



Martian dust storms as a possible sink of atmospheric methane

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[1] Recent laboratory tests, analog studies and numerical simulations all suggest that Martian dust devils and larger dusty convective storms generate and maintain large-scale electric fields. Such expected E-fields will have the capability to create significant electron drift motion in the collisional gas and to form an extended high energy ($u \gg kT$) electron tail in the distribution. We demonstrate herein that these energetic electrons are capable of dissociating any trace CH_4 in the ambient atmosphere thereby acting as an atmospheric sink of this important gas. We demonstrate that the methane destruction rate increases by a factor of 10^{12} as the dust storm E-fields, E , increase from 5 to 25 kV/m, resulting in an apparent decrease in methane stability from $\sim 10^{10}$ sec to a value of ~ 1000 seconds. While destruction in dust storms is severe, the overall methane lifetime is expected to decrease only moderately due to recycling of products, heterogeneous effects from localized sinks, etc. We show further evidence that the electrical activity anticipated in Martian dust storms creates a new harsh electro-chemical environment. **Citation:** Farrell, W. M., G. T. Delory, and S. K. Atreya (2006), Martian dust storms as a possible sink of atmospheric methane, *Geophys. Res. Lett.*, *33*, L21203, doi:10.1029/2006GL027210.

1. Introduction

[2] The discovery of trace amounts of methane in the Martian atmosphere [Formisano *et al.*, 2004; Krasnopolsky *et al.*, 2004; Mumma *et al.*, 2004] has generated great excitement in the Mars science community. While geological origin of methane is an attractive possibility [Formisano *et al.*, 2004; Atreya *et al.*, 2004; Oze and Sharma, 2005; Atreya *et al.*, 2006a], there is a non-unique likelihood that the methane source is biogenic in nature [Chappelle *et al.*, 2002; Krasnopolsky *et al.*, 2004; Atreya *et al.*, 2004, 2006a]. To date, the primary atmospheric loss processes considered for methane are through photochemistry and surface effects, with methane photochemical stability estimated to be on the order of several hundreds of years [Summers *et al.*, 2002; Wong *et al.*, 2003]. Such relatively long lifetimes suggest that any methane might become well-mixed in the Martian atmosphere. In this work, we introduce a second possible very active methane loss process: direct electron dissociation of methane in the high E-field environments expected in Martian dust devils, larger convective dust storms, and dust fronts. This highly

seasonal and quasi-local loss process could play a role in the non-uniformity of methane on the planet.

[3] Dust storms on Mars are expected to generate and maintain large-scale electric dipole fields, with interior E-field values approaching the atmospheric breakdown levels of ~ 25 kV/m [Melnik and Parrot, 1998; Farrell *et al.*, 2003, 2006; Zhai *et al.*, 2006]. The E-fields form via grain-grain contact electrification that tends to leave smaller dust particles with a net negative charge and larger sandy grains with a net positive charge [Ette, 1971]. Vertical winds in the storm then mass-stratify (and charge-stratify) the grain distribution as a function of height, creating a downward-directed electric dipole moment and large-scale dipole electric field structure [Crozier, 1964; Farrell *et al.*, 2004].

[4] Evidence for this charge creation/separation process is in the form of analytical models [Melnik and Parrot, 1998; Farrell *et al.*, 2003, 2006; Zhai *et al.*, 2006] and terrestrial analog studies [Freier, 1960; Crozier, 1964; Schmidt *et al.*, 1998; Delory *et al.*, 2002; Farrell *et al.*, 2004; Jackson and Farrell, 2006]. The former modeling studies all suggest that E-fields at many tens of kV/m can be generated in a convective Martian storm with charging exponential growth time scales on the order of 10's of seconds under ideal conditions. The latter analog studies consistently find relatively large electric fields in small terrestrial dust devils and saltating dust fronts, with dust devil fields > 100 kV/m and dust front fields > 150 kV/m. The E-fields in terrestrial dust devils/fronts are not large enough to create atmospheric breakdown on Earth, but well above the atmospheric breakdown fields of ~ 25 kV/m for the low-pressure Martian atmosphere. Given that very similar analogous aeolian processes occur on Mars, large fields approaching breakdown are anticipated in that planet's dust devils/storms and dust frontal systems.

[5] A complementary set of papers by Delory *et al.* [2006] and Atreya *et al.* [2006b] recently examined the behavior of ambient electrons in the Martian atmosphere under the influence of large E-fields (like that in dust devils/storms/fronts). They found that the electrons evolve in three ways: First, the electron density increases geometrically with increasing E , this due to increasing CO_2 ionizations from energetic E-field driven electrons. Second, the electron drift velocity steadily increases with E reaching 5×10^5 m/s near 20 kV/m. Finally, a distinct high energy electron tail develops in the electron distribution, with its power-law rolloff in the 10's of eVs decreasing directly with increasing E [Nighan, 1970; Delory *et al.*, 2006]. Basically, a collisional plasma develops in a mature dust devil/storm in the low pressure CO_2 atmosphere. This plasma may even glow [Eden and Vonnegut, 1973; Farrell *et al.*, 2005].

