

Is Mars Alive?

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Mars long has been considered a cold, dead planet. However, recent reports of methane in the Martian atmosphere [Formisano *et al.*, 2004; Krasnopolsky *et al.*, 2004; Mumma *et al.*, 2004] suggest that methane currently is being produced, since its calculated atmospheric lifetime of 400 years or less [Nair *et al.*, 2005] requires a constant resupply. Possible subsurface sources for this resupply are geological, or even microbiological, in nature. So the question is: Is Mars alive, biologically or geologically speaking?

If either geological or microbiological sources of methane on Mars can be confirmed, there will be profound implications for astrobiology and the U.S. space program. If the existence of active microbiology were established, it would not be surprising if NASA reorganized its mission plan to follow-up on such a discovery. Additionally, current geological processes that result in the formation of methane would be in locations that are warm and wet, and thus likely habitable. If key nutrients such as nitrogen and phosphorus—in addition to liquid water—also were available, such locations could support life, and not necessarily just methane-producing organisms.

However, if these environments were found not to be inhabited, fundamental astrobiological notions about the requirements for the presence of life would be challenged. Such a conclusion would greatly reduce the expectations for life elsewhere in the galaxy. Therefore, an understanding of the processes producing Martian atmospheric methane, and the places on Mars from which it arises, will have wide scientific and sociological implications.

There are several different processes on Earth, both biogenic and abiogenic, that form methane at rates that can contribute to a detectable atmospheric presence. Techniques used to characterize these various terrestrial sources can guide planning for future Martian investigations and flight missions.

By M. ALLEN, B. SHERWOOD LOLLAR, B. RUNNEGAR, D. Z. OEHLER, J. R. LYONS, C. E. MANNING, AND M. E. SUMMERS

Terrestrial Methane Formation: Potential Analogues for Martian Processes

Biogenic methane production results from extant biological activity (microbial methanogenesis) as well as from the thermal processing of complex organic remnants of past life (thermogenesis).

In the first instance, methane is the metabolic by-product of a single related group of microorganisms known as methanogens. Microbial methanogenesis results both from the reduction of carbon dioxide (CO₂) by hydrogen to form methane and water, and by the fermentation of a variety of organic substrates, including methanol, methyl amines, methyl sulfides, and methyl acetate. Methyl acetate is particularly interesting because it may decompose into methane and CO₂ without the addition of hydrogen. Microbes employing these different metabolic pathways variously emit—in addition to methane—molecular hydrogen, carbon dioxide or carbon monoxide, hydrogen sulfide or sulfur dioxide, methyl mercaptan, and ammonia.

The recycling of deeply buried insoluble organic material (kerogen) through thermogenesis is a delayed form of biogenic methane formation. In addition to methane, thermogenesis also can produce a series of light hydrocarbon gases (ethane, propane, butane). On Mars, more shallowly buried organic material from putative past life could be processed by thermogenesis initiated during impact events [Oehler *et al.*, 2005] or by heat from igneous intrusions.

Alternatively, terrestrial methane may be produced abiogenically in water-rock reactions in zones proximate to mantle-derived magma and in crustal contexts. The features that differentiate mantle-related from crust-derived abiogenic methane are as follows: (1) The temperature at which the relevant water-rock reaction occurs is higher in the former than in the latter; and (2) the source of carbon is CO₂ degassed from nearby magma in the former case and is crustal carbon (CO₂ or carbonate) in the latter.

