

Mars Methane Detection and Variability at Gale Crater

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Abstract: Reports of plumes or patches of methane in the Martian atmosphere that vary over monthly timescales have defied explanation to date. From in situ measurements made over a 20-month period by the Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM) instrument suite on Curiosity at Gale Crater, we report detection of background levels of atmospheric methane of mean value 0.69 ± 0.21 ppbv at the 95% confidence interval (CI). This abundance is lower than model estimates of ultraviolet (UV) degradation of accreted interplanetary dust particles (IDP's) or carbonaceous chondrite material. Additionally, in four sequential measurements spanning a 60-sol period, we observed elevated levels of methane of 7.19 ± 1.99 (95% CI) ppbv implying that Mars is episodically producing methane from an additional unknown source.

One Sentence Summary: Mars methane has been detected at background levels of ~0.7 ppbv and at a transient elevated abundance of ~10 times this value over a 60-sol period.

Main Text:

Because Earth's atmospheric methane is predominantly biologically-produced (1), determining the abundance and variability of methane in the current Martian atmosphere is critical to assessing the contribution from a variety of potential sources or reservoirs that may be biological (such as methanogens (2,1)) or abiotic (1). These latter processes include: geological production such as serpentinization of olivine (3), UV degradation of meteoritically-delivered organics (4,5,6), production by impacts of comets (7), release from subsurface clathrates (8) or regolith-adsorbed gas (9,10), erosion of basalt with methane inclusions (11), or geothermal production (12). Several detections of Mars methane have been published. Ground-based observations from the Canada-France-Hawaii Telescope (CFHT) in 1999 found a global average value of 10 ± 3 ppbv (2), and those using the NASA IRTF telescope in 2003 reported (13) methane release in plumes from discrete sources in Terra Sabae, Nili Fossae, and Syrtis Major that showed seasonal changes with a summer time maximum of ~45 ppbv near the equator. This work also reported simultaneous detections of methane and carbon dioxide in 2005, and an upper limit of 3 ppbv in 2006, from which its' rapid destruction since 2003 was inferred (13). The Planetary Fourier Spectrometer (PFS) on the Mars Express (MEX) spacecraft reported detection in 2004 (14) with an updated global average abundance of 15 ± 5 ppbv (15), with indications of discrete localized sources and a summer time maximum of 45 ppbv in the north polar region. From the Thermal Emission Spectrometer (TES) of Mars Global Surveyor (MGS), methane abundances from 5 to 60 ppbv were deduced (16) as intermittently present over locations where favorable geological conditions such as residual geothermal activity (Tharsis and Elysium) and strong hydration (Arabia Terrae) might be expected. Using data from NASA-IRTF acquired in February 2006, (17) reported a detection of 10 ppbv at mid-latitudes (42-7°N) over Valles Marineris but an upper limit of 3 ppbv outside that region; in December 2009 they obtained an upper limit of 7-8 ppbv and noted that data from both observations agreed with those of (13). More recent ground-based observations report methane mixing ratios that have diminished considerably since 2004-2006 to a two-sigma upper limit of 5 ppbv (17,18,19), suggesting a very short lifetime for atmospheric CH₄ and contradicting the MEX claim that methane persisted from 2004-2010. At Curiosity's Gale Crater landing site (4.5°S, 137°E), published maps of PFS data (15) show an increase from ~15 ppbv in fall to ~30 ppbv in winter, whereas the TES trend (16) is opposite: ~30 ppbv in fall and ~5 ppbv in winter.

Observational evidence for methane on Mars has been questioned in the published literature (20,21,22) because photochemical models are unable to reconcile the observed amounts with their reported spatial gradients and temporal changes over months compared with the expected ~300 year methane lifetime. 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 (13) were questioned (22) on the basis of a possible misinterpretation from methane lines whose positions coincided with those of terrestrial isotopic ¹³CH₄ lines. Krasnopolsky (7) argued that cometary and volcanic contributions were not sufficient to explain high methane abundances, noting for the latter possibility the lack of current volcanism or hot spots in thermal imaging (23), and the extremely low upper limit for Mars SO₂ that in Earth's volcanic emissions is orders of magnitude more abundant than CH₄, as predicted for Mars (24). Model calculations including expected atmospheric transport and circulation (20,25) are to date all unable to reproduce the spatial and temporal characteristics of the observed high concentration methane plumes, whether resulting from possible clathrate release (8), surface adsorption by or desorption from the regolith (9) or for ultraviolet (UV) degradation of surface organics (4,5,6), despite the introduction of a variety of putative loss mechanisms (26,27,28).

