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Icarus 172 (2004) 537–547

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Detection of methane in the martian atmosphere: evidence for life?

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Received 29 March 2004; revised 1 July 2004

Abstract

Using the Fourier Transform Spectrometer at the Canada–France–Hawaii Telescope, we observed a spectrum of Mars at the P-branch of the strongest CH_4 band at 3.3 μm with resolving power of 180,000 for the apodized spectrum. Summing up the spectral intervals at the expected positions of the 15 strongest Doppler-shifted martian lines, we detected the absorption by martian methane at a 3.7 sigma level which is exactly centered in the summed spectrum. The observed CH_4 mixing ratio is 10 ± 3 ppb. Total photochemical loss of CH_4 in the martian atmosphere is equal to 2.2×10^5 cm^{-2} s^{-1}, the CH_4 lifetime is 340 years and methane should be uniformly mixed in the atmosphere. Heterogeneous loss of atmospheric methane is probably negligible, while the sink of CH_4 during its diffusion through the regolith may be significant. There are no processes of CH_4 formation in the atmosphere, so the photochemical loss must therefore be balanced by abiogenic and biogenic sources. Outgassing from Mars is weak, the latest volcanism is at least 10 million years old, and thermal emission imaging from the Mars Odyssey orbiter does not reveal any hot spots on Mars. Hydrothermal systems can hardly be warmer than the room temperature at which production of methane is very low in terrestrial waters. Therefore a significant production of hydrothermal and magmatic methane is not very likely on Mars. The calculated average production of CH_4 by cometary impacts is 2% of the methane loss. Production of methane by meteorites and interplanetary dust does not exceed 4% of the methane loss. Methane cannot originate from an extinct biosphere, as in the case of "natural gas" on Earth, given the exceedingly low limits on organic matter set by the Viking landers and the dry recent history which has been extremely hostile to the macroscopic life needed to generate the gas. Therefore, methanogenesis by living subterranean organisms is a plausible explanation for this discovery. Our estimates of the biomass and its production using the measured CH_4 abundance show that the martian biota may be extremely scarce and Mars may be generally sterile except for some oases.

Keywords: Mars, atmosphere; Exobiology; Atmospheres, composition; Spectroscopy; Infrared observations

1. Introduction

Half a century ago, seasonal variations of the reflectivity of Mars at low and middle latitudes were ascribed to vegetation, and attempts were made to detect the chlorophyll bands and other "bands of life." G.A. Tikhov, a Russian scientist, suggested the term astrobotany in 1945 for that new field and published a book with this title in 1949 and followed it in 1953, with a book entitled "Astrobiology." It was recognized subsequently that the observed seasonal variations are caused by windblown dust. However, even after the careful and detailed but unsuccessful search for life by the Viking instruments, Mars still represents our greatest if not only hope to achieve a nonhypothetical subject for astro- or exobiology.

It is currently thought that methanogenesis is a highly likely metabolic pathway for possible microbial life on Mars (McCollom, 1999; Weiss et al., 2000; Jakosky et al., 2003; Varnes et al., 2003). The probable existence of subsurface liquid water on Mars (Mellon and Phillips, 2001) would provide protected habitats for such organisms, perhaps similar to the microbial communities thriving in many places

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0019-1035/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.icarus.2004.07.004

deep beneath the Earth's surface (Chapelle et al., 2002). The detection of atmospheric methane is a way to deduce the existence of this type of life.

The strictest upper limit to CH_4 in the martian atmosphere was obtained by summing up 1747 infrared spectra from the Mariner 9 orbiter (Maguire, 1977). No absorption of Mars thermal radiation was observed at the CH_4 band at 1306 cm^{-1}, and this resulted in an upper limit of 20 parts per billion (ppb). This limit corresponds to the absorption at a level of twice the noise equivalent radiance, that is, 0.1%, measured with resolving power $\nu/\delta\nu = 550$ (ν is wavenumber).

An indication of a possible presence of methane in the martian atmosphere was obtained by Krasnopolsky et al. (1997). To search for HDO, they observed a spectrum of Mars at 2650–2800 cm^{-1} with resolving power of 270,000 using the Fourier transform spectrometer at the Kitt Peak National Observatory. Methane was a by-product in that search, and a weak signal from possible methane at 70 ± 50 ppb was below the two-sigma limit.

A spectrum of Mars at 2.4–45 μm was observed with the short-wavelength spectrometer at the Infrared Space Observatory with resolving power of 2000 near 3.3 μm. No methane absorption was detected, and the upper limit to methane was 50 ppb (Lellouch et al., 2000).

We report here our observations which resulted in a detection of methane on Mars. We will discuss sources and sinks of methane on Mars and its relevance to the problem of life. An abstract of this work with its basic results was submitted to and published by the European Geosciences Union (Krasnopolsky et al., 2004), and the submission deadline, 11 January 2004, was on the second day of operation of the Planetary Fourier Spectrometer (PFS) on board the Mars Express orbiter (Formisano et al., 2004). Later, Kerr (2004) reported that the PFS team also announced a detection of methane at a press conference in March 2004. Attempts to detect methane on Mars were made even earlier by Mumma et al. (2003). However, no results of their observations have been published in that abstract.

2. Observation

We searched for CH_4 on Mars using the P-branch of its strongest band at 3020 cm^{-1}. This band is stronger than the band at 1306 cm^{-1}, which was used by Maguire (1977) to establish his upper limit, by a factor of 2.2. Reflection of solar light by Mars with the mean surface albedo of 0.1 (Erard and Calvin, 1997) dominates the planet's spectrum near 3020 cm^{-1} and further doubles the effect of absorption because of the two-way path in the atmosphere. However, our observations were ground-based and possible martian lines of CH_4 must therefore be observed against the very strong telluric methane lines. This required the highest spectral resolution, maximum Doppler shift from the velocity of Mars relative to the Earth, and a high elevation to reduce both the abundance of telluric methane and its line widths, which are proportional to atmospheric pressure. We found that the best instrument to search for CH_4 on Mars was the Fourier Transform Spectrometer (FTS) at the Canada–France–Hawaii Telescope (CFHT). The telescope site at Mauna Kea (elevation 4.2 km), size (3.6 m), and the FTS apodized resolving power $\nu/\delta\nu = 180{,}000$ were the main factors in our choice.

The observations were made on 24 and 27 January 1999, when Mars' helio- and geocentric distances were 1.66 and 1.24 AU, diameter 7.6 arcs, solar longitude $L_S = 88°$, i.e., near the summer solstice, and telluric airmass 1.14–1.27. We used a diaphragm of 5 arcs and a filter with a band pass of 2840–3020 cm^{-1} at half maximum. Our diaphragm reduced the signal from Mars but also removed a significant uncertainty which could arise from the inclusion of the Mars limb. This would require some assumptions on the limb brightening of the atmosphere and darkening of the surface and corrections for light scattering on the limb. The observing conditions were very good with relative humidity $< 5\%$ and a temperature of -3 to $-6\,°C$. However, a strong wind of up to 30 knots blurred the image and reduced the signal-to-noise ratio.

Difference between the geocentric velocities for the two nights was less than 0.03 $km\,s^{-1}$, which corresponds to 3×10^{-4} cm^{-1}, and the observed interferograms were simply coadded and apodized. The final interferogram was processed to obtain an oversampled spectrum with sampling intervals of 0.00171 cm^{-1}. The total effective exposure time was 4.75 h, and we achieved a signal-to-noise ratio of 110 at the peak of the filter transmission in the regions without atmospheric absorption. A small part ($\approx 3\%$) of the observed spectrum is shown in Fig. 1.

