comparison. Additionally, the temperature of the mineral samples during the organic oxidation reaction in our study and in the Viking LR experiment is fairly similar: $3 \text{ }^\circ\text{C}$ in this study vs. $\sim 10 \text{ }^\circ\text{C}$ inside the experimental cells of the Viking Landers (Levin and Straat, 1981).

In Fig. 4 we normalize the CO_2 produced from vials A_{org} ($\text{TiO}_2 \cdot \text{H}_2\text{O}_2 + \text{organic solution}$) and E_{org} (JSC-Mars-1+ $\text{H}_2\text{O}_2 + \text{organic solution}$) to a 0.83 g sample mass and compare our oxidation rates to the results of the LR experiment onboard Viking Landers 1 and 2 (VL1 and VL2). For each of the experimental analogs, we divide the nmol of CO_2 produced by organic oxidation by a constant to quantify the enhanced reactivity of the analogs relative to Martian soil. It can be seen in Fig. 4 that $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ is about 125 times more oxidizing than the Martian regolith, and JSC-Mars-1 combined with H_2O_2 is about 30 times more oxidizing. Quinn and Zent (1999) also found $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ to be about 100 times more reactive than the Martian surface with respect to the organic solution, and suggested that this two order of magnitude difference could be due to the 1% abundance of TiO_2 in the Martian regolith (Clark et al., 1977). The $30 \times$ greater reactivity of the JSC-Mars-1+ H_2O_2 sample could be due to mineralogical differences between this palagonitic material and the actual Martian soil, or due to the greater H_2O_2 content of our sample.

Despite the large difference in the magnitude of reactivity between the oxidative analogs studied ($\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1+ H_2O_2) and the Martian regolith, the overall reactivity of the analogs appears to be similar to that observed by VL1 and VL2, namely, the oxidation of the organic solution proceeds via a rapid initial release of CO_2 followed by a slower, prolonged release. The diminished rate of production of CO_2 is perhaps due to the decrease in available organic reagent.

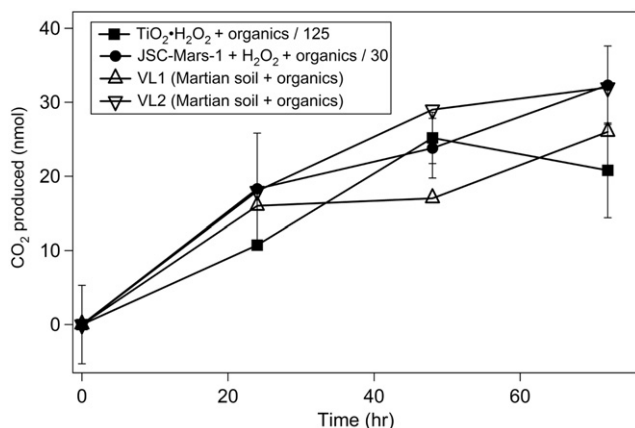


Fig. 4. Comparison of the oxidation rates of the organic solution by the $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1+ H_2O_2 analogs (this work) and by the Martian surface during the Viking LR experiment (Quinn and Zent, 1999). All data is normalized to a 0.85 g sample mass. For the two lab analogs, the CO_2 produced by organic oxidation is divided by a constant to determine the enhanced reactivity of the analogs relative to the Martian surface. It can be seen that $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ is about 125 times more oxidizing than the Martian soil, and JSC-Mars-1+ H_2O_2 is about 30 times more oxidizing. Although both analogs used in this study are more reactive than the actual Martian regolith, the overall behavioral trend (rapid initial release followed by a slower, prolonged increase) is similar.

Although both of these systems ($\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1+ H_2O_2) were able to oxidize the organic solution to CO_2 , no CO_2 was observed to be produced as a result of CH_4 oxidation. As a result, only an upper-limit reaction coefficient for the oxidation of CH_4 by these mineral surfaces can be determined. This reaction coefficient (α) is defined as the fraction of collisions of CH_4 with the surface of the mineral that result in complete oxidation to CO_2 . The perchlorate salts did not evolve any CO_2 from CH_4 , nor did they oxidize the organic solution to any measureable extent. However, as we were not able to perform BET surface area analysis on the perchlorate salts, values of α could not be determined for CH_4 oxidation by these salts. Therefore, in the following section we only determine upper limit values of α for CH_4 on $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1+ H_2O_2 .