The Tunable Laser Spectrometer (TLS) of the Sample Analysis at Mars (SAM) (29) instrument suite on Curiosity rover has a spectral resolution (0.0002 cm^{-1}) that offers unambiguous identification of methane in a unique fingerprint spectral pattern of 3 well-resolved adjacent ¹²CH₄ lines in the 3.3-μm band (30). 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 channel uses a near-IR tunable diode laser at 2.78 μm that has yielded robust data on carbon, oxygen and hydrogen isotopic ratios on Mars (31). The second channel uses an interband cascade (IC) tunable laser at 3.27 μm for methane detection alone, scanning across seven rotational lines that includes the R(3) triplet used in this study. This laser 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 (~ 7 mbar) for “full cell” runs. Our methane determination is made by differencing the measured methane abundances in our sample cell when filled with Mars atmosphere from measurements of the same cell evacuated, as detailed in the Supplementary Material (SM) (32).

From our first six observations spanning a 234-sol period (1 sol = 1 Mars day = 24 hrs 27.3 mins), we previously reported (33) a mean value of 0.18 ± 0.67 ppbv that was not precise enough to claim detection of Mars methane, but instead set an upper limit of 1.3 ppbv (95% CI) that was significantly lower than those reported (5 ppbv, 95% CI) from recent ground-based observations (17,18,19).

We have now reprocessed our entire data set (with a small modification explained in (32)). Our data set now extends the measurement period over 605 sols, including 11 direct ingest measurements and two recent measurements using a “methane enrichment” experiment run on sols 573 and 684. In this latter procedure, the atmospheric methane is effectively enriched by 23 ± 1 times by flowing the ingested gas slowly over a carbon dioxide scrubber material. Prior to running on Mars, the instrument script was optimized using the test-bed SAM suite (32). Results from the complete data set are given in Table 1 and plotted in Fig. 1. We partition our data points of Fig. 1 into 3 groups for independent analysis: (i) the “low methane” direct ingest results of sols 79, 81, 106, 292, 313 and 684; (ii) the “low methane” enrichment results for sols of 573 and 684; and (iii) and the four sequential “high methane” runs of sols 466, 474, 504, and 526, as there is no statistically-significant variation within each grouping. Mean values for these grouped data sets (final three lines, Table 1) form the basis for our analysis and conclusions. We note the good agreement between the direct and enriched experiments that were run back to back on sol 684. The daytime run of sol 306 is not included in group (iii) because it was not part of the high methane sequence, nor is it included in the low methane group (i) since it is clearly higher than the background average.

Our “low methane” enrichment experiments produce a mean value for atmospheric methane of 0.69 ± 0.21 (95% CI) ppbv, as described in (32). The higher precision, direct-ingest (non-enrichment) group yields a mean methane value of 0.89 ± 1.83 (95% CI) ppbv, agreeing with the lower precision enrichment value within error. For the “high methane” abundance seen in direct-ingest we measure a mean value of 7.19 ± 1.99 (95% CI) ppbv for the four sols 466, 474, 504, and 526. In the SM (32), we provide arguments to rule out the possibility of terrestrial contamination, and therefore conclude that the enrichment result and the “high methane” result independently produce detection of methane at two levels of abundance. Although TLS samples only the very lowest part (~ 1 m) of the Mars atmosphere in the Gale Crater region, the atmospheric mixing time of a few months suggest that our measured value of 0.69 ± 0.21 (95% CI) ppbv is likely representative of the mean background level for Mars atmospheric methane abundance, which is only expected to vary significantly and seasonally over the winter poles (20).

