

## Non-Detection of Methane in the Mars Atmosphere by the Curiosity Rover

C. R. Webster, P. R. Mahaffy, S. K. Atreya, G. J. Flesch and K. A. Farley

By analogy with Earth, methane in the atmosphere of Mars is a potential signature of ongoing or past biological activity on the planet<sup>1</sup>. During the last decade, Earth-based telescopic<sup>2,3</sup> and Mars orbit remote sensing instruments<sup>4,5</sup> have reported significant abundances of methane in the Martian atmosphere ranging from several to tens of parts-per-billion by volume (ppbv). Observations from Earth showed “plumes” of methane<sup>3</sup> with variations on timescales much faster than expected and inconsistent with localized patches seen from orbit, prompting speculation of sources from sub-surface methanogen bacteria, geological water-rock reactions or infall from comets, micro-meteorites or interplanetary dust<sup>1</sup>. From measurements on NASA’s Curiosity Rover that landed near Gale Crater on 5<sup>th</sup> August 2012, we here report no definitive detection of methane in the near-surface Martian atmosphere. Our *in situ* measurements were made using the Tunable Laser Spectrometer (TLS) in the Sample Analysis at Mars (SAM) instrument suite<sup>6</sup> that made three separate searches on Martian sols 79, 81 and 106 after landing. The measured mean value of  $0.39 \pm 1.4$  ppbv corresponds to an upper limit for methane abundance of 2.7 ppbv at the 95% confidence level. This result is in disagreement with both the remote sensing spacecraft observations taken at lower sensitivity and the telescopic observations that relied on subtraction of a very large contribution from terrestrial methane in the intervening observation path. Since the expected lifetime of methane in the Martian atmosphere is hundreds of years<sup>2,13</sup>, our results question earlier observations and set a low upper limit on the present day abundance, reducing the probability of significant current methanogenic microbial activity on Mars.

The first reports of the detection of methane (CH<sub>4</sub>) on Mars were published in 2004. They were based on ground-based Fourier Transform Spectrometer (FTS) observations by Krasnopolsky et al.<sup>2</sup> from the Canada-France-Hawaii Telescope (CFHT) and the Planetary Fourier Spectrometer (PFS) observations of Formisano et al.<sup>4</sup> from Mars Express (MEX) spacecraft in orbit around Mars since 2003. The FTS-CFHT observations searched for methane in the P-branch of the 3.3  $\mu\text{m}$  band of CH<sub>4</sub> at a resolution of  $\sim 0.03 \text{ cm}^{-1}$ , and found a global average value of  $10 \pm 3$  ppbv. The PFS/MEX observations covered the central Q-branch of the same band at  $3018 \text{ cm}^{-1}$  at a resolution of  $\sim 2 \text{ cm}^{-1}$ , and found a global average abundance of  $10 \pm 5$  ppbv. The PFS data also indicated discrete localized sources. The global average value was subsequently updated<sup>5</sup> to  $15 \pm 5$  ppbv following analysis of a much larger data set of more than 500,000 spectra from 2003-2010. These authors<sup>5</sup> also reported a summer time maximum of 70 ppbv in the north polar region and seasonal variations with values dropping below the PFS detection limit of 5 ppbv in winter. A global methane value of 10 ppbv was also reported<sup>7</sup> from averaging of thousands of spectra collected by the Thermal Emission Spectrometer (TES) of Mars Global Surveyor (MGS), covering the 7.7  $\mu\text{m}$  band of CH<sub>4</sub> at  $1306 \text{ cm}^{-1}$  at a resolution of  $\sim 8 \text{ cm}^{-1}$ . Mumma et al.<sup>3</sup> searched for the R0 and R1 spectral lines of CH<sub>4</sub> in its 3.3  $\mu\text{m}$  CH<sub>4</sub> band using the Cryogenic Echelle Spectrograph on the Infrared Telescope Facility (IRTF) and Near Infrared Spectrometer on Keck-2 telescope, all with a resolution of  $\sim 0.07 \text{ cm}^{-1}$ . They reported that methane is released in plumes from discrete sources in Valles Marineris, Nili Fossae and Syrtis Major, with the largest plume containing 19,000 tons of CH<sub>4</sub> in March 2003, but in January 2006 the global abundance represented about half the amount released in 2003 implying rapid destruction of methane<sup>3</sup>. Mumma et al. also reported seasonal changes with a summer time

