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Supplementary Information for

Modeling barometric pumping of martian methane: Implications for *Perseverance* sample timing and gas loss from drilled cores

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Text S1. Core methane loss rates: considerations for timing of sample tube seal

There has been some latency between the collection of a sample by *Perseverance* and the sealing of the tube. In some cases this has been due to the original cap not creating a seal; in others it has been due to samples not fitting correctly in the tube, so some time was required to push the sample in farther. If the sample tubes are not capped relatively quickly, there is a risk of losing most or all methane contained in the pores. We attempt to quantify how quickly the tubes should be sealed to preserve the collected pore gas by performing a simple analysis below.

The governing equation is the 1-D mass diffusion equation through a porous medium:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C is concentration in units mass per unit volume, t is time, D_e is the effective diffusivity of methane through the porous medium, and x is the horizontal spatial coordinate. The effective diffusivity takes in the binary molecular diffusivity of the gas species and modifies it as a function of porosity, tortuosity, and contributions from other relevant diffusion effects such as Knudsen diffusion (Equations 4-6).

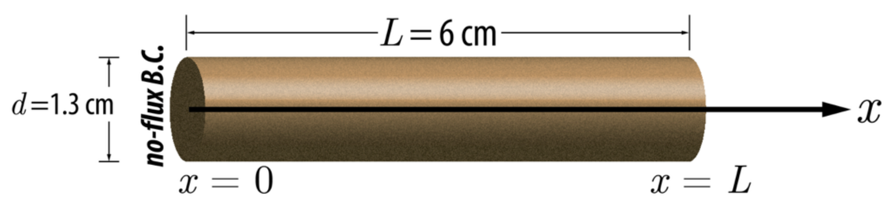

Figure S1. Schematic of the 1D diffusion problem domain. Note that the radial dimension is used only to calculate the mass loss rate based on initial pore concentration (C_0). Mass can leave the core via the boundary on $x = L$.

We assume an intact cylindrical core sample (Figure S1) with length (L) 6 cm and radius (r) 0.65 cm (Kronyak et al., 2024). We assume that the sample has been placed in the sample tube, which is closed at one end. The core has an arbitrary initial concentration C_0 of methane uniformly distributed along the length of the core: $C(x, t = 0) = C_0$. The system is assumed to be 1-D, so the tracer mass is uniformly distributed across the cross-sectional area of the core.

As a gross simplification, we assume that methane can only escape the core from one end of the core – the end corresponding to the unsealed tube opening. In actuality, methane can seep out of the radial boundary of the core as well, which would increase the rate of gas loss from the sample. However, depending on how tightly the sample tube surrounds the core, methane seeping from the radial boundary will populate the sample tube air surrounding the core with methane gas, creating locally high methane concentrations. This may slow the overall loss of methane via diffusive flux out the radial boundary and even create regions where escaped methane back-diffuses in to the core. The boundary conditions are therefore:

$$\left.\frac{dC}{dx}\right|_{x=0} = 0 \qquad (2)$$

and

$$C(L,t) = 0. \qquad (3)$$

The diffusive transport equation is solved numerically using a backward Euler finite-difference, which is implicit in time (pyDiffusionFDM; Ortiz, 2025).

Because of the unknown nature of pore sizes, geometries, and porosity, we sample a range of effective diffusivities derived from kinetic theory of gases and the free-air molecular diffusivity of methane under known Earth conditions. The free-air molecular diffusion coefficient of methane under standard conditions (D_0) is approximately 1.6×10^{-5} m^2/s. Scaling to Mars average surface conditions this becomes ~1.4×10^{-3} m^2/s. The low ambient air pressure at Mars is sufficiently low that the mean free path of gas molecules is comparable to or larger than the average pore diameter within rocks and regolith. In this Knudsen regime, collisions with pore walls dominate over molecule-molecule collisions. The Knudsen diffusivity (D_K) is given by:

$$D_K = \frac{2}{3} r_p \sqrt{\frac{8RT}{\pi M}} \qquad (4)$$

where r_p is the pore radius, R is the universal gas constant, T is temperature, and M is the molar mass of methane (0.016 kg/mol). Assuming a pore size of 1 μm and average ambient conditions on Mars, we get an approximate $D_K \approx 3.6 \times 10^{-4}$ m^2/s.

