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Key Points:
- Nighttime SAM-TLS seasonal cycle enrichment measurements and TGO sunset/sunrise measurements are not in opposition
- Microseepage fluxes must be local to Gale, range from 0.82 to 4.6 kg/sol, and are consistent with a constant source at depth
- Little of Mars experiences microseepage unless a fast destruction mechanism exists or Gale is very unusual

Supporting Information:
- Supporting Information S1

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The Methane Diurnal Variation and Microseepage Flux at Gale Crater, Mars as Constrained by the ExoMars Trace Gas Orbiter and Curiosity Observations

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Abstract The upper bound of 50 parts per trillion by volume for Mars methane above 5 km established by the ExoMars Trace Gas Orbiter, substantially lower than the 410 parts per trillion by volume average measured overnight by the Curiosity Rover, places a strong constraint on the daytime methane flux at the Gale crater. We propose that these measurements may be largely reconciled by the inhibition of mixing near the surface overnight, whereby methane emitted from the subsurface accumulates within meters of the surface before being mixed below detection limits at dawn. A model of this scenario allows the first precise calculation of microseepage fluxes at Gale to be derived, consistent with a constant 1.5×10^{-10} kg·m^{-2}·sol^{-1} (5.4×10^{-5} tonnes·km^{-2}·year^{-1}) source at depth. Under this scenario, only 2.7×10^{4} km^{2} of Mars's surface may be emitting methane, unless a fast destruction mechanism exists.

Plain Language Summary The ExoMars Trace Gas Orbiter and the Curiosity Rover have recorded different amounts of methane in the atmosphere on Mars. The Trace Gas Orbiter measured very little methane (<50 parts per trillion by volume) above 5 km in the sunlit atmosphere, while Curiosity measured substantially more (410 parts per trillion by volume) near the surface at night. In this paper we describe a framework which explains both measurements by suggesting that a small amount of methane seeps out of the ground constantly. During the day, this small amount of methane is rapidly mixed and diluted by vigorous convection, leading to low overall levels within the atmosphere. During the night, convection lessens, allowing methane to build up near the surface. At dawn, convection intensifies and the near-surface methane is mixed and diluted with much more atmosphere. Using this model and methane concentrations from both approaches, we are able—for the first time—to place a single number on the rate of seepage of methane at Gale crater which we find equivalent to 2.8 kg per Martian day. Future spacecraft measuring methane near the surface of Mars could determine how much methane seeps out of the ground in different locations, providing insight into what processes create that methane in the subsurface.

1. Introduction

One of the key questions in Martian environmental chemistry is the origin and fate of the trace gas methane. Methane is a sensitive tracer of processes in the subsurface such as water-rock reactions, decomposition of clathrates or ancient accumulated meteoritic organics, or perhaps even current or past microbial activity (Oehler & Etiope, 2017). Initially, the first near-surface measurements from the Sample Analysis at Mars Tunable Laser Spectrometer (SAM-TLS) onboard the Curiosity rover (Webster et al., 2013; Webster et al., 2015) reported less than 1.3 ppbv of methane but later reported 7- to 9-ppbv spikes in 2013. Using a spot-tracking mode from orbit, the Planetary Fourier Spectrometer onboard Mars Express (Giuranna et al., 2019) simultaneously recorded a 15-ppbv plume over and around Gale crater. As such, there is strong evidence of episodic and significant emissions of methane on Mars of perhaps as much as 19,000 tons of material at a time (Mumma et al., 2009). SAM-TLS also has observed a seasonal pattern—repeated over 3 Mars years—of methane with an average concentration of 410 parts per trillion by volume (pptv; 0.41 ppbv;