maximum of ~45 ppbv near the equator, contrary to the polar maximum of MEX-PFS, and decreasing below 3 ppbv in spring. From an analysis of additional data, Villanueva et al.<sup>8</sup> find no detectable methane since 2006, with global upper limit of 7 ppbv, consistent with the December 2009 data of Krasnopolsky<sup>9</sup> who found an upper limit of 8 ppbv. However, from independent IRTF-CSHELL observations, Krasnopolsky also reported a detection of 10 ppbv methane in 2006 at  $L_s = 10^\circ$  from  $45^\circ\text{S}$  to  $7^\circ\text{N}$  and  $63$  to  $93^\circ\text{W}$ .

Taken at face value, the above ground-based (CFHT, IRTF, Keck-2) and orbital (MEX, MGS) observations suggest a global methane mixing ratio of approximately 10 ppbv, ranging up to 70 ppbv, discrete sources, seasonal changes, and a very short lifetime for  $\text{CH}_4$  in the atmosphere. Although no direct observations exist specifically for Curiosity's Gale Crater landing site ( $4.5^\circ\text{S}$ ,  $137^\circ\text{E}$ ), published maps of methane distribution covering broad areas that encompass Gale crater or interpolation of maps suggest between 5-20 ppbv of  $\text{CH}_4$  above Gale Crater corresponding to the time of our measurements in the southern spring. Caution should be exercised in interpreting earlier data, however. The MEX and MGS data suffer from very poor spectral resolution, unidentified spectral features of similar or higher strength, and averaging over very wide areas which cast doubt on the validity of seasonal and spatial variations. Although the ground-based observations by Mumma et al.<sup>3</sup> are done at relatively high spectral resolution, two-way optical transmission through the earth's atmosphere that is rich in methane - a million times more than any methane on Mars, and averaging over large areas also raise questions<sup>10,11</sup> about the fine details of absolute methane abundance and the reported seasonal and spatial changes. Nevertheless, prior to our measurements reported here, these<sup>3</sup> ground-based telescopic data were the best-available in support of possible presence of methane on Mars.

The Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM)<sup>6,12</sup> instrument suite on Curiosity rover has spectral resolution ( $0.0002\text{ cm}^{-1}$ ) far superior to the ground-based telescopic and orbiting spectrometers. TLS is a two-channel tunable laser spectrometer that uses direct and second harmonic detection of IR laser light absorbed by gas in a sample cell. One laser source is a near-IR tunable diode laser at  $2.78\text{ }\mu\text{m}$  that can scan two spectral regions containing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  isotopic lines (reported elsewhere); the second laser source is an interband cascade (IC) laser at  $3.27\text{ }\mu\text{m}$  used for methane detection alone, scanning across the triplet of rotational lines that make up R(3) (see Fig. 1 and Table S1). The IC laser beam makes 81 passes of a 20-cm long Herriott cell fitted with high-vacuum microvalves that allow evacuation with a turbomolecular pump for "empty cell" scans, or filled to Mars ambient pressure ( $\sim 7\text{ mbar}$ ) for "full cell" runs. During data collection, the Herriott cell and other optics are kept at  $47\pm 3\text{ }^\circ\text{C}$  using a ramped heater that thermally stabilizes the cell and also spoils any interference fringes during the 2-minute sample period. The laser scans every second through the methane spectral region (Fig. 1) and each spectrum is co-added on board to downlink sequential 2-minute averaged spectra during a given run of  $\sim 1$ -2 hours in duration. Typically, we record and download twenty-six 2-minute "empty cell" spectra followed by twenty-six 2-minute "full cell" spectra, then finally five additional 2-minute empty cell spectra (see Fig. S1). Our measurement is a difference method described in the Fig.1 caption and supplementary material. This experiment has been repeated on three separate Martian sols (days) to date (Martian sols 79, 81, & 106 after landing in August 2012). The inlet to the SAM-TLS instrument is a 3/16" internal diameter stainless steel tube heated to  $50^\circ\text{C}$  containing a dust filter of sintered Inconel 0.5 micron particles that is located on the rover side  $\sim 1\text{ m}$  above the Martian surface. For sampling on sols 79, 81 and 106, the inlet was pointing either into or out of the nominal wind direction.