The principal sources of organics delivered exogenously to Mars are isotropically-accreted interplanetary dust particles (IDP's) and low-mass carbonaceous chondrites containing up to 10% organics by weight (1,4,5,6). Recent observations by SAM on Curiosity have detected the presence of chlorobenzene and simple chlorinated alkanes (34) in a drilled martian mudstone in Gale Crater. Laboratory studies of meteoritic materials have shown that UV irradiation of organic molecules can produce methane either directly (5) or through secondary photochemical reaction (35), and that certain molecules can form a photoresistant layer leading to methane over extended time periods (6). Constrained by laboratory production rates, models have assessed the rate and size of infall of meteoritic material such as IDP's, carbonaceous chondrites and other sources of organic carbon to the martian surface that might reproduce methane observations under Mars-like UV conditions. The UV/CH₄ model of isotropically accreted IDP organics of Schuerger et al. (4) predicts that the UV-induced production of methane is carbon-limited, and over geological time can produce a globally-averaged methane abundance of 2.2 ppbv methane for a 20% conversion rate of organic carbon to methane. No significant diurnal or seasonal changes are predicted by this model, which cannot explain the variability of methane over relatively short timescales observed in earlier studies (12,14). Even with consideration of single large bolide impacts or multiple airburst events, the models struggle to emplace sufficient carbon over the large surface areas of the plume observations, and more importantly cannot supply methane fast enough to create plumes over the observed timeframe (5).

Our background methane abundance reported here of 0.69 ± 0.21 ppbv from the low methane enrichment is significantly lower than the 2.2 ppbv obtained from the Schuerger UV/CH₄ model estimate (5) described above,

despite the fact that measured surface UV levels from Curiosity's REMS instrument (32,36) agree with the model values (5). This implies that either the quantity of delivered carbon or its conversion efficiency to methane is one-third the model estimates or that an indigenous source may be having an effect. It is also likely that the fresh analog material used by Schuerger et al. (5) is not completely representative of the bulk of material (UV-processed IDP's) being delivered to Mars.

As detailed in (32), our high methane result of 7.19 ± 1.99 ppbv (95% CI) shows no significant quantitative correlation with relative humidity, atmospheric pressure (carbon dioxide abundance), ground or air temperature, inlet pointing, or radiation levels measured by other Curiosity instruments: the Rover Environmental Monitoring Station (REMS (36)), the Chemistry and Camera complex (ChemCam (37)), and the Radiation Assessment Detector (RAD (38)). The REMS observations suggest a plausible anti-correlation with water abundance, air and ground temperatures and both REMS and the Curiosity mast camera (MastCam (39)) show a possible anticorrelation with atmospheric opacity (32), but our first enrichment measurement on sol 573 spoils this. However, all methane measurements (including sol 573) support an anti-correlation of methane abundance with column measurements of oxygen abundance and water vapor as measured by the ChemCam instrument (see Fig. S9), the latter contrasting with the weak positive correlation observed by the Mars Express PFS (8, 40). However, the lack of O₂ and H₂O data for the range Ls = 160-220 spoils this comparison, and we must await future measurements to assess this fully.

Concerning the possibility of spatially-variable methane abundance, although the high methane measurements were observed within 200-300 m of each other (Fig. S10), the rover had not traveled far (~1 km) since the lower value of sol 466, and the high methane disappeared after traveling only a further ~1km away. Typical ground winds of ~7 m/sec (25) would cover that distance in only 2 minutes, and given rotation of diurnal wind, it's impossible to isolate one location from another. This suggests a short-duration event that is either local and weak, or more distant and stronger. The persistence of the high methane values over 60 sols and their sudden drop 47 sols later is not consistent with a well-mixed event, but rather with a local production or venting that, once terminated, disperses quickly. Most of our data is taken at night, when prevailing winds are likely from the south. The marginally higher daytime values suggested in sols 306 and 526 indicate a source to the rover's north, because prevailing daytime winds would advect toward the rover location. The change in rover location is therefore unimportant as this is a temporal, not locational variation. With a concern that Curiosity transit over varying surface materials (identified by the Alpha Particle X-ray Spectrometer (APXS (41)) measurements) could be associated with the high methane observations, we studied rover stand-time and local terrain composition (32) and rule out such potential contributions. While we cannot rule out possible clathrate release (8) or surface adsorption into the regolith with subsequent release (9), both these mechanisms do not support the local, short timescale variation we observe.

