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Science **306**, 1758 (2004);
DOI: 10.1126/science.1101732

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Detection of Methane in the Atmosphere of Mars

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We report a detection of methane in the martian atmosphere by the Planetary Fourier Spectrometer onboard the Mars Express spacecraft. The global average methane mixing ratio is found to be 10 ± 5 parts per billion by volume (ppbv). However, the mixing ratio varies between 0 and 30 ppbv over the planet. The source of methane could be either biogenic or nonbiogenic, including past or present subsurface microorganisms, hydrothermal activity, or cometary impacts.

Methane (CH_4) is an important tracer of possible biological, internal, or atmospheric processes on Mars. The possibility of methane-producing bacteria or microorganisms on Mars has been suggested in the past (*1*, *2*). The source of methane could also be in water/rock reactions in the martian interior (*3*, *4*) or volcanic hot spots (*5*). Another possibility is external sources such as cometary impacts (*6*).

The Planetary Fourier Spectrometer (PFS) (*7*) operates in the infrared, covering a wavelength range of 1.2 to 45 μm (220 to 8190 cm^{-1}) in two spectral channels: the short wavelength (SW), from 1.2 to 5.5 μm, and the long wavelength (LW), from 5.5 to 45 μm (*8*, *9*). The spectral resolution is 1.3 cm^{-1} and the spatial resolution is ~10 km near the pericenter. Sampling is done every 1.02 cm^{-1}. Four bands of methane lie within the spectral range of the PFS, at 1300, 3000, 4400, and 6000 cm^{-1}. The 6000 cm^{-1} band is not suitable for detecting weak CH_4 signatures by the PFS because of the presence of many strong solar Fraunhofer lines and the lack of a reference solar spectrum in this region to subtract these lines. In the 4400 and 1300 cm^{-1} regions, there is some evidence of spectral signatures of minor species. However, the signal-to-noise ratio (SNR) (*10*) of the PFS is much greater in the 3000 cm^{-1} region. Therefore, we have searched for methane in this band (ν_3), centered at 3018 cm^{-1}, which is also the strongest fundamental band of methane. To increase the SNR, we first averaged data from 16 orbits obtained in January-February 2004 (*11*), covering the entire longitude range. For 16 orbits, about 100 spectra were selected in the equatorial region where a high radiance level is expected, and a total of 1680 spectra were averaged together to obtain a global spectrum (Fig. 1A). An average of 2931 spectra taken in 24 orbits during a following period in May 2004 is shown in Fig. 1B.

The electronic noise of the instrument providing a 1σ (67%) confidence level in the measurements was computed from measurements of deep space. For the SW channel of the PFS, deep space corresponds to a source of radiance intensity zero; hence it provides a measure of the instrumental noise (*10*). The noise equivalent radiance (NER) of a single spectrum at 3000 cm^{-1} is 0.01 erg/(s sr cm^2 cm^{-1}). Accordingly, the S/N ratios for our two data sets are about 1300 (Fig. 1A) and 1500 (Fig. 1B), respectively. A number of solar and water vapor lines can be identified in the spectrum. However, certain features, particularly the ones at 3006.5, 3009, and 3018 cm^{-1}, are not associated with any presently known molecules of the martian atmosphere. Figure 2, A and B, shows a comparison of the averaged data, with synthetic spectra calculated with a mean H_2O mixing ratio of 350 parts per million (ppm). With a depth of about 1% (that is, more than 10 times above the noise level), the line at 3018 cm^{-1} is significant, because it corresponds to the line position of maximum methane absorption in this wavenumber region (ν_3-Q branch). We identified this feature with methane by comparing it to a synthetic spectrum (*12*, *13*) (red curve in Fig. 2), and determined the abundance of methane in the atmosphere from the line depth. Other methane lines present in this region have been checked but are found to be less intense than the one presented here by at least a factor of 3 to 4. Many are hidden in water or solar lines. One of them, at 3028 cm^{-1}, is shown in the figures. Its behavior is similar to that of the main line at 3018 cm^{-1}; however, it is too weak for evaluating the mixing ratio, and it is also partially contaminated by water vapor lines.

At 3011 cm^{-1}, on the left side of a strong solar line, the discrepancy between the observed and synthetic spectra reflects an instrumental ("overshooting") effect that is frequently present in the PFS spectra in the red wing of single strong lines. Apart from this departure, a possible explanation for the discrepancies observed at other frequencies (3002, 3007, and 3009 cm^{-1}) is that they are due to unidentified minor molecular species. Further discrepancies can be due to (i) H_2O spectroscopic parameters or insufficient mixing ratio or (ii) surface albedo (which, in the 3000 cm^{-1} range, can be affected by mineralogic signatures of hydrated minerals). However, we believe that the identification of methane at 3018 cm^{-1} is definite, in view of the good fit of its wavenumber position.