To date we have no definitive detection of methane. Individually, each of our 3 data sets produces a mean methane value of  $\leq 1.3$  ppbv; the complete data set produces a measured value of  $0.39 \pm 1.4$  ppbv (1 std error). At the 95% confidence level this provides an upper limit on mars atmospheric methane of 2.7 ppbv.

The very short methane lifetime of 0.4-4 years derived by Mumma et al.<sup>3</sup> from their 2003-06 observations, compared to the photochemical lifetime of several hundred years<sup>2,13</sup> requires powerful destruction mechanisms. Although electrochemical models have been proposed for removal of methane by oxidants, such as hydrogen peroxide and perchlorates or by superoxides derived from their mineral reactions<sup>1,14,15</sup> and directly by electric fields generated in dust devils<sup>16</sup>, their efficacy at Mars remains to be tested. Moreover, it is not clear whether any of these processes can reduce the lifetime of methane by a factor of 100 or more. In the absence of rapid destruction, global methane resulting from the methane plumes of 2003 reported by Mumma et al.<sup>3</sup> should remain relatively unchanged, i.e. tens of ppbv today, considering also that the time for methane to spread uniformly over Mars is only a few months<sup>17</sup>. However, the TLS measurements show no evidence of such large methane abundance above Gale Crater or even the 7-8 ppbv global upper limits of the 2006-2009 ground-based observations<sup>8,9</sup>. However, the 2.7 ppbv upper limit set by the TLS could still be consistent with a very small amount of methane on Mars, whose origin would be unknown at present.

Three possible origins of methane on Mars have been proposed previously: geologic, biotic, and exogenous<sup>2,4,17</sup> as illustrated in Fig. 2. The geologic origin of methane is commonly seen in hydrothermal vents in terrestrial oceans including high-temperature black smokers and also at vents with relatively mild temperatures. Methane is produced by the process of serpentinization which is actually a two-step process where hydration of Fe, Mg, or Cr-rich silicate minerals such as olivine or pyroxene first liberate hydrogen. The hydrogen in turn combines with carbon or carbon-bearing molecules in metal-catalyzed Fischer-Tropsch reactions to produce methane<sup>17</sup>. All necessary minerals and volatiles for low-temperature serpentinization are present on Mars, and liquid water and warmer conditions once existed in the past and could still exist in the subsurface. Methane so produced could be stored for later release to the atmosphere<sup>18</sup>. Biology – past or present – is responsible for 90-95% of all methane on Earth. Mars too is likely to have met key requirements for microbial life<sup>1</sup> – energy (sunlight and chemical), nutrients (CO, CO<sub>2</sub>, H<sub>2</sub>), and medium (liquid water) to facilitate biochemical reactions and transport of nutrients. However, presence of methane alone does not signify presence of life. Finally, methane could also result from exogenous sources<sup>4,17</sup>. Laboratory simulations show that up to a few ppbv may be produced by UV degradation of carbonaceous meteorites<sup>19</sup> or interplanetary dust particles<sup>20</sup>, depending on the efficiency of the process and oxidation of exogenous organic material by surface oxidants. The upper limit of methane determined by the TLS is so low that if any methane is present on Mars, it could have originated from any one of the above three sources or a combination thereof. Future plans for Curiosity include a methane enrichment experiment that will increase sensitivity by at least an order of magnitude and facilitate investigation of diurnal and seasonal changes in methane should it be detected.

1. Atreya, S. K. et al. Methane on Mars: Current observations, interpretation, and future plans. *Planet. Space Sci.* **59**, 133-136 (2011).
2. Krasnopolsky, V. A., Maillard, J. P. & Owen, T. C. Detection of methane in the martian atmosphere: evidence for life? *Icarus* **172**, 537-547 (2004).
3. Mumma, M. J. et al. Strong release of methane on Mars in northern summer 2003. *Science* **323**, 1041-1045 (2009).