The observed spectrum consists mostly of telluric CH_4 lines. The spectroscopic database HITRAN 2000 gives 24,000 lines of CH_4 in the range of 2840–3020 cm^{-1}. Fortunately, most of these lines are very weak, and only 1500 of them result in telluric absorption exceeding 1%. For example, a weak telluric line of methane at 2975.74 cm^{-1} is seen in Fig. 1. The number of CH_4 lines of similar or greater strength is 338 in our spectral range. Four components of the CH_4 P4 line are also shown in Fig. 1. Each of these components is stronger than the line at 2975.74 cm^{-1} by a factor of ≈ 400. Evidently, a wing of only the bluest of these four components may be studied to search for methane on Mars. 29 strong but unsaturated lines of telluric methane were used to measure a wavenumber correction, which was equal to a factor of $1 + (4.75 \pm 0.12) \times 10^{-6}$, that is, 0.01425 ± 0.0004 cm^{-1} at 3000 cm^{-1}.

Figure 1 demonstrates also a few strong lines of telluric water vapor. The only martian lines immediately seen in the spectrum are weak Doppler-shifted satellites to strong telluric H_2O lines (Fig. 1). We will use these lines to determine the effective spectral resolution and Doppler shift, which may differ from that for Mars' mass center because of the

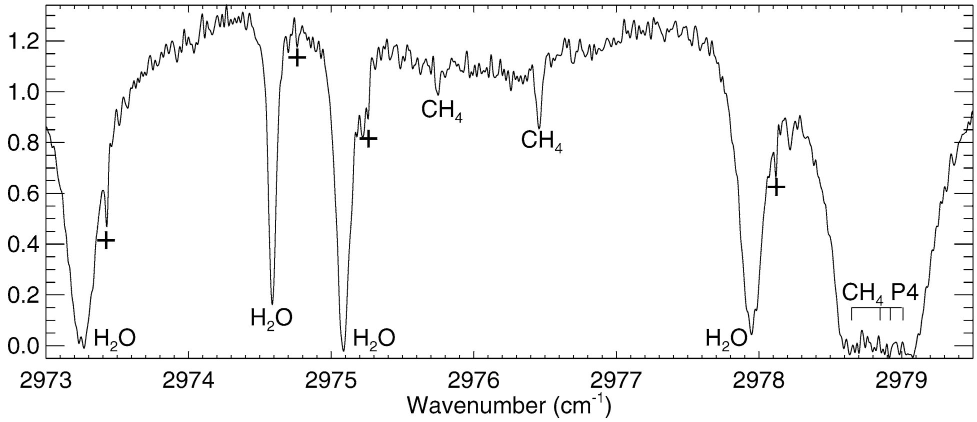

Fig. 1. A small part (3%) of the CFHT/FTS spectrum of Mars. Telluric lines of CH_4 and H_2O are the major features in the spectrum. Martian H_2O lines (crosses) are weak, narrow, and shifted to the blue by 0.1762 cm^{-1}.

projection of Mars rotation which is variable within the field of view, and some fine instrumental effects.

Fitting of the telluric H_2O line at 2973.25 cm^{-1} by the collisional line shape

$$t(\nu) = A \exp\left(-\frac{\eta N S \Delta\nu_c}{\pi[(\nu-\nu_0)^2 + \Delta\nu_c^2]}\right)$$

is shown in Fig. 2. Here $t(\nu)$ is the transmission at wavenumber ν, ν_0 is the central wavenumber, η is the telluric airmass, N is the column abundance, S is the line strength, $\Delta\nu_c$ is the collisional line width, and A is the scaling factor. The chosen line is the strongest H_2O line in our spectrum, and its fitting results in $\Delta\nu_c = 0.058$ cm^{-1} and $N = 3 \times 10^{21}$ cm^{-2}, that is, 0.9 mm of precipitated water. This value confirms the dry conditions on Mauna Kea during the observations.

Using the Viking measurements of seasonal variations of the atmospheric pressure (Hess et al., 1980; Tillman, 1988) and the MGS/MOLA surface elevations, we find that the mean pressure in our field of view was 6 mbar. Using the MGS/TES observations at the same martian season (Smith, 2004), we found that the mean atmospheric temperature was very close to 200 K in our field of view at a level of 3 mbar (half total pressure).

The fitting in Fig. 2 makes possible an accurate extraction of the martian line using a ratio of the observed spectrum and fitting near the martian line. Its Doppler shift corresponds to a geocentric velocity of -17.79 $km\,s^{-1}$. We find from the fitting of 8 lines that the mean value of the geocentric velocity is -17.76 ± 0.06 $km\,s^{-1}$.

The equivalent width of the martian H_2O line in Fig. 2 is 0.00903 cm^{-1}, and the line strength is 1.41×10^{-22} cm at 200 K from HITRAN 2000. We retrieved a water vapor abundance of 13 μm of precipitated water in the martian atmosphere using the standard curve-of-growth technique (Chamberlain and Hunten, 1987; Krasnopolsky, 1986). The measured H_2O abundance on Mars is close to that observed for the same season and latitudes from the Viking orbiters (Jakosky and Farmer, 1982) and slightly smaller than the 17 pr. μm obtained from the Mars Global Surveyor (Smith, 2002). The difference may be due to annual variations or to absorption and scattering by dust, hazes, and clouds, which are weak for the far infrared observations of water from the Mars Global Surveyor, but become stronger at the shorter wavelengths of the Viking and our observations.

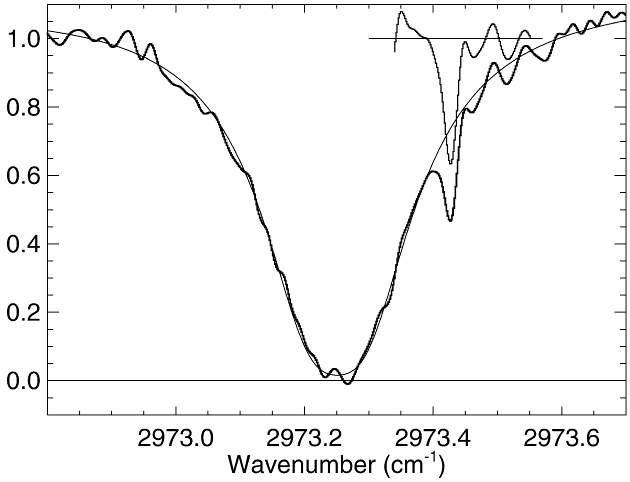

Fig. 2. Fitting of the telluric H_2O line at 2973.25 cm^{-1} by the collisional line shape. This fitting determines the water abundance of 0.9 pr. mm above Mauna Kea during the observation. Ratio of the observed spectrum and fitting near the martian H_2O line makes it possible to deduce the H_2O abundance of 13 pr. μm on Mars.

The line full width at half maximum FWHM is equal to 14 points in Fig. 2. Its optical depth is $\tau_0 = 2.1$ in the line center, therefore it is wider than a weak line in the martian atmosphere. A mean FWHM of the four lines with $\tau_0 < 0.5$ is 10.5 ± 1.6 points $= 0.0180 \pm 0.0027$ cm^{-1}. The expected width of a weak martian line is $(2\pi)^{1/2}\Delta\nu_D = 0.0076$ cm^{-1}. Here $\Delta\nu_D = 3.04 \times 10^{-7}\nu(T/\mu)^{1/2}$ is the Doppler line width, $T = 200$ K is the temperature of Mars atmosphere at a half pressure level of 3 mbar, and $\mu = 18$ is the molecular mass. The measured FWHM reflects the effects of the line width and the spectral resolution, which appears to be equal to $(0.0180^2 - 0.0076^2)^{0.5} = 0.0163$ cm^{-1}. The unapodized resolution is expected to be 0.0134 cm^{-1}, and a weak apodization applied resulted in some degradation of the spectral resolution. The resolving power of the apodized spectrum is $\nu/\delta\nu = 180{,}000$.