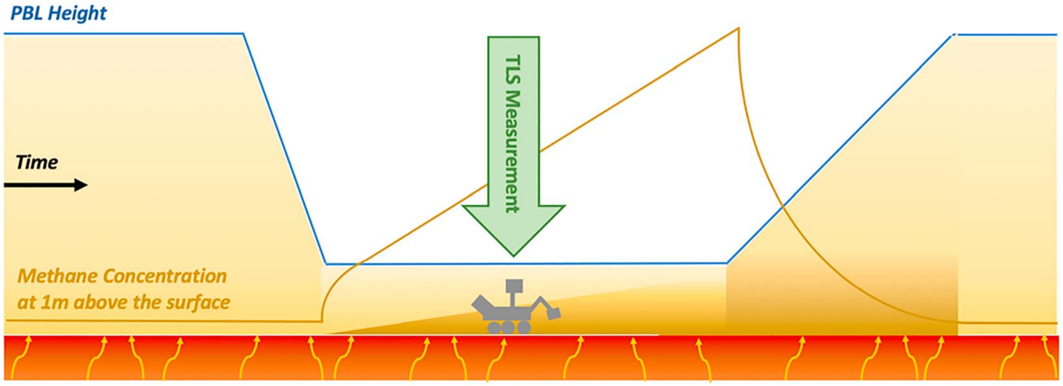

Figure 1. Schematic concept of how atmospheric concentrations of methane (shown by the Gold curve, not to scale) at 1 m should react to a constant low level of microseepage if the background concentration of methane in the atmosphere is close to zero. The PBL thickness, which corresponds to the layer of well-mixed air next to the surface, is shown by the blue curve and is not to scale with nighttime values in meters compared to kilometers during the day. Note how concentrations of methane rise overnight once atmospheric mixing can no longer distribute this material throughout the column. As indicated by the green arrow, it is at these times that the Sample Analysis at Mars-TLS enrichment runs have all been obtained. In the morning, this small amount of methane is mixed and diluted with the methane-free air above. PBL = Planetary Boundary Layer; TLS = Tunable Laser Spectrometer.

Webster et al., 2018), which has been interpreted as indicating adsorption-mediated reactions (Moores et al., 2019). This seasonal cycle implied a pattern of exchange with the surface that allowed the first limits to be placed on microseepage of methane out of the subsurface at Gale crater; specifically, an upper limit of 0.03 kg·km^{-2}·year^{-1} (Moores et al., 2019) was estimated. However, this model was ignorant of the methane content of the portion of the Martian atmosphere capable of mixing with the near-surface air (within 1 m of the surface) at Gale crater which allowed the microseepage rate to be constrained only within several orders of magnitude.

Recent results from the Trace Gas Orbiter's (TGO) Atmospheric Chemistry Suite and Nadir and Occultation for Mars Discovery instruments onboard ExoMars have now provided a robust upper limit on methane in the atmosphere above 5 km of <50 pptv (Korablev et al., 2019) with values below 12 pptv observed at clear northern latitudes down to 3 km above the surface. This upper limit, in turn, places a strong constraint on the methane content of the bulk of the Martian atmosphere through the vigorous atmospheric mixing thought to occur on Mars, based on atmospheric models (Waugh et al., 2019). Indeed, Korablev et al. (2019) correctly point out that when combining together (1) the ~1-sol daytime mixing timescale required for the air within Gale crater to mix with outside air (Moores et al., 2016; Rafkin et al., 2016) with (2) persistent values measured within Gale that average ~410 pptv and (3) the ~300-year expected photochemical lifetime of methane on Mars (Atreya et al., 2007), that the flux of methane out of Gale crater should be approximately 30 kg/sol or 6×10^{-4} tonnes·km^{-2}·year^{-1} (Korablev et al., 2019), 20 times higher than the estimate of Moores et al. (2019). Such a large emission should be visible to TGO, yet it is not observed.