4. Formisano, V., Atreya, S. K., Encrenaz, T., Ignatiev, N. & Giuranna, M. Detection of methane in the atmosphere of Mars. *Science* **306**, 1758-1761 (2004).
5. Geminale, A., Formisano, V., & Sindoni, G. Mapping methane in Martian atmosphere with PFS-MEX data. *Planet. Space Sci.* **59**, 137-148 (2011).
6. Mahaffy, P. R. et al. The Sample Analysis at Mars Investigation and instrument Suite. *Space Sci. Rev.* **170**, doi:10.1007/s11214-012-9879-z (2012).
7. Fonti, S. & Marzo, G. A. Mapping the methane on Mars, *Astron. Astrophys.* **512**, A51, doi:10.1051/0004-6361/200913178 (2010).
8. Villanueva, G. L. et al. A sensitive search for Organics (CH<sub>4</sub>, CH<sub>3</sub>OH, H<sub>2</sub>CO, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>), hydroperoxyl (HO<sub>2</sub>), nitrogen Compounds (N<sub>2</sub>O, NH<sub>3</sub>, HCN) and chlorine species (HCl, CH<sub>3</sub>Cl) on Mars using ground-based high-resolution infrared spectroscopy. *Icarus*, **223**, 11-27 (2013).
9. Krasnopolsky, V. A., Search for methane and upper limits to ethane and SO<sub>2</sub> on Mars *Icarus* **217**, 144-152 (2012).
10. Lefevre, F. & Forget, F. Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics. *Nature* **460**, doi:10.1038/nature08228 (2009).
11. Zahnle, K. J., Freedman, R. S. & Catling, D. C. Is there methane on Mars? *Icarus* **212**, 493-503 (2011).
12. Webster, C. R. & Mahaffy, P. R. Determining the local abundance of Martian methane and its' <sup>13</sup>C/<sup>12</sup>C and D/H isotopic ratios for comparison with related gas and soil analysis on the 2011 Mars Science Laboratory (MSL) mission. *Planet. Space Sci.* **59**, 271-283 (2011).
13. Wong, A. S., Atreya, S. K. & Encrenaz, T. Chemical markers of possible hot spots on Mars. *J. Geophys. Res.* **108**, doi:10.1029/2002JE002003 (2003).
14. Atreya, S. K. et al. Oxidant Enhancement in Martian Dust Devils and Storms: Implications for Life, and Habitability. *Astrobiology* **6**, 439-450 (2006).
15. Delory, G. T. et al. Oxidant Enhancement in Martian Dust Devils and Storms: Storm Electric Fields and Electron Dissociative Attachment. *Astrobiology* **6**, 451-462 (2006).
16. Farrell, W. M., Delory, G. T., Atreya, S. K. Martian Dust Storms as a Possible Sink of Atmospheric Methane. *J. Geophys. Res.* **33**, doi:10.1029/2006GL027210 (2006).
17. Atreya, S. K., Mahaffy, P. R. & Wong, A. S. Methane and related trace species on Mars: Origin, loss, implications for life, and habitability. *Planet. Space Sci.* **55**, 358-369 (2007).
18. Chassefire, E. Metastable methane clathrate particles as a source of methane to the martian atmosphere. *Icarus* **204**, 137-144 (2009).
19. Keppler, F. Ultraviolet-radiation-induced methane emissions from meteorites and the Martian atmosphere. *Nature* **483**, 93-96, doi:10.1038/nature11203 (2012)
20. Schuerger, A. C., Moores, J. E., Clausen, C. A., Barlow, N. G. & Britt, D. T. Methane from UV-irradiated carbonaceous chondrites under simulated Martian conditions, *J. Geophys. Res.* **117**, doi:10.1029/2011JE004023 (2012).