[6] As described by Delory *et al.* [2006] and Atreya *et al.* [2006b], the energetic electrons also affect the ambient molecules in the low pressure gas. Specifically, electron dissociation of CO_2 into CO and O^- occurs near 4.4 eV.

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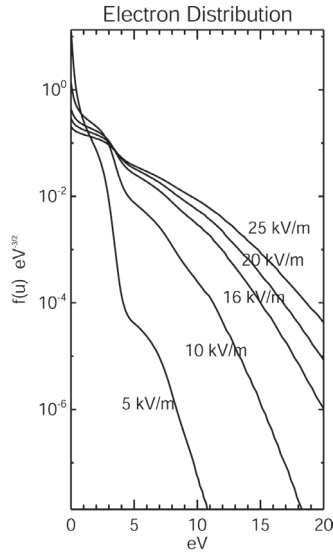


Figure 1. Electron distribution in the collisional CO₂ atmosphere for E-fields at Martian atmospheric pressures.

Without the E-field, the electrons do not possess the intrinsic energy to dissociate the molecule. However, with an electric field, an energetic portion of the electron population now exists (i.e., the tail of the distribution) with the required energy to dissociate the CO₂ and this population (between 4 and 5 eV) is found to increase geometrically with increasing E. Water also undergoes a similar electron dissociation attachment at a number of resonant energies between 6 and 12 eV (the narrow resonance at 6.6 eV is dominant), and *Delory et al.* [2006] found that the production of dissociated water products OH and H⁻ also geometrically increases with increasing E-field. *Atreya et al.* [2006b] examined the subsequent recombination pathways for the dust storm E-field created species CO, O⁻, OH, and H⁻ in the Martian near-surface atmosphere and found that anomalously large amounts of the reactive species H₂O₂ can be created in the atmosphere at concentrations exceeding 200 times that of regular photochemical production. The reactive product H₂O₂ was found to be at condensation levels and hence they conclude that the peroxide coats aeolian dust and the surface, and may possibly account for the presumed highly-reactive soil found by the Viking landers [*Oyama et al.*, 1977].

[7] These tandem models suggest that the atmospheric conditions in Martian dust devils/storms/fronts are relatively harsh, with large E-fields, the creation of a collisional plasma (energetic electrons, CO₂⁺, and negative ions), and the formation of reactive species. Given this new meteorology-driven electrochemical environment on Mars that is so very different from the fair-weather photochemical environment, we ask an obvious question: What is the stability of methane in Martian dust storms?

2. Model and Results

[8] The behavior of electrons in a low pressure CO₂ gas requires the solution of the Boltzmann equation with inclusion of inelastic and elastic collisions. The resulting electron distribution has been derived by *Nighan* [1970] and *Delory et al.* [2006] with similar results. Figure 1 shows the

distribution from *Delory et al.* [2006] for the case of electrons in the Mars near-surface atmosphere. Note the development of an extended high energy electron tail (energy, $u > 4$ eV) that increases in population with increasing E-field.

[9] The electron impact ionization of CO₂ occurs for those electrons with energies, $u > 14$ eV. Each impact will create an added electron thereby allowing exponential growth in electrons density defined by:

$$n_e = n_{e0} \exp(\alpha x) \quad (1)$$

where α is Townsend's first ionizing coefficient (in units of inverse length) and x is an anode/cathode distance (or separation of the charging centers). The inverse of α represents the distance required for an electron to impact-ionize CO₂ thereby freeing a second electron. As quantified by *Delory et al.* [2006, equations 7 and 8 and Figure 4], this distance ranges from 10¹⁰ cm for fields at 5 kV/m to 3 cm at 25 kV/m. We note that expression (1) applies for E-fields in pre-breakdown conditions. To consider discharges/full breakdown situations, a denominator term of the form $(1 - F(\omega))$ would then be included in (1), where $F(\omega)$ is a function dependent upon the number of secondary electrons produced per unit length, ω . Note that when enough secondaries are produced to have $1 - F(\omega) = 0$, the electron density becomes infinite, signifying complete breakdown of the gas. Since any modeled secondary processes is not unique and would create an unnecessary contrivance, we simply exclude breakdown/discharge situations in our model (set $F(\omega) = 0$), and consider our formalism in (1) as applicable to the pre-breakdown electrostatic environment in the dust devil.

