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REPORT

PLANETARY SCIENCE

Background levels of methane in Mars' atmosphere show strong seasonal variations

Christopher R. Webster^{1*}, Paul R. Mahaffy², Sushil K. Atreya³, John E. Moores⁴, Gregory J. Flesch¹, Charles Malespin², Christopher P. McKay⁵, German Martinez⁶, Christina L. Smith⁴, Javier Martin-Torres^{6,7}, Javier Gomez-Elvira⁸, Maria-Paz Zorzano^{6,8}, Michael H. Wong², Melissa G. Trainer², Andrew Steele⁹, Doug Archer Jr.¹⁰, Brad Sutter¹⁰, Patrice J. Coll¹¹, Caroline Freissinet¹², Pierre-Yves Meslin¹³, Raina V. Gough¹⁴, Christopher H. House¹⁵, Alexander Pavlov², Jennifer L. Eigenbrode², Daniel P. Glavin², John C. Pearson¹, Didier Keymeulen¹, Lance E. Christensen¹, Susanne P. Schwenzer¹⁶, Rafael Navarro-Gonzalez¹⁷, Jorge Pla-García^{8,18}, Scot C. R. Rafkin¹⁹, Álvaro Vicente-Retortillo³, Henrik Kahanpää²⁰, Daniel Viudez-Moreiras⁸, Michael D. Smith², Ari-Matti Harri²⁰, Maria Genzer²⁰, Donald M. Hassler¹⁹, Mark Lemmon²¹, Joy Crisp¹, Stanley P. Sander¹, Richard W. Zurek¹, Ashwin R. Vasavada¹

Variable levels of methane in the martian atmosphere have eluded explanation partly because the measurements are not repeatable in time or location. We report in situ measurements at Gale crater made over a 5-year period by the Tunable Laser Spectrometer on the Curiosity rover. The background levels of methane have a mean value 0.41 ± 0.16 parts per billion by volume (ppbv) (95% confidence interval) and exhibit a strong, repeatable seasonal variation (0.24 to 0.65 ppbv). This variation is greater than that predicted from either ultraviolet degradation of impact-delivered organics on the surface or from the annual surface pressure cycle. The large seasonal variation in the background and occurrences of higher temporary spikes (~7 ppbv) are consistent with small localized sources of methane released from martian surface or subsurface reservoirs.

Methane is produced in Earth's atmosphere predominantly through biological processes (1, 2). Its existence in an oxidizing atmosphere such as Mars' is recognized as a potential biosignature whose putative sources could include methanogenic bacteria (1, 3, 4). Alternative nonbiological methane production mechanisms include geological processes such as serpentinization of olivine or pyroxene (5), ultraviolet (UV) degradation of indigenous or meteoritically delivered organics (6, 7), formation by the impact of comets (8), release from subsurface clathrates (9) or gas absorbed in the regolith (10, 11), erosion of basalt with methane inclusions (12), or geothermal processes (13). As a strong greenhouse gas, methane bursts on early Mars may have been responsible for intermittent

lake-forming climates—a process which could be ongoing today (14).

There have been numerous reports of methane in Mars' atmosphere by Earth-based remote sensing and from Mars orbit since 2004. None of those observations show a repeatable seasonal, temporal, or spatial trend. From Earth telescopes, a global average value of 10 ± 3 parts per billion by volume (ppbv) was observed in 1999 (3), whereas observations in 2003 showed plumes of methane from discrete sources with a summertime maximum of ~45 ppbv near the equator (4), but only an upper limit of 7.8 ppbv 3 years later in January 2006 (15). Further data taken in February 2006 yielded a detection of 10 ppbv at 45°S to 7°N over the Valles Marineris region, but an upper limit of 3 ppbv outside that