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**Author information:**

Correspondence and requests for materials should be addressed to C.R. Webster, [Chris.R.Webster@jpl.nasa.gov](mailto:Chris.R.Webster@jpl.nasa.gov)

**Affiliations:**

**Jet Propulsion Laboratory, California Institute of Technology, Pasadena CA 91109:**

Christopher R. Webster, Gregory J. Flesch

**NASA Goddard Space Flight Center (GSFC), Greenbelt, MA 20771:** Paul R. Mahaffy

**University of Michigan, Ann Arbor, MI 48109:** Sushil K. Atreya

**California Institute of Technology, Pasadena CA 91125:** Kenneth A. Farley

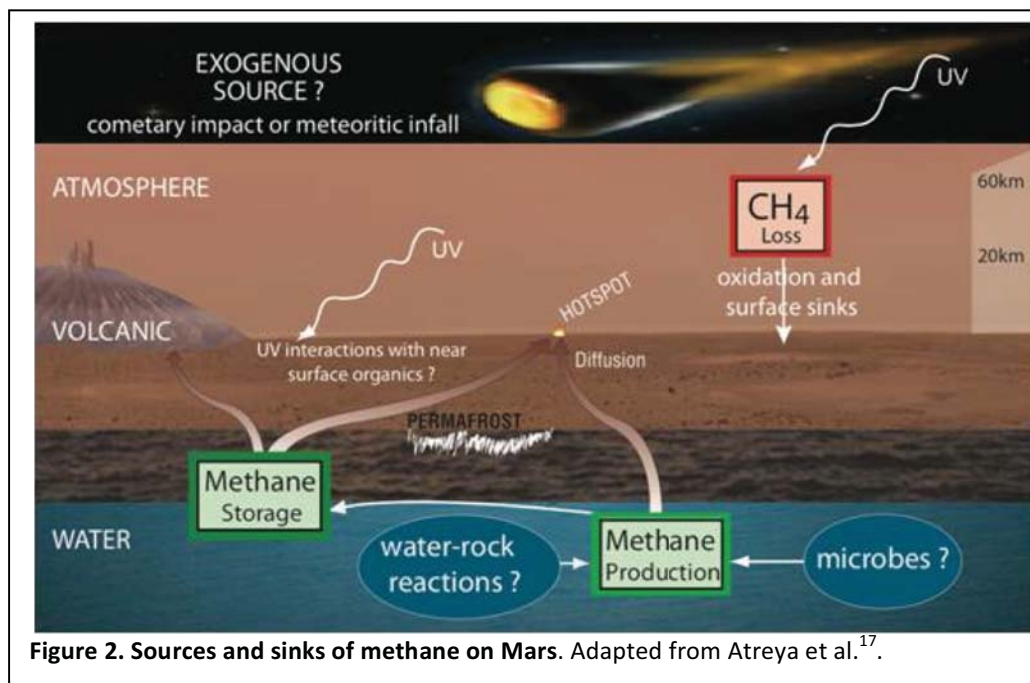
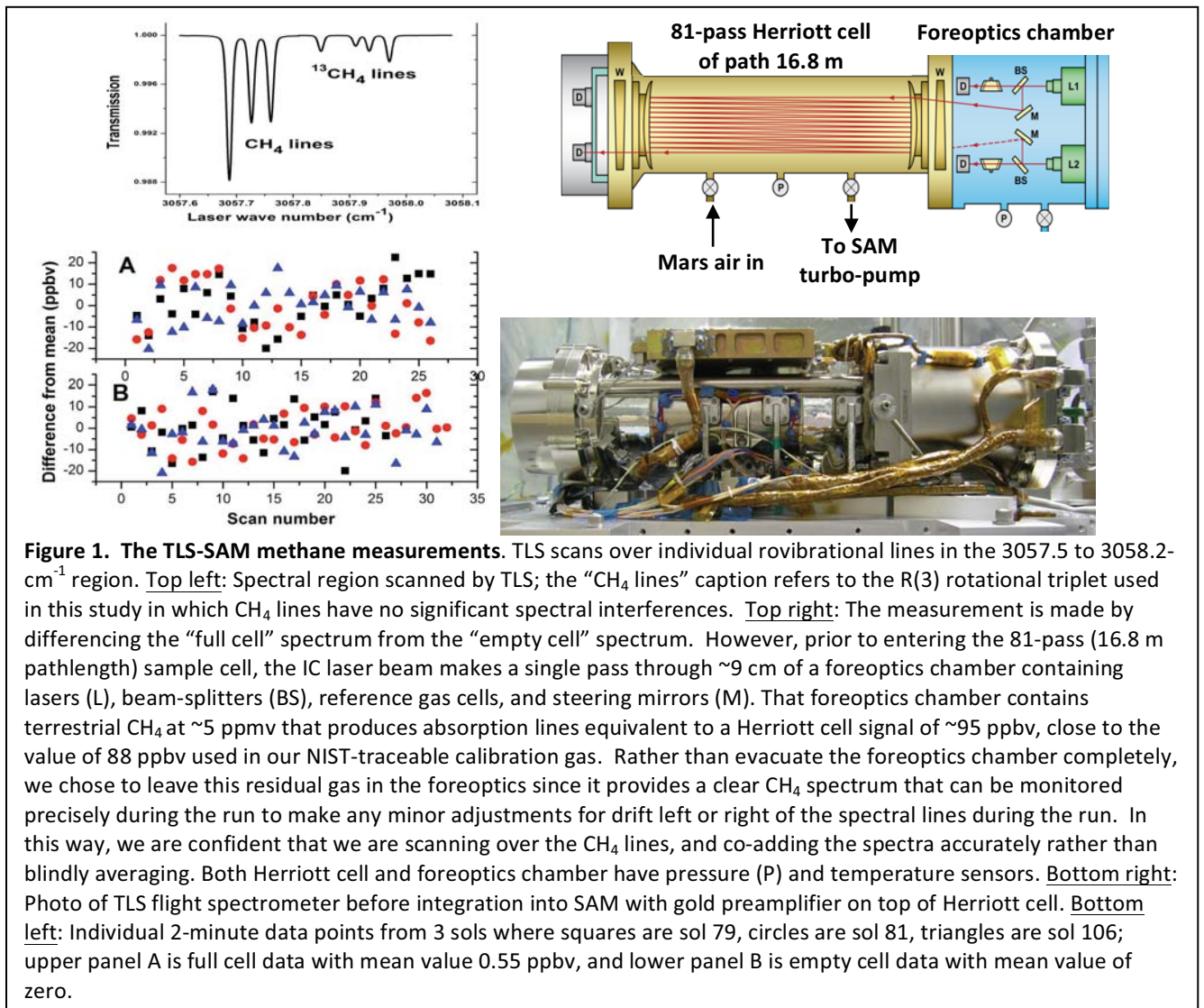
**Contributions:**