However, the calculation of Korablev et al. (2019) neglects the timing of the SAM-TLS enrichment gas ingests which all begin within 2 hr of local midnight (Webster et al., 2018) due to rover energy considerations. Korablev et al. (2019) assume that the values measured by SAM-TLS are representative of the entire volume of Gale crater during the entire diurnal period in which they are acquired, as Moores et al. (2019) also assumed. Had the SAM-TLS enrichment run gas ingests taken place during the daytime when atmospheric mixing homogenizes trace-gas concentrations throughout the Planetary Boundary Layer (PBL), this would be a reasonable inference. However, at night, the PBL collapses from a few kilometers down to tens of meters (Guzewich et al., 2017), and the diffusivity of the Martian atmosphere may fall as low as the molecular limit. This effectively traps any methane emitted after sundown within, at most, a few tens of meters of the Martian surface and perhaps even less (Guzewich et al., 2017). A similar behavior is found for H_2O molecules at Gale crater, which are trapped in the lowest very stable air layers at night and then get mixed throughout the rapidly growing convective boundary layer during daytime (Savijarvi et al., 2015). As a result of this barrier to vertical mixing, methane may build up to much greater concentrations near the surface where the SAM-TLS inlet is located than it would during the daytime as shown schematically in Figure 1.

While the methane concentration in this layer may be high, the total mass of methane required to produce the SAM-TLS signal would be relatively small and once the PBL begins to build again at dawn would be mixed away, nearly to the background level observed by TGO. Indeed, because the mass of methane involved is so low, much lower than the mass of a plume, it would be invisible to nadir-pointing orbital observations (e.g., Giuranna et al., 2019).

Such a mechanism is plausible because the rate of methane emission into the atmosphere depends more on the subsurface temperature profile than the temperature right at the surface. Indeed, at adsorption enthalpies of 32–37 kJ/mol (Hu et al., 2016; Moores et al., 2019) and below (Gough et al., 2010; Meslin et al., 2011), the kinetics of methane on the surface require several sols for equilibration with the atmosphere, meaning that the cold surface does not appreciably inhibit methane release through microseepage at night. This letter will therefore use models of the diffusivity of the Martian atmosphere across diurnal cycles and season to determine what flux of methane at the surface is required to produce the observed concentration of methane at the SAM-TLS inlet at midnight on the nights when enrichment experiments were performed. We will then use the numerical code of Moores et al. (2019) to test whether or not the fluxes observed are consistent with a steady seep at depth, and if so, the strength of that seep will be calculated. These values will, in turn, be used to determine how much of the Martian surface is emitting methane through microseepage in light of the helpful constraint levied by the TGO measurement (Korablev et al., 2019).

2. Modeling Diffusivity in the Nighttime Martian Atmosphere

At most times of the day, mixing within the Martian atmosphere is driven by turbulent convection; thus, the dispersal of gasses should be modeled using eddy diffusivity, not molecular diffusion. When the PBL is fully developed, values of the eddy diffusivity may approach values of several thousands of square meters per second, (e.g., Pathak et al., 2008; Taylor et al., 2007) within the PBL (though not at the surface) which is 6 orders of magnitude greater than typical molecular diffusivities of ~10^{-3} m^2/s. However, once the surface temperature becomes colder than the air above it, as a result of nighttime radiative cooling, turbulent mixing becomes inhibited and molecular diffusivity can become competitive with or perhaps even larger than turbulence resulting from buoyancy (the Monin-Obukhov length) for dispersing and mixing materials from the surface. For methane in a carbon dioxide atmosphere, the binary mass diffusivity, D_{AB} (m^2/s^1), can be expressed, as adapted from Fuller et al. (1966)

$$D_{AB} = \frac{1.0110\times10^{-7}T^{1.75}\sqrt{\left({}^{1}/_{M_A} + {}^{1}/_{M_B}\right)}}{P\left[\left(\sum V_A\right)^{1/3} + \left(\sum V_B\right)^{1/3}\right]^2} \tag{1}$$

Here, T is the temperature of the gas mixture (K), P is the pressure (bar), M_A and M_B are the molecular masses of each gas (g/mol), and $\sum V_A$ and $\sum V_B$ are the diffusion volumes of species A and B, respectively. For CH_4 and CO_2, where the molecular masses are 16.06 and 44.04 g/mol and the diffusion volumes are 24.4 and 26.9, respectively, this expression becomes

$$\mathrm{D}_{\mathrm{CH4-CO2}} = 8.48\times10^{-10}\,\frac{T^{1.75}}{P} \tag{2}$$

