THE MUDDY MATTER OF METHANE ON MARS. K. J.. Zahnle[1], R. S. Freedman[1], and D. C. Catling[2], [1]NASA Ames Reseacr Center (MS 245-3 NASA Ames Research Center Moffett Field CA 94043), [2]University of Washington (Box 351310, Dept. Earth & Space Sciences, Univ. of Washington, Seattle, WA).

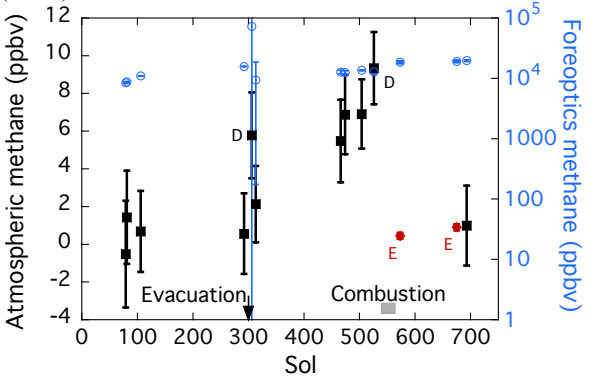
Introduction: The story of methane on Mars begins with its first discovery in 1969. That announcement, based on a spectrum obtained 48 hours earlier by Mariner 7, was greeted by "a general gasp from the [assembled] scientists and newsmen" and a front page story in the New York Times [1]. It was only after getting some sleep that the team realized they had actually seen a forbidden band in frozen CO2 [2]. But the fascination with methane – the simplest, most stable, and most abundant organic molecule in the cosmos – has not gone away. Methane does not have a known chemical source in an atmosphere like Mars's, and its lifetime – standard photochemistry predicts 300 years [3] – is short enough that its presence in the atmosphere almost demands an exciting source. Pursuit has been vigorous and there have been many subsequent discoveries of variable credibility and consistency [3-6]. The reports describe an ephemeral gas with a lifetime of weeks or months rather than the expected 300 years, and the best of them describes phenomena seen only during the winter of 2003 [5]. We have previously questioned whether these reports are compelling [7]; we will briefly review why.

Its back! The TLS/SAM experiment on the MSL Curiosity rover was intended to resolve the matter by looking for a distinctive pattern of spectral lines that uniquely identifies methane [8]. The TLS gets its sensitivity by reflecting an infrared laser beam dozens of times across the length of the cell holding the gas sample. The wavelength of the laser can be varied enough to map out a thin but extremely highly resolved sliver of spectrum carefully chosen to measure CH4. The good news is that a lot of methane is seen. The bad news is that little of the methane is martian. Most is in the foreoptics to the sample cell, and comes from several sources, known and unknown, in the rover itself. The small difference between the signal obtained when there is martian air in the cell and the signal obtained when the cell is empty is attributed to methane of Mars.

Figure 1 of Webster et al [9] chronicles the story of these differences. At first no martian methane was seen, both while the rover was awash in stowaway Florida air and then after the foreoptics were evacuated. But later, as methane slowly built up again inside the foreoptics, apparently martian methane was seen in four samples of Mars air at levels on the order of 7 ppbv. The statistics of any one measurement are marginal but the four measurements are self-consistent. After the fourth sighting, TLS/SAM performed the first of two higher-sensitivity enrichment experiments, only to find the methane nearly gone. A second enrichment experiment done 3 months later gives a low but nonzero CH4 abundance of 0.9 ppbv. Although 0.9 ppbv may not seem like much, it is more than can be easily explained by degrading incoming exogenic organic matter. Even at 0.9 ppbv, CH4 is exciting.

The yellow tape: William of Ockham would warn us to be wary of peekaboo methane when a known source – the rover – is so near at hand. Number crunching data given in the tables in the supplemental online material reveals that the concentration of methane inside the foreoptics is 1000X higher than in the martian air; it would not take much, and the stowaway Florida air establishes that there are leaks. But it would be a mistake to be too confident that indigenous methane was never there. We know very little about Mars. A synchronous report that O2 (!) is seasonally variable (from Chemcam, another Curiosity instrument, reported in [9]) sends a clear warning that theory may be missing something fundamental about Mars's atmosphere. Methane could be caught up in this.

References: [1] Sullivan W., *N. Y. Times,* Aug. 8 (1969). [2] Herr K. and Pimentel G., *Science 166,* 496 (1969). [3] Krasnopolsky V. et al., *Icarus 172,* 537 (2004). [4] Formisano V. et al., *Science 56,* 1758 (2004). [5] Mumma M. et al., *Science 323,* 1041 (2009). [6] Fonti S. and Marzo G., *Astron. Astrophys. 512,* A51 (2010). [7] Zahnle K. et al., *Icarus 212,* 493 (2011). [8] Webster C. and Mahaffy P. *Planet Sp. Sci. 59*, 271 (2010). [9] Webster C. et al., *Science 347,* 415 (2015).



Redraft of Fig. 1, Webster et al [9]. "D" are daytime measurements, "E" enrichment. Foreoptics CH4 – FL air before evacuation, rover sources thereafter – computed from table S2 in SOM [9].