

COLD-TRAPPED METHANE IN REGIONS OF PERMANENT SHADOW (PSRs). C. M. Ferrari-Wong¹, P. G. Lucey¹, and C. I. Honniball², ¹Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa (cfw@hawaii.edu), ²NASA Goddard Space Flight Laboratory.

Background: Abell et al. (1971) used mass spectroscopy, gas chromatography, and combined gas chromatography-mass spectroscopy to analyze lunar samples from the Apollo 11 and Apollo 12 missions and found that all of the samples of fines (<1 mm) contained indigenous methane. They hypothesized that reactions between solar wind hydrogen and carbon could be a major source of methane on the lunar surface.[1]

A mass peak of 16 corresponding to methane was detected in the lunar exosphere in measurements by the Apollo 17 Lunar Atmosphere Composition Experiment [2] and again in 2016 when the Lunar Atmosphere and Dust Environment Explorer (LADEE) spacecraft's neutral mass spectrometer formally identified methane in the lunar exosphere.[3] The methane was detected on the dayside, peaking at around 0700 h local time, with peak concentrations of approximately 400-450 molecules cm⁻³. No methane was detected in the exosphere over the local nighttime surface, which is consistent with methane being cold-trapped on the nighttime surface.

On the lunar night side, a cold silicate surface can trap molecules. As the sun rises, the surface warms up, releasing the trapped molecules through thermal desorption. Depending on its velocity, a released molecule may escape from the Moon or follow a ballistic trajectory; the molecule also may be lost to ionization.[4] If a ballistic molecule interacts with a warm surface, the process will repeat until the molecule is trapped by a cold surface. This random process ensures that some molecules will eventually reach the Permanently Shadowed Regions (PSRs), where they can reside for extended periods of time due to the low surface temperatures.

The Diviner Lunar Radiometer made direct temperature measurements of the south pole's PSRs, showing a range of temperatures from around 120K to less than 40K.[5] Due to these low temperatures, methane molecules can adsorb onto the surfaces of grains in the PSRs and remain there indefinitely. Because the supply of methane is continuous, it may build up on the surface until it reaches saturation at a monolayer. Some of this methane may be sequestered through regolith overturn, which also exposes unsaturated soil to the incoming methane leading to a possibly thick deposit of methane-enriched regolith.

Abundance Estimation: To estimate the amount of CH₄ that can saturate the PSRs, we find the amount of CH₄ the surface of an average lunar grain can contain. To calculate the mass per unit area of a monolayer of methane (M_{mono}), we use the following:

$$M_{mono} = \frac{M_{CH_4}}{A_{mono}} = \frac{M_{CH_4}}{d_{CH_4}^2 * N_0}$$

Molar mass of methane (M_{CH_4})	16.04 g/mol
Diameter of a methane molecule (d_{CH_4})	~3.5 Å
Avogadro's Number (N_0)	6.022*10 ²³

$$M_{mono} = 2.17 \times 10^{-4} \text{ g/m}^2/\text{mol}$$

Multiplying this number by the average surface area of lunar soils at **0.5 m²/g** [6,7], we find that the lunar surface can hold **~110 ppm CH₄** at 100% monolayer in the PSRs.

Using the same calculation above, we estimate the amount of hydrogen due to methane molecules at 100% monolayer in the PSRs to be **~27 ppm**. In a recent paper by Lawrence et al 2022 [8], Lunar prospector hydrogen abundances can range up to a maximum of 117 ppm. Methane could account for approximately 20% of that signal.

At very cold temperatures, could methane condensation be a factor in the PSRs? Conducting a similar calculation to Zhang and Paige (2009) [9,10] and using the constants provided in Brown and Ziegler (1980) [11], methane's sublimation rate is ~2m/Gyr at 25K. Thus as expected, methane condensation is not a factor anywhere in the PSRs.

Spectroscopic Detection of Methane: Two upcoming missions will search for methane in the PSRs: Lunar Trailblazer [12] and VIPER. Lunar Trailblazer carries an IR spectrometer that could detect a 3.4-micron methane band in the permanent shadow if it is present.

On the VIPER mission, co-author Honniball proposed using VIPER's tungsten illumination lamp to deliberately heat the lunar surface while monitoring the release of volatiles. The VIPER NIRVSS instrument will monitor spectral changes, and the MSolo mass spectrometer will detect methane evolved from the warming surface. Before heating, NIRVSS and MSolo will observe the surface and continue measurements

throughout the heating experiment. NIRVSS will measure changes in the methane band at 3.4 microns as the surface heats.

In Figure 1, we have modeled spectra of methane with increasing abundance. Methane has a band at 3.4, so we should see a methane band of ~1% strength.

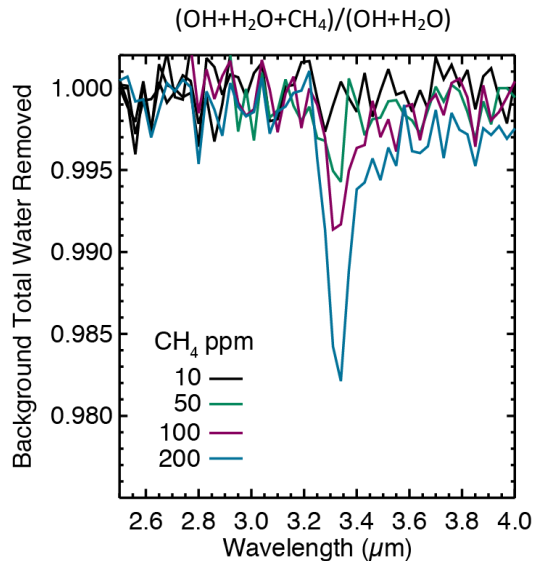


Figure 1 Model spectra of methane adsorbed onto a hydroxyl-bearing substrate with increasing abundance. The noise is modeled VIPER NIRVSS noise.

Experimental Work: There are currently no laboratory IR measurements of the spectrum of adsorbed methane. To address this issue, we are designing and building an environment chamber that allows us to measure the reflectance of a cooled particular surface and direct methane gas onto the sample (Figure 2). We repurposed a small infrared detector liquid nitrogen Dewar for this purpose and equipped the chamber with a pair of windows for IR illumination and measurement at a phase angle of 90 degrees. A copper cold finger supports a small sample cup for cooling to LN₂ temperatures. Particulate samples are highly insulating, so the optical surface tends to reach radiative equilibrium with the warm chamber walls.[6] To reduce this effect, we placed the sample in a small internal chamber with calcium fluoride windows that admit IR illumination and allow us to view the sample but block most thermal radiance since they do not transmit past 7 microns. There will be a small amount of heating from the surroundings and the illuminator, which we will measure using particulate olivine as a thermometer.

Once the Dewar cover is removed and the sample is placed on the cold finger in its radiative control chamber, we evacuate the Dewar and fill it with liquid nitrogen to allow it to equilibrate. Once the system is in



Figure 2 Methane adsorption chamber. Windows are 1.5 inches in diameter for scale.

thermal equilibrium, we introduce small titers of methane gas into the chamber through a small pipe directed at the sample surface. We collect data with the vacuum pump engaged in removing any methane gas that is not cold-trapped. For completeness, we will measure samples of varying albedos and lunar simulants, mostly anorthosite but others with lower albedos. We will present our preliminary findings at this year's conference.

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