CRW and PRM led the development and build of the TLS instrument with responsibility for performance and calibration. GJF wrote the flight instrument and data analysis software, and with CRW analyzed the spectra to produce methane abundances. KAF conducted the statistical analysis of the retrieved methane abundances. SKA developed measurement strategies, provided comparison of results by interpolation of other available data sets, and worked with CRW and PRF on the interpretation of results.

Figures 1 and 2 appear on the next page.

Supplemental information:

Text plus Tables S1 and S2, and Figures S1 and S2.



## **SUPPLEMENTAL INFORMATION:**

### **Non-Detection of Methane in the Mars Atmosphere by the Curiosity Rover**

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#### **Methane spectroscopy and laser parameters:**

The TLS interband cascade (IC) laser scans through a triplet of lines associated with R(3) in the  $\nu_3$  band identified in Table S1 by both the HITRAN data base<sup>a</sup> and laboratory measurements.

Spectral line center (cm <sup>-1</sup> )	Line-strength (cm <sup>-1</sup> / (molecule·cm <sup>-2</sup> ) at 296 K)	Ground-state energy (cm <sup>-1</sup> )	Assignment
3057.687285	2.085E-19	62.8781	R(3)
3057.726529	1.245E-19	62.8768	R(3)
3057.760524	1.245E-19	62.8757	R(3)

The IC laser operated near 245 K stabilized by a two-stage TEC cooler producing single-mode (>99%) continuous-wave output power with a linewidth retrieved from low-pressure (Doppler limited) spectra of ~10 MHz. This light was collimated using an efficient triple-lens collimator to produce ~1 mW laser power. Prior to entering the Herriott cell, the beam was attenuated by a factor of ~20 by a thin mylar sheet to reduce optical fringing and detector non-linearity.