At Gale crater, typical overnight temperatures of 180 K and pressures of 8 mbar as measured by the Rover Environmental Monitoring Station (Martínez et al., 2017) would yield a binary diffusivity of 9.4×10^{-4} m^2/s, which suggests that the mixed layer can be no thicker, Δz, than

$$z = \sqrt{6D_{\mathrm{CH4-CO2}}t} \tag{3}$$

or approximately 16 m if we take the timescale of diffusion, Δt, to be at most 12 hr. This value is in excellent agreement with the overnight PBL thickness of 18 m calculated from MarsWRF Grid A simulations (Newman et al., 2017).

Using the binary diffusion coefficient, it therefore becomes possible to simulate the dispersal and subsequent trapping of any methane released from the subsurface at night by considering two end-members. First, we could consider this near-surface layer to be well mixed. Because the wind speed at night can be on the order of a few meters per second (Newman et al., 2017), the thickness of the laminar sublayer (a few millimeters) is substantially smaller than the thickness of the diffusion front. This would allow the small amount of turbulence generated by nighttime winds or buoyancy to help to homogenize the very thin PBL in which this methane becomes trapped, as demonstrated by the similarity between calculations of turbulent kinetic energy through MarsWRF and molecular diffusion. As a second end-member, the near-surface air could be considered completely static and stably stratified with only molecular diffusion able to move material vertically. In this case, a gradient in the methane concentration, C_{CH4}, with height, z, will exist within the near-surface layer, following the classical solution to the diffusion of molecules away from a surface

$$C_{\mathrm{CH4}}(z) = C_{\mathrm{CH4}}(0)\mathrm{erfc}\left[^{z/z}\right] \tag{4}$$

Here erfc is the complimentary error function. The SAM-TLS inlet is located at 1 m above the surface (Mahaffy et al., 2012), and the value measured for methane concentration at this height can be used to determine the entire profile within the layer at the time of gas ingest.

Either the concentration of methane is the same throughout the mixed layer, as in the first end-member, or it follows the profile of equation (4), as in the second end-member. In both cases, it becomes possible to determine how much methane is located within the near-surface layer, and assuming that this methane has been accumulated since dynamical conditions stabilized in the evening, the flux can be directly calculated. Regardless of which end-member is selected, we must add the residual amount left over in the atmosphere from the previous day's vigorous mixing and dilution throughout the PBL and out of Gale crater as a background. As TGO's measurements suggest that this background value (Korablev et al., 2019) is negligible compared to the SAM-TLS enrichment measurements (Webster et al., 2018), it will be taken to be zero in the results presented in section 3 and discussed in section 4.

3. Results

3.1. Converting the SAM-TLS Concentrations to Methane Flux

For each of the SAM-TLS measurements, Table 1 describes each quantity important for constraining the methane flux as per section 2. First, we calculate amount of time, Δt, between the dynamical stabilization of the lower atmosphere until the middle of the SAM-TLS ingest, 1 hr after the observation begins. This stabilization time is defined as the time when the surface temperature becomes colder than the air temperature, and both are measured by Rover Environmental Monitoring Station (Martínez et al., 2017). Next, the thickness of the layer where turbulent and molecular diffusion are important is calculated using the stabilization time according to equation (3). Next the total mass of methane in the layer is calculated using both stably stratified and well-mixed models along with the flux that this mass of methane represents. Finally, for ease of description and comparison with the calculations of Korablev et al. (2019), an integrated value throughout the day that assumes equivalent microseepage production throughout Gale is also provided, though the inhibition of vertical mixing overnight would also apply to horizontal mixing. Note that this table includes two measurements acquired since Webster et al. (2018) on sol 2076 and 2446. The concentration of methane in the sol 2076 run was 0.55 ± 0.13 ppbv, and in the sol 2446 run, the concentration was 0.23 ± 0.13 ppbv. Uncertainties on these measurements are 1 SEM (Standard Error of the Mean), and individual values do not include the 8% systematic uncertainty in the enrichment factor of 25 ± 2. A separate plume of methane was also recently observed and is discussed further in section 4.2 and Figure S2 in the supporting information.