The slope of the synthetic spectrum of the martian atmosphere (Fig. 2, A and B) indicates the presence of water ice clouds in the equatorial region of Mars. Indeed, the quality of the fits improves when such clouds are included in the synthetic spectra. In the synthetic spectra, the water ice cloud particles have an effective dimension of 1.25 μm (*14*), and optical constants from (*15*) have been used. From the direct comparison between the PFS spectra and the synthetic spectra (Fig. 2, A and B), we find that the observed line depth corresponds to a methane mixing ratio of approximately 10 parts per billion by volume (ppbv) or somewhat greater. Considering the uncertainty of the fitting with the synthetic spectrum (*10*), we derive a conservative CH_4 mixing ratio of 10 ± 5 ppbv (*16*). The synthetic calculations also show that because the individual lines are not saturated, the depth of the ν_3-Q branch should increase almost linearly with increasing mixing ratio, and this fact can be used to identify and study variations of the methane mixing ratio.

An examination of orbits with a higher air-mass factor can provide greater confidence in our analysis, because the methane line depth should increase with increasing amounts of CH_4 along the line of sight. This is possible to do because occasionally Mars Express does not point to the nadir, its normal operation mode, but at a slant angle due to its inertial attitude. This results in an increased air mass in the line of sight, which implies that the line of sight abundance of methane should also increase, whereas its mixing ratio is expected to remain unchanged. The average spectrum over 121 measurements taken during the

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pericenter pass of orbit 145, with an air-mass factor of 1.12, is shown in Fig. 3. Upon taking into account the air-mass factor, we obtain a methane mixing ratio of 30 ± 5 ppbv. This value is higher than the global average ratio of 10 ± 5 ppbv and indicates that the methane mixing ratio may be variable. Motivated by this possibility, we have examined several other orbits, including orbit 68, 202, and 72, for which the air-mass factors are, respectively, 1.03, 1.33, and 2.1. We discovered that orbit 72, for which the air-mass factor (2.1) was even greater than in orbit 145 (1.12), gives another extreme in CH_4. Because the number of measurements for this case (120) is close to those in orbit 145, a similar sigma value is obtained. Figure 4 gives the average PFS spectrum for orbit 72. However, there is no indication of the methane line, and the synthetic spectrum with no methane fits the data nicely. Because the synthetic spectrum fitting orbit 72 data has been computed using the same solar spectrum as we used for other fits, this indicates that the 3018 cm^{-1} line was not due to the Sun. From the four orbits 68, 145, 202, and 72, with respective air-mass factors of 1.03, 1.12, 1.33, and 2.1, methane mixing ratios of 9, 30, 30, and 0 ppbv are derived by comparing the observed methane line depth to synthetic spectra, after taking into account the air-mass factors. In the case of orbit 72, we conclude that the methane abundance is below our detectability limit: lower than 5 ppbv.

The above variation in CH_4 could represent either spatial or temporal changes or both. Because the time span of our observations (January through May 2004) is short compared to the martian year (almost 2 Earth years) and seasons (about 6 months each), the CH_4 variation mentioned above can be studied versus spatial changes. Space variations could be present because of localized sources and/or localized surface sinks. We can attempt to determine whether the spatial variations occur over a large range of longitude by dividing our original 16 orbits (or 24 orbits) into three longitudinal ranges: longitudes –55° to –170° (orbits 10, 30, 32, 41, *44*, and *202*); longitudes +52° to –55° (orbits 20, 61, 100, 103, *145*, and 148); and longitudes +52° to +190° (orbits 24, 71, *72*, and 97) (the numbers in italics represent inertial orbits) (Fig. 5). The three sets of orbits for the second group are as follows: longitudes –55° to –170° (orbits *390*, 386, 394, 397, *400*, and 401); longitudes +52° to –55° (orbits *404*, 405, *408*, *410*, 411, 426, 427, *428*, *429*, 430, and *431*); longitudes +52° to +19° (orbits *414*, *417*, 418, 420, 421, 424, and 425) (the numbers in italics represent inertial orbits). The three sets of longitudes are presented in different colors in Fig. 5.

The methane mixing ratio decreases from group 1 to group 3 (Fig. 6). The best fit is obtained for the methane mixing ratios of 25 ± 5, 15 ± 5, and 10 ± 5 ppbv, respectively, for the three longitude ranges, going from eastern longitudes to western longitudes. However, orbit 145 in group 2 has the highest mixing ratio of any individual orbit, implying that methane concentrations can be high in smaller regions within these longitudinal ranges.