[10] The energetic electrons are also capable of dissociating CO₂ at energies near 4.4 eV [*Delory et al.*, 2005]. At this resonance, an electron will dissociate CO₂ into CO and O⁻. The production of CO/O⁻ is describable via

$$\frac{dn_{\text{CO/O}^-}}{dt} = k_{e/\text{CO}_2} n_{\text{CO}_2} n_e \quad (2)$$

where k_{e/CO_2} is the chemical rate for the reaction and n is the density of the designated species. The chemical rate is [*Ferreira*, 1983]

$$\begin{aligned} k_{e/\text{CO}_2} &= \langle \sigma_d v \rangle = (2e/m_e)^{1/2} \int_{u_0 - \delta u/2}^{u_0 + \delta u/2} \sigma_d(u) u f(u) du \\ &\sim (2e/m_e)^{1/2} \sigma_d(u_0) u_0 f(u_0) \delta u \end{aligned} \quad (3)$$

where σ_d is the (e, CO₂) dissociation cross section of $\sim 0.15 \times 10^{-22} \text{ m}^2$ [*Itakawa*, 2002], at u_0 of 4.4 eV and δu is the relatively-narrow cross section width of ~ 1.0 eV. We make use of the narrow line width to derive the approximate form of k in (3). *Delory et al.* [2006] found that the E-field production of CO/O⁻ ranged from 10¹⁰ m⁻³ s⁻¹ at 5 kV/m to $\sim 10^{18}$ m⁻³ s⁻¹ at 25 kV/m. A similar calculation was made therein for (e, H₂O), and subsequent products OH/H⁻ were found to be at 10⁷ m⁻³ s⁻¹ at 5 kV/m to $\sim 10^{15}$ m⁻³ s⁻¹ at 25 kV/m (for a water loss $\Delta n/n$ of $\sim 10^{-5}$ every second in large fields). As described in the complementary paper of *Atreya et al.* [2006b], the enhanced production of O and H

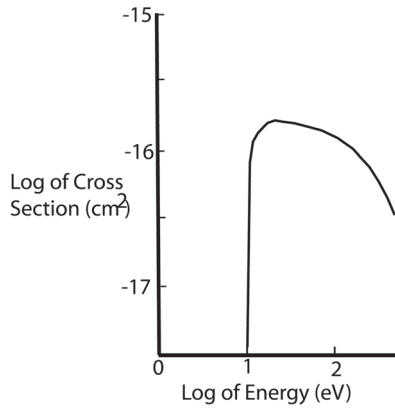


Figure 2. Cross section for electron dissociation of CH₄ (data from *Ohmori et al.* [1986]).

in large E-fields was used as inputs to an atmospheric chemistry model which found that for large electric fields the atmospheric abundance of the recombination product H₂O₂ may exceed 200 times that of maximum photochemical model, with column density values of H₂O₂ at $7 \times 10^{17} \text{ cm}^{-2}$ and intermediate product OH at $8 \times 10^{13} \text{ cm}^{-2}$ [*Atreya et al.*, 2006b]. This enhancement of the peroxide has implications in the biogeochemistry of Mars soil/surface (see discussion therein). Clearly, the electro-chemistry model indicates that the collisional plasma that forms in dust storms is a harsh electrochemical environment creating very reactive species via subsequent recombination of electron-dissociated products.

[11] Energetic electrons are also capable of dissociating methane at energies > 10 eV. Figure 2 shows the methane

dissociation cross section (adapted from *Ohmori et al.* [1986]). Unlike CO₂ and H₂O, the methane dissociation cross section is relatively broad, starting near 10 eV, peaks at 20 eV, and slowly decreasing beyond 100 eV. The methane loss via electron dissociation can be described via

$$dn_{\text{CH}_4}/dt = -k_{e/\text{CH}_4} n_{\text{CH}_4} n_e \quad (4)$$

where

$$k_{e/\text{CH}_4} = \langle \sigma_d v \rangle = (2e/m_e)^{1/2} \int_0^\infty \sigma_d(u) u f(u) du \quad (5)$$

where $\sigma_d(u)$ is the methane dissociation cross section shown in Figure 2 and $f(u)$ is shown in Figure 1. The electron density is defined by equation (1) and we assume that the ambient density of CH₄ is $n_{\text{CH}_4} \sim 10 \text{ ppb} \sim 2 \times 10^{15} \text{ m}^{-3}$.

[12] Figure 3 shows the destruction of methane (Figure 3a) and methane destruction time ($(k_{e/\text{CH}_4} n_e)^{-1}$) (Figure 3b) as a function of dust devil/storm/front electric field. The line in Figure 3b indicates the photochemical lifetime of 10^{10} seconds (~ 300 years). Note that as the E-field increases, the CH₄ destruction time geometrically decreases and is close to ~ 1000 seconds for large E-fields (Figure 4).