The spectral resolution of 0.0163 cm^{-1} corresponds to 9.5 sampling points. Compared to the Nyquist sampling of two points per resolution element, our spectrum is oversampled by a factor of 5.

3. Detection of methane

All possible martian CH_4 lines of interest are on the blue wings of the strong telluric CH_4 lines. To search for methane, we choose those CH_4 lines, which are weakly contaminated by other telluric lines at the expected positions of the martian lines. We consider all available methane lines with strengths exceeding a given limit, which we choose at 6×10^{-20} and 1.5×10^{-20} cm. The numbers of lines exceeding the two limits are 5 and 15, respectively. The peak opacity from a line with $S = 1.5 \times 10^{-20}$ cm using a methane abundance of 10 ppb is

$$2\eta_0 f_{\mathrm{CH}_4}\frac{SN_0}{\delta\nu} = 0.9\%,$$

where η_0 is the airmass in the martian atmosphere which is equal to ≈ 2.5 in our field of view, f_{CH_4} is the methane mixing ratio, $N_0 = 2.2 \times 10^{23}$ cm^{-2} is the column abundance of gas molecules for the pressure of 6 mbar on Mars, and the factor of 2 is because the resolution interval $\delta\nu$ refers to half maximum. A signal at the position of the martian line is typically a third of the maximum signal, therefore the expected absorption of $0.009 \times 110/3$ is a third of the noise level. Evidently, inclusion of the weaker lines in the extraction of methane is not helpful.

We fit the blue wings of each of the chosen telluric CH_4 line with cubic polynomials for the spectral intervals of 75 points centered at the martian lines. The fitting does not include 15 central points where the martian line is expected. This fitting for the strongest martian CH_4 line in our spectrum is shown in Fig. 3. The wing of the telluric line has a wave-like structure, and the greatest wave exactly coincides with the expected position of the martian line. This wave is of the proper sign and exceeds the other waves by more than a factor of 1.8. The local noise is equal to standard deviation (sigma) of the fit and shown with intervals of three points. Excluding the central points, approximately a third of the remaining points exceed the standard deviation, in accord with the Gauss statistics.

Deviations from the fits for the chosen lines are summed up using statistical weights. According to the rules of statistics, these weights should be proportional to the squares of ratios of line intensity to local noise, and the line intensity should be proportional to the line strength and local continuum. The summing of the lines with $S > 6 \times 10^{-20}$ cm is shown in Fig. 4. While some spectra show peaks and minima exceeding that at the position of the martian line, the latter

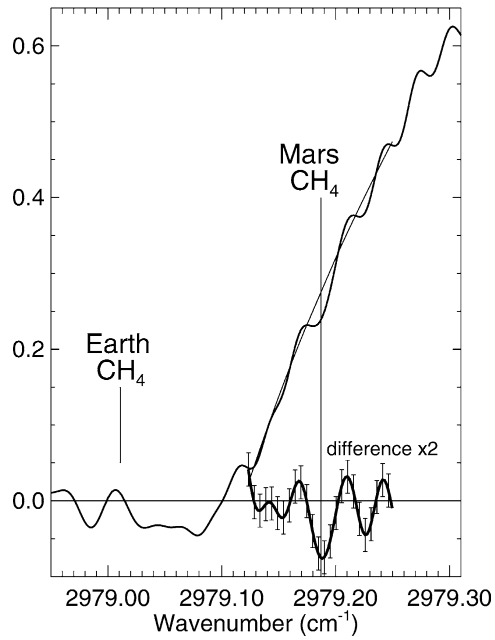

Fig. 3. Blue wing of the strongest methane telluric line in our spectrum. The expected positions of the line center and the Doppler-shifted martian line are shown. 75 points near the martian line are fitted by a cubic parabola (thin line). Difference between the measured points and the fitting is also shown. The greatest difference is exactly centered at the expected position of the martian line, is of the proper sign, and exceeds the other minima and maxima by more than a factor of 1.8.

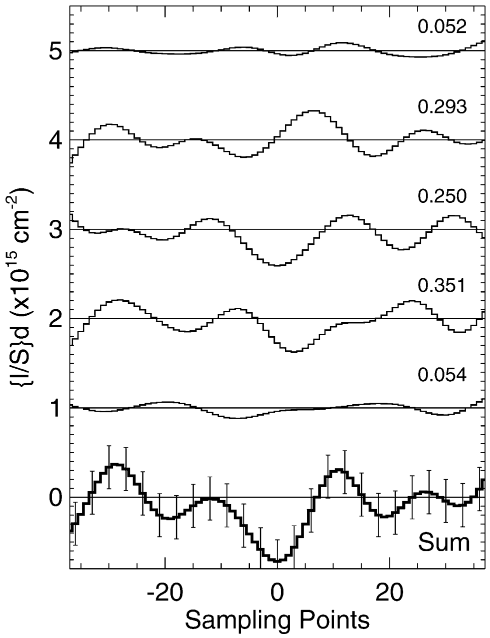

Fig. 4. Summing of the weighted spectra centered on all lines with $S > 6 \times 10^{-20}$ cm. Weights are shown near each line, and the spectra are displaced vertically. The absorption is exactly centered at the expected position of the martian line and exceeds the other minima and maxima by more than a factor of 2. $d = 0.00171$ cm^{-1} is the sampling interval.

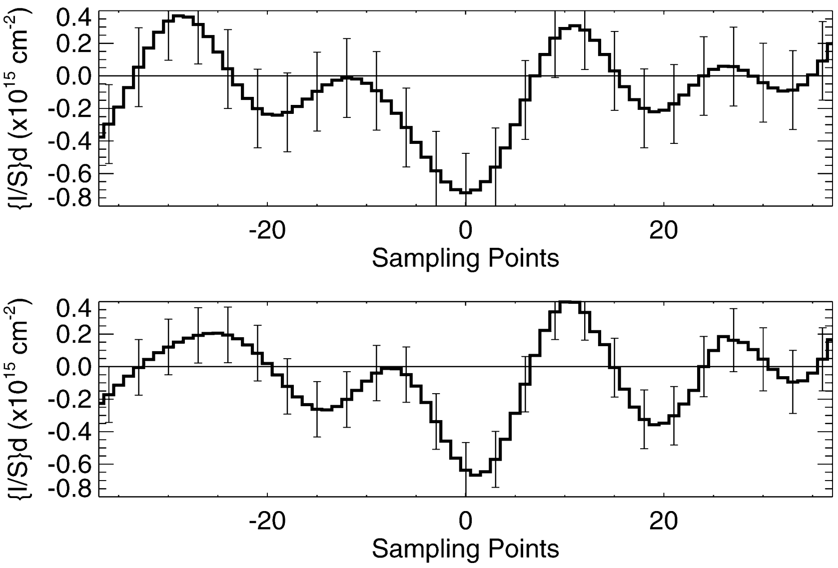

Fig. 5. Weighted-mean spectra of 5 and 15 strongest martian lines of CH_4 (upper and lower panels, respectively). The absorption peak is shifted by 10% of the resolution element in the lower spectrum. The absorption peaks correspond to the methane detection at levels of 3.0 and 3.7 sigma, respectively.

clearly dominates in the sum. Also, though the absorption is significantly shifted in the individual spectra, it exactly coincides with the expected position in the sum.