Within an individual pore, we combine the molecular diffusion and Knudsen diffusion using a simplified form of the Dusty Gas Model (DGM):

$$\frac{1}{D_p} = \frac{1}{D_0} + \frac{1}{D_K} \qquad (5)$$

where D_p is the pore diffusivity. Using the previously calculated values, we get a $D_p \approx 2.9 \times 10^{-4}$ m^2/s. Finally, we calculate the effective gas diffusion coefficient (D_e) of methane through the porous medium using Millington-Quirk model, a tortuosity-based relationship originally reported in Millington and Quirk (1961) and later modified by Jury et al (1991):

$$D_e = \frac{D_p \theta_a^{10/3}}{\phi^2} \qquad (6)$$

where ϕ is porosity, and θ_a is the volumetric air content, defined as the volume of air divided by the total volume of rock (alternatively, $\theta_a = (1 - S_w)\phi$, where S_w is the water saturation, which we assume to be zero). Calculating D_e at three porosities (ϕ: $[0.1, 0.2, 0.3]$) yields a range of effective diffusivities: $1.4 \times 10^{-5} < D_e < 5.8 \times 10^{-5}$ m^2/s. However, because we do not know the rock porosity, pore size distribution, or pore geometry at Jezero crater, we input a range of values for D_K in Equation 4 and porosities in Equation 5 to characterize the potential range of effective diffusivities that could be in collected samples. Extending this range to account for other unknowns, we examined the following range in our simulations: $4.6 \times 10^{-7} < D_e < 2.0 \times 10^{-3}$ m^2/s. These results are presented in Figure S2.

We calculate a time of sample failure (t_{fail}) to use as a metric to gauge how quickly the sample tube needs to be sealed effectively trap inside the methane from the core. We arbitrarily calculate t_{fail} as the time when 10% of the initial mass (M_0) of pore methane remains

$\left(\frac{M(t)}{M_0} = 0.1\right)$. As shown in Figure S2, t_{fail} can occur between ~2 s to 1.8 h. Earlier t_{fail} occurs for rocks with higher porosity and larger pore radii, with the converse conditions yielding later t_{fail}.

