THE PARADOX OF MARS METHANE. K. Zahnle[1], D. C. Catling[2]. [1]Space Science and Astrobiology Division, NASA/Ames Research Center, Moffett Field, CA, 94086. [2]Earth & Space Sciences/ Astrobiology Program, Univ. of Washington, Seattle WA 98195-1310.

Methane on Mars continues to attract a great deal of attention. In 2019 alone, methane has been both confirmed [1] and denied [2]. To satisfy everyone, methane must react 1000 times more quickly with martian materials than can be deduced from laboratory experiments performed on Earth [3,4], which is surprising given that methane and its interactions have been exceptionally well-studied on Earth. The simplest solution to the apparent paradox is that the detections are mistaken. Here we present Mars Science Laboratory (MSL, aka Curiosity Rover) data in possibly unfamiliar ways. We report, you decide.

The recent history of methane observations on Mars is plotted in Figure 1. Detections and upper limits are plotted. The overall trend is that methane's abundance has declined in lockstep with the accuracy of the observations. The most recent, made independently by the Nadir and Occultation for MArs Discovery (NOMAD) and Atmospheric Chemistry Suite (ACS) instruments on the Roscosmos-ESA Trace Gas Orbiter (TGO), are by far the most sensitive, numerous, and spatially comprehensive. These set the lowest upper bounds, with the most stringent of these being 0.05 ppbv [2].

Of the detections, *in situ* measurements made by the Tunable Laser Spectrometer (TLS) in the Sample Analysis at Mars (SAM) instrument package on MSL have received the most attention [5-7]. SAM-TLS reports methane at levels well above what is believed to be the instrument's performance floor [6,7]. SAM-TLS employs two different measurement strategies: a "direct ingest" mode that directly samples martian air, and an "enhanced" mode in which CO2 is removed to concentrate unreactive gases [6]. The modes give different results and are plotted separately on Fig. 1.

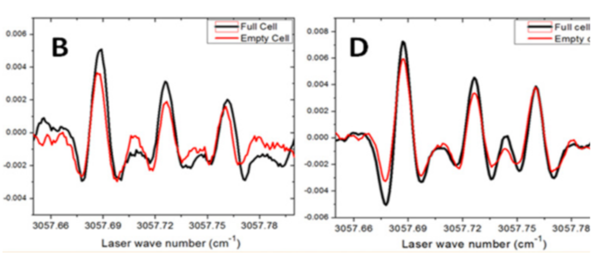

Figure 2. Screenshots of two strong CH4 detections [6]. "B" sums all reported data for Sol 474 (direct). "D" sums data (as edited by [6]) from Sols 573 and 684, the first two enrichment experiments. Mars CH4 is retrieved from the **difference** between the red and black curves. Almost all the methane seen here is instrumental background, as discussed in [7].

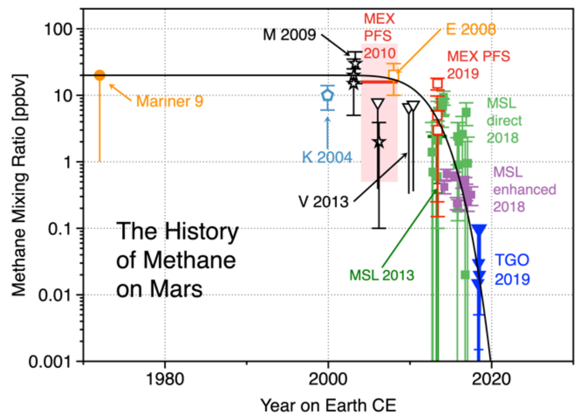

Figure 1. Reported detections and upper limits of methane mixing ratios on Mars. Mariner 9 upper bound used the 7.8 micron band [8]; the others are obtained at 3.3 microns. Ground-based telescopic measurements are reported by [3,9-11]. Several orbiter-based reports [12-15] use the MEX (Mars Express) PFS (Planetary Fourier Spectrometer). PFS results from 2004-2008 scatter randomly between 0 and 61 ppbv, with a mean of 15 ppbv [12-14]; these are plotted as a box and a solid line, respectively. "E2008" refers to an MEX-PFS retrieval presented with great skepticism [15]. Three iterations of *in situ* measurements [5-7] use the SAM-TLS instrument package on MSL. "Direct-ingest" and "enhanced" modes give different results and are plotted separately. Recent stringent upper limits [2] obtained by TGO are plotted at three epochs in 2018. "MEX PFS 2019" uses an improved model of Mars's atmosphere transmission to treat observations taken at roughly the same time and place as Sol 306 *in situ* observations made by MSL [1]. The black line is our arbitrary curve fit to the ensemble, and of course implies nothing, although extrapolation bodes ill for methane in the future.

Figures 2-6 document methane detections made by MSL in the two modes. Figure 2 shows what the cumulative data look like for two of the strongest methane detections [6]. Figures 3 and 4 are histograms of the individual measurements of empty and filled sample cells for these detections. The scatter is used to estimate errors in the means assuming Gaussian noise [6]. The reported detections are the differences between the filled and empty means. Figure 5 and 6 compare the results obtained by the direct and enhanced modes [7]. Figures 5 and 6 imply that measurement uncertainties are not due to random noise.