Fuchs and Sutugin (1971) show α can be calculated by Eq. (1):

$$\frac{J_{\text{net}}}{J_{\text{total}}} = \frac{0.75\alpha(1 + Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha} \quad (1)$$

where J_{net} is the net flow of CH_4 to the entire mineral surface area (i.e., the flow that either sticks or reacts) and J_{total} is the total flow to the mineral surface area assuming the system is in the continuum regime. In this regime, the Knudsen number (Kn), the ratio of the mean free path of a gas molecule (λ) to the particle radius (R_p), is small (< 1) and these conditions subsequently dictate the properties of molecular transport to the surface of a particle. As λ is 79 nm at atmospheric pressure and the mineral particle diameters range from 1 to $10 \mu\text{m}$, $Kn \ll 1$ and the experimental system is in the continuum regime. Eq. (2) was used to find the following:

$$J_{\text{total}} = \frac{D_{\text{CH}_4}}{R_p} (c_\infty - c_s) SA \quad (2)$$

where J_{total} is the total flow (molecules s^{-1}) toward the entire mineral surface area present in the vial assuming the system is in the continuum regime, D_{CH_4} is the diffusivity of CH_4 inside the vial, c_∞ and c_s are the concentrations of CH_4 far away from the particle and on the surface of the particle, respectively (Seinfeld and Pandis, 1998), and SA is the total surface area present in the vial. Based on SEM images of $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and JSC-Mars-1, R_p is $2.5 (\pm 1) \mu\text{m}$ on average for both minerals. The diffusivity of CH_4 at room temperature is $0.2 \text{ cm}^2 \text{ s}^{-1}$ and was calculated using $D_{\text{CH}_4} = 0.5v\lambda$, where v is the mean molecular speed (m s^{-1}) of CH_4 at a temperature T given by the Maxwell-Boltzmann distribution of gas velocities, $v = (8RT/\pi M_w)^{1/2}$ (Seinfeld and Pandis, 1998). Although no oxidation of CH_4 was observed, we assume we are simply measuring an upper limit of the heterogeneous reaction that is occurring; thus, c_s is 0 and c_∞ is the bulk gas phase concentration of CH_4 in the vial ($2.4 \times 10^{18} \text{ molecules cm}^{-3}$). The total surface area (SA) for each mineral was found by multiplying the mineral's BET specific surface area (SSA_{BET}) ($\text{m}^2 \text{ kg}^{-1}$) by the sample mass (kg). Given the error in the estimation of R_p in the mineral sample, J_{total} is equal to $4 \times 10^{26} (\pm 2 \times 10^{26}) \text{ molecules s}^{-1}$ for $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ and $1 \times 10^{27} (\pm 5 \times 10^{26}) \text{ molecules s}^{-1}$ for JSC-Mars-1+ H_2O_2 , with the difference due to the larger sample mass, and thus total surface area, of JSC-Mars-1.

Next, an upper limit of the net flow of CH_4 to all mineral particles in the vial, or the upper limit of total CH_4 that is oxidized to CO_2 , J_{net} , can be derived from the detection limit of the experiment. The smallest amount of CO_2 that could be reasonably detected by the TCD is 7.7 nmol . As not even this small amount of CO_2 was present in the 1.0 cm^3 sample of vial headspace injected into the GC during the final measurement, less than 65.5 nmol of total CO_2 were present in the 8.5 cm^3 vial by the end of the 72 h experiment ($7.7 \text{ nmol cm}^{-3} \times 8.5 \text{ cm}^3 = 65.5 \text{ nmol total}$). However, since there was leakage of atmospheric CO_2 in some vials, a more conservative upper limit is 150 nmol per

8.5 cm³ corresponds to the mixing ratio of CO₂ in Earth's atmosphere). If more than this amount of CO₂ was formed in the vial headspace, we were certain to detect it. As less than 150 nmol CO₂ was produced after 72 h, $J_{\text{net}} < 3.5 \times 10^{11}$ CH₄ molecules s⁻¹ assuming a 1:1 reaction stoichiometry between CH₄ and CO₂. From Eq. 1, α is less than $\sim 3.7 \times 10^{-17}$ for TiO₂·H₂O₂ and less than $\sim 1.6 \times 10^{-17}$ for JSC-Mars-1+H₂O₂.

