GAS-SOLID INTERACTIONS IN THE ATMOSPHERE OF MARS AND THEIR EFFECT ON METHANE AND TRACE-GAS EVOLUTION

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Introduction: Recent observations of the evolution of trace gasses near the surface of Mars have suggested a puzzle in atmospheric chemistry. Oxygen, carbon monoxide and methane all increase and decrease over the year in a similar way (e.g. Trainer et al., 2019), which is unexpected of such different chemical species. Meanwhile, concentrations of methane in the near-surface atmosphere (Webster et al., 2015; 2021) suggest more production of the gas than can reasonably be destroyed by known mechanisms.

Several groups have posited a fast-destruction mechanism to account for this imbalance in production and destruction of methane and the strange behavior of other gasses. Tantalizingly, many of the proposed mechanisms rely on Gas-solid interactions either with airborne dust or other surface materials. For instance, Jensen et al. (2014) have proposed chemisorption of methane onto grain surfaces. Meanwhile Thøgersen et al (2019) have proposed triboelectric destruction of methane between grains and Atreya et al (2011;2006) and Delory et al (2006) propose the chemical removal of methane by surface oxidants. Furthermore, Atreya et al. (2021) and Trainer et al. (2019) both suspect a surface-atmosphere process to be responsible for the remarkable shifts seen in oxygen concentration and Korablev et al. (2021) have linked the uplift of salt-rich surface materials to the surprising atmospheric concentration of HCl observed by TGO.

Regardless of the specific mechanism, a critical step to determining the rate of change of the concentration of any gas will be the rate at which gas molecules encounter a surface where reactions can take place. This rate of interaction will change throughout the day and season, creating patterns in measured gas concentrations. Those changes, in turn, will provide evidence of gas-solid chemistry.

Grain Encounter Model: To estimate the rate of grain encounters for any putative gas molecule, a simple model is constructed.

First, all dust grains are assumed to be equidistant from one another, an assumption which is likely true on average. Based on the dust loading described by Moores et al. (2007) which found that 3 x 10^6 particles m^{-2} were required to explain typical optical depths of 0.5 and assuming constant dust/gas mixing ratio with height, we find that grains should be ~7 mm apart on average. If those grains are organized as the vertices of a cube, it becomes possible to calculate how long a gas molecule would be expected to take to diffuse from its start location to any one of the vertices.

The path of the diffusing molecule is modelled as an expanding sphere. As this sphere passes each dust particle (located at each vertex), the probability of an encounter between the gas molecule and the dust particle is calculated based upon the fraction of the surface of that sphere which is occupied by the cross-section of the dust particle. For the purposes of our model, we use the modal grain size which is close to 0.5 microns in radius (Moores et al., 2007).

Once the expanding diffusion sphere touches the most distant dust particle, the probabilities of an encounter with all dust particles are summed to give an overall likelihood of an encounter with any of the dust particles over the time required to diffuse to the final grain. As the grid is a regular one, it becomes possible to determine how long it would take to raise the probability of an encounter to 1 by continuing to expand the diffusion sphere. This is simply the time to diffuse to the most distant grain divided by the probability of an encounter along the way. It is necessary to obtain a probability of 1 because the diffusion front itself is an expression of the root mean square distribution of the molecular distances. This process is repeated at 1,000,000 different positions of gas molecules interior to the cube with dust grains as vertices. The average over the 1,000,000 gas molecules gives a good estimate of the time required for any one gas molecule to have an encounter with a dust grain.

The diffusion distance and the time required are linked through the diffusivity. If the daytime is selected for calculation, the diffusion front is defined by the eddy diffusivity, approximately 2000 m^2 s^{-1}, as described in Taylor et al. (2007). This yields a typical time between gas-dust interactions of 0.47 seconds. If nighttime is selected, we use the molecular diffusivity of 9.4 x 10^{-4} m^2 s^{-1}, consistent with numerical model results for nighttime PBL behavior. This yields a typical time between gas-dust interactions of 9.9 x 10^5 seconds or ~11 sols.

