

METHANE ADSORPTION ON MARTIAN SOIL ANALOGS: A POSSIBLE ABIOGENIC EXPLANATION FOR METHANE VARIABILITY. R. V. Gough¹, M. A. Tolbert¹, C. P. McKay² and O. B. Toon³, ¹Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309 (raina.gough@colorado.edu), ²NASA Ames Research Center, Division of Space Sciences and Astrobiology, Moffett Field, CA 94035, ³Laboratory for Atmospheric and Space Physics and Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO 80309.

Introduction: Trace amounts of methane (CH_4) have recently been discovered in the Martian atmosphere [1-3]. Additionally, several studies have also reported significant variability in the atmospheric concentration of this CH_4 [1, 4-6]. This is a surprising result as the lifetime of CH_4 on Mars with respect to the currently known loss pathways (photolysis, gas phase oxidation) is on the order of hundreds of years; therefore one would expect the CH_4 to be well mixed. It is thus possible that there are currently unknown CH_4 sources and sinks with much shorter lifetimes, perhaps even less than one year [4, 6].

One possible sink that is poorly understood is heterogeneous interaction with the dusty Martian surface. It is not known if non-negligible adsorption or reaction occurs, as these processes have been neither experimentally nor theoretically investigated. We have performed a series of laboratory experiments at the low temperature and pressure conditions found on the surface of Mars in order to understand and quantify the heterogeneous interaction between CH_4 and the Martian regolith.

Experiments performed and results: Methane uptake studies were performed on JSC-Mars-1, a terrestrial material thought to be a suitable analog for the Martian surface [7]. Experiments were performed using a high-vacuum Knudsen cell which has been previously described in the literature [8]. A typical experiment involved cooling the sample to a desired temperature, exposing the sample to gas phase CH_4 for a given period of time, and then using temperature programmed desorption with mass spectrometry (MS) detection to quantify the adsorbed CH_4 . To understand the factors which affect the adsorption process, experiments were performed as a function of temperature, CH_4 dose (pressure \times time), and sample mass.

As seen in Fig. 1, we found that the number of desorbed CH_4 molecules, N_{des} , decreased exponentially with increasing temperature for a given CH_4 dose and sample mass, an expected result for simple adsorption. The value of N_{des} was used as a measurable lower limit for the number of adsorbed molecules, a property that is not measurable with our experimental technique.

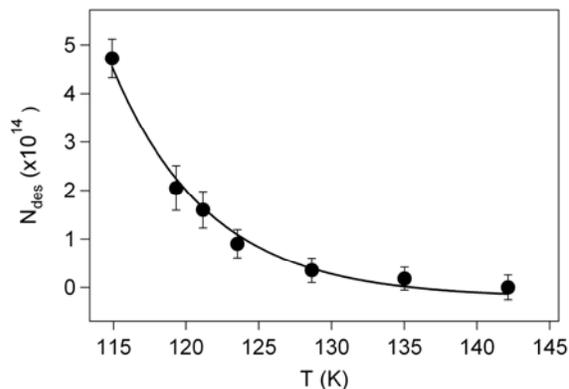


Figure 1. Amount of CH_4 desorbed as a function of sample temperature.

From N_{des} and the specific surface area (SSA) of the sample we can calculate the fractional CH_4 coverage (θ) present on the sample surface prior to desorption. Next, from the relationship between θ and dose, we can find the uptake coefficient, γ , which represents the fraction of collisions with the surface that result in net loss of CH_4 from the gas phase. As we were only able to experimentally measure γ between 115 and 135 K due to the detection limit of our instrument, an extrapolation to Martian temperatures is required. The temperature dependence of γ and the extrapolation to higher temperatures is shown in Fig. 2.

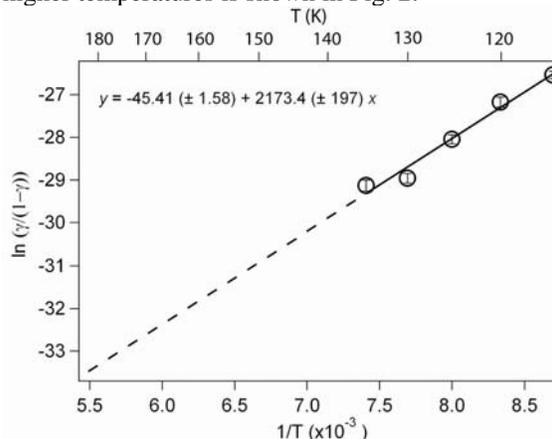


Figure 2. Exponential relationship between experimentally determined uptake coefficient and inverse temperature. The linear fit and function used to extrapolate to warmer temperatures are shown.