No matter which end-member model is used, the values obtained for the methane flux are substantially smaller than the value of 30 $\mathrm{kg \cdot Gale^{-1} \cdot sol^{-1}}$ suggested by Korablev et al. (2019) by at least an order of magnitude. This is not unexpected, as Korablev et al. (2019) assume that the values measured by SAM-TLS are indicative of daytime values. However, since microseepage would be expected to be active at all times of the day, any methane emitted from the subsurface in this way would be more concentrated in the near surface at night. In the daytime, when this near-surface methane is mixed with the entire PBL, the amount of mass described would produce a methane concentration of no more than a few parts per trillion by volume on any individual sol.

Table 1
Methane Flux Needed to Explain SAM-TLS Observations Using TGO-ACS/NOMAD Constraints

SAM ingest[a]	Δt[b] ($\times 10^4$ s)	Diffusive layer thickness (m)	CH_4 column mass ($\times 10^{-11}$ kg/m^2)		CH_4 flux ($\times 10^{-11}$ kg·m^{-2}·sol^{-1})		Integrated CH_4 flux (kg·Gale^{-1}·sol^{-1})[c]	
573.08	3.52	14.7	2.92[d]	5.29[e]	7.38[d]	13.3[e]	1.34[d]	2.42[e]
684.06	3.72	16.5	4.83	8.83	11.6	21.1	2.10	3.83
965.99	1.93	12.2	3.06	5.45	14.1	25.1	2.56	4.55
1,086.06	2.66	12.7	1.42	2.52	4.72	8.41	0.856	1.53
1,169.02	2.72	12.6	1.38	2.47	4.52	8.06	0.820	1.46
1,322	3.44	16.2	3.55	6.47	9.16	16.7	1.662	3.03
1,451.06	3.93	16.5	3.56	6.47	8.04	14.6	1.459	2.65
1,527.06	2.79	13.5	2.08	3.74	6.62	11.9	1.20	2.16
1,579	1.89	11.5	1.21	2.14	5.67	10.0	1.03	1.82
1,709	3.08	14.6	1.97	3.57	5.70	10.3	1.03	1.87
2,076.06	4.08	17.5	3.81	6.98	8.31	15.2	1.51	2.76
2,446.12	3.47	15.3	1.49	2.71	3.83	6.95	0.695	1.26
Average					7.47	13.5	1.35	2.45

Note. SAM-TLS = Sample Analysis at Mars Tunable Laser Spectrometer; TGO-ACS = Trace Gas Orbiter-Atmospheric Chemistry Suite; NOMAD = Nadir and Occultation for Mars Discovery.
[a] Sol, from Webster et al. (2018). Decimal portion of the sol is used so that, for instance, sol 573.08 represents local time 01:57. [b] Time between Planetary Boundary Layer collapse (dynamical stabilization of the near-surface atmosphere) and the middle of the TLS-SAM ingest, 1 hr after the start time shown in column 1. [c] Flux integrated over the entire area of Gale crater (approximately 18,600 km^2) for ease of comparison. [d] This column describes values obtained by considering the near-surface layer to be stably stratified. [e] Values obtained by considering the near-surface layer to be well mixed.