region, and no detection (<8 ppbv) in December 2009 (16). From Mars orbit, the Planetary Fourier Spectrometer (PFS) on the Mars Express spacecraft measured a global average abundance of 15 ± 5 ppbv from 2004 to 2010 (17, 18). The Thermal Emission Spectrometer on the Mars Global Surveyor spacecraft measured abundances ranging from 5 to 60 ppbv (19), although the claims of local variations were later withdrawn (20). Published maps of PFS data (18) at Curiosity's landing site in Gale crater (4.5°S, 137°E) show an increase over 1 year from ~15 ppbv in Autumn to ~30 ppbv in winter. In situ measurements of Mars methane began soon after the August 2012 landing of the Mars Science Laboratory (MSL) Curiosity rover at Gale crater. The Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM) instrument suite initially reported (21) a low methane abundance at Gale crater with an upper limit of 1.3 ppbv [95% confidence interval (CI)]. Subsequent observations over a 20-month period showed (22) a background level of 0.69 ± 0.25 ppbv and revealed unexpected occasional spikes to 7.2 ± 2.1 ppbv (95% CI).

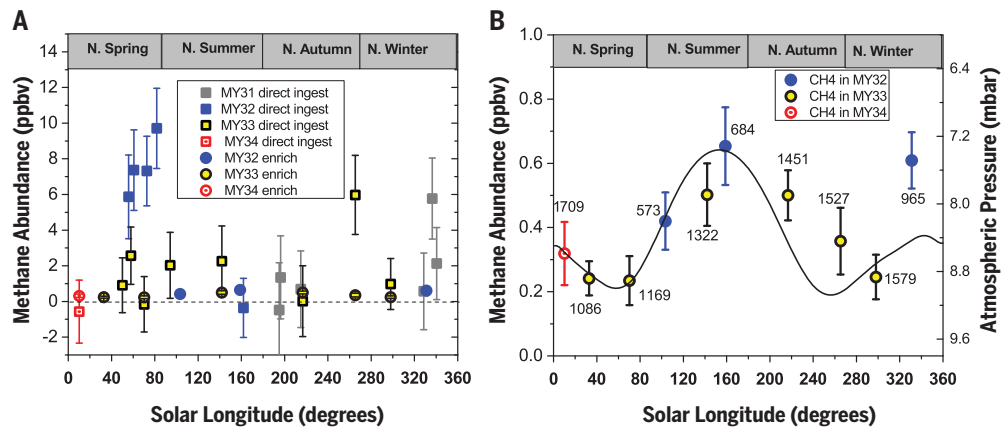
Existing models including atmospheric transport and circulation (23–26) are unable to reproduce the reported high concentrations of methane and its spatial and temporal variability, even when including possible clathrate release (9), surface/regolith adsorption/desorption (10), seasonally variable production from UV breakdown of surface organics (6, 7), or proposed mechanisms of rapid loss (27, 28). Analysis of all methane measurements up to 2016 (29) provides little evidence for any correlation between meteor streams and methane plumes as previously suggested (30).

The TLS-SAM instrument (31) is a two-channel tunable laser spectrometer that uses both direct and second harmonic detection of absorbed infrared (IR) laser light. One channel uses a near-IR tunable diode laser at 2.78 μm to measure carbon, oxygen, and hydrogen isotopic ratios in both the Mars atmosphere and from gases evolved from rock pyrolysis (32, 33). The high spectral resolution provides high sensitivity to methane by resolving its distinct fingerprint spectral pattern of three adjacent R(3) $^{12}\text{CH}_4$ lines in the 3.3- μm band (32). An interband cascade semiconductor laser source reflects 81 times between two spherical mirrors in a 20-cm-long sample cell of the Herriott design. The sample cell is fitted with high-vacuum microvalves to control evacuation by a SAM turbomolecular pump for empty cell scans or is filled to Mars

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Fig. 1. The TLS-SAM methane measurements versus martian solar longitude. All plotted values are listed in table S2, have error bars of ± 1 SEM, and are corrected to global mean annual values. MY, Mars year. **(A)** All measurements up to 27 May 2017, including those from direct ingestions (squares) and enrichment ingestions (circles with smaller error bars). **(B)** Background measurements from enrichment ingestions show strong seasonal variation. The atmospheric pressure (inverted scale at right) from REMS is plotted for comparison, the solid line representing the mean values over the 3 Mars years.