Martian implications: With an experimentally determined or extrapolated value of γ at a given surface temperature, the kinetics of adsorptive loss can be determined for a given system. For example, with information about the number of collisions between CH_4 and the mineral surface per unit time that occur on Mars, we can use simple collision theory to estimate a time scale over which a column of CH_4 can be removed from the gas phase (i.e.: the atmosphere). We assume that neither vertical transport through the atmosphere nor diffusion through the regolith are limiting processes, as we show both are likely to occur on faster time scales than adsorption.

Figure 3 shows the lifetime of an atmospheric CH_4 column with respect to adsorption onto mineral surfaces, τ_{ads} , as a function of surface temperature. Accessible soil depths (d_{soil}) of 1 and 10 m are shown. The upper and lower limits of each shaded depth band represent low and high values, respectively, for SSA values which could exist in the Martian regolith.

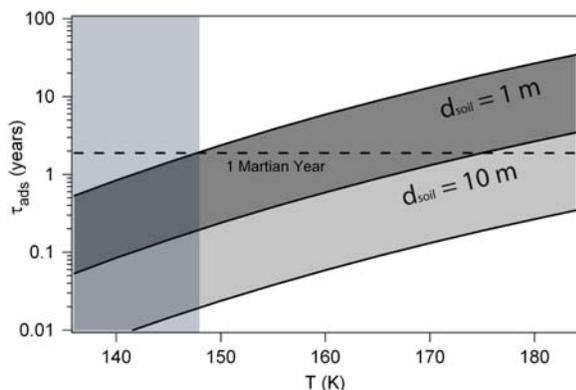


Figure 3. Lifetime of CH_4 adsorption as a function of temperature if CH_4 can diffuse to $d_{soil} = 1$ m and 10 m. The shaded area at $T < 148$ K indicates conditions below the CO_2 frost point on Mars.

It can be seen that colder surface temperatures, deeper diffusion depths, and high surface area soil would all contribute to quicker atmospheric CH_4 loss. It is important to note that under certain conditions, this CH_4 depletion would indeed occur in less than a Martian year. Both observations and theory confirm that such conditions could occur in the regolith at certain latitudes at certain times during the seasonal cycle. Although shallow ice table depths would prevent significant CH_4 loss in the coldest areas of Mars (the polar regions), the mid latitudes (± 50 - 60°) experience similarly cold temperatures (150 K) during the winter [9, 10] and have at least 1 meter of dry, ice-free soil above the ice table and available for CH_4 adsorption [10].

Few details have been reported thus far regarding the observed variability of the CH_4 in the Martian atmosphere and any dependence on time of day, season, latitude, or elevation that may exist. Mumma et al. [6] find the variability may be seasonal and “consistent with episodic release”. Mumma et al. [3] and Geminale et al. [4] both report that the CH_4 may be positively correlated with atmospheric H_2O vapor. Both observations would be expected in the case of temperature-dependant CH_4 adsorption, as CH_4 and H_2O would both adsorb to mineral surfaces when surface temperatures drop in the winter, and would then desorb as surface and subsurface temperatures rise again in the spring and summer.

It should be noted that while this proposed adsorption process could contribute to the observed CH_4 variability, it is likely to be fully reversible on an annual time scale, and is only recycling the Martian CH_4 . There is no net destruction of CH_4 , and thus no required increase in the magnitude of a potential CH_4 source to account for the observed mixing ratio.

Conclusions: We have experimentally determined values for the uptake coefficient (γ) on JSC-Mars-1 under low-temperature and low-pressure conditions, and extrapolated our results to the temperatures present in the Martian regolith. Although the values we have determined are small (e.g.: $\gamma = 4 \times 10^{-14}$ at 150 K), the available mineral surface area below an atmospheric CH_4 column is quite large. We show that the surface and sub-surface temperatures likely to exist during the Martian winter could cause significant atmospheric CH_4 to be adsorbed to soil grains in the regolith. Although biogenic production of CH_4 is still a possibility which could explain the recent observations, we suggest an abiotic process which could explain the variability of CH_4 as well.

References: [1] Formisano, V. et al. (2004) *Science*, 306(5702), 1758-1761. [2] Krasnopolsky, V. A. et al. (2004) *Icarus*, 172(2), 537-547. [3] Mumma, M. et al. (2004) *Bull. Amer. Astron.*, 36(4), 1127. [4] Geminale, A. et al. (2008) *Planet. Space Sci.*, 56(9), 1194-1203. [5] Mumma, M. et al. (2005) *Bull. Amer. Astron.*, 37(3), 669. [6] Mumma, M., et al. (2008) *Mars Atmosphere: Modeling and Observations*. [7] Singer, R. B., (1982) *JGR*, 87, 159-168. [8] Frinak, E. K., et al. (2004) *J. Phys. Chem. A*, 108(9), 1560-1566. [9] Tokano, T. (2003) *Icarus*, 164(1), 50-78. [10] Mellon, M. T., et al. (2004) *Icarus*, 169(2), 324-340.