Our measurements of a background methane abundance of ~0.7 ppbv can be reconciled with photochemical models that include an exogenous source such as UV degradation of organics (5) because model results likely represent upper limits with extensive UV processing in space prior to delivery to Mars. Like the earlier plume measurements, our higher transient methane amounts of ~7 ppbv require an additional source of methane, in our case suggesting advection to the rover location from a local unidentified source. If that source were a recent bolide impacting Gale Crater and producing 1% methane, we estimate that it would have to be several meters in size and leave a crater of tens of meters in diameter, but no new impact craters have been observed within Gale Crater from Mars orbit time-series imaging (42) since landing. Our measurements spanning a full Mars year indicate that trace quantities of methane are being generated on Mars by more than one mechanism or a combination of proposed mechanisms -- including methanogenesis either today or released from past reservoirs, or both.

References and Notes

1. S. K. Atreya, P. R. Mahaffy, and A. S. Wong, Methane and related trace species on Mars: Origin, loss, implications for life, and habitability. *Planet. Space Sci.* **55**, 358-369 (2007).
2. V. A. Krasnopolsky, J.P. Maillard, and T.C. Owen, Detection of methane in the martian atmosphere: evidence for life? *Icarus* **172**, 537-547 (2004).
3. C. Oze and M. Sharma, Have olivine, will gas: Serpentinization and the abiogenetic production of methane on Mars, *Geophys. Res. Lett.* **32**: doi10.1029/2005GL022691 (2005).

4. F. Keppler, I. Vigano, A. McLeod, U. Ott, M. Früchtl, and T. Röckmann, Ultraviolet-Radiation-Induced Methane Emissions From Meteorites and the Martian Atmosphere, *Nature* **486**, no. 7401: 93–96. doi:10.1038/nature11203 (2012).
5. A. Schuerger, J.E. Moores, C.A. Clausen, N.G. Barlow and D.T. Britt, Methane from UV-irradiated Carbonaceous Chondrites under Simulated Martian Conditions, *J. Geophys. Res.* **117**, doi: 10.1029/2011JE004023, (2012).
6. O. Poch, S. Kaci, F. Stalport, C. Szopa and P. Coll, Laboratory Insights into the Chemical and Kinetic Evolution of Organic Molecules under Simulated Mars Surface UV Radiation Conditions, *Icarus*, doi: <http://dx.doi.org/10.1016/j.icarus.2014.07.014>, (2014).
7. V. A. Krasnopolsky, Some problems related to the origin of methane on Mars, *Icarus* **180**, 359–367 (2006).
8. E. Chassefière, Metastable Methane Clathrate Particles as a Source of Methane to the Martian Atmosphere, *Icarus*, **204**, 137-144 (2009).
9. P.-Y. Meslin, R. Gough, L. Lefevre, F. Forget, Little variability of methane on Mars induced by adsorption in the regolith, *Planet. Space Sci.* (2010), DOI:10.1016/j.pss.2010.09.022 (2010).
10. R.V. Gough et al., Methane Adsorption on a Martian Soil Analog: an Abiogenic Explanation for Methane Variability in the Martian Atmosphere, *Icarus*, **207**, 165-174 (2010).
11. S. McMahon, J. Parnell, and N.J.F. Blamey, Sampling methane in basalt on Earth and Mars, *Internat. J. Astrobiol.* **12**, 113-122 (2013).
12. G. Etiope, D. Z. Oehler, C. C. Allen, Methane Emissions from Earth's Degassing: Implications for Mars, *Planet. Space Sci.* **59**, 182-195 (2011).
13. M. J. Mumma, et al., Strong release of methane on Mars in northern summer 2003. *Science* **323**, 1041-1045 (2009).
14. V. Formisano, S. K. Atreya, T. Encrenaz, N. Ignatiev, and M. Giuranna, Detection of methane in the atmosphere of Mars. *Science* **306**, 1758-1761 (2004).
15. A. Geminale, V. Formisano, and G. Sindoni, Mapping methane in Martian atmosphere with PFS-MEX data. *Planet. Space Sci.* **59**, 137-148 (2011).
16. S. Fonti and G. A. Marzo, Mapping the methane on Mars, *Astron. Astrophys.* **512**, A51, doi:10.1051/0004-6361/200913178 (2010).
17. G. L. Villanueva, et al., A sensitive search for Organics (CH₄, CH₃OH, H₂CO, C₂H₆, C₂H₂, C₂H₄), hydroperoxyl (HO₂), nitrogen Compounds (N₂O, NH₃, HCN) and chlorine species (HCl, CH₃Cl) on Mars using ground-based high-resolution infrared spectroscopy, *Icarus*, **223**, 11-27 (2013).
18. V. A. Krasnopolsky, Search for methane and upper limits to ethane and SO₂ on Mars, *Icarus* **217**, 144-152 (2012).
19. V. A. Krasnopolsky, A sensitive search for methane and ethane on Mars, *EPSC abstracts* **6**, 49 (2011).
20. F. Lefèvre and F. Forget, Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics, *Nature* **460**, doi:10.1038/nature08228 (2009).
21. S. K. Atreya et al., Methane on Mars: Current Observations, Interpretations, and Future Plans, *Planet. Space Sci.* **59**, 133-136 (2011).
22. K. J. Zahnle, R.S. Freedman, and D.C. Catling, Is there methane on Mars? *Icarus* **212**, 493-503 (2011).
23. P. R. Christensen, Mars as seen from the 2001 Mars Odyssey Thermal Emission Imaging System experiment, *EOS Trans. AGU Fall Meet. Suppl.* **84** (46), Abstract P21A-02, 2003.
24. F. Gaillard et al., Geochemical Reservoirs and Timing of Sulfur Cycling on Mars, *Space Sci. Rev.*, **174**, 251-300 (2013).
25. M. Mischna, M. I. Richardson, C. E. Newman, A. D. Toigo, Atmospheric Modeling of Mars Methane Surface Releases, *Planet. Space Sci.* **59**, 227-237 (2011).
26. S. K. Atreya et al., Oxidant Enhancement in Martian Dust Devils and Storms: Implications for Life, and Habitability. *Astrobiology* **6**, 439-450 (2006).
27. G. T. Delory et al., Oxidant Enhancement in Martian Dust Devils and Storms: Storm Electric Fields and Electron Dissociative Attachment. *Astrobiology* **6**, 451-462 (2006).
28. W. M. Farrell, G. T. Delory, and S. K. Atreya, Martian Dust Storms as a Possible Sink of Atmospheric Methane. *J. Geophys. Res.* **33**, doi:10.1029/2006GL027210 (2006).
29. P. R. Mahaffy et al., The Sample Analysis at Mars Investigation and Instrument Suite. *Space Sci. Rev.* **170**, 401-478 (2012).
30. C.R. Webster and P.R. Mahaffy, Determining the Local Abundance of Martian Methane and Its' ¹³C/¹²C and D/H Isotopic Ratios for Comparison with Related Gas and Soil Analysis on the 2011 Mars Science Laboratory (MSL) Mission, *Planet. and Space Sci.*, **59**, 271-283 (2011).