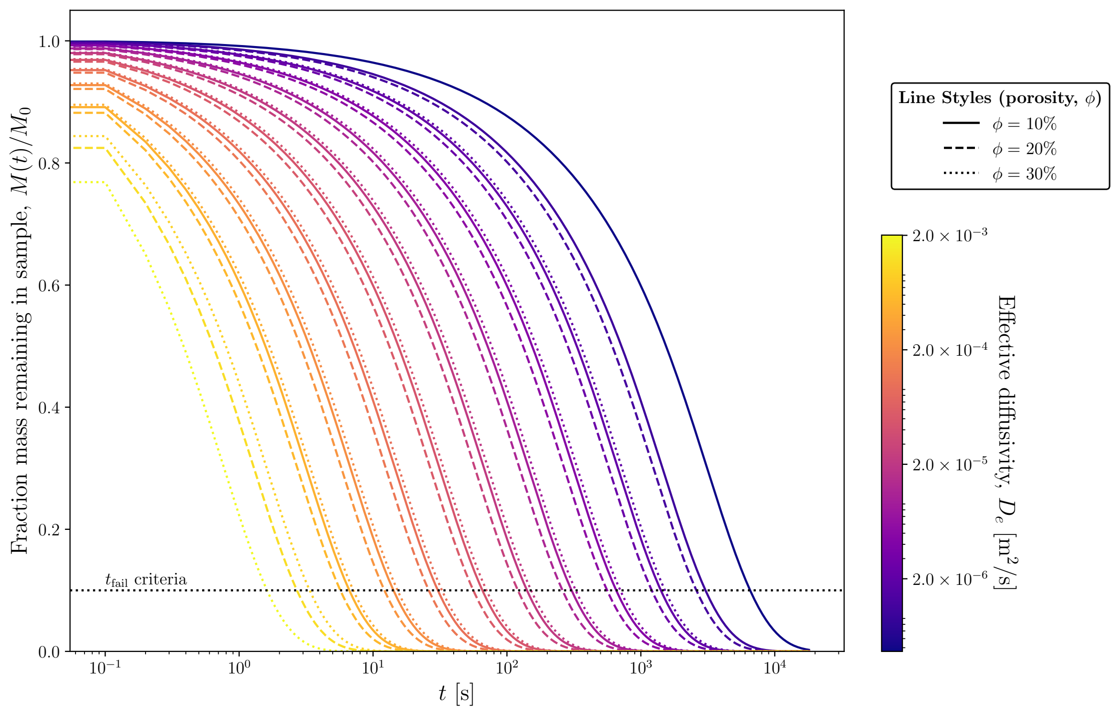

Figure S2. Modeled fraction of mass remaining in collected core samples depending on porosity and effective diffusivity. Horizontal dotted line indicates an arbitrarily chosen time of sample failure criterion (t_{fail}).

To further examine the range of t_{fail} for collected cores, we use a Monte Carlo approach to simulate diffusive loss. We draw pore radius values from a lognormal distribution with parameters consistent with terrestrial basalts (Stavropoulou et al., 2024) and porosity values from a uniform distribution. Using 20,000 realizations, we calculate t_{fail} as before from transport simulations using derived effective diffusivity D_e (Equations 4-6) based on the values of each randomly sampled pair of r_p and ϕ. Sampled and derived values are given in Figure S3a-c, and the determined range of values of t_{fail} is given in Figure S3d. Values of t_{fail} can be approximated using a lognormal distribution:

$$f(x;\mu,\sigma) = \frac{1}{x\,\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln x - \mu)^2}{2\sigma^2}\right), \quad x > 0 \qquad (7)$$

where x is the random variable (t_{fail}), μ is the mean of $\ln(x)$, and σ is the standard deviation of $\ln(x)$. The distribution of t_{fail} can be described with lognormal parameters $\mu = 265$ s and $\sigma = 375$ s. For lognormally distributed data, better descriptors of central tendency and spread are the geometric mean (approximately the median for lognormal data; $\exp(\mu)$) and $\pm 1\sigma$ interval (the ± 1 standard deviation in log space; [lower, upper] $= \exp(\mu \pm \sigma)$). We calculate a geometric mean of 144 s and a spread of 49 s to 427 s. The range of t_{fail} values is 20 s to 4.2 h.

