Is there Methane on Mars? Part II

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There have been several reports of transient methane in the martian atmosphere at 10-60 ppbv [1-5]. The credibility of the reports has been enhanced by their independence and mutual consistency. Here we review why abundant variable methane on Mars should be seen as an extraordinary claim and show why the published reports fall short of providing extraordinary evidence.

An extraordinary claim

If present, methane on Mars is highly variable both in time and place [2-5]. The variability demands that methane's lifetime in the atmosphere be short, weeks or months at most [6]. Variability implies both a strong source and a strong sink. Most discussions of methane on Mars have focused on possible sources [1-4,7-12]. On the other hand, the sink must act in the open, either in the atmosphere or at the surface, and can be addressed in the context of what is known about Mars [13].

Conventional atmospheric chemistry predicts that methane should have a 200-300 year lifetime on Mars [14-16]. The experimental basis of methane's chemistry is well established in Earth's atmosphere at conditions that do not differ greatly from those of Mars. Thus it is extraordinary that methane's life on Mars should be measured in weeks or months rather than the hundreds of years that terrestrial experience would predict.

Speculation has focused on oxidation at the surface or on grains, possibly involving exotic oxidants or electric discharges or both [10,13]. Any such mechanism would be expected to oxidize CO more easily, yet at $\sim$800 ppmv, CO remains abundant. It is also important to recognize that powerful martian oxidants have their origin in the atmosphere, and that the primary source of the oxidants is hydrogen escape following water vapor photolysis. Electric discharges create oxidants and reductants in equal number. The latter must be channelled into hydrogen escape if electric discharges are to have a net oxidizing effect. Whether methane is oxidized in the atmosphere or on the surface, methane oxidation must ultimately consume oxidants generated in the atmosphere.

Persistent short-lived methane at a mean abundance of 15 ppbv [3] would also have major consequences for the martian atmosphere as a whole. To illustrate the problem, consider oxidation of 30 ppbv methane to 0 ppbv methane in four months. This equates to a methane destruction rate of 6.5×10^8 cm^{-2}s^{-1}, equivalent to an O_2 destruction rate of 1.3×10^9 cm^{-2}s^{-1}. At this rate the $\sim$1300 ppm of O_2 in Mars's atmosphere would be destroyed in 7000 years. This is an order of magnitude faster than H_2O photolysis and subsequent H escape ($2 \times 10^8 - 4 \times 10^8$ H atoms cm^{-2}s^{-1}) can create new O_2 [16,17]. In other words, if methane is both persistent [3,5] and variable on the reported time scale, the *two* biggest terms affecting the chemistry of the Martian atmosphere — methane oxidation *and* the unknown but necessary source of oxidizing power to react with the methane — have *both* been overlooked. This is alarming given that conventional models do a good job of accounting for the abundances of known trace species in Mars's atmosphere [17-19].

It is of course possible to invoke intermittent methane releases that are rare enough not to overwhelm the redox budget of the atmosphere. Methane's mean mixing ratio could then be less than 1 ppbv, which would be small enough to fit under the cap set by hydrogen escape to space. But doing so rejects the spacecraft evidence that the mean methane abundance is 15 ppbv [3]. A large part of what makes methane on Mars seem credible to a wider community is that the methane was seen independently from Mars orbit and from Earth. The case for methane is considerably weakened if the space-based observations are spurned.

It is also imaginable that methane condenses and evaporates seasonally as an adsorbate or in clathrates, and thus is not consumed. Such processes are not constrained by atmospheric chemistry [19,20]. However, methane is outcompeted for adsorption sites by more abundant polar molecules such as H_2O and H_2O_2 and by some nonpolar molecules, including CO_2 and xenon. At $\sim$60 ppbv, Xe is more abundant than methane. The continued presence of Xe in the atmosphere suggests that methane adsorption could not be effective. Methane can enter clathrates, but the CH_4/CO_2 ratio in the clathrate would be lower than in the atmosphere. Thus quantitative removal of methane in clathrates would be accompanied by quantitative removal of CO_2 into clathrates. Similar arguments apply for Xe clathrate, which is more stable than either CO_2 or CH_4 clathrate. Finally, GCM simulations show no correlation between the reported spatial patterns of methane variability and the computed spatial patterns of CO_2 condensation [6].

A biological sink fails to account for why rare CH_4 is eaten but abundant CO is not.

Extraordinary evidence?

Spacecraft observations [2,3] use the PFS instrument on *Mars Express.* Spectral resolution is coarse (1.3 cm^{-1}) and the putative signal weak. Methane is inferred indirectly by adding CH_4 to a multi-parameter radiative transfer model. Despite the low resolution, the computed methane feature (essentially the width of the Q branch) is twice that of the purported 3018 cm^{-1} methane feature. The effect of adding methane is comparable to the mismatch between model and data seen at other wavelengths.