The sums for 5 lines with $S > 6 \times 10^{-20}$ cm and 15 lines with $S > 1.5 \times 10^{-20}$ cm are shown in Fig. 5. The absorption in the lower panel is shifted by one point which is 10% of the resolution element. Deviations of approximately a quarter of the points in both spectra exceed one sigma, which is within the uncertainty of the Gauss statistics. Deviations of three of 60 points exceed two sigma in the lower spectrum, again in accord with the statistics. (Here we exclude 15 central points.) Oversampling does not affect a percent of points exceeding, say, one or two sigma. The oversampling is a factor of 5 in our spectra, the number of points for the Nyquist sampling would be 12 instead of 60, and one point in the lower spectrum would exceed two sigma. The Gauss statistics predicts $0.05 \times 12 = 0.6$ point with uncertainty of $0.6^{1/2} = 0.8$ point.

The peak values are equal to 3.0 sigma in the upper spectrum and 3.7 sigma in the lower spectrum. They exceed the largest deviations in the spectra by factors of 2.02 and 1.65, respectively. Both of the summed spectra show a detection of martian CH_4 absorption near the standard detection criterion of 3 sigma. Summing 15 central points, the CH_4 mixing ratio is 12.6 ± 4.2 and 9.2 ± 2.5 ppb from the upper and lower spectra, respectively. The weighted-mean value is 10.05 ± 2.9 ppb. The uncertainties of the two values are not statistically independent and therefore are averaged linearly, not as squares. The recommended value for the methane mixing ratio in the martian atmosphere is 10 ± 3 ppb.

Since these data were obtained, the Fourier transform spectrometer has been decommissioned at the CFHT, and it is impossible to repeat our observation. Probably, currently the best instrument for detection of methane on Mars is the PHOENIX spectrograph (Mumma et al., 2003), which is now at the South Gemini Observatory. However, its resolving power is lower by a factor of 2.5 and its range is smaller by a factor of ≈ 10 than those of the FTS/CFHT.

4. Photochemical loss of methane

The observed abundance of methane is too small to affect the abundances of major photochemical species. We found four reactions for the photochemical loss of methane on Mars (Table 1). The main process is direct photolysis by solar Lyman-alpha radiation. The mean Lyman-alpha photon flux is $I_{1216} = 3.7 \times 10^{11}$ cm^{-2} s^{-1} at 1 AU (Woods et al., 1996), and the CH_4 and CO_2 cross sections at 1216 Å are $\sigma_{CH_4} = 1.85 \times 10^{-17}$ cm^2 and $\sigma_{CO_2} = 7.4 \times 10^{-20}$ cm^2 (Huebner, http://espsun.space.swri.edu/amop). Absorption of Lyman-alpha photons occurs near 80 km in the martian atmosphere, and the mixing time is much shorter than the CH_4 lifetime relative to photolysis at these heights. Therefore, the CH_4 mixing ratio is constant with height near 80 km, and the loss of CH_4 by photolysis is

$$L_{1216} = \frac{I_{1216}}{4r^2} \frac{\sigma_{CH_4}}{\sigma_{CO_2}} f_{CH_4} = 1.0 \times 10^5 \text{ cm}^{-2}\,\text{s}^{-1}.$$

Here $r = 1.52$ AU is the mean Mars heliocentric distance, 4 is the ratio of the sphere to disk areas, and $f_{CH_4} = 10^{-8}$ is the CH_4 mixing ratio. The three other loss processes are the reactions with OH, O, and O(^{1}D). Column rates for these reactions are calculated using the data of photochemical models by Nair et al. (1994) and Krasnopolsky (1995). Different approaches were used in these models to fit the experimental data, and the models are significantly different. The total lifetime of CH_4 on Mars is 250 and 430 years,

Table 1
Photochemical loss of CH_4 in the martian atmosphere

Reaction	Rate coefficient ($cm^3\ s^{-1}$)	Column rate ($cm^{-2}\ s^{-1}$)	
$CH_4 + h\nu$ (1216 Å) $\rightarrow$ products	–	1.0×10^5	1.0×10^5
$CH_4 + OH \rightarrow CH_3 + H_2O$	$2.45 \times 10^{-12} \exp(-1775/T)$[a]	1.0×10^5	1.2×10^4
$CH_4 + O \rightarrow CH_3 + OH$	$8.3 \times 10^{-12}(T/300)^{1.56} \exp(-4270/T)$[b]	560	120
$CH_4 + O(^1D) \rightarrow CH_3 + OH$	1.5×10^{-10} [a]	7.8×10^4	5×10^4
Total		2.8×10^5	1.6×10^5

The second column does not refer to photolysis of CH_4, which is discussed in the text, and to the total loss. Column rates for the three reactions are calculated using the photochemical models of Nair et al. (1994, Fig. 15) and Krasnopolsky (1995, Fig. 2a) in the left and right columns, respectively.

[a] Sander et al. (2003).

[b] Baulch et al. (1992).

and the total loss is 2.8×10^5 and $1.6 \times 10^5\ cm^{-2}\ s^{-1}$, respectively. We will use the mean values of 340 years and $2.2 \times 10^5\ cm^{-2}\ s^{-1}$, that is, 270 $t\ y^{-1}$ (tons per year).

We have not found any data on the heterogeneous loss of methane in the literature. The heterogeneous reaction probability must be equal to $\gamma = 6 \times 10^{-9}$ to double the loss of methane calculated above. (We assumed a uniformly mixed dust with opacity of 0.5 to calculate this value.) It may be compared to the gas reaction probability of 2×10^{-11} in the collisions between CH_4 and O. Comparison with some other heterogeneous reactions (Sander et al., 2003) results in a conclusion that the heterogeneous loss of atmospheric methane is probably negligible on Mars.

Time of vertical mixing is $H^2/K \approx 10^6$ s $\approx$ 10 days in the martian lower atmosphere. Time of horizontal mixing is $\approx 5R/V \approx 0.5$ y. Here $H \approx 10^6$ cm is the scale height, $K \approx 10^6\ cm^2\ s^{-1}$ is the eddy diffusion, $R = 3.4 \times 10^8$ cm is Mars' radius, $V \approx 100\ cm\ s^{-1}$ is the meridional wind speed, and $V/5$ is the chaotic component of the wind speed. Both times of vertical and horizontal mixing are much shorter than the CH_4 lifetime of 340 y. Therefore methane should be well mixed with the constant mixing ratio of 10 ± 3 ppb throughout the whole atmosphere on Mars.

Methane is more abundant than other hydrocarbons in the atmospheres of the outer planets and satellites by three orders of magnitude and more, and the expected abundances of the other hydrocarbons are negligible on Mars. Wong et al. (2003) calculated that formaldehyde H_2CO, which is the most abundant product of methane chemistry on Mars, is less abundant than methane in the martian atmosphere by six orders of magnitude, and the products of methane chemistry are not helpful as tracers of methane.

5. Diffusion of methane through regolith

Diffusion of gas through the martian regolith (Weiss et al., 2000) is of the Knudsen type, when molecular collisions with the walls of the pores dominate in the transport process. The calculated diffusion coefficient (Weiss et al., 2000) may be approximated as $D = 1.37\mu^{-1/2}\ cm^2\ s^{-1}$, and μ is the molecular mass in atomic units.