5. Martian implications

The upper limit parameter α can be used to determine the kinetic importance of heterogeneous CH₄ oxidation on Mars. To quantify such CH₄ loss, first we approximate the CH₄ flux, F_{CH_4} (molecules m⁻² s⁻¹), to any surface on Mars. As the atmospheric pressure on Mars is low, heterogeneous processes are occurring in the kinetic/molecular regime and so F_{CH_4} can be found using

$$F_{\text{CH}_4} = \frac{1}{4} v n_{\text{CH}_4} \quad (3)$$

where n_{CH_4} is the number density of CH₄ on Mars (molecules m⁻³). On the surface of Mars, the average observed CH₄ mixing ratio of 10 ppbv corresponds to $n_{\text{CH}_4} = 2.2 \times 10^{15}$ molecules m⁻³, yielding an approximate value of F_{CH_4} of 3×10^{17} molecules m⁻² s⁻¹ at 210 K. We can then estimate a lower limit oxidation timescale, τ_{ox} , over which a column of CH₄ could be permanently removed from the atmosphere via oxidation by H₂O₂ complexed to mineral surfaces:

$$\tau_{\text{ox}} = \frac{N_{\text{CH}_4}}{\alpha F_{\text{CH}_4} \text{SSA}_{\text{soil}} \rho_{\text{soil}} d_{\text{H}_2\text{O}_2}} \quad (4)$$

where N_{CH_4} is the CH₄ column abundance above 1 m² of regolith (molecules m⁻²), SSA_{soil} and ρ_{soil} are the specific surface area (m² kg⁻¹) and density (kg m⁻³) of the Martian soil, respectively, and $d_{\text{H}_2\text{O}_2}$ is the depth (m) of the surface soil layer that contains adsorbed or complexed H₂O₂. A uniform mixing ratio of 10 ppbv at Martian surface gravity and pressure conditions corresponds to $N_{\text{CH}_4} = 2.2 \times 10^{19}$ CH₄ molecules m⁻². We use a value for ρ_{soil} of 1650 kg m⁻³ (Feldman et al., 2004) and a value for SSA_{soil} of 1.7×10^4 m² kg⁻¹ (Ballou et al., 1978). We assume that this entire specific surface area is available to oxidize CH₄ and the H₂O₂ is homogeneously distributed from the surface down to $d_{\text{H}_2\text{O}_2}$.

The depth of Martian soil that contains H₂O₂ is a difficult parameter to constrain, as the H₂O₂ production mechanism(s), flux from the atmosphere to the surface, rates of adsorption and destruction upon interaction with the soil, and lifetime in the subsurface have only been estimated or theoretically calculated. However, as the gas chromatograph–mass spectrometer onboard Viking Lander 2 failed to detect any organic compounds in a sample collected at a depth of 10 cm (Biemann, 1979), it seems likely that the layer of strongly oxidizing soil extends at least 10 cm below the surface. Bullock et al. (1994) found that even if the lifetime of H₂O₂ in the soil is long (10⁵ years), little H₂O₂ will penetrate below a depth of 3 m due to significant adsorption of H₂O₂ to soil grains. Impact gardening, aeolian activity, or triboelectric processes could overturn the surface of the regolith and provide a mechanism for H₂O₂ to reach greater depths. However, it is highly unlikely that these processes could turn over meters of Martian soil every few years. It is therefore difficult to constrain a reasonable maximum value for $d_{\text{H}_2\text{O}_2}$, although at some depth the oxidation of CH₄ molecules will be limited by the timescale needed to diffuse to such depths. For example, it would take almost 3 years for CH₄ to reach depths of 100 m (Formisano et al., 2004; Gough et al., 2010), so values of $d_{\text{H}_2\text{O}_2}$ greater than this are unrealistic. However, we do not specifically consider the