3. Conclusions

[13] The meteorological-driven electrochemical environment in dust devils/storms/fronts is a clear sink of atmospheric methane. The molecular destruction time of methane exponentially decreases with driving electric field as $t(E) \sim t_0 \exp(-\beta(E - E_0))$ where t_0 is 10^{11} seconds, E_0 is 10 kV/m and β is $1.2 \times 10^{-3} \text{ m/kV}$. The value of $1/\beta$ represents an e-folding of the value of t every $\sim 1 \text{ kV/m}$. We note that the global methane lifetime, even with dust storm losses, may only display a moderate decrease since we have not included sources from recycling of dissociated products back into CH₄, including but not limited to such unexplored processes as reactions between energetic (hot) hydrogen atoms and methyl radicals, heterogeneous chemistry, atmospheric dynamics, etc. Also, the volumetric regions of largest E-fields still remained undefined for Mars. Once

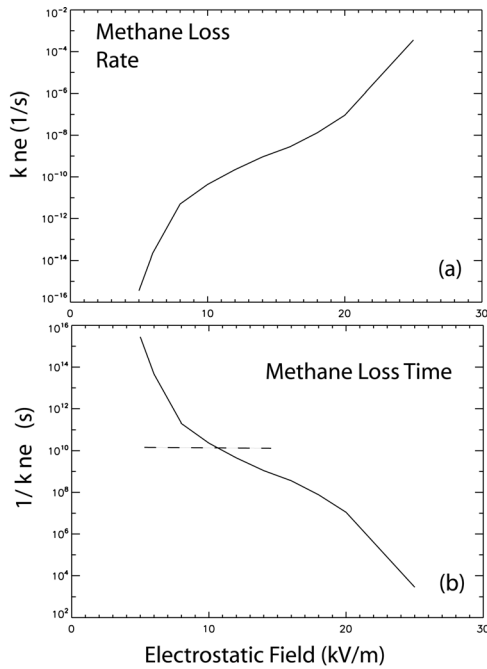


Figure 3. Methane destruction rate and destruction time as a function of storm electrostatic field. Note that the loss time drops from > 300 year ($\sim 10^{10}$ sec) to less than 1000 seconds in storms with large E-fields.

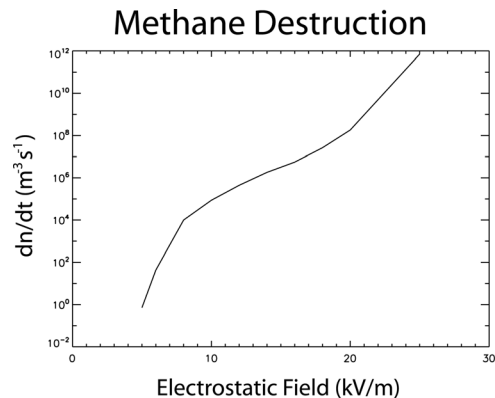


Figure 4. Methane destruction as a function of electrostatic field, assuming methane concentrations at 10 ppb.

these elements of the problem become known, a new large-scale lifetime can be derived.

[14] It has been proposed (via the Mars Scout program) to fly a high resolution atmospheric composition spectrometer from orbit specifically targeting the sources and sinks of methane. Given the results herein, such an orbiting spectrometer should see temporal and spatial variations in CH₄ in association with dust activity. At the largest time and spatial scales, we suggest that the global content of methane may have a seasonal dependence, with abundance being smaller during and immediately following the major dust storm season (just after southern summer), depending upon how fast methane recovers. On intermediate temporal/spatial scales (weeks/100s km), it is anticipated that methane concentrations will decrease in spatial regions behind dust fronts and in the near-vicinity of the dusty “cores” that form in the southern highlands in southern summer, just prior to the onset of major dust storms. Mesoscale missions that examine atmospheric composition in a region (i.e., airplane, balloon) should observe a correlation between passing dust storms and fronts, E-fields, and methane production. On the small temporal/spatial scales (10's minutes/~1km), methane concentrations are anticipated to decrease at locations of local dust devil activity. This smallest scale might not be resolvable via orbiting spectrometers. However, landed assets such as the mass spectrometer and the tunable laser spectrometer that are part of the Sample Analysis at Mars (SAM) suite on the 2009 Mars Science Laboratory (MSL) are expected to note some decrease in methane with the passing of a moderate sized dust devil (lasting a few minutes) or in conjunction with a set of dust devils like that recently observed passing in succession by MER (http://marsrovers.jpl.nasa.gov/gallery/press/spirit/20050819a/dd_enhanced_568b-B558R1.gif). Laboratory simulation studies and further modeling are required to fully characterize the effect of electric fields on the nature of methane on Mars.

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