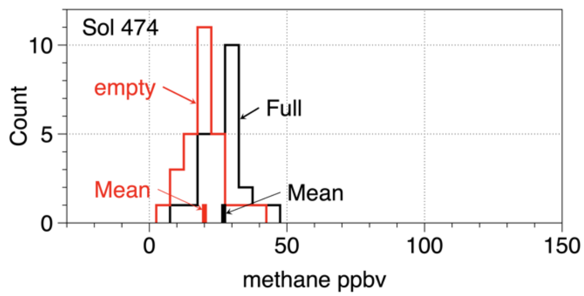

Figure 3. Histograms of the individual measurements of the Herriot cell (sample chamber) when empty and when filled with the direct-ingest atmospheric sample on Sol 474, derived from supplementary material to ref. [6]. The difference between the means corresponds to detection of 6.88±2.11 (one sigma).

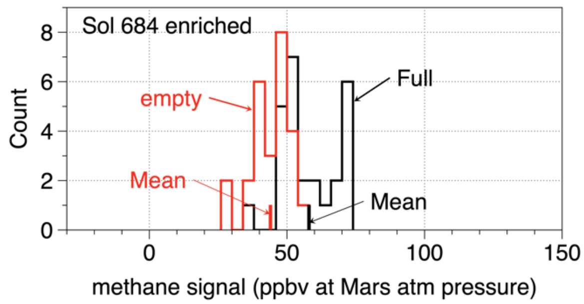

Figure 4. Histogram of individual measurements on Sol 684 using an enriched sample, derived from the supplementary material to ref. [6]. The "full" distribution is bimodal. It arguably contains information exceeding that of Gaussian noise centered on the mean. Sol 684 gave the largest SAM-TLS CH4 abundance measured by the enrichment method to date (0.653±0.121, [7]).

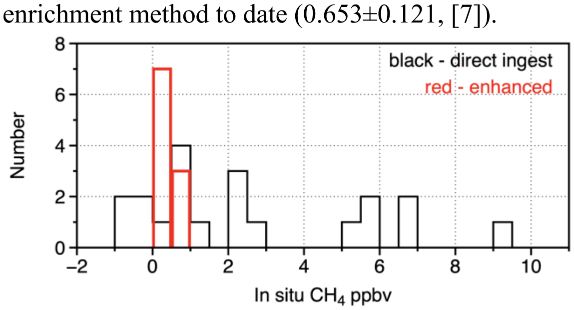

Figure 5. Histograms of all 30 MSL measurements of methane on Mars, reported as concentrations in Martian air (Table S2, ref. [7]). The two distributions are mutually inconsistent. Half the direct measurements exceed 2 ppbv, while all enhanced measurements have less than 0.7 ppbv. The odds that the two distributions sample the same parent distribution are of the order of 10^{-3}. Alternatively, the error in the direct ingest measurements must be of the order of 5 ppbv to provide the observed scatter, i.e., the uncertainty has the same order of magnitude as the reported detections.

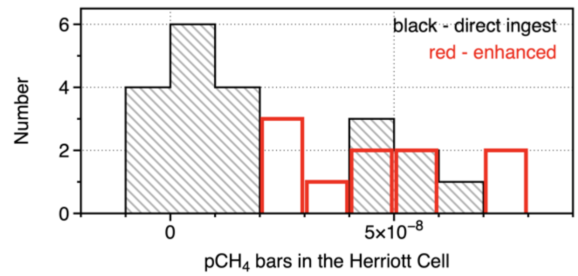

Figure 6. Histograms of what was actually inferred to be in the Herriot cell for the same 30 measurements; i.e., we are reconstructing what was actually measured. We account for the higher concentrations but lower pressures in the Herriot cell during the enhanced measurements using supplemental information to ref. [6]. These two histrograms less dissimilar, and there is considerable likelihood that they sample the same parent distribution. This is consistent with MSL methane being artifacts of the measurement process or of the data reduction process.

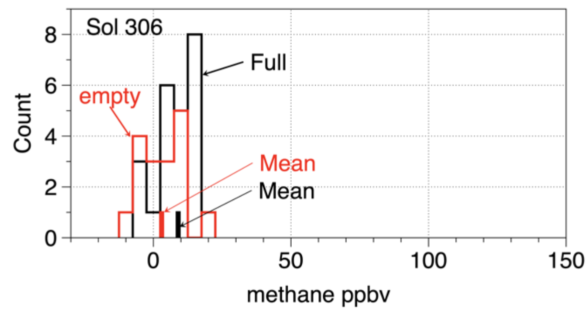

Figure 7. Histogram of individual measurements on Sol 306, after the "empty" data were revised, using supplemental information to ref. [6]. The difference in means is 5.78±2.27 (one sigma). Sol 306 was initially listed as -2.21±0.94 [5] before the abherent data were deleted. The difference of 8 ppbv in the same measurement suggests that this is the magnitude of SAM-TLS systematic uncertainties. MEX-PFS report a detection of 15±2.5 on this date [1].

References:

[1] Giurrana et al. (2019) Nat. Geosci. 12, 326. [2] Korablev et al (2019) Nature 568, 517. [3] Krasnopolsky et al. (2011) Planet. Sp. Sci. 59, 52. [4] Zahnle et al. (2011) Icarus 212, 493. [5] Webster et al. (2013) Science 342, 355. [6] Webster et al. (2015) Science 347, 415. [7] Webster et al. (2018) Science 360, 1093. [8] Maguire (1977) Icarus 32, 85. [9] Krasnopolsky et al. (2004) Icarus 172, 537. [10] Mumma et al. (2009) Science 323, 1041. [11] Villanueva et al. (2013), Icarus 223, 11. [12] Formisano et al. (2004), Science 306, 1758. [13] Geminale et al. (2008), Planet. Sp. Sci. 56, 1194. [14] Geminale et al. (2011), Planet. Sp. Sci. 59, 137. [15] Encrenaz (2008), Adv. Space Res. 42, 1.