Table 2
Times of methane diffusion

Depth	10 m	100 m	1 km	10 km
Thin layer	0.33	7.5	490	46,000
Thick layer	0.16	3	170	15,000

Times are in years, and thick layer extends from the surface to a given depth.

The equation of diffusion from a thin layer at depth d to the surface may be integrated to give the diffusion time

$$t = \frac{n_0 d}{\Phi} + \frac{d^2}{2D}.$$

Here $\Phi = 2.2 \times 10^5\ cm^{-2}\ s^{-1}$ is the CH_4 flow and $n_0 = 2 \times 10^9\ cm^{-3}$ is the CH_4 surface density. Diffusion time from a layer which extends from the surface to depth d may be calculated by a further integration:

$$\tau = \frac{n_0 d}{2\Phi} + \frac{d^2}{6D}.$$

The calculated diffusion times (Table 2) are long, so the existence of a heterogeneous sink for methane during its diffusion through the regolith to the atmosphere is a distinct possibility. Therefore, the production of methane may significantly exceed the very weak flow of $2.2 \times 10^5\ cm^{-2}\ s^{-1}$ from the regolith to the atmosphere. This flow is thus a lower limit to the production of methane in the regolith.

6. Abiogenic sources of methane

6.1. Hydrothermal and magmatic methane

There are no processes of methane formation in the atmosphere, so the loss of $2.2 \times 10^5\ cm^{-2}\ s^{-1}$ must therefore be balanced by abiogenic and biogenic sources. Welhan (1988) considered sources of methane in the hydrothermal systems on the Earth. He discussed two abiogenic sources of methane, from magmatic outgassing and high-temperature chemical reactions within a hydrothermal fluid. For example, methane may form in the following equilibria:

$$CO_2 + 2H_2O = CH_4 + 2O_2,$$

$$8FeO + 2H_2O + CO_2 = 4Fe_2O_3 + CH_4,$$

$2C + 2H_2O = CO_2 + CH_4,$

$CO_2 + 4H_2 = CH_4 + 2H_2O.$

If the first equilibrium dominates (Holland, 1984), then abiogenic methane is negligible on Mars.

Gas-phase reactions between stable molecules at room temperatures are extremely slow. For example, a rate coefficient of the reaction between H_2 and O_2 is $2.4 \times 10^{-10} \times \exp(-28{,}500/T)$ cm^3 s^{-1} (Tsang and Hampson, 1986), that is, 1.3×10^{-51} cm^3 s^{-1} at 300 K, and a mixture of H_2 and O_2 could exist for a period exceeding the age of the Solar System by a factor of 5×10^{14}. Therefore, the reactions occurring in hot fluids are only of interest here.

Welhan (1988) considered the outgassing from the hydrothermal systems at mid-oceanic ridges where pressure is hundreds bars, temperature reaches 350 °C (620 K), and concentrations of methane are higher than those in the mean ocean water by a factor of up to a million. The outgassing is traced using the rare isotope ^{3}He, which represents juvenile helium trapped during the Earth's accretion. The mantle helium is enriched in ^{3}He by a factor of 8 (Welhan, 1988) relative to the atmospheric helium, which has $^3He/^4He = 1.4 \times 10^{-6}$. Concentrations of CH_4 in the mid-oceanic ridge fluids are smaller than those of He by a factor of ≈ 90 (Welhan, 1988). We combine these data with the known ^{3}He global-mean outgassing rate of 4 cm^{-2} s^{-1} (Prather and McElroy, 1983), based on the measurements of gas dissolved in the ocean. Then the abiogenic outgassing of methane on the Earth is as low as $4/(8 \times 90 \times 1.4 \times 10^{-6}) = 4000$ cm^{-2} s^{-1} = 17 t y^{-1}.

H_2O and CO_2 are the most abundant volcanic gases on the Earth. Thermochemical equilibrium in the first of the above reactions at high temperature of magma ($\approx$ 1400–1500 K on Earth) results in a release of methane by the volcanic eruptions. Its mixing ratio is typically a few ppm (Etiope and Klusman, 2002) in the erupted gases. The annual eruption rate of magma is 4 km^3 on Earth, the erupted gases are $\approx 5\%$ of this mass (Geist, 1992), and this corresponds to a methane production of $\approx 3 \times 10^5$ cm^{-2} s^{-1} = 1300 t y^{-1}.

Geothermal emission of methane is typically ignored in the budget of terrestrial methane which is accurately documented (Yavitt, 1992; Yung and DeMore, 1999). It is very much weaker than the biogenic production of methane on the Earth (511 megatons per year = 1.2×10^{11} cm^{-2} s^{-1}) and therefore very uncertain. Etiope and Klusman (2002) estimated a global CH_4 flux from gas vents as 0.01–1 Mt y^{-1} = $2.4 \times 10^6 - 2.4 \times 10^8$ cm^{-2} s^{-1}. This estimate exceeds the two values given above, and our discussion with G. Etiope has not revealed any error in our values and methods.

Outgassing from Mars is weaker than that from the Earth by an order of magnitude (Krasnopolsky et al., 1994). The youngest lava flows which represent the last case of martian volcanism are at least 10 million years old (Hartmann and Berman, 2000), far greater than the methane lifetime, and the released methane disappeared since that time. The thermal emission imaging system (THEMIS) at the Mars Odyssey orbiter (Christensen, 2003) does not reveal any hot spots on Mars. Hypothetical hydrothermal systems can hardly be warmer than the room temperature at which methane is very low abundant in terrestrial waters. Based on these facts, a significant production of hydrothermal and magmatic methane is not very likely on Mars.

6.2. Cometary methane on Mars

Methane may be brought to Mars by cometary impacts. The methane abundance in the cometary ice is $\approx 1\%$ (Gibb et al., 2003). The impact frequency on the Earth for comets with sizes exceeding 1 km is 2.2×10^{-6} y^{-1} (Shoemaker et al., 1994). Impacts of bodies with mass exceeding 4×10^{16} g remove the atmosphere above the plane tangential to the impact (Rahe et al., 1994). We assume that the gases from the comet ice are removed by the blast if the comet mass exceeds 10^{16} g.

There are three populations of comets, which contribute almost equally to the impacts on the Earth (Shoemaker et al., 1994): the Jupiter family, the Halley family, and long-period and new comets. We included extinct comets in our calculation, though those comets may lose some of their ice. We adopted the mean density of nuclei of 1 g cm^{-3} and the mass of ice as half the nucleus mass. The mass of a comet with diameter of 1 km is 5×10^{14} g, and the number of comets exceeding mass m is proportional to $m^{-0.58}$ for $m < 3 \times 10^{17}$ g (Rahe et al., 1994). Then the frequency of impacts on the Earth is

$$f = 2.2 \times 10^{-6} \left(\frac{5 \times 10^{14}}{m} \right)^{0.58} \text{y}^{-1}.$$

The impact cross-section of Mars is 0.2 of the Earth cross-section (Chyba et al., 1994) because of the smaller geometric cross section and the gravitational potential. The number of comets crossing Mars orbit is greater than those for the Earth, however, this number refers to the area, which is greater by a factor of $1.52^2 = 2.3$. (Mars orbit is at 1.52 astronomic units.) Therefore, the densities of the cometary flux are approximately equal near Mars and Earth.