ambient pressure (~ 7 mbar) for full cell runs. Because the instrument's foreoptics chamber contains residual terrestrial methane gas, an atmospheric determination is made by subtracting an empty cell measurement from each full cell run (34). We used two methods of atmospheric ingestion: The first is a direct ingest method, in which gas is fed into the evacuated sample cell through an inlet port located on the side of the Curiosity rover, taking ~ 20 min to fill to ~ 7 mbar and producing uncertainties of ~ 2 ppbv for each measurement (34). The second is an enrichment method that ingests atmospheric gas through a second inlet port, which is passed over a CO_2 scrubber to fill the sample cell more slowly (~ 2 hours) to the same pressure of ~ 7 mbar. The latter method efficiently removes incoming CO_2 and H_2O but not methane, effectively enriching its abundance by a factor of 25 ± 4 (34). This reduces the overall uncertainty correspondingly, allowing more precise determination of low background levels. Along with other monitoring data, the Herriott cell pressure is recorded every 3 s during the entire ingestion process and data collection.

All our measurements to 27 May 2017 (values listed in table S2), over a period of 55 (Earth) months spanning 3 martian years, are shown in Fig. 1A. We consider values above 3 ppbv to be high spikes of methane; these were occasionally observed in the direct ingest mode. For the high methane spike seen in direct ingest on the four sols (martian days since rover landing) 467, 475, 505, and 525, our improved analysis (34) produces a mean value of 7.6 ± 1.6 ppbv (95% CI), which is slightly higher than the 7.2 ppbv previously reported (22). All high-precision measurements in the enrichment mode are below 0.7 ppbv and identify the background levels and their associated seasonal variation. These individual background level measurements are given in Table 1, with a mean value of 0.41 ± 0.16 (95% CI) and a variation that ranges from 0.24 to 0.65 ppbv, an increase of nearly a factor of 3 from its lowest value.

As shown in Fig. 1B, the background methane levels have a strong seasonal cycle, peaking near the end of the northern summer/southern winter (Gale crater at 4.5°S , 137.4°E is near the equator).

There is no large variation in the mean background level from year to year over this period. The direct ingest measurements with values below 3 ppbv produce a mean value of 0.59 ± 0.54 (95% CI), which is consistent with the higher precision enrichment mean value. This rules out some potential contamination sources because direct ingest uses a different inlet and plumbing from the enrichment runs. Indeed, for the many occasions (table S2) when a direct ingest measurement was run soon after an enrichment run (~ 4 hours between sample midpoints), the two results agree within the uncertainty of the direct ingest measurement, with only one exception on sol 1527 [solar longitude (L_s) = 265.3°]. On this sol, a 20-min direct atmospheric ingest started 3 hours after the end of a 2-hour atmospheric enrichment ingest. The direct sample contained 5.98 ppbv CH_4 , whereas the enriched sample contained 0.27 ppbv CH_4 . We attribute this to the arrival at Curiosity of a high spike from a location that could have been up to tens of kilometers away, according to model wind fields (34). The enrichment value at $L_s = 331^\circ$ of 0.61 ppbv appears higher than expected for a single modal seasonal variation shape, so we cannot rule out that this may be due to the atmosphere in recovery from a higher spike sometime before that measurement.

An earlier report (22) ruled out several mechanisms that may have caused false TLS readings—namely, methane left over from evolved-gas pyrolysis of rock samples, incomplete pumping of the Herriott cell, reactive coatings inside the Herriott cell, wheel degradation or rock-crushing release during transit, and varying surface material under the rover. We argue against the possibility (35) that the rover itself is a source of methane because we cannot identify any source large enough to produce even an instantaneous cloud of ~ 7 ppbv methane in a 10-m-diameter sphere around the rover, which would require $\sim 10^{18}$ methane molecules (34). With typical Mars wind speeds of ~ 3 to 5 m/s (36) replenishing the air around the rover, a supply of $\sim 10^{24}$ methane molecules would be needed over the 2-month duration of the highest spike period. Although the TLS-SAM fore-optics chamber contains some terrestrial methane

[$\sim 10^{15}$ molecules (34)], this is too small an amount to be considered as a bulk source for later ingestion even if somehow contained within the rover instrumentation. By monitoring the fore-optics chamber pressure and methane content over the 5-year period on Mars, we see no evidence of gross leakage from the foreoptics chamber.