Ground-based observations must contend with Earth's atmosphere, which is ∼60 times thicker than Mars's and contains ∼1.8 ppmv methane. Thus it is necessary to exploit the Doppler shift when Mars is approaching or receding from Earth. If we accept for argument that there are 20 ppbv methane on Mars, there are 5400 terrestrial methane molecules to look through to see one martian methane molecule. In practice it is not quite so bad as that (the sunlight passes twice through Mars's atmosphere, and one observes from a mountaintop), but still it is to be expected that the terrestrial $^{12}CH_4$ lines are 2000 times stronger than their putative martian counterparts. Even terrestrial $^{13}CH_4$ lines are 20 times stronger than the martian $^{12}CH_4$ lines.

Krasnopolsky et al [1] observed one component of ν_3 $^{12}CH_4$ P4 in blueshift. The retrieved methane signal does not obviously exceed the noise background, and it appears embedded in a wavelet pattern suggestive of instrumental ringing. If this be methane, it would be consistent with an abundance of 10 ppbv.

Mumma et al [4] used the R0 and R1 lines of the ν_3 band of $^{12}CH_4$. The apparent methane signature is easy to see in their Fig. 1. These observations were made when Mars was in approach at 15-16 km/s in January of 2003, so that the putative martian lines were blueshifted by 0.15-0.16 cm^{-1}. Significant methane was not detected at R0 and R1 three years later when Mars was receding at 16-17 km/s from the Earth, for which the martian lines were in redshift [4]. The upper limit appears to be ∼3 ppbv.

The redshift/blueshift dichotomy is interesting. It suggests that there might be an explanation other than seasonality. We looked at the HITRAN database and found that strong $^{13}CH_4$ R1 and R2 lines are superposed on the blue wings of the $^{12}CH_4$ R0 and R1 lines. The separations between line centers are 0.10 and 0.12 cm^{-1}, respectively. These separations are comparable to the Doppler blueshifts of 0.15-0.16 cm^{-1} of the 2003 observations, and lumps the telluric and martian lines within the 0.08 cm^{-1} spectral resolution of the instrument. Because the telluric $^{13}CH_4$ lines are ∼20 times stronger than the putative martian $^{12}CH_4$ lines, the correction for telluric $^{13}CH_4$ — which depends entirely on a model of transmission through Earth's atmosphere [4] — needs to be extremely good if the much weaker martian lines are to be retrieved. The redshift observations do not suffer from this problem.

Martian methane was also reported in $^{12}CH_4$ P2 at a blueshift of 0.11 cm^{-1} [4]. The blueshift superposes the martian line on a stronger and extremely temperature-sensitive telluric H_2O line. Given the variable humidity and temperature in Earth's atmosphere, modeling transmission through this line would be extremely challenging.

Summary

Abundant methane on Mars would be an extraordinary result. However, none of the reported detections provide extraordinary evidence. The strongest reported signals are at frequencies where telluric interference is especially difficult to remove. By contrast, the most favorable of the published observations, of the $^{12}CH_4$ ν_3 R0 and R1 lines taken in redshift in 2006, are consistent with no methane on Mars at the 3 ppbv level [4]. We conclude that there is as yet no compelling evidence for methane on Mars, and that the upper limit may be as small as 3 ppbv.

References [1] Krasnopolsky V, Maillard J, Owen T (2004) *Icarus 172,* 537. [2] Formisano V, Atreya SK, Encrenaz T, Ignatiev N, Giuranna M (2004) *Science 306,* 1758. [3] Geminale A, Formisano V, Giuranna M (2008) *Planet. Space Sci. 56,* 1194. [4] Mumma M, Villanueva G, Novak R, Hewagama T, Bonev B, DiSanti M, Mandell A, Smith M (2009) *Science 323,* 1041. [5] Fonti S, Marzo G (2010). *Astron. Astrophys. 512,* id.A51. [6] Lef'evre F and Forget F (2009) *Nature 460,* 720. [7] Lyons J, Manning C, Nimmo F (2005) *Geophys. Res. Lett. 32,* L13201. [8] Bar-Nun A, Dimitrov V. (2006). *Icarus 181,* 320. [9] Krasnopolsky V (2006) *Icarus 180,* 359. [10] Atreya S, Mahaffy P, Wong A (2007) *Planet. Space Sci. 55,* 358. [11] Chastain B, Chevrier V (2007) *Planet. Sp. Sci. 55,* 1246. [12] Chassefière E (2009) *Icarus 204,* 137. [13] Farrell W, Delory G, Atreya S (2006) *Geophys. Res. Lett. 33,* L21203. [14] Summers M, Lieb B, Chapman E, & Yung Y (2002) *Geophys. Res. Lett. 29,* 2171. [15] Wong A, Atreya S, Encrenaz T (2003) *J. Geophys. Res. 108,* 5026. [16] Krasnopolsky V (2006). *Icarus 185,* 153. [17] Nair H, Allen M, Anbar A, Yung Y, Clancy R (1994) *Icarus 204,* 137. [18] Zahnle K, Haberle R, Catling D, Kasting J (2008) *J. Geophys. Res. 113,* E11004. [19] Yung Y, Russell M, Parkinson C (2010) *J. Cosmo. 5,* 1121. [20] Gough R, Tolbert M, McKay C, Toon O (2010) *Icarus 207,* 165.