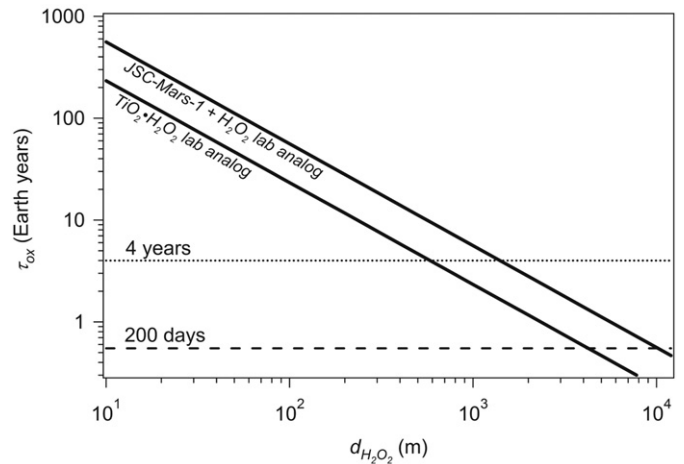


Fig. 5. The lifetime of a CH₄ column in the Martian atmosphere due to heterogeneous oxidation by H₂O₂ adsorbed to soil (τ_{ox}) as a function of soil depth ($d_{\text{H}_2\text{O}_2}$). Results are shown for both experimentally determined values of α : CH₄ on TiO₂·H₂O₂ (lower diagonal line) and CH₄ on JSC-Mars-1+H₂O₂ (upper diagonal line). The horizontal dotted line represents $\tau_{\text{ox}}=4$ years, which is the upper limit lifetime consistent with the ground-based observations of Mumma et al. (2009). The horizontal dashed line corresponds to $\tau_{\text{ox}}=200$ days, which is the CH₄ lifetime needed to explain the observed atmospheric variability (Lefevre and Forget, 2009). Very large depths of oxidized soil ($d_{\text{H}_2\text{O}_2} > 500$ m) are needed for the CH₄ lifetime to be consistent with observations of the Martian atmosphere.

diffusion time of CH₄ through the regolith during this calculation of τ_{ox} .

In Eq. (4), the reaction coefficient, α , is the upper limit value we have experimentally determined for either TiO₂·H₂O₂ ($\alpha < 3.7 \times 10^{-17}$) or JSC-Mars-1+H₂O₂ ($\alpha < \sim 1.6 \times 10^{-17}$). In Fig. 5 we plot the CH₄ lifetime (τ_{ox}) as a function of the depth of the soil layer that contains H₂O₂ ($d_{\text{H}_2\text{O}_2}$) using the two experimentally determined, upper limit values for α . It can be seen in Fig. 5 that τ_{ox} decreases with increase in $d_{\text{H}_2\text{O}_2}$. The horizontal dotted and dashed lines in Fig. 5 correspond to CH₄ lifetimes of 4 years and 200 days, respectively. These lines represent the two different CH₄ lifetimes which have been proposed: the ground-based observations of Mumma et al. (2009) are consistent with a CH₄ lifetime of 4 years or less; however, Lefevre and Forget (2009) find these observations could actually suggest a lifetime of about 200 days.

In the case of both analogs, it can be seen in Fig. 5 that the CH₄ lifetime is very long for any reasonable oxidant depth. Even in the case of the more reactive analog (TiO₂·H₂O₂), more than 500 m of oxidized soil are required in order to remove CH₄ from the atmosphere in time scales of 4 years or less. At these depths, however, subsurface diffusion would limit the kinetics of CH₄ loss and therefore it is unlikely that H₂O₂ adsorbed to soil grains could be responsible for the rapid CH₄ loss which has been recently reported.

We have no way to accurately quantify the decreased reactivity of the Martian regolith toward CH₄ relative to the laboratory analog. However, the soil on Mars is likely to be less reactive than either of these analog materials as the analogs oxidized the organic solution much more rapidly than the actual Martian surface oxidized the organics during the LR experiment. Therefore, these upper limit α values are certainly an over-estimation which will yield lower limit lifetimes. Additionally, the heterogeneous oxidation of CH₄ would most likely occur more slowly on Mars than in our study due to the lower temperatures present on the Martian surface. This correlation between reaction kinetics and temperature is predicted by both collision theory and transition state theory (Finlayson-Pitts and Pitts, 2000) and could increase the CH₄ lifetime even further beyond what could be relevant to the Martian CH₄ cycle.

It is important to point out that we assume CH₄ loss on Mars would be constant as a function of time over the entire calculated lower limit lifetime (τ_{ox}), which represents a different behavior than the decreased reactivity observed after a few days in our organic oxidation experiments. This plateauing, observed even more dramatically in similar experimental studies by Levin and Straat (1981) and Quinn and Zent (1999), is likely due to the large excess of organic molecules beginning to deplete the oxidant (H₂O₂). In the case of CH₄ oxidation on Mars, we do not believe the reaction would level off after a few days, as the oxidant (perhaps H₂O₂) would not be the limiting reagent. Estimates of soil H₂O₂ content on Mars vary from 1.4×10^{23} H₂O₂ molecules m⁻³ (Bullock et al., 1994) to 5.8×10^{26} H₂O₂ molecules m⁻³ (Levin and Straat, 1981), indicating there is enough oxidant in less than 200 μ m depth of soil, at least stoichiometrically, to oxidize the 2.2×10^{19} molecules of CH₄ in a 1 m² atmospheric column above this regolith, assuming a 10 ppbv mixing ratio. Therefore, we do not believe that H₂O₂ would be depleted to any relevant extent during the reported 4 year (or shorter) CH₄ lifetime and thus the oxidation rate would not be expected to decrease.