#### **Calibration:**

The absolute methane abundances reported here are calibrated using NIST-traceable methane in air provided by the NOAA-CMDL laboratory (provided by Jim Elkins group) specified to contain  $88 \pm 0.5$  ppbv. By injecting this gas into the TLS Herriott cell during pre-launch calibration runs of TLS and SAM in the NASA GSFC environmental chamber, we record both direct absorption and 2f signal sizes using the same conditions (e.g. laser scan, modulation, flight electronics and software, Herriott cell temperature and pressure, ramp heater) used on Mars. During the calibration run, the foreoptics is pumped out so that there is no contribution from foreoptics gas. The path length of the Herriott cell was verified to be 81 passes based on direct absorption measurements of these same methane lines using a second calibration cylinder (same provider) at 1800 ppbv. In addition, by adding pure methane gas at low pressures so that the lines are bleached to zero light transmission at line centers, the mode purity during the scan is verified. No change in alignment or detector signal sizes has been detected since pre-launch. Normalizing the mean value retrieved to 88 ppbv gives us a calibration result and uncertainty of  $88.0 \pm 1.13$  ppbv. We note that this uncertainty does not carry forward in our difference method described below, since it would only serve to change the mean value and upper limit slightly (1 part in 88).

#### **Difference method:**

The difference method is described in the body of the main paper, and the sequence shown in Fig. S1. During the empty or full cell periods, the foreoptics and Herriott cell pressures are very stable; during a typical run (Sol 106) the temperatures and foreoptics pressure are stable to 0.02%, and the Herriott cell pressure during the full cell section is stable to 0.1%.

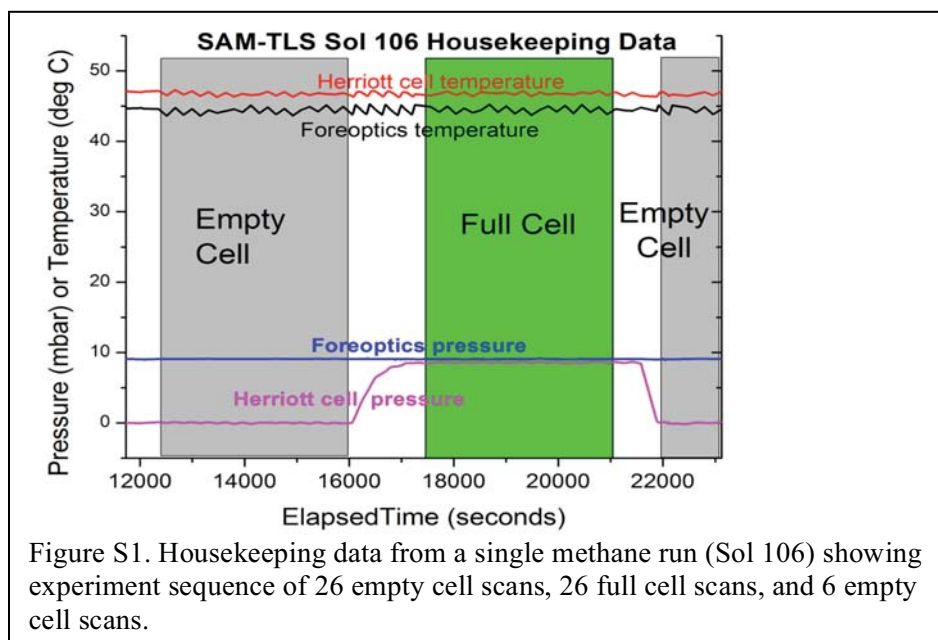


Figure S1. Housekeeping data from a single methane run (Sol 106) showing experiment sequence of 26 empty cell scans, 26 full cell scans, and 6 empty cell scans.

### Statistical analysis of data:

The TLS measurements include methane absorption occurring both in the Herriot cell and along the optic path prior to entry into the cell, as described in the main text. The foreoptics region has terrestrial methane in it, allowing confident identification of the methane absorption lines and continuous monitoring of scan-to-scan line shifts. The foreoptics methane signal also introduces a substantial blank signal which must be removed to compute the amount of methane in the Mars atmosphere in the Herriot cell.