Modeling Fast Destruction Mechanisms with the Grain Encounter Model: As an example, we use the model to consider the evolution of methane by deriving an atmospheric lifetime. When these lifetimes are input to the model of Moores et al. (2019), the effect is equivalent to adding a fast destruction mechanism. Even those molecules which encounter a grain are not captured or destroyed with perfect efficiency, so different lifetimes for methane in the atmosphere and different amounts of background methane, perhaps derived from external plumes are used in model runs. In all runs, the model has been extended so that it continues past the time of the SAM ingest and completes an entire diurnal

cycle. Figure 1 shows these runs using the sol 1709 SAM-TLS ingest from Moores et al. (2019).

The upper panel of figure 1 shows two model runs with no background methane present. The black curve shows the baseline case with a methane lifetime of 329 years (e.g. Atreya et al., 2006) while the red curve shows an exceptionally fast destruction mechanism with an exponential lifetime of only 3600 seconds (1 hour). Overnight, both curves are identical as there are few gas-solid interactions and therefore, the fast destruction mechanism does not operate. As a result, the changes that occur in methane concentration are due entirely to the accumulation of methane into the near surface layer.

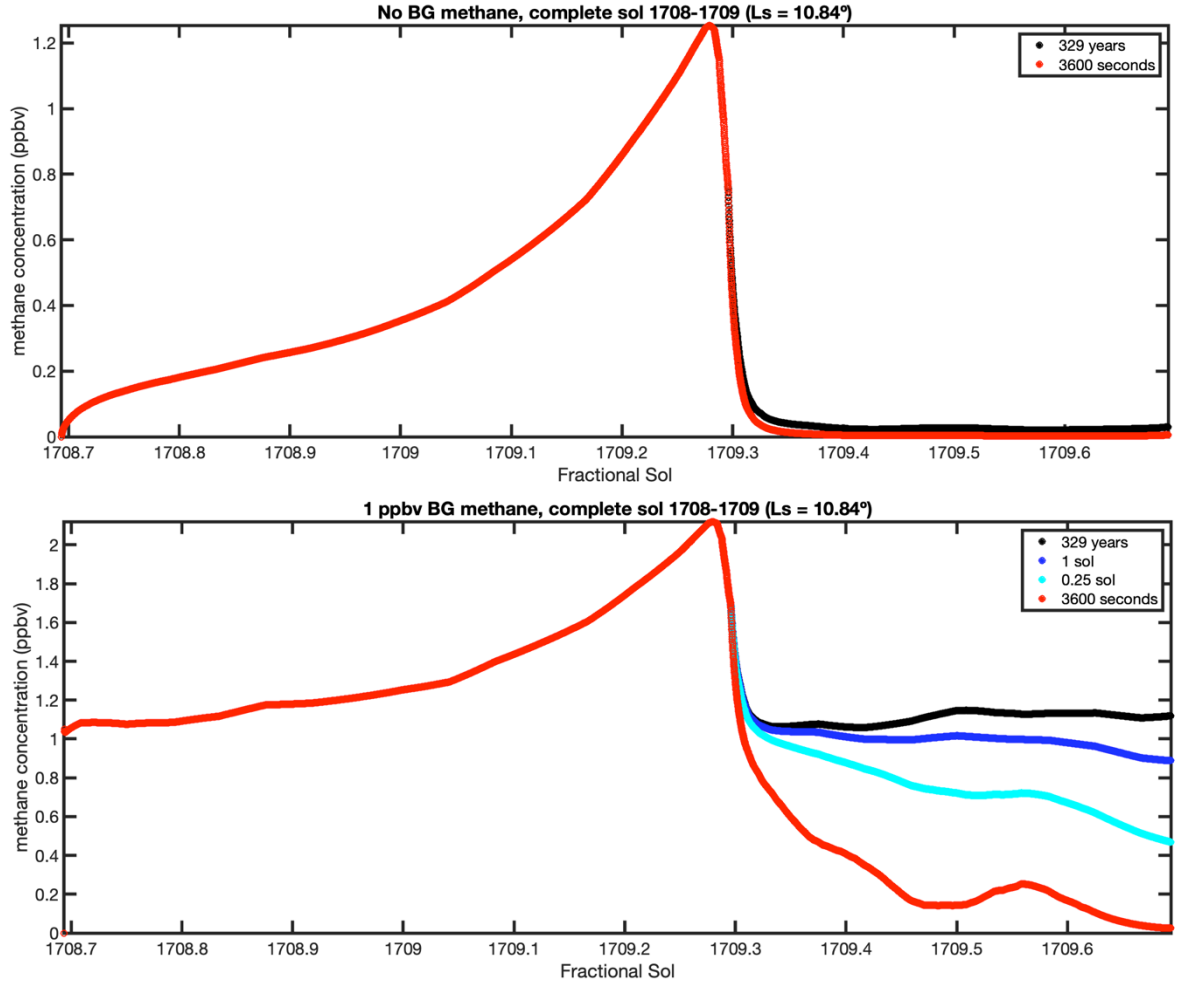

Figure 1. *Evolution of methane concentration under different background levels and fast destruction mechanisms. In the top panel, there is no background methane and even fast destruction mechanisms that operate more quickly than any proposed produce very little change in concentration. In the bottom panel, the evolution of the concentration at 1 m overnight is the result of micro-seepage, whereas the daytime evolution is due to the fast destruction mechanism.*

During the daytime, these curves are separated slightly but remain nearly indistinguishable. While the scenario (red curve) with an exceptionally fast destruction mechanism declines at dawn more quickly than does the baseline case (black curve), the separation between the two is only 0.05 ppbv (50 pptv) at most. Not only is achieving this level of sensitivity in a flight instrument incredibly difficult, but measurements would need to be acquired every few minutes to quantify the effect. Instead, the rapid decline in methane levels observed is due almost entirely to the effect of dilution with methane-free air above. As such, while micro-seepage can be quantified if background levels are low, the fast destruction mechanism is nearly impossible to measure.

