

Methane on Mars

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Finally, the Eureka Moment!

In 2004, the first reports of methane (CH₄) in Mars' atmosphere, by both *Mars Express* and ground-based observations, stirred up excitement in the scientific community [1,2]. These detections (at 10 ppbv level) immediately raised questions regarding the origin of methane. On Mars, oxidants and UV radiation destroy atmospheric methane in approximately 300 yrs [3]. Therefore, the presence of atmospheric methane requires ongoing or recent methane emission. On Earth, methane is almost entirely of (live and fossil) biological origin, while abiotic sources, believed to be predominantly volcanic and/or hydrothermal, account for the rest (a few percent) of the total CH₄ flux into the atmosphere [4]. The conventional understanding of Mars is in stark contrast: decades of exploration have not found life or active volcanism, although localized outgassing sources cannot be ruled out, and we know that past Martian volcanism until perhaps only a few million years ago had existed [5]. Consequently, a methane detection impacts Mars science and astrobiology in very fundamental ways. It turns the theoretical musing of possible life on Mars into a necessary investigation component for interpreting observational data. It elevates the possibility of hydrothermal activity on Mars, which can be habitable environments providing liquid water and redox energy to sustain life. Moreover, it compels new research directions to explore novel processes that can produce methane on Mars.

Subsequent to the 2004 reports, several teams reported high spatial and temporal variability, including plumes of up to 60 ppbv methane. The variability posed an even greater theoretical challenge than the sheer presence of CH₄. Methane's predicted 300-year atmospheric lifetime is far longer than global mixing time of about a month [6-9]. Hence, methane should be uniformly distributed in the Martian atmosphere. Introducing novel, much more efficient sinks can shorten the predicted lifetime [10]. However, a strong sink, whatever its nature, would also require a source that seems implausibly strong. Indeed, Lefevre and Forget [9] stated that the observed variations of methane on Mars are not explained by known atmospheric chemistry and physics at the time. However, these previous remote-sensing detection claims have been called into question, due to interference from telluric absorption in the ground-based observations, low spectral resolution in the orbital observations, and contradictions between the locations of maxima reported from ground-based observations and maps inferred by the Planetary Fourier Spectrometer (PFS) and Thermal Emission Spectrometer (TES) [9,11,12].

Therefore, a definitive measurement from the Mars Science Laboratory (MSL) had been highly anticipated. In particular, MSL's Tunable Laser Spectrometer (TLS) instrument has superb spectral resolution to definitively measure methane on Mars.

Lo and behold, TLS's latest measurements indicate a background CH₄ mixing ratio of 0.7 ppbv and a pulse of 7 ppbv observed over two months [13]. These findings suggest at least two types of methane emission are at work, a constant emission producing the background level and a pulse mechanism. Some time is required for the scientific community to fully vet these results to rule out any possible sources of error [14]. If it is borne out, this discovery becomes one of the greatest

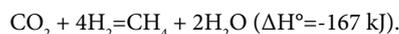
Eureka moments in the half century of robotic exploration of Mars, beginning with the first success of Mariner 4 in 1965 and reaching such ambitious milestones as the Viking landers [15-17] and *Curiosity* rover [18]. These intriguing findings promise to compel a new era of Mars and astrobiological research to explain methane's existence and variability in the Martian atmosphere.

Potential Origins

The question regarding the origin of methane raises tantalizing possibilities regarding potential life and habitability on Mars. As discussed above, methane's atmospheric existence requires a recent or continually replenishing source, which challenges the conventional framework of a geologically and biologically dead Mars [19].

Furthermore, methane's high variability, despite an atmospheric mixing rate that is much shorter than its chemical lifetime [3,9,10,20,21], defies explanation to date. This discovery necessarily opens a new era of research pursuing answers to the questions: What is generating methane? How is it destroyed or sequestered on Mars?

Extrapolating our knowledge of terrestrial biotic sources to Mars, many consider methanogens (a type of Archaean microbe) as a probable analog to Martian life forms [22-24]. Some methanogens are able to utilize inorganic compounds (H₂ and CO₂) as their only source of energy through the following methane-generating redox reaction [4,22]:



Being independent of sunlight/photosynthesis for subsistence, methanogens thrive in deep subsurface locales where CO₂ is the predominant oxidant and H₂ (aq) is abundant from water-rock interactions (ferrous-ion reduction of H₂O to H₂ during serpentinization). H₂ may also come from photochemical dissociation of H₂O in the atmosphere [23]. In fact, methanogens thrive in some of the harshest environments on Earth, including extremely acidic environments and inside Greenland glacial ice 3-km deep, which is analogous to Martian subsurface ice environments [25-28].

Alternatively, many researchers favor Fischer-Tropsch-type (FTT) reactions as a potential methane source [4,10,29]. FTT is the most widely posited abiotic source of methane on Earth. Catalyzed by transition metals (Ni, Fe, Co, Cr, Ru) and related oxides, these reactions have the same overall chemical equation as the methanogenesis reaction above,

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and take place in hydrothermal environments [30]. Abundant evidence indicates that volcanism and hydrothermal environments existed, and might still exist, on Mars [5,31,32]. If these environments do exist on current Mars, they may provide warmth and liquid water to support FTT and/or microbial methane production. Thus, CH₄ in Mars' atmosphere can point to either serpentinization or the existence of life itself, both of which are associated with a hydrothermal, habitable backdrop.