Using the limiting mass is 10^{16} g, the mass influx from the impacts on Mars is

$$\Phi_m = 0.2 \int_0^{10^{16}} m \frac{df}{dm} dm = 10^9 \text{ g y}^{-1}.$$

The calculated mean delivery of methane by comets is 5 t y^{-1}, that is, 2% of the total loss. This also means that the observed methane may be mostly due to a recent impact of comet, but probability of this event is $\approx 2\%$.

6.3. Methane from meteorites

Delivery of meteoritic carbon to Mars was considered by Flynn (1996). The total mass flux is 12×10^9 g y^{-1} delivered mostly by interplanetary dust particles smaller than

10^{-2} g. Some part of this flux is melted and vaporized, some is subject to pyrolysis, and 2.4×10^9 g y^{-1} is the unaltered fraction of the delivered meteoritic matter. Flynn (1996) assumed that the average carbon content of interplanetary dust is 10%. Then the total carbon delivery is 1.2×10^8 g y^{-1} and the delivery of polymeric organic matter known as kerogen (Benner et al., 2000) is at a rate of 240 t y^{-1} of reduced carbon (Benner et al., 2000). This rate is comparable to the photochemical loss of methane.

Gerasimov (2002) simulated the high-temperature decomposition of meteorites impacting a planet using a laser beam with a power density of 10^5–10^7 W cm^{-2}. The measured total yield of gases varied with a mean value of $(8 \pm 4) \times 10^{-7}$ g J^{-1}. For a mean velocity of the impacting bodies of ~ 15 km s^{-1} their energy is equal to 10^5 J g^{-1}. A product of these values is 0.08 and exceeds the abundance of volatiles in meteorites. Therefore most of the meteorite volatiles are released during the impact, in accord with the estimate of Flynn (1996). Carbon is released mostly as CO and CO_2 with a yield of 0.9% for CH_4 (Gerasimov, 2002).

No organic matter was detected by the Viking gas chromatograph—mass spectrometer (Biemann et al., 1977). This is explained by its decomposition due to solar ultraviolet radiation or oxidation by the regolith (Flynn, 1996; Benner et al., 2000). Methane cannot form in any of these ways. Therefore the yield of 0.9% from Gerasimov (2002) corresponds to an upper limit to the production of methane from the meteoritic carbon on Mars. This upper limit is equal to 11 t y^{-1}, that is, 4% of the required production.

7. Methanogenesis on Mars

We are therefore led to consider a biogenic origin of methane on Mars. "Natural gas" on Earth is related to the extinct macroscopic life forms, which were and are impossible on Mars, given the exceedingly low limits on organic matter in the soil set by the Viking landers (Biemann et al., 1977) and the dry recent history of the planet. The major source of atmospheric methane on the Earth (Yavitt, 1992) is the microbial methanation of dead macroscopic biota:

$$2CH_2O \rightarrow CH_4 + CO_2.$$

There are presumably no macroscopic biota to decompose, so this process cannot occur on Mars; therefore we will discuss production of methane on Mars by methanogenic organisms in the soil.

Max and Clifford (2000) consider a possible accumulation of significant abundances of methane by methanogenic bacteria in the liquid saline groundwater layer which they suppose to exist near a depth of 6 km on Mars. Though they do not rule out abiogenic methane from aqueous alteration of basalt, they conclude that "the detection of substantial quantities of subsurface methane, as either gas or hydrate, would by itself provide persuasive evidence that an Earth-like subsurface biosphere evolved on early Mars." Max and Clifford do not see "how the life once established in this niche could become extinct." They consider formation of methane hydrate $CH_4 \cdot 6.1\ H_2O$ as a form of underground methane. However, diffusion through the regolith to the atmosphere (Section 5) may inhibit the formation of hydrate.

Summers et al. (2002) adopted the maximum potential fluxes $\Phi_{CO} = -8.8 \times 10^9$ cm^{-2} s^{-1} and $\Phi_{H_2} = -8.6 \times 10^8$ cm^{-2} s^{-1} from Weiss et al. (2000) (though they confused them and gave without explanation and reference) and a conversion efficiency of 10^{-4} for these species to CH_4 by methanogenic bacteria. Then they found that a flow of CH_4 of $10^{-4} \times 8.8 \times 10^9 = 8.8 \times 10^5$ cm^{-2} s^{-1} results in the CH_4 mixing ratio of 15 ppb using the photochemical model by Nair et al. (1994). Actually abundance of CH_4 is just a product of its flow and lifetime, and their values correspond to the lifetime of 120 years, though they wrote twice in the paper that the lifetime is 300 years and our calculations for the model by Nair et al. (1994) resulted in 250 years (Section 4). According to their paper, if all CH_4 molecules hitting the surface are lost, then the CH_4 mixing ratio would decrease by 30%. Our calculations similar to that in Section 4 show that the CH_4 mixing ratio would be halved if the probability of heterogeneous loss on the surface is as low as 10^{-8}.

7.1. Biomass production

In our discussion of methanogenesis on Mars, we will rely on what is known about such organisms on the Earth, keeping in mind that martian microbes may employ very different biochemistry to achieve the same result.

Methanogens consume metabolic energy from the summary reactions

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + 1.71\ \text{eV}\ (39.35\ \text{kcal mol}^{-1}),$$

$$2H_2O + 3CO \rightarrow CH_4 + 2CO_2 + 0.48\ \text{eV}\ (11.04\ \text{kcal mol}^{-1}).$$

The H_2-based methanogenesis is more effective energetically and met on the Earth. However, CO is more abundant than H_2 in the martian atmosphere where their mixing ratios are equal to 800 and 15 ppm (Krasnopolsky and Feldman, 2001), respectively, and the CO-based methanogenesis may be important on Mars.

The required fluxes of 9×10^5 cm^{-2} s^{-1} for H_2 and 7×10^5 cm^{-2} s^{-1} for CO are much smaller than the photochemical production of these species (5.7×10^8 and 3.3×10^8 cm^{-2} s^{-1} for H_2 and 1.1×10^{12} and 8.3×10^{11} cm^{-2} s^{-1} for CO from the models by Nair et al. (1994) and Krasnopolsky (1995)). They are also much smaller than the potential fluxes of 8.6×10^8 cm^{-2} s^{-1} for H_2 and 8.8×10^9 cm^{-2} s^{-1} for CO calculated for a biotic layer at a depth of 10 m in Weiss et al. (2000). However, there is a significant uncertainty in the fluxes consumed and released by the bacteria on Mars because of the lack of the data on heterogeneous loss of CH_4, H_2, and CO in the martian soil.

The lower limit for the CH_4 production of 2.2×10^5 cm^{-2} s^{-1} corresponds to the metabolic energy of $3.8 \times$

10^5 and 1.1×10^5 eV cm^{-2} s^{-1} for the H_2- and CO-based methanogenesis, respectively. It may be readily converted to biomass production if a mass per energy yield of methanogenesis is known. However, we have not found this yield in the literature and therefore assume that it is similar to that of photosynthesis on Earth,

$$CO_2 + H_2O + 2h\nu \rightarrow CH_2O + O_2.$$

Two visible photons have total energy of 5 eV, and the yield is 6 u eV^{-1} where u is the atomic mass unit. Then the biomass production rate by methanogenesis on Mars exceeds 1.2×10^{-10} and 3×10^{-11} g cm^{-2} y^{-1}, that is, 170 and 50 t y^{-1}, respectively.