This situation changes if there is a plume event nearby which raises the total amount of background methane in the atmosphere. The lower panel of Figure 1 shows this case with the baseline (black) compared to a 1-sol lifetime (blue), as suggested by Lefèvre and Forget (2009), plus a 0.25 sol lifetime (cyan) and a 3600 second lifetime (red). As with the no background methane case, all curves are the same overnight when the fast destruction mechanism does not operate, but during the day each curve exhibits different rates of change with the 3600 second case achieving zero methane by the end of the day and even a 1-sol lifetime yielding a detectable 0.2 ppbv (200 pptv) decline. Note that in this model, the evo-

lution of methane depends highly on the PBL height as a rising PBL mixes down 1 ppbv of methane into the near-surface. As such, the relative coarseness of the bottom panel as compared to the top panel is the result of the relative coarseness of the PBL model inputs from Newman et al. (2017) as compared to the 10 s timestep used in the model shown here.

As such, a surface spacecraft could measure the micro-seepage rate on any day during the night, whereas quantifying the fast destruction mechanism would require daytime measurements and would need a plume to be present to make useful observations. While such measurements of a declining plume could in principle also be made from orbit, having a surface station as well would provide a unique perspective on the rate of change and would be important to help determine not only the rate of the fast destruction mechanism but whether it primarily operates near the surface or throughout the column.

Gas-solid interactions can amplify many fast destruction mechanisms. A fast destruction mechanism would allow for more methane destruction to occur for the same measured concentration than would otherwise be possible, allowing for more areas on Mars to emit methane via micro-seepage (Moores et al., 2019) with the increase proportional to the efficacy of the destruction mechanism. Such a process must be periodically overwhelmed by larger releases which are seen at all levels of the atmosphere, but also decay away quickly, within months of their observation or faster (Mumma et al, 2009; Giuranna et al, 2019; Webster et al., 2015; 2021).

If gas-dust interactions are important to the fast destruction mechanism, the process of PBL growth and collapse described in Moores et al. (2019) and confirmed by Webster et al. (2021) would lead to an amplification. This occurs because the frequency of dust-particle interactions is directly related to the atmospheric diffusivity – the same parameter driving the bulk convection and mixing of the PBL.

As such, not only does daytime mixing dilute any methane emitted near the surface, but such mixing would also increase by orders of magnitude the reaction rate of any destruction mechanism. At night, not only would emitted methane be trapped near the surface, but any gas-solid chemistry-based fast destruction mechanism would further be halted from acting, revealing the true micro-seepage rate from the subsurface (Moores et al., 2019). If such a mechanism exists for methane, it is likely to be important for other species as well, providing a novel window into atmospheric chemistry on Mars.

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