3.2. Testing Consistency With a Constant and Stable Seep at Depth

The values provided in Table 1 have validity only at the time of measurement. However, if microseepage is the cause of the observed variation in flux shown in Table 1, then the flux should vary over the day and from day to day. As such, to constrain the total amount of flux into the atmosphere above Gale crater averaged over an entire year, it is necessary to examine these results to see if they are consistent with a model of constant microseepage at depth. Moores et al. (2019) describe such a model which was modified in two ways to address the current scenario under discussion in this letter: first, the background methane concentration—which had not previously been measured—was set to zero, as suggested by Korablev et al. (2019); second, the temporal grid was adjusted to be finer overnight to allow the diffusive front in the atmosphere to be considered explicitly. The model and the modifications are explored more fully in the supporting information provided.

The Moores et al. (2019) diffusive-adsorptive microseepage model, modified in this way, provides profiles of how the methane concentration measured at 1 m should evolve up until the SAM-TLS ingest and beyond, as demonstrated for the sol 1709 measurement in Figure 2a. In this panel, the model is shown as the red line, the measurement made by SAM-TLS is shown in black, and the final point on the red line is retained as the model prediction. This exercise is repeated for each SAM-TLS methane enrichment measurement, taking into account the time of night when that measurement was acquired. The resulting model predictions and the SAM-TLS results over the entire Martian year are shown as Figure 2b. By fitting this model to the measurements of the individual observations, the average flux over the day and over the year may be calculated. The resulting value for the average flux is 1.5×10^{-10} kg·m^{-2}·sol^{-1} (5.4×10^{-5} tonnes·km^{-2}·year^{-1}). A sensitivity analysis of this result has been included as Figure S1.

The fit is of relatively good quality overall with the value of the $\chi_\nu{}^2$ statistic of 1.28 corresponding to a goodness of fit of 0.165, if the point at $L_S = 331°$ is excluded. Since the goodness of fit value is greater than 0.1, the statistics suggest that the constant seepage assumption should be accepted (Press et al., 1997). It is noteworthy that if the point at $L_S = 158°$ is excluded in addition to the clear outlier at $L_S = 332°$, the quality of the fit improves to $\chi_\nu{}^2 = 0.820$ and the goodness of fit rises to 0.547. While it is certainly possible that the $L_S = 158°$ point also represents a small or decaying plume, it is more difficult to exclude this point purely on the statistics or shape of the seasonal cycle.

A surprise in model runs with a methane-free external atmosphere was that a close examination of microseepage within the nighttime PBL requires different thermophysical properties of methane than did the