Correlations of the high methane spikes with other measurements were investigated in an earlier publication (22). We compare our background values with the same parameters measured by Curiosity's instruments (34): pressure, surface temperature, relative humidity, inferred water vapor abundance, and surface UV from the Rover Environmental Monitoring Station (REMS) instrument; dust opacity from REMS and the Mastcam instrument; radiation flux from the Radiation Assessment Detector (RAD) instrument; and argon measurements from SAM's Quadrupole Mass Spectrometer (QMS).

The rough seasonal trend of a maximum near the end of northern summer is seen in several parameters—including the atmospheric pressure, surface UV, surface temperature, and argon abundance—but comparing these small seasonal changes with our methane background measurements produces no significant bivariate linear correlation (figs. S3 to S38) (34).

As with all Solar System bodies, Mars is expected to receive material exogenously (from outside the planet) as infalling dust, micrometeorites, and cometary sources containing organic materials that can partially survive (or be reexposed during atmospheric entry) on the surface, later releasing methane from UV photolytic processes either directly (7) or through secondary photochemical reaction (37). One such UV/CH_4 model (7) predicts that production is carbon-limited and over very long time periods can produce 2.2 ppbv methane in the martian atmosphere. We considered models of methane arising from exogenous material but found that they are inconsistent with the observed background value, its disproportionality with the UV flux, and the size of its seasonal variation (34).

The Mars atmosphere has a seasonal surface pressure cycle due to a combination of the

Table 1. Curiosity TLS-SAM methane enrichment measurements at Gale crater (4.5°S, 137.4°E) over a 38-month period. SEM, standard error of the mean; EF, enrichment factor; L_s , solar longitude; CI, confidence interval. The global pressure multiplier is derived from in situ REMS pressure measurements; it is the number by which the original measured in situ values of methane (given in table S3) were multiplied to correct the results to the global mean annual mixing ratio given in the right two columns. Earth dates refer to the time when the gas ingest was started. The decimal portion of the sol is used so that sol 573.08 represents local time 01:57.

Martian sol after landing on 6 August 2012	Earth date	L_s (degrees)	Global pressure multiplier	CH ₄ (ppbv)	Error ± 1 SEM (ppbv)
573.08	17 March 2014	103.48	0.970	0.419	0.089
684.06	9 July 2014	158.61	0.877	0.653	0.121
965.99	25 April 2015	331.57	1.003	0.609	0.088
1086.06	26 August 2015	32.81	1.050	0.241	0.053
1169.02	19 November 2015	70.57	1.062	0.235	0.076
1322.00	24 April 2016	142.46	0.881	0.502	0.097
1451.06	4 September 2016	216.58	1.007	0.500	0.078
1527.06	21 November 2016	265.78	1.076	0.357	0.104
1579.00	13 January 2017	298.76	1.036	0.246	0.069
1709.00	27 May 2017	10.84	1.020	0.319	0.098
				Mean value ± 1 SEM (68% CI) = 0.408 ± 0.049 ppbv	
				Mean value including EF error ± 1 SEM (68% CI) = 0.408 ± 0.082 ppbv	
				Mean value ± 2 SEM (95% CI) = 0.41 ± 0.16 ppbv	