We also consider the possibility that H₂O₂ adsorbed to mineral dust aerosol in the atmosphere could act as a CH₄ sink. However, even at the high optical depths (OD) present during dust storms, the surface area of mineral dust in the Martian atmosphere is relatively small. For example, Martin (1995) calculated that a localized dust storm monitored by the Viking orbiter (OD=0.83) resulted in an atmospheric dust enhancement of 18,000 kg km⁻², corresponding to a 6 μ m layer of dust if compacted. Even if this atmospheric mineral aerosol was coated with H₂O₂ to a greater extent than the regolith material due to condensation of electrostatically produced oxidant (Atreya et al., 2006; Delory et al., 2006), it can be seen in Fig. 5 that this effective depth is many orders of magnitude too small to impact atmospheric CH₄ concentrations on a seasonal time scale.

It is therefore unlikely that H₂O₂ adsorbed to mineral grains in the Martian regolith or atmosphere is responsible for the rapid CH₄ destruction reported by Mumma et al. (2009) or the spatial and temporal variability observed by Geminale et al. (2008) and Fonti and Marzo (2010). As a CH₄ lifetime of less than 4 years is required to cause this reported variability (Mumma et al., 2009), some other loss process is likely occurring. It has been suggested that CH₄ is not being destroyed by H₂O₂, but rather by ·OH formed during mineralogical processing of H₂O₂. Processes such as the Fenton reaction, which oxidizes Fe²⁺ to Fe³⁺ while reducing H₂O₂ to ·OH, could be occurring on or in the iron-rich Martian regolith. Other proposed oxidants include superoxide (O₂⁻) ions (Yen et al., 2000), iron (IV) salts (Tsapin et al., 2000), or peroxonitrite compounds (Plumb et al., 1989). Incident UV radiation could play a role in the destruction of CH₄ directly through a surface-enhanced destruction process or indirectly through photochemical formation of oxidants on surfaces of minerals or ices. Perhaps chlorine species such as the reactive intermediate anionic chlorine oxides (ClO⁻, ClO₂⁻, and ClO₃⁻) exist in the regolith and could destroy organics or methane. It is also possible that the reactive components of the regolith or the mechanisms occurring have not yet been identified. Either way, more work must be done towards identifying chemical species or minerals that are reactive towards CH₄ over very short time scales (less than 4 years).

6. Conclusions

We have performed a series of experiments analyzing the reactivity of several oxidizing analogs toward CH₄. Perchlorate salts and H₂O₂ are thought to exist on Mars although their geographic distribution is not known. These species, especially peroxides, have

been proposed to rapidly destroy CH₄, possibly resulting in a CH₄ lifetime short enough to explain the observations of Mumma et al. (2009) (less than 4 years) and the model results of Lefevre and Forget (2009) (200 days). However, we have shown that ClO₄⁻ salts are unreactive towards both CH₄ and the organic compounds used during the Viking LR experiment and are thus very unlikely to destroy CH₄ over these time scales on Mars. Hydrogen peroxide, complexed with TiO₂ and also added to JSC-Mars-1 soil analog, was able to oxidize the Viking organic solutions to CO₂ with greater reactivity than the Martian surface. However, even the most reactive oxidative analog, TiO₂·H₂O₂, did not oxidize CH₄ to CO₂ during a 72 h experiment within the detection limit of the GC instrument used. A calculated upper limit reaction coefficient, α , is less than $\sim 3.7 \times 10^{-17}$ for TiO₂·H₂O₂ and less than $\sim 1.6 \times 10^{-17}$ for JSC-Mars-1+H₂O₂. When these experimental results are extrapolated to Martian conditions, the CH₄ lifetimes calculated are too long to be relevant to the Martian CH₄ cycle. Depths of oxidized soil greater than 500 m are needed for the CH₄ lifetime to be consistent with observations of the Martian atmosphere. Moreover, these reactions are likely temperature dependent and will be slower at Martian temperatures.

This study was not a comprehensive study of all possible mineral analogs and all possible H₂O₂ complexation or stabilization mechanisms. However, we have shown that neither ClO₄⁻ salts nor H₂O₂ alone are likely to be directly responsible for the recently observed rapid destruction and high temporal and spatial variability of atmospheric CH₄ on Mars.

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