A greater value of the biomass yield may be obtained using another scheme (Jakosky and Shock, 1998) with a molecule such as adenosine triphosphate (ATP) with a yield of ATP of 0.1 mol kcal^{-1} and production of 1 g of cells from 0.02 mol ATP. Converting units to eV and u, this corresponds to a biomass yield of 115 u eV^{-1}, which is greater than that of photosynthesis by a factor of 20. Accordingly, the lower limits to the biomass production rate by methanogenesis are 2.3×10^{-9} and 6×10^{-10} g cm^{-2} y^{-1} (3300 and 940 t y^{-1}) for the two reactions, respectively, by this scheme.

A minimal energy requirement to maintain a biomass is $\approx 10^{-5}$ kcal (g dry weight)$^{-1}$ s^{-1} = 4.4×10^{-7} eV u^{-1} s^{-1} (Weiss et al., 2000). Then methanogenesis can support 1.5×10^{-12} and 4×10^{-13} g cm^{-2} (2 and 0.6 t) of dry biomass, respectively. Total biomass exceeds the dry biomass by an order of magnitude.

The long diffusion time calculated in Section 5 (Table 2) is also applicable to the diffusion of atmospheric H_2 and CO into the soil to feed the methanogens. These species are reducing and may be lost in the long contact with oxidizing minerals in the soil. Therefore, the martian biotic layer may be comparatively thin, for example, ≈ 100 m. Then the lower limits to the biomass production by methanogenesis are 1.2×10^{-14}–2.3×10^{-13} g cm^{-3} yr^{-1} for the H_2 methanogenesis and 3×10^{-15}–6×10^{-14} g cm^{-3} yr^{-1} for the CO methanogenesis. The limits to the dry biomass are 1.5×10^{-16} and 4×10^{-17} g cm^{-3}, respectively. These limits are lower by a few orders of magnitude than those from the Viking gas chromatograph with mass spectrometer (GCMS), whose maximum sensitivity was 10^{-11} g cm^{-3} for some organic species (Biemann et al., 1977). The mass of a small terrestrial microbe is $\approx 10^{-15}$ g (Brock and Madigan, 1991), and media with a microbe population less than ≈ 10 cm^{-3} are considered as sterile. Therefore, the above limits show that the martian biota may be exceptionally scarce and Mars may be almost sterile relative to methanogens if the heterogeneous sink of methane is ineffective.

7.2. *Search for possible oases*

The biomass distribution is highly irregular on the Earth and may be even more irregular on Mars. If life is concentrated in a few (≈ 10) oases on Mars, each oasis has a size comparable to the uncertainty of landing on Mars (say, ±1°), and locations of the oases could be properly determined, then the derived limits are higher for the oases by three orders of magnitude, and the oases may have a detectable biota.

The very long lifetime of methane in the martian atmosphere and short times of vertical and horizontal mixing are not encouraging for detection of the oases by observing methane above them. Let us assume that the total production of methane is concentrated in n vents each with radius r. Then the CH_4 flux in a vent is equal to

$$\Phi_V = \frac{4\Phi}{n}\left(\frac{R}{r}\right)^2,$$

where $\Phi = 2.2 \times 10^5$ cm^{-2} s^{-1} is the global-mean production rate and R is Mars radius. The accumulation time is $t \approx 2r/V$ where $V \approx 1$ m s^{-1} is the mean wind velocity. An excess in the CH_4 abundance above the vent over the mean atmospheric abundance is by a factor of

$$\frac{\Phi_V t}{\Phi \tau_a} = \frac{8R^2}{nVr\tau_a} = \frac{8600}{nr},$$

where $\tau_a = 10^{10}$ s is the methane lifetime in the atmosphere and r is in meters. The expected methane abundance above the vents is $86/nr$ ppm. If the vent number is ≈ 10 and their radii are ≈ 10 m, then the methane abundance is ≈ 1 ppm above them. The calculated excess refers to the densities measured in situ. Remote observations involve column abundances where the excess above the vents becomes extremely low, and detection of the oases and vents by measurements of methane will present a difficult problem.

8. Conclusions

We observed a spectrum of Mars at the P-branch of the strongest CH_4 band at 3.3 μm with resolving power of 180,000 for the apodized spectrum. Summing up the spectral intervals at the expected positions of the strongest Doppler-shifted martian lines, we detected methane at a level which is slightly above the standard detection criterion of 3 sigma. The observed CH_4 abundance is 10 ± 3 ppb. Photochemical loss of methane is 2.2×10^5 cm^{-2} s^{-1} and corresponds to its lifetime of 340 years.

Outgassing from Mars is low, the latest martian volcanism is at least 10 million years old, and thermal emission imaging from the Mars Odyssey orbiter does not reveal hot spots on Mars. Hypothetical hydrothermal systems can hardly be warmer than the room temperature at which methane production is very low. Based on these facts, a significant production of hydrothermal and magmatic methane is not very likely on Mars.

Delivery of methane by comets is near 2% of its loss. Methane from meteorites and interplanetary dust is smaller than 4% of its loss. Therefore, we have not found any significant abiogenic source of methane and methanogenesis by living subterranean organisms is a plausible explanation for this discovery. If life on Mars resembles terrestrial methanogens, we can anticipate an enhancement of $^{12}C/^{13}C$ in the methane by as much as a few per cent (Welhan, 1988). The search for such an enhancement would be a worthy goal for a suitably designed in situ experiment and certainly for studies of a returned atmospheric sample. Our estimates show that Mars is generally sterile except for some oases.

Acknowledgment

We are grateful to G.R. Gladstone for some helpful comments.

References

Baulch, D.L., 11 colleagues, 1992. Evaluated kinetic data for combustion modeling. J. Phys. Chem. Ref. Data 21, 411–429.

Benner, S.A., Devine, K.G., Matveeva, L.N., Powell, D.H., 2000. The missing organic molecules on Mars. Proc. Natl. Acad. Sci. USA 97, 2425–2430.

Biemann, K., 11 colleagues, 1977. The search for organic substances and inorganic volatile compounds in the surface of Mars. J. Geophys. Res. 82, 4641–4658.

Brock, T.D., Madigan, M.T., 1991. Biology of Microorganisms. Prentice–Hall, Englewood Cliffs, NJ.

Chamberlain, J.W., Hunten, D.M., 1987. Theory of Planetary Atmospheres. Academic Press, San Diego, CA.

Chapelle, F.H., O'Neill, K., Bradley, P.M., Methe, B.A., Ciufo, S.A., Knobel, L.L., Lovley, D.R., 2002. A hydrogen-based subsurface microbial community dominated by methanogens. Nature 415, 312–315.

Christensen, P.R., 2003. Mars as seen from the 2001 Mars Odyssey Thermal Emission Imaging System experiment. EOS Trans. AGU Fall Meet. Suppl. 84 (46). Abstract P21A-02.

Chyba, C.F., Owen, T.C., Ip, W.H., 1994. Impact delivery of volatiles and organic molecules to Earth. In: Gehrels, T. (Ed.), Hazards Due to Comets and Asteroids. Univ. of Arizona Press, Tucson, AZ, pp. 9–58.

Erard, S., Calvin, W., 1997. New composite spectra of Mars, 0.4–5.7 μm. Icarus 130, 449–460.

Etiope, G., Klusman, R.W., 2002. Geologic emissions of methane to the atmosphere. Chemosphere 49, 777–789.

Flynn, G.J., 1996. The delivery of organic matter from asteroids and comets to the early surface of Mars. Earth Moon Planets 72, 469–474.

Formisano, V., the PFS Team, 2004. First preliminary results of PFS-MEX at Mars. Geophys. Res. Abstracts 6, 07336.