Examples of water-rock reactions include the high-temperature reequilibration of mantle-derived CO₂ at temperatures of 500–600°C at mid-ocean ridges [Welhan and Craig, 1983], the thermal decomposition of carbonates at 300°C [McCollom, 2003], and serpentinization (a reaction between olivine and water that liberates hydrogen) followed by the reduction of CO₂ or carbon monoxide at

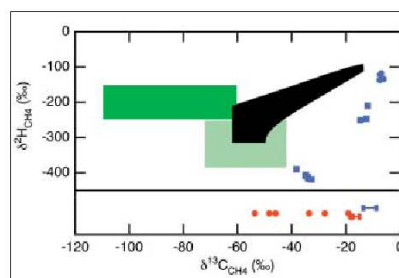


Fig. 1. Correlation of $\delta^2\text{H}$ values of methane with $\delta^{13}\text{C}$ values of methane from different terrestrial sources [after Onstott *et al.*, 2006]. Microbial methanogenic methane produced by the enzymatic reduction of CO₂ with hydrogen (solid green area) is isotopically lighter in carbon than methane produced by fermentation (hatched green area). Methane produced by thermogenesis (black area), derived from high-temperature water-rock reactions (red points) and derived from low-temperature water-rock reactions (blue points), have similar carbon isotope ranges but may differ significantly in hydrogen isotope composition. For some measurements, only $\delta^{13}\text{C}$ values are available (lower box).

lower temperatures ($\leq 200^\circ\text{C}$) [Abrajano *et al.*, 1990; Kelley *et al.*, 2005].

On Mars, igneous intrusions rising near to the surface or the geothermal gradient may provide heating sufficient for the presence of subsurface liquid water and consequently for water-rock reactions that lead to the abiogenic production of methane [Lyons *et al.*, 2005; Oze and Sharma, 2005]. Additionally, if the mantle of Mars is more reducing than the terrestrial mantle, direct degassing of methane is possible.

How to Distinguish Between Methane Source Processes?

On Earth, the relative abundances of methane carbon and hydrogen isotopologues (forms of methane differing in isotopic composition) and gaseous alkanes with up to four carbon atoms may be used to distinguish the various source processes. The three most common approaches (Figures 1–3) are based on (1) the correlation between the carbon ($\delta^{13}\text{C}$) and hydrogen ($\delta^2\text{H}$) stable isotope ratios of methane, (2) the correlation between the ratio of the abundance of methane (CH₄) to the sum of the abundances

of ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}) versus the $\delta^{13}C$ of the methane, and (3) the correlation between the $\delta^{13}C$ and δ^2H values for the first four alkanes (methane, ethane, propane, butane). Following normal convention, $\delta^{13}C$ and δ^2H are defined as

$$\delta^{13}C(\text{‰}) = \left[\frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{standard}}}{(^{13}C/^{12}C)_{\text{standard}}} \right] \times 1000 \quad (1)$$

$$\delta^2H(\text{‰}) = \left[\frac{(^2H/^1H)_{\text{sample}} - (^2H/^1H)_{\text{standard}}}{(^2H/^1H)_{\text{standard}}} \right] \times 1000 \quad (2)$$

Figure 1 shows that $\delta^{13}C$ values alone do not clearly distinguish between the different sources of methane, except when the $\delta^{13}C$ value is highly depleted in ^{13}C ($< -70\text{‰}$). However, the distribution of terrestrial $\delta^{13}C$ values is heavily weighted to values greater than -70‰ ; most analyses are therefore ambiguous. However, knowledge of δ^2H as well as $\delta^{13}C$ does separate samples with similar $\delta^{13}C$ values. Potentially, unique identification of the methane source may be possible by taking these two variables into account.

The ratio of the abundance of methane to ΣC_n (the sum of the abundances of C_2H_6 , C_3H_8 , and C_4H_{10}) clearly differentiates between microbial methanogenic and thermogenic origins of methane, particularly when this ratio is correlated with $\delta^{13}C$ (Figure 2). However, the separation between thermogenic and abiogenic products is not large and makes unique characterization difficult.

