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Low Upper Limit to Methane Abundance on Mars

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By analogy with Earth, methane in the Martian atmosphere is a potential signature of ongoing or past biological activity. During the last decade, Earth-based telescopic observations reported "plumes" of methane of tens of parts-per-billion by volume (ppbv), and those from Mars orbit showed localized patches, prompting speculation of sources from sub-surface bacteria or non-biological sources. From in situ measurements made by the Tunable Laser Spectrometer (TLS) on Curiosity using a distinctive spectral pattern unique to methane, we here report no detection of atmospheric methane with a measured value of 0.18 ±0.67 ppbv corresponding to an upper limit of only 1.3 ppbv (95% confidence level) that reduces the probability of current methanogenic microbial activity on Mars, and limits the recent contribution from extraplanetary and geologic sources.

Methane is the most abundant hydrocarbon in our solar system, and is found in the atmospheres of several planets and satellites (*1*). On Earth, 90-95% of atmospheric methane is biologically-produced, either from extant or fossil sources, and is easy to identify and quantify with confidence using spectroscopic methods (*2*). For Mars, three possible origins have been proposed: geologic, biotic, and exogenous (*3*–*5*). Over the last decade, there have been several reports of methane detection from Earth and from Mars orbit. Observations with the Canada-France-Hawaii Telescope (CFHT) found a global average value of 10 ±3 ppbv (*5*). The Planetary Fourier Spectrometer (PFS) on the Mars Express (MEX) spacecraft found a global average abundance of 10 ±5 ppbv (*4*), later updated (*6*) to 15 ppbv, with indications of discrete localized sources (*4*), and a summer time maximum of 45 ppbv in the north polar region. A search for methane from the Infrared Telescope Facility (IRTF) and the Keck-2 telescope reported methane release in plumes (*7*) from discrete sources in Terra Sabae, Nili Fossae and Syrtis Major, with the largest plume containing 19,000 tons of CH_4 in March 2003; seasonal changes with a summer time maximum of ~45 ppbv near the equator were seen. Methane abundances later retrieved (*8*) from a second instrument in Mars orbit, the Thermal Emission Spectrometer (TES) of Mars Global Surveyor (MGS), reported methane abundances as intermittently present (1999-2003), ranging from 5 to 60 ppbv in locations where favorable geological conditions such as residual geothermal activity (Tharsis and Elysium) and strong hydration (Arabia Terrae) are expected. More recent observations report methane mixing ratios that have diminished considerably since 2004-6 to upper limits of 7-8 ppbv (*9*–*11*), suggesting a very short lifetime for atmospheric CH_4 and contradicting the MEX claim that methane persisted from 2004-2010. Ground-based observations favor episodic injection of methane in 1999 and 2003, 10 ppbv at Valles Marineris in Feb. 2006 (*9*, *11*), and <8 ppbv in Jan. 2006 (*10*), 2009 and 2010; while orbital data from PFS and TES suggest a more regular behavior with latitudinal, seasonal and interannual variabilities. At Curiosity's Gale Crater landing site (4.5°S, 137°E), published maps of PFS data (*6*) show an increase from ~15 ppbv in fall to ~30 ppbv in winter, whereas the TES trend (*8*) is opposite: ~30 ppbv in fall and ~5 ppbv in winter.

The Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM) (*12*, *13*) instrument suite on Curiosity rover has a spectral resolution (0.0002 cm^{-1}) - far superior to the ground-based telescopic and orbiting spectrometers- that offers unambiguous identification of methane in a unique fingerprint spectral pattern of 3 well-resolved adjacent $^{12}CH_4$ lines in the 3.3 μm band (Fig. 1). The in situ technique of tunable laser absorption in a closed sample cell is simple, non-invasive and sensitive. TLS is a two-channel tunable laser spectrometer that uses both direct and second harmonic detection of IR laser light. One laser source is a near-IR tunable diode laser at 2.78 μm that can scan two spectral regions containing CO_2 and H_2O isotopic lines that have been used to report $^{13}C/^{12}C$, $^{18}O/^{17}O/^{16}O$ and D/H ratios in the Martian atmosphere (*13*). The second laser source is an interband cascade (IC) laser at 3.27 μm used for methane detection alone, scanning across seven rotational lines that includes the R(3) triplet used in this study (see Fig. 1 and table S1). The IC laser beam makes 81 passes of a 20-cm long sample cell of the Herriott design fitted with high-vacuum microvalves that allow evacuation with a turbomolecular pump for "empty cell" scans, or filled to Mars ambient pressure (~8 mbar) for "full cell" runs. During data collection, the cell and other optics are kept at 47 ± 3°C using a heater that thermally stabilizes the cell but is ramped up and down within these temperature limits to increase gas sensitivity by spoiling the accumulation of optical interference fringes during the 2-min period of spectrum collection. Our methane determination is made by comparing the measured methane abundances in our sample cell when filled with Mars atmosphere to those of the same cell evacuated, as detailed in (*14*). The laser scans every second through the methane spectral region and each spectrum is co-added on board to downlink sequential 2-min. averaged spectra during a given run of ~1-2 hours in duration. Typically, we record twenty-six 2-min. "empty cell" spectra followed by twenty-six 2-min. "full cell" spectra, then finally five additional 2-min. empty cell spectra. For each 2-min. spectrum, we retrieve methane abundances from three spectral lines (*14*) individually and combine the results to produce a weighted average value. By subtracting all retrieved abundances (full and empty cell) from the empty cell mean value for that sol run, we are left with 31 differences for the empty cell and 26 for the full cell. For our statistical analysis we analyze the empty cell and full cell differences for all the sols taken as one data set (*14*). For Sols 79, 81, 106 and 292 the foreoptics chamber contained residual terrestrial air (see Table 1 pressures) including CH_4 that produced absorption line signals in the sample cell detector channel, as described in (*14*). For Sols 306 and 313 the foreoptics was evacuated. Both sample cell and foreoptics chamber have pressure and temperature sensors. This experiment has been repeated on six separate Martian sols (days) to date (Martian sols 79, 81, 106, 292, 306, and 313 after landing in August 2012). The inlet to the TLS is a stainless steel tube (*14*) heated to 50°C and located on the rover side ~1 m above the Martian surface, and was pointed at a variety of directions relative to the nominal wind direction. Mars atmospheric gas was ingested during the night for sols 79, 81, 106, 292, and 313; and during the day for sol 306 (Table 1). Our measurements correspond to southern spring (sols 79, 81, 106) and mid-late summer (sols 292, 306, 313) on Mars.

To date we have no detection of methane. Individually (Table 1), each of our 6 data sets produces a mean methane value ranging from -2.2 to 1.7 ppbv. Combining the individual sol results with equal weighting yields a mean and standard error of 0.11 ± 0.67 ppbv. Alternatively, combining all of the individual measurements from all sols yields a grand mean and standard error of 0.18 ± 0.67 ppbv. At the 95% confidence level either approach (*14*) yields an upper limit on Mars atmospheric methane of 1.3 ppbv. Curiosity's low upper limit is not expected given observations only a few years ago of large methane plumes, and calculations (*7*) that the plume dispersion should produce global values of ~6 ppbv after the 6-month period (*3*, *15*) needed to mix uniformly across the planet that would persist with a photochemical lifetime of several hundred years (*3*, *5*, *16*).

Prior to Curiosity's landing on Mars in August 2012, observational evidence for methane on Mars was questioned in the published literature (*15*, *17*, *18*). Contradictions were noted between the locations of maxima reported from ground-based observations and maps inferred by PFS and TES from Mars orbit. The plume results (*7*) were questioned (*17*) on the basis of a possible misinterpretation from methane lines whose positions coincided with those of terrestrial isotopic $^{13}CH_4$ lines. Krasnopolsky (*19*) argued that cometary and volcanic contributions were not sufficient to explain high methane abundances, calculating a cometary contribution of only ~0.1 ppbv, and noting the lack of current volcanism, lack of hot spots in thermal imaging (*20*), and the extremely low upper limit for Mars SO_2 (*9*, *21*) that in Earth's volcanic emissions is orders of magnitude more abundant than CH_4 (*5*).