Other proposed sources of Martian methane include volcanic/magmatic degassing [33,34], exogenous delivery [35-39] and release from clathrates [40]. It would be premature to adopt or dismiss any of these hypotheses, or to suppose there can be no others.

Potential Sinks

From the surface to 60 km altitude, excited oxygen atoms, O(¹D), and OH destroy methane. As mentioned above, the resulting methane lifetime is about 300 years, so the observed variability on timescales of months to years is unexpected. Introducing novel, much more efficient sinks can shorten the predicted lifetime [10]. It is worth noting that MSL's ChemCam instrument reported anomalous O₂ depletion that appears to be temporally correlated with CH₄ enhancements, evoking questions of whether an unknown oxidizing sink exists on Mars [41]. However, a strong sink, whatever its nature, would require a source that seems implausibly strong [9]. Sequestration is another possibility [42,43], especially if we can find a mechanism that is both efficient enough, and reversed by changing conditions on Mars, to produce the observed methane-abundance variations.

The Pulsing Sources

While there is more than one explanation for the steady background CH₄ of about 0.7 ppbv, the pulse of 7 ppbv defies a simple explanation. Because a serpentinization source would likely be located a few kilometers below the surface [30], it is difficult to concoct a release mechanism that is so confined in time. The transport from the source region to the planetary surface is a steady diffusive process and no model has produced a localized pulse. Similarly, the action of UV on organics is a diffuse process [37-39] and is not expected to prefer a particular location or time.

Analogy with the CH₄ emission from terrestrial permafrost may be illuminating. Episodic bursts of CH₄ from Arctic tundra have been observed during several weeks of thawing and freezing [44,45]. Each short-lived pulse of CH₄ emission often equals the integral of the background emission from the rest of the year. Most of the CH₄ is of microbial origin, and is produced and sequestered in the first few centimeters of soil, and then released to the atmosphere as the near-surface thaws or freezes. Potential future investigations involving, e.g., abundance correlations with ground temperature and temporal-spatial patterns in methane abundance and stable-isotope compositions can shed light on whether or not such seasonal cryo-trapping is at work on Mars [46].

Journey into the Unknown

Resolving the methane sources and sinks on Mars will require an exploration and technology-development strategy. Existing hypotheses of Martian methane sources include gas-water-rock chemistry [30] and microbes (methanogens) [23]. If proven, the former implies the existence of environs offering liquid water and chemical sources of energy—i.e. habitability—while the latter implies the discovery of life on Mars. Solving these planetary-scale puzzles requires a concerted

research effort across many disciplines. Resulting hypotheses regarding Martian methane's sources and sinks will undoubtedly call for major technological advancements, including new measurement and exploration capabilities and methodologies.

The foregoing overview points to a myriad of interrelated questions that impact future Mars exploration such as:

- Do methane-producing organisms exist in the Martian subsurface?
- Are there geological hotspots or hydrothermally-active environments generating methane on Mars?
- Are there sinks or sequestration sites for methane on Mars?
- What are the measurable signatures for hypothesized methane sources and sinks/sequestration sites?
- How does one distinguish biotic and abiotic sources using a combination of existing tools and novel methodologies?
- Can the ultraviolet degradation of accreted interplanetary or carbonaceous material explain the observed pulse of elevated methane?

Answers to these important questions dictate fundamental aspects of future Mars exploration strategy and mission design, including landing site selection, requirements for drilling capability, requirements on deployable platforms (e.g. higher mobility rovers, balloons/airships), requirements for instrument capabilities to detect relevant (e.g. molecular, isotopic, thermal, morphological) signatures, and mission durations relevant to expected dynamical time-scales. In particular, it is already clear that major advancements in instrument technology will surely be needed. Past and existing orbiting instruments have had difficulties producing convincing evidence to answer first-order questions: Does methane exist and how much? In-situ, MSL-TLS accomplished this feat and also observed temporal variability, but it had to reach deep into its capability. The next level of questions, regarding sources, sinks, sequestration, and transport, will demand major new measurement and exploration capabilities.

A future Mars exploration program will have to bring together complementary expertise that is necessary to generate synergy in creating innovative ideas and a comprehensive roadmap. Advances in the fields of Mars exploration and instrumentation will be driven, augmented and supported by an improved understanding of deep-subsurface biogeochemistry, astrobiology, planetary geology, atmospheric chemistry, atmospheric dynamics, and remote sensing, as well as the study of Mars climate evolution, clumped-isotope analysis, stable-isotope analysis, origins of life, biosignatures, methane emissions from permafrost, and hydrothermal processes and signatures.

May the Eureka moment crystallize into a new phase of exploration with further expansion of the interdisciplinary enterprise of life and environment on Mars [47]!

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