condensation and sublimation of carbon dioxide in the polar caps, an effect arising from the difference in mean surface altitude of the two hemispheres, and a dynamical effect resulting from the balance between mass and wind field (38). At equatorial locations like Gale crater, the pressure cycle is dominated by the polar cap contribution, although departures from regular seasonal trends can be present locally, sometimes because of dust storms (39). In situ measurements from REMS show pressures that range from 7.3 to 9.1 mbar (Fig. 1B), with a mean value of 8.4 mbar. When reporting gas mixing ratios, it is customary to correct in situ values to produce global mean annual mixing ratios, as we have done for the TLS-SAM data (Table 1 and Fig. 1). The observations of spatial and temporal variations (such as the spikes) indicate that normalization to a global mean value may not be appropriate, although this correction is at best only ~15% of the observed amplitude. To explain the large amplitude of the background methane observations, we considered whether large quantities of poorly mixed subliming CO₂ could reach the low latitudes of Gale crater during the higher pressures and thereby result in low mixing ratios locally; this scenario is not borne out by modeling (36) nor by the QMS-SAM in situ measurements of argon (34), which can be considered a long-lived tracer of atmospheric transport and mixing.

The Mars Regional Atmospheric Modeling System (MRAMS) (34) shows that both horizontal mixing and vertical transport play a role in the transport of air into and out of Gale crater. For a small (~2° latitude/longitude area) short (~1 hour) methane release inside Gale crater, all methane is gone (reduced by an order of magnitude) within 6 to 8 hours; when released outside the crater, methane is diluted by several orders of magnitude in similar time, regardless

of the season. Mixing time scales are ~1 sol regardless of season, which is much faster than previously thought (34). For steady-state release in a small to medium area (~2° to 10° latitude/longitude area) mimicking expectations for release inside or outside the crater, MRAMS shows daily variations of an order of magnitude occurring because of nighttime/daytime differences in flows between crater rim and floor.

With ancient atmospheric pressures of several hundred millibars (40), large amounts of methane may be stored in the cold martian subsurface as clathrates in a stability zone several times thicker than that of Earth (41–43). Although the seasonal signature of the TLS-SAM measurements is not consistent with direct clathrate release, clathrates may provide a source of surface microseepage (diffuse exhalations without any specific morphological structure that may vent from outcropping of rocks or river or lake beds) (43–45). On Mars, such seepage would occur preferentially through permeable pathways, such as faults, fractures, or in breaches in sealing lithologies; this would not require identifiable geomorphological structures on the surface. Weak microseepage exhalations could explain background and plume methane anomalies observed on Mars (43), perhaps near the dichotomy boundary and at Gale crater, where there is fractured sedimentary rock. Microseepage flux may vary over time, depending on variations of gas pressures along the subsurface migration pathway or on seasonal changes in the soil, or even where microbial activity may consume methane.

Regardless of the subsurface origin, methane that finds its way to surface layers over long time periods (42, 43) may be expected to show seasonal variation. We consider a process that retains methane at the surface temporarily before releasing it through a process linked to the surface temperature. That process could be ad-

sorption on a surface with a high surface area-to-volume ratio, such as dust or soil. Although mineral dust cannot serve as a methane sink, it can moderate the release (11, 12). Adopting an energy barrier of ~20 to 35 kJ/mol—which is somewhat higher than that reported for the physical adsorption of methane into clays (46), zeolites (47), and Mars analog soil (12)—we found that large seasonal variations are expected (fig. S41). Plausible correlations of the background methane values with atmospheric water vapor and with surface temperatures point to physical or chemical surface (or dust) processes, or microseepage release. The amplitude of the seasonal cycle indicates that there remain unknown atmospheric or surface processes occurring in present-day Mars.

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SUPPLEMENTARY MATERIALS

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Background levels of methane in Mars' atmosphere show strong seasonal variations

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Measuring martian organics and methane

The Curiosity rover has been sampling on Mars for the past 5 years (see the Perspective by ten Kate). Eigenbrode *et al.* used two instruments in the SAM (Sample Analysis at Mars) suite to catch traces of complex organics preserved in 3-billion-year-old sediments. Heating the sediments released an array of organics and volatiles reminiscent of organic-rich sedimentary rock found on Earth. Most methane on Earth is produced by biological sources, but numerous abiotic processes have been proposed to explain martian methane. Webster *et al.* report atmospheric measurements of methane covering 3 martian years and found that the background level varies with the local seasons. The seasonal variation provides an important clue for determining the origin of martian methane.

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