The very short methane lifetime of 0.4-4 years derived from the 2003-06 observations (*7*) requires powerful destruction mechanisms that have not been identified to date. Although models have been proposed for rapid removal of methane by oxidants, such as hydrogen peroxide and perchlorates or by superoxides derived from their mineral reactions (*22*–*24*) and directly by electric fields generated in dust devils (*25*), there remains no evidence for their existence at Mars. Moreover, it has not been demonstrated that any of these processes can reduce the lifetime of methane by the required factor of 100 or more compared to its photochemical lifetime. Our reported upper limit of 1.3 ppbv is significantly lower than the methane abundances reported from Mars remote sensing spacecraft observations and those from Earth telescopic observations, including both the earlier high values of typically tens of ppbv and the more recently reported upper limits of 7-8 ppbv (*9*, *10*). Although TLS samples only the very lowest part (~1 m) of the Mars atmosphere compared to the other observations that are vertical column-integrated results, the atmospheric scale height (~10 km) and mixing time (~few months) suggests that our measured upper limit is representative of the global mean background level. With an expected photochemical lifetime of methane in the Martian atmosphere of hundreds of years (*3*, *5*, *16*), there currently remains no accepted explanation (*15*, *17*) for the existence and distribution of the reported plumes, nor of the apparent disappearance of methane over the last few years. Our result sets an upper limit that is ~6 times lower than other recent measurements and greatly reduces the probability of significant methanogenic microbial activity on Mars and recent methane production by serpentinization or from exogenous sources including meteoritic, interplanetary dust and cometary infall.

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Supplementary Materials
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Materials and Methods
Figs. S1 to S5
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References (*26*, *27*)

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Table 1. Curiosity SAM-TLS methane measurements at Gale Crater (4.5 S, 137.4 E) over an 8-month period. SEM, standard error from the mean; Ls, solar longitude.

Martian Sol after landing on Aug 6th 2012	Earth date	Ls (deg)	Gas ingest time/cell pressure (mbar)/foreoptics pressure (mbar)	Mean value ± 1 SEM (ppbv)
79	Oct 25th 2012	195.0	Night/8.0/11.5	1.62 ± 2.03
81	Oct 27th 2012	196.2	Night/8.0/11.5	1.71 ± 2.06
106	Nov 27th 2012	214.9	Night/8.5/10.9	-0.55 ± 1.45
292	June 1st 2013	328.6	Night/8.7/9.2	0.60 ± 1.74
306	June 16th 2013	336.5	Day/8.1/0.0	-2.21 ± 0.94
313	June 23rd 2013	340.5	Night/8.7/0.0	-0.50 ± 0.94
	Mean of individual sol results			0.11 ± 0.56
	Mean for entire aggregated data set			0.18 ± 0.67

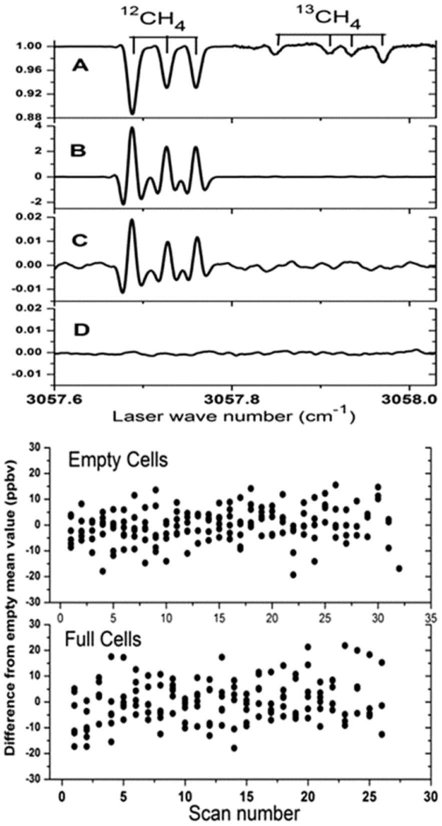

Fig. 1. The TLS-SAM methane measurements. (**Top**) Examples of flight spectra downloaded from Curiosity. (**A**) Spectrum recorded during an unrelated Evolved Gas Analysis (EGA) run (*14*) showing location of $^{12}CH_4$ and $^{13}CH_4$ lines, in which the second half has been vertically expanded by x20 to show the weaker $^{13}CH_4$ lines; (**B**) Same as (A) but second harmonic (2f) spectrum (*14*) without vertical expansion; (**C**) Averaged full cell 2f spectrum for Sol 106 (nighttime ingest) with foreoptics contribution (*14*); (**D**) Averaged full cell 2f spectrum for Sol 306 (daytime ingest) with foreoptics evacuated. [Spectra A and B are shown here in part because they were taken after the atmospheric runs and show that our CH_4 lines have not moved, and the instrument continued to work well with consistent capability to detect methane.] (**Bottom**) Individual 2-min data points from 6 sols: upper panel is empty cell data with mean value of 0.0 ppbv, and lower panel is full cell data with mean value of 0.18 ppbv.