31. C. R. Webster et al., Isotope Ratios of H, C and O in CO₂ and H₂O of the Martian Atmosphere, *Science* **341**, 260 (2013).
32. This paper, supplementary online material – reference website.
33. C. R. Webster, P. R. Mahaffy, S. K. Atreya, G. J. Flesch, K. A. Farley, Low Upper Limit to Methane Abundance on Mars, *Science* **342**, 355 DOI: 10.1126/science.1242902 (2013).
34. C. Freissinet et al., Organic Molecules in the Sheepbed Mudstone of Gale Crater, Mars, *8th International Conf. on Mars*, Abstract No. 1349 (2014).
35. J.R.C. Garry et al., Analysis and Survival of Amino Acids in Martian Regolith Analogs, *Meteorit. Planet. Sci.* **41**, 391-405 DOI: 10.1111/j.1945-5100.2006.tb00470.x (2006).
36. Gómez-Elvira et al., Curiosity's Rover Environmental Monitoring Station: Overview of the First 100 Sols, *J. Geophys. Res.*, DOI: 10.1002/2013JE004576 (2014).
37. T. H. McConnochie et al., ChemCam Passive Spectroscopy of Atmospheric O₂ and H₂O, *8th International Conf. on Mars*, Abstract #1328 (2014).
38. D. M. Hassler et al., *Space Sci. Rev.* **170**.1-4, 503-558. (2012).
39. M. T. Lemmon, The Mars Science Laboratory Optical Depth Record, *8th International Conf. on Mars*, Abstract #1338 (2014).
40. A. Geminal et al., Methane in Martian Atmosphere: Average Spatial, Diurnal and Seasonal Behavior, *Planet. Space Sci.* **56**, 1194-1203, (2008).
41. M. E. Schmidt, et al., Geochemical Classification of Rocks in Gale Crater with APXS to sol 360: Sediment provenance, mixing, and diagenetic processes, 45th Lunar and Planet. Sci. Conf. Abstr. #1504 (2014).
42. Fred Calef, JPL, personal communication (2014).
43. L. S. Rothman et al., The HITRAN 2008 Molecular Spectroscopic Database, *J. Quant. Spectr. Rad. Transfer* **110**, 533-572 (2009).
44. C. R. Webster, R. T. Menzies, and E. D. Hinkley, "Infrared laser absorption: theory and applications," *Laser Remote Chemical Analysis*, R.M. Measures, ed., Wiley, New York, Chap. 3, (1988).