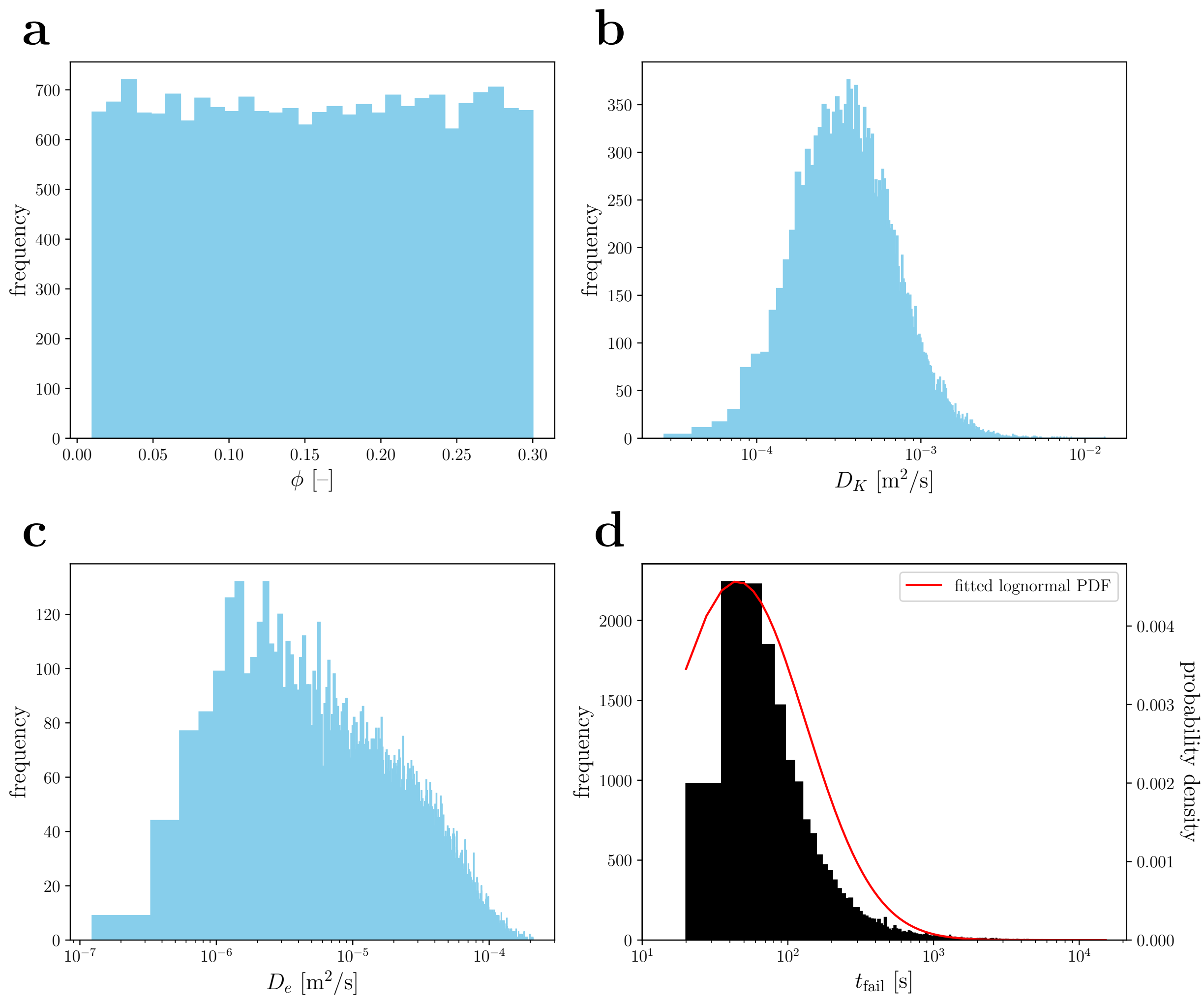

Figure S3. Composite figure of sampled and derived values from a Monte Carlo approach to quantifying methane loss: (a) porosity values drawn from a uniform distribution on [0.01, 0.30]; (b) derived Knudsen diffusivity calculated using Equation 4 based on the r_p values sampled from a lognormal distribution; (c) derived D_e values used in the methane loss simulations calculated using Equations 4-6; (d) calculated t_{fail} for collected cores based on simulations of diffusive loss using sampled ϕ and r_p values. t_{fail} can be approximated using a lognormal distribution (red line; Equation 7).

The current tube capping procedure requires human verification of sample retention by ground operators, which can take upwards of 24 hours. Because of the relatively short timeframe required to seal the sample before significant methane loss occurs for the average sample (i.e., on the order of minutes to at most a few hours), most previously collected samples likely would not have retained pore methane. A more sophisticated analysis of methane loss from collected samples could be used to determine whether the coincidence with decreasing temperatures at nightfall would increase methane adsorption to the pore walls, which could slow gas loss in the short term.

Text S2. Discussion of the possibility of instrument methane contamination

A recent study (Viscardy et al., 2025) raises doubts about the findings of methane detections suing the Tunable Laser Spectrometer (TLS) onboard NASA's *Curiosity* rover. The study analyzed TLS data to assess the reliability of past methane measurements. Their analysis showed show pressure instabilities in the instrument, hinting at potential leaks, which is significant as the the foreoptics chamber contains methane levels 3–4 orders of magnitude higher than those in the sample cell, raising the potential for contamination. Self-contamination of atmospheric samples by *Curiosity* would cast uncertainty on our subsurface-atmospheric modeling of methane at Gale crater, which was based on TLS-SAM measurements. However, addressing this potential issue is outside the scope of the present study.

However, as was noted in Swindle et al (2025), there is value in attempting to collect methane using other instruments, such as sample tubes, as this would provide a means of determining whether terrestrial contamination has occurred, once the head-space gas and sample volatiles are analyzed. They posited the value of collecting an atmospheric sample of methane, i.e., containing only gas and no rock. We add that, given the possibility that certain times of day may be more likely to yield methane in the rock pore space, consideration of the timing of samples has the potential to bolster the usefulness of rock samples as another means of testing for sample contamination.

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