Geist, D.J., 1992. Volcanoes. In: Nierenberg, W.A. (Ed.), Encyclopedia of Earth System Science, vol. 4. Academic Press, San Diego, CA, pp. 427–436.

Gerasimov, M.V., 2002. Toxins produced by meteorite impact and their possible role in a biotic mass extinction. In: Koerbel, C., MacLeod, K.G. (Eds.), Catastrophic Events and Mass Extinctions: Impacts and Beyond. Geological Society of America, Boulder, CO, pp. 705–716. Special Paper 356.

Gibb, E.L., Mumma, M.J., dello Russo, N., DiSanti, M.A., Magee-Sauer, K., 2003. Methane in Oort cloud comets. Icarus 165, 391–406.

Hartmann, W.K., Berman, D.C., 2000. Elysium Planitia lava flows: crater count chronology and geological implications. J. Geophys. Res. 105, 15011–15025.

Hess, S.L., Ryan, J.A., Tillman, J.E., Henry, R.M., Leovy, C.B., 1980. The annual cycle of pressure on Mars measured by Viking Landers 1 and 2. Geophys. Res. Lett. 7, 197–200.

Holland, H.D., 1984. The Chemical Evolution of the Atmosphere and Oceans. Princeton Univ. Press, Princeton, NJ.

Jakosky, B.M., Farmer, C.B., 1982. The seasonal and global behavior of water vapor in the martian atmosphere: complete global results of the Viking atmospheric water detector experiment. J. Geophys. Res. 87, 2999–3019.

Jakosky, B.M., Shock, E.L., 1998. The biological potential of Mars, the early Earth, and Europa. J. Geophys. Res. 103, 19359–19364.

Jakosky, B.M., Nealson, K.H., Bakermans, C., Ley, R.E., Mellon, M.T., 2003. Subfreezing activity of microorganisms and the potential habitability of Mars' polar regions. Astrobiology 3 (2), 343–350.

Kerr, R.A., 2004. Life of volcanic belching on Mars? Science 303, 1953.

Krasnopolsky, V.A., 1986. Photochemistry of the Atmospheres of Mars and Venus. Springer-Verlag, New York.

Krasnopolsky, V.A., 1995. Uniqueness of a solution of a steady state photochemical problem: applications to Mars. J. Geophys. Res. 100, 3263–3276.

Krasnopolsky, V.A., Feldman, P.D., 2001. Detection of molecular hydrogen in the atmosphere of Mars. Science 294, 914–917.

Krasnopolsky, V.A., Bowyer, S., Chakrabarti, S., Gladstone, G.R., McDonald, J.S., 1994. First measurement of helium on Mars: implications for the problem of radiogenic gases on the terrestrial planets. Icarus 109, 337–351.

Krasnopolsky, V.A., Bjoraker, G.L., Mumma, M.J., Jennings, D.E., 1997. High-resolution spectroscopy of Mars at 3.7 and 8 μm: a sensitive search for H_2O_2, H_2CO, HCl, and CH_4, and detection of HDO. J. Geophys. Res. 102, 6525–6534.

Krasnopolsky, V.A., Maillard, J.P., Owen, T.C., 2004. Detection of methane in the martian atmosphere: evidence for life. Geophys. Res. Abstracts 6, 06169.

Lellouch, E., Encrenaz, T., de Graauw, T., Erard, S., Morris, P., Crovisier, J., Feuchtgruber, H., Girard, T., Burgdorf, M., 2000. The 2.4–45 μm spectrum of Mars observed with the Infrared Space Observatory. Planet. Space Sci. 48, 1393–1405.

Maguire, W.C., 1977. Martian isotopic ratios and upper limits for possible minor constituents as derived from Mariner 9 infrared spectrometer data. Icarus 32, 85–97.

Max, M.D., Clifford, S.M., 2000. The state, potential distribution, and biological implications of methane in the martian crust. J. Geophys. Res. 105, 4165–4171.

McCollom, T.M., 1999. Methanogenesis as a potential source of chemical energy for primary biomass production by autotrophic organisms in hydrothermal systems on Europa. J. Geophys. Res. 104, 30729–30742.

Mellon, M.T., Phillips, R.J., 2001. Recent gullies on Mars and the source of liquid water. J. Geophys. Res. 106, 23165–23179.

Mumma, M.J., Novak, R.E., DiSanti, M.A., Bonev, B.P., 2003. A sensitive search for methane on Mars. Bull. Am. Astron. Soc. 35, 937.

Nair, H., Allen, M., Anbar, A.D., Yung, Y.L., Clancy, R.T., 1994. A photochemical model of the martian atmosphere. Icarus 111, 124–150.

Prather, M.J., McElroy, M.B., 1983. Helium on Venus: implications for uranium and thorium. Science 220, 410–411.

Rahe, J., Vanisek, V., Weissman, P.R., 1994. Properties of cometary nuclei. In: Gehrels, T. (Ed.), Hazards Due to Comets and Asteroids. Univ. of Arizona Press, Tucson, AZ, pp. 597–634.

Sander, S.P., Friedl, R.R., DeMore W.B., Golden, D.M., Kurylo, M.J., Hampson, R.F., Huie, R.E., Moortgat, G.K., Ravishankara, A.R., Kolb, C.E., Molina, M.J., 2003. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 14. JPL Publication 02-25.

Shoemaker, E.M., Weissman, P.R., Shoemaker, C.S., 1994. The flux of periodic comets near Earth. In: Gehrels, T. (Ed.), Hazards Due to Comets and Asteroids. Univ. of Arizona Press, Tucson, AZ, pp. 313–335.

Smith, M.D., 2002. The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer. J. Geophys. Res. 107 (E11), 5115.

Smith, M.D., 2004. Interannual variability in TES atmospheric observations of Mars during 1999–2003. Icarus 167, 148–165.

Summers, M.E., Lieb, B.J., Chapman, E., Yung, Y.L., 2002. Atmospheric biomakers of subsurface life on Mars. Geophys. Res. Lett. 29 (24), 2171.

Tillman, J.E., 1988. Mars global atmospheric oscillations: annually synchronized, transient normal-mode oscillations and the triggering of global dust storms. J. Geophys. Res. 93, 9433–9451.

Tsang, W., Hampson, R.F., 1986. Chemical kinetic database for combustion chemistry. Part 1. Methane and related compounds. J. Phys. Chem. Ref. Data 15, 1087–1248.

Varnes, E.S., Jakosky, B.M., McCollom, T.M., 2003. Biological potential of martian hydrothermal systems. Astrobiology 3 (2), 407–414.

Weiss, B.P., Yung, Y.L., Nealson, K.H., 2000. Atmospheric energy for subsurface life on Mars? Proc. Natl. Acad. Sci. USA 97, 1395–1399.

Welhan, J.A., 1988. Origins of methane in hydrothermal systems. Chem. Geology 71, 183–198.

Wong, A.S., Atreya, S.K., Encrenaz, T., 2003. Chemical markers of possible hot spots on Mars. J. Geophys. Res. 108 (E4), 5026.

Woods, T.N., 15 collegues, 1996. Validation of the UARS solar ultraviolet irradiances: comparison with the ATLAS 1 and 2 measurements. J. Geophys. Res. 101, 9541–9569.

Yavitt, J.B., 1992. Methane, biogeochemical cycle. In: Nierenberg, W.A. (Ed.), Encyclopedia of Earth System Science, vol. 3. Academic Press, San Diego, CA, pp. 197–207.

Yung, Y.L., DeMore, W.B., 1999. Photochemistry of Planetary Atmospheres. Oxford Univ. Press, New York/Oxford.