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Supporting Online Material

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Materials and Methods

Figs. S1-S13.

Tables S1, S2.

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Table 1. Curiosity TLS-SAM methane measurements at Gale Crater (4.5 S, 137.4 E) over a 20-month period.
SEM=standard error of the mean. L_s=solar longitude. CI=confidence interval.

Martian Sol after landing Aug 6 th 2012	Earth date	L _s (deg)	Gas ingest time/cell pressure (mbar)/foreoptics pressure (mbar)	Mean value ± 1SEM (ppbv)	Mean value ± 95%CI (ppbv)
79	Oct 25 th 2012	195.0	Night/8.0/11.5	-0.51 ± 2.83	-0.51 ± 5.55
81	Oct 27 th 2012	196.2	Night/8.0/11.5	1.43 ± 2.47	1.43 ± 4.84
106	Nov 27 th 2012	214.9	Night/8.5/10.9	0.68 ± 2.15	0.68 ± 4.24
292	Jun 1 st 2013	328.6	Night/8.7/9.2	0.56 ± 2.13	0.56 ± 4.17
306	Jun 16 th 2013	336.5	Day/8.1/0.0	5.78 ± 2.27	5.78 ± 4.45
313	Jun 23 rd 2013	340.5	Night/8.7/0.0	2.13 ± 2.02	2.13 ± 3.96
466	Nov 29 th 2013	55.7	Night/8.0/2.3	5.48 ± 2.19	5.48 ± 4.29
474	Dec 6 th 2013	60.6	Night/7.9/2.3	6.88 ± 2.11	6.88 ± 4.14
504	Jan 6 th 2014	72.7	Night/8.1/2.3	6.91 ± 1.84	6.91 ± 3.63
526	Jan 28 th 2014	81.7	Day/7.5/2.3	9.34 ± 2.16	9.34 ± 4.23
573	Mar 17 th 2014	103.4	Night/5.3/2.3	0.47 ± 0.11	0.47 ± 0.21
684	Jul 9 th 2014	158.8	Night/4.5/2.7	0.90 ± 0.16	0.90 ± 0.31
684	Jul 9 th 2014	158.8	Night/6.8/2.7	0.99 ± 2.08	0.99 ± 4.08
Mean value of “low methane” sols 79, 81, 106, 292, 313, 684 =				0.89 ± 0.92	0.89 ± 1.83
Mean value of “low methane” enrichment results for sols 573 and 684 =				0.69 ± 0.10	0.69 ± 0.21
Mean value of “high methane” sols 466, 474, 504, 526 =				7.19 ± 1.02	7.19 ± 1.99

Figure 1. The TLS-SAM methane measurements vs. martian sol. Plotted values are from Table 1, with error bars representing ±1 SEM. Those with larger error bars are the direct ingest results, and the two with smaller error bars labelled EN are the values retrieved from the “methane enrichment” runs. All measurements are made from nighttime ingest, except the two marked “D” that are ingested during the day and analyzed at night. The last direct ingest value (plotted near sol 700) occurred during the same sol 684 as the last enrichment run, but is offset to higher sol value to separate the points for visual clarity. The shaded boxes show the occurrence and duration of the SAM evolved gas analysis (EGA) runs for RK=Rocknest, JK=John Klein, CB=Cumberland and combustion during which gases evolved from rock samples were introduced into SAM and a portion fed into the TLS sample cell for analysis.