In an attempt to develop a more diagnostic method for distinguishing between thermogenic and abiogenic methane, terrestrial studies have focused on $\delta^{13}C$ plus δ^2H signatures for detectable alkanes (Figure 3). The trends in isotopic fractionation with carbon number show distinct differences between formation processes. While more experimental work confirming the range of isotopic variation associated with abiogenic water-rock reactions is necessary, these results suggest that having measurements of both $\delta^{13}C$ and δ^2H may discriminate between the two sources. Rather than comparing absolute $\delta^{13}C$ variations among samples, this approach focuses on deriving mechanistic information about reaction processes by comparing isotopic values among species in a reaction series [Sherwood Lollar *et al.*, 2002]. Such approaches, independent of source $\delta^{13}C$ values, will be particularly important for Mars methane studies where the absolute $\delta^{13}C$ values may lie far from terrestrial values due to planetary differences in the bulk isotopic composition.

The application of these terrestrial values to Martian investigations is ambiguous for two reasons: (1) The isotopic composition of methane and other molecules released by subsurface processes is directly related to the isotopic composition of the sources (feedstocks) from which these gases are formed; the latter is rarely known, and the large scatter in terrestrial values for a given process (Figure 1) is partly a result of differences in the isotopic composition of the

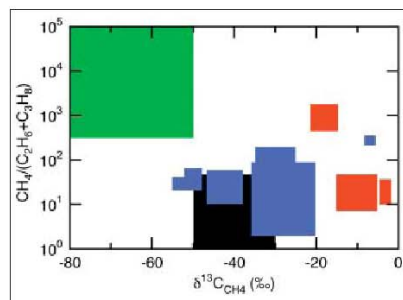


Fig. 2. Correlation of the ratio methane/(ethane + propane) with $\delta^{13}C$ (methane) for various sources of terrestrial methane, color-coded as in Figure 1. Microbial methanogenesis (green) due to either reduction of CO_2 or fermentation shows similar values for the alkane ratio. Note the clear discrimination between methane produced by microbial methanogenesis versus the various abiogenic sources. Modified after Horita and Berndt [1999].

source materials. (2) The large scatter also results from systems with multiple processes; separation of the contributions due to each typically has not been accomplished.

Deducing the source of Martian methane and estimating the magnitude of the source (e.g., the size of any biosphere) from atmospheric observations of the abundances of methane and its average isotopic composition are complicated by several factors. First, the Martian feedstock isotopic ratios may be hard to determine. Second, methane-consuming microbes, if they were to exist in or above the methane source region, could serve as a sink for methane, reducing the observed CH_4 flux from the level emitted in the source zone and modifying its isotopic composition. Finally, once methane enters the atmosphere, its decomposition processes may be isotopologue-dependent and introduce an additional isotopic fractionation in the residual fraction of methane of the atmosphere [Nair *et al.*, 2005].

What More Needs to Be Done?

The current approaches for identifying sources of terrestrial methane are mostly empirically derived and open to revision as new systems are investigated. For example, one experimental study suggests that biogenic isotopic fractionation has been found to decrease at elevated temperatures [House *et al.*, 2003]. However, one clear conclusion is that the measurement of the $\delta^{13}C$ value for Martian methane alone will not sufficiently distinguish geological from biology-related processes. While the presence of ethane, propane, and butane, in addition to methane, is widely held to distinguish a geological versus microbial origin for hydrocarbon gases, the $CH_4/\Sigma C_n$ ratio cannot distinguish between ancient biogenic (thermogenic) processes and abiogenic sources related to water-rock reactions (Figure 2).

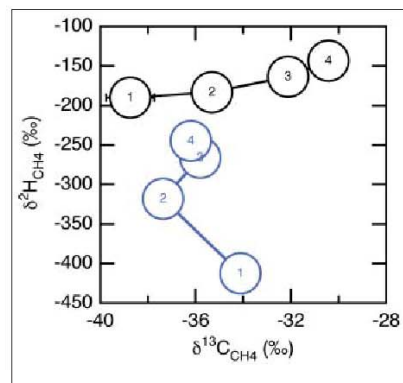


Fig. 3. Isotopic patterns in δ^2H and $\delta^{13}C$ as a function of alkane carbon number; alkanes derived from thermogenesis (black) compared with abiogenic alkanes produced via water-rock reactions (blue) [after Sherwood Lollar *et al.*, 2002]. The values for methane, ethane, propane, and butane are indicated by numerals 1, 2, 3, and 4, respectively.