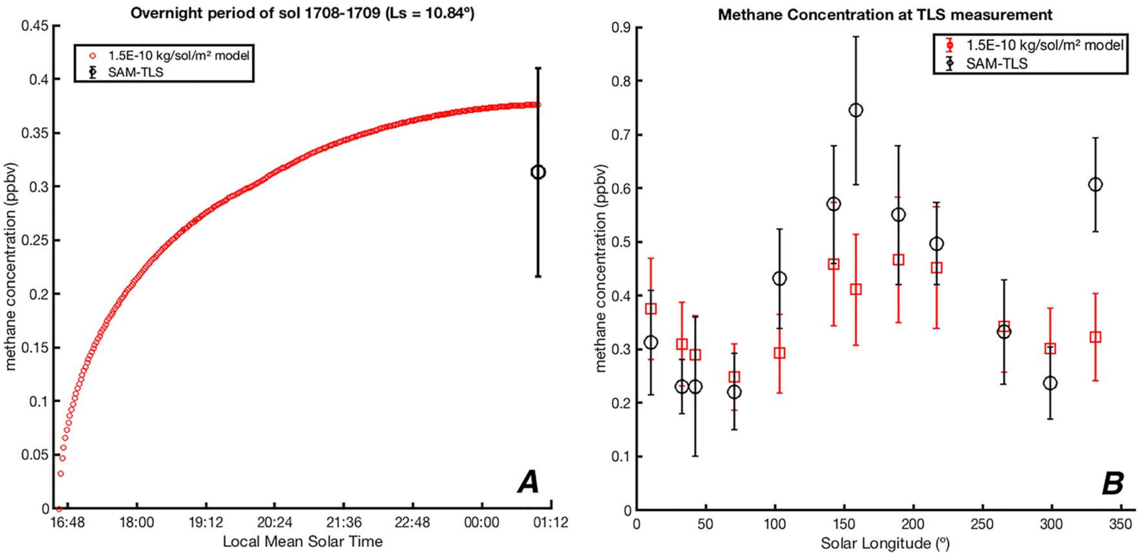

Figure 2. (a) A detailed examination of a single overnight simulation for the sol 1709 ($L_S = 10.8^\circ$) case from the time of Planetary Boundary Layer collapse up until the middle of the TLS ingest at 1:12 LMST. Note how levels of methane rise quickly near the surface once vigorous mixing ends. Error bars on the model are derived from Rover Environmental Monitoring Station data as in Moores et al. (2019). Error bars on the measurement are 1 SEM (Standard Error of the Mean), and individual values do not include the 8% systematic uncertainty in the enrichment factor of 25 ± 2. (b) A comparison between modeled values of methane concentration using a modified version of the microseepage model of Moores et al. (2019) with the enthalpy of adsorption set to 25 kJ/mol and the seepage rate set to 1.5 $\times 10^{-10}$ kg·m^{-2}·sol^{-1}. The quality of fit shown in this panel is $\chi_v{}^2 = 1.28$ when the point at $L_S = 331^\circ$ is excluded as an outlier that may represent a small plume. SAM-TLS = Sample Analysis at Mars Tunable Laser Spectrometer.

previous less constrained work of Moores et al. (2019) or the plume analysis of Hu et al. (2016). The value of 25 kJ/mol derived in the sensitivity analysis of Figure S1 is significantly closer to agreement with laboratory work, lying only 5 kJ/mol above the range described by Gough et al. (2010). Furthermore, where the previous work had supposed that the lack of a fit for three of the points at $L_S = 10.9^\circ$, 266°, and 298° was the result of changing atmospheric dynamics due to a change in the altitude of the rover and had excluded those points, it is now possible to incorporate these measurements directly into the overnight model. The lower amount of methane observed in these three cases instead results from the shorter elapsed time since PBL collapse to the SAM-TLS ingest.

4. Discussion

4.1. How Much of Mars's Surface Emits Methane?

As in previous work, the rate of seepage calculated in section 3 has significance for how much of the surface of Mars could exhibit microseepage at the rate described. If no unusual chemistry is assumed, which is to say that the lifetime of methane in the Martian atmosphere is on the order of ~300 years (Atreya et al., 2007), then it becomes possible to place a limit on how much methane can be emitted through microseepage over the entire planet while the bulk atmosphere remains below the 50 pptv upper limit set by TGO. Korablev et al. (2019) set this limit at ~4.0 kg/sol which implies that no more than 2.7×10^4 km^2 of the surface may be emitting methane. This is an exceptionally small area, approximately 143% the area of Gale crater itself.

Gale crater is an unusual geological context on Mars. It is located on a portion of the dichotomy boundary where pressure gradients could exist within the subsurface and near where extensional faults have previously been mapped (Oehler & Etiope, 2017). Furthermore, the history of Gale indicates that it once had habitable standing liquid water (Grotzinger et al., 2014), the sediments of which are now located on and below the surface of Gale crater. At the very least, such an environment could have collected organic carbon from interplanetary dust particles and protected them from their initial UV-mediated destruction (e.g., Moores et al., 2017), providing a substantial source of raw materials for methane production (Eigenbrode et al., 2018).

However, Gale crater is not unique in these properties. Indeed, no matter which attribute of Gale's geological history is assumed correlated with methane seepage, substantially more than 2.7×10^4 km^2 of Mars's surface (Oehler & Etiope, 2017) also would be included as a likely emission location. Indeed, as Etiope and Oehler (2019) have recently argued, a fast destruction or sequestration mechanism is necessary for any of these mechanisms to avoid the problem of excess methane building up in the Martian atmosphere, above the levels observed by TGO. By effectively decreasing the lifetime of methane in the Martian atmosphere, a fast destruction (e.g., Atreya et al., 2006; 2011; Delory et al., 2006) or sequestration process (e.g., Jensen et al., 2014) would allow a substantially larger area to be emitting methane than what we have calculated here.