The spacecraft returns two-minute averaged signals for each of the three spectral absorption lines given in Table S1. We treat each of these lines as a separate estimate of the absorption attributable to methane somewhere along the optic path. These absorptions were converted into an apparent methane mixing ratio in the Herriot cell by assuming that this is the only region in which methane occurs. We thus obtained between 78 and 96 independent measurements of the empty cell and of the full cell methane abundance on each of the three measurement sols (Table S2). On sol 81 two measurement cycles of the empty cell yielded three obvious outliers (see Fig. S2), and these have been excluded from further consideration. Note that the empty cell contributions arise overwhelmingly from methane in the foreoptics region rather than in the Herriott cell itself which is pumped out to  $<10^{-3}$  mbar. The difference between the full cell and the empty cell measurements is then the abundance of methane attributable to the martian atmosphere.

Results for each of the three measurement sols are shown in Table S2. The empty cell signal on all three sols is about 95 ppbv, with a typical standard error of about 1.6 ppbv. This signal is the background above which we seek to measure the atmospheric signal. As shown in the table, subtraction of this signal from the full cell data yields apparent atmospheric methane mixing ratios of 1.2, 1.3, and -1.0 ppbv on sols 79, 81, and 106, respectively. On all three sols the 95%

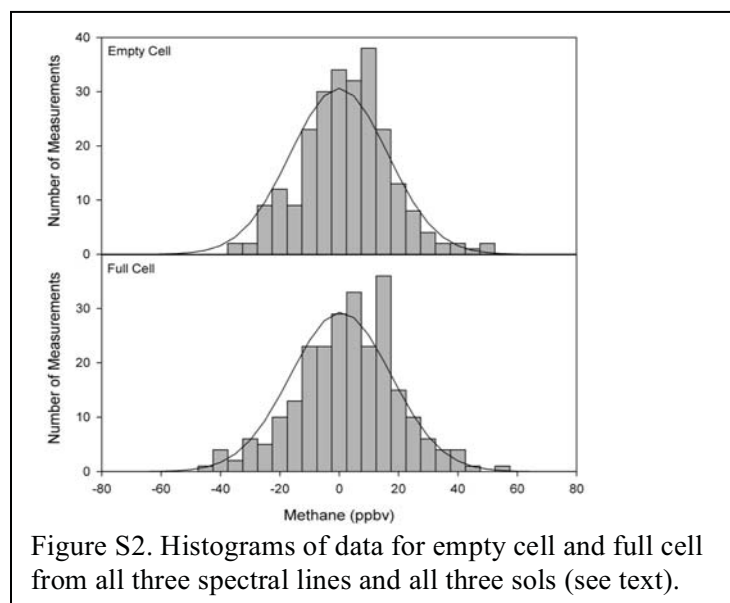


confidence interval ranges from about -4 to +6 ppbv, i.e., the concentration of methane detected is within error of zero.

In the absence of any notable difference in the atmospheric methane abundances retrieved on the three sols, we chose to merge the three individual data sets to obtain best estimates of the atmospheric methane amount, its uncertainty, and our instrumental detection limit. For this calculation we subtracted the mean blank signal on each sol from the measured signals on that sol. The results are shown in Figure S2 as a pair of histograms, one each for the aggregated 3-sol data sets for the empty cell and the full cell runs. These histograms are broadly Gaussian distributions with statistically equivalent variance. The mean empty cell value is by definition zero, with a standard error of the mean of 0.96 ppbv, while the blank-corrected full cell mean is  $0.39 \pm 1.07$  ppbv. A student's t-test on these two distributions yields a value of 0.77 and  $P = 0.79$ , implying that the difference between these two populations is not statistically significant. These data imply an upper limit with 95% confidence of 2.7 ppbv for the methane concentration of the Martian atmosphere.

Table S2. Statistical data for each sol.

Sol	Foreoptics+Empty Cell			Foreoptics+Full Cell			Observed (ppbv)	SEM (ppbv)
	n	Mean (ppbv)	SEM (ppbv)	n	Mean (ppbv)	SEM (ppbv)		
79	78	87.28	1.48	78	88.49	2.17	1.21	2.6
81	90	92.08	1.67	78	93.34	1.93	1.25	2.5
106	78	104.20	1.70	93	103.20	1.54	-1.00	2.3
All data (blank corrected)	246	0	0.96	249	0.39	1.07	<b>0.39</b>	<b>1.4</b>



**Supplemental Reference:**

- a. L.S. Rothman et al., The HITRAN 2008 Molecular Spectroscopic Database, *J. Quant. Spectr. Rad. Transfer* 110, 533-572 (2009).