Further terrestrial field and laboratory measurements of the carbon and hydrogen isotopologues of methane and C_n alkanes are needed to confirm which correlations provide the most unique separation between the various hydrocarbon-producing reactions (Figure 3). Much less well constrained at present are the relative abundances of other cogenerated molecules, such as sulfur and nitrogen compounds, for various methane sources and any unique patterns of isotopic fractionation in these cogenerated species.

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References

- Abrajano, T.A., *et al.* (1990), Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, *Philippines, Appl. Geochem.*, 5, 625-630.
- Formisano, V., *et al.* (2004), Detection of methane in the atmosphere of Mars, *Science*, 306, 1758-1761.

- Horita, J., and M.E. Berndt (1999), Abiogenic methane formation and isotopic fractionation under hydrothermal conditions, *Science*, 285, 1055–1057.
- House, C.H., et al. (2003), Carbon isotopic fractionation by Archeans and other thermophilic prokaryotes, *Org. Geochem.*, 34, 345–356.
- Kelley, D.S., et al. (2005), A serpentinite-hosted ecosystem: The lost city hydrothermal field, *Science*, 307, 1428–1434.
- Krasnopolsky, V.A., et al. (2004), Detection of methane in the Martian atmosphere: Evidence for life?, *Icarus*, 172, 537–547.
- Lyons, J.R., et al. (2005), Formation of methane on Mars by fluid-rock interaction in the crust, *Geophys. Res. Lett.*, 32, L13201, doi:10.1029/2004GL022161.
- McCollom, T.M. (2003), Formation of meteorite hydrocarbons from thermal decomposition of siderite (FeCO₃), *Geochim. Cosmochim. Acta*, 67, 311–317.
- Mumma, M.J., et al. (2004), Detection and mapping of methane and water on Mars, *Bull. Am. Astron. Soc.*, 36, 1127.
- Nair, H., et al. (2005), Isotopic fractionation of methane in the Martian atmosphere, *Icarus*, 175, 32–35.
- Oehler, D.Z., et al. (2005), Impact metamorphism of subsurface organic matter on Mars: A potential source for methane and surface alteration, paper presented at the 36th Lunar and Planetary Science Conference, Lunar and Planet. Inst., Houston, Tex., 14–18 March.
- Onstott, T.C., et al. (2006), Martian CH₄ sources, flux, and detection, *Astrobiology*, 6, 377–395.
- Oze, C., and M. Sharma (2005), Have olivine, will gas: Serpentinization and the abiogenic production of methane on Mars, *Geophys. Res. Lett.*, 32, L10203, doi:10.1029/2005GL022691.
- Sherwood Lollar, B., et al. (2002), Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs, *Nature*, 416, 522–524.
- Welhan, J.A., and H. Craig (1983), Methane and helium in deep Earth gases, *Abstr. Pap. Am. Chem. Soc.*, 186, 14-GEOC.
- Allen@jpl.nasa.gov; Barbara Sherwood Lollar, Department of Geology, University of Toronto, Canada; Bruce Runnegar, NASA Astrobiology Institute, NASA Ames Research Center, Moffett Field, Calif.; Dorothy Z. Oehler, NASA Johnson Space Center, Houston, Tex.; James R. Lyons, Institute of Geophysics and Planetary Physics, University of California, Los Angeles (UCLA); Craig E. Manning, Department of Earth and Space Sciences, UCLA; and Michael E. Summers, Department of Physics and Astronomy, George Mason University, Fairfax, Va.

Author Information

Mark Allen, Jet Propulsion Laboratory, California Institute of Technology, Pasadena; E-mail: Mark.