4.2. How to Test the Diurnal Theory

The diurnal theory can be tested relatively easily by near-surface in situ measurements but would be a severe challenge for orbiting instruments which lack the sensitivity to detect such small amounts of methane in either limb or nadir sounding modes. It seems likely that microseepage should occur on Mars (Oehler and Etiope, 2018) and would contribute to the signal at Gale and that an increase in the amount of methane due to microseepage would be observed overnight in many places. The strongest signal would be observed just before sunrise. Furthermore, by capturing the entire diurnal cycle, the amount of microseepage at any location on Mars where measurements could be obtained would allow methane seepage to be quantified. Such a measurement scheme allows for global estimates of how much methane is emitted into the atmosphere of Mars and how this varies geographically, potentially illuminating the relative contributions of different processes in the subsurface.

However, the cadence of measurements would need to be frequent in order to separate the effect of different processes. At a minimum, measurements from future missions should be acquired every few degrees of L_S, with the time of day varied to build up a complete diurnal picture, as is presently done with meteorological measurements. Preferably, several measurements would be acquired each sol to completely characterize the diurnal cycle and disentangle the buildup and decaying phases of any plumes, aiding in characterizing the two major features of methane observed in the Martian near-surface atmosphere. This measurement strategy would provide enough data to clearly confirm or refute subsurface models, atmospheric transport models, and other theories about the creation, destruction, and movement of methane on Mars. Based on the measurements acquired by SAM-TLS, useful observations of methane microseepage in this way can be accomplished with measurements made at a precision of 100 pptv, achievable for many varieties of multipass, cavity ring-down, and related optical absorption cells of reasonable size.

An early attempt to test the diurnal theory onboard Curiosity was carried out on 20 June 2019. In this case, the gas ingest start was advanced to 03:53 LMST (sol 2442.16): as late in the morning as possible, given the constraints of the instrument and Curiosity mission operations. At this time, a value of ~0.5 ppbv would have been expected based on the model presented here. However, instead, the methane concentration observed was 19 ± 0.18 ppbv (see Figure S2), the largest measurement yet acquired by SAM-TLS on Mars, suggesting the presence of a plume. This result therefore argues directly for high-cadence future observations of methane to disentangle the effects of plumes and microseepage.

5. Conclusions

A diurnal microseepage process was developed that could account for the increased concentration of methane in the near-surface atmosphere observed by the Curiosity Rover overnight at Gale crater without violating the low concentration constraint set on the bulk Martian atmosphere by TGO observations. This framework allowed the flux of methane at the surface to be determined. These fluxes were seen to average 1.5×10^{-10} kg·m^{-2}·sol^{-1} (5.0×10^{-5} tonnes·km^{-2}·year^{-1}), approximately an order of magnitude lower than the flux that would be required if the methane concentration does not vary over diurnal timescales. As such, if known chemistry for methane is assumed, with an atmospheric lifetime of over 300 years, no more than 2.7×10^4 km^2 of the surface may be emitting methane.

The flux itself was seen to vary over the year from 3.83 to 11.6×10^{-11} kg·m^{-2}·sol^{-1} for a completely stably stratified model and 6.95 to 25.1×10^{-11} kg·m^{-2}·sol^{-1} for a well-mixed near-surface model. A subsurface adsorptive-diffusive model of microseepage was tested against this variation, and the best fit was obtained for a flux at depth of 1.5×10^{-10} kg·m^{-2}·sol^{-1}, close the simple average of the results at the surface. These results were consistent with a constant source at depth; however, due to a lack of measurements, it is not possible to effectively separate small plumes from the microseepage background. This ambiguity could be resolved with more frequent measurements of methane at the Martian surface from future landed vehicles.

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