Previously, an upper limit of 20 ppbv of methane was obtained by Mariner 9 (*17*), and another one of 70 ± 50 ppbv was inferred from ground-based observations (*18*). However, recently two ground-based detections of methane were reported (*19*, *20*) with a mixing ratio of 11 ± 4 ppbv (*20*), in agreement with the Mars Express PFS result for the global methane mixing ratio.

On Earth, the dominant source of methane is biogenic sources such as termites and cattle (*21*). Other sources of terrestrial methane include marshes, rice paddies, natural gas, lakes, and oceans. On Mars, methane could be derived from biogenic sources such as subsurface microorganisms (*1*) or nonbiogenic sources such as the slow release of methane stored in subsurface reservoirs, outgassing from volcanic/hydrothermal reservoirs, or the destruction of meteoritic or cometary material during infall. We estimated the global methane mixing ratio produced by each of these sources. The observed global average mixing ratio of 10 ppbv amounts to a column abundance of 2.2 × 10^{15} cm^{-2} CH_4 molecules at the surface of Mars. Assuming a CH_4 photochemical lifetime of ~2 × 10^{10} s near the surface (*5*, *23*) we estimate that a flux of ~1 × 10^5 molecules cm^{-2} s^{-1} would be required to explain a CH_4 mixing ratio of 10 ppb on Mars (*16*). Integrated over the planet, this would amount to a methane source strength of ~4 g s^{-1}; that is, ~1.26 × 10^5 kg $year^{-1}$ or ~126 tons $year^{-1}$.

The flux of micrometeoritic dust at Mars is estimated to be ~300 g s^{-1} or ~9000 tons $year^{-1}$ (*24*). Most of it would burn up in the atmosphere, but allowing for a generous 25% surviving to the surface (*24*), nearly 2300 tons $year^{-1}$ could reach the surface of Mars. If all of the micrometeoritic dust is assumed to be from carbonaceous chondrites, then organic materials would comprise about 3% of the flux (*25*): ~70 tons $year^{-1}$. If all of the organic materials could be converted to methane, then micrometeoritic sources of methane would be roughly comparable to that needed to explain

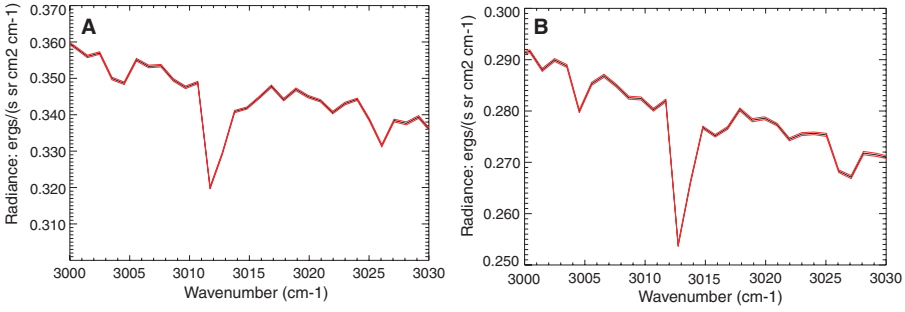


Fig. 1. (**A**) A portion of the first averaged PFS spectrum (January-February 2004, black curve), with ±1σ confidence (red lines). The SNR is about 1300. Methane is identified at 3018 cm^{-1}. There are three water lines (at 3003.5, 3022, and 3026 cm^{-1}) and two solar lines (at 3012 and 3014 cm^{-1}). The continuum slope is due to water ice clouds in the atmosphere. The small peak at the left of the main solar line is due to instrumental response function. (**B**) The second averaged PFS spectrum (May 2004) in the same frequency interval. The caption is the same as for (A). The SNR is about 1500.

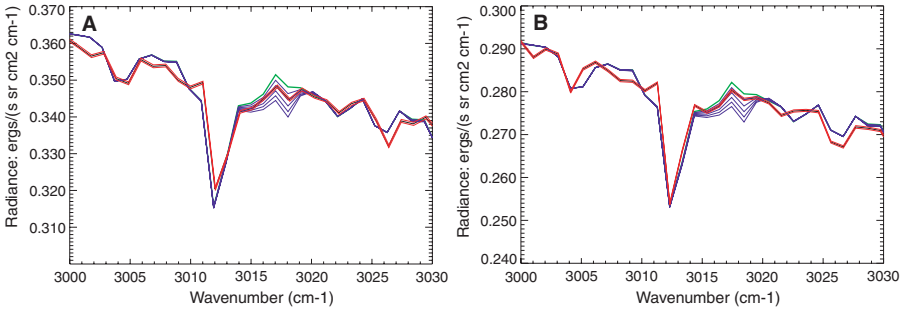


Fig. 2. (**A**) Synthetic spectra computed for 0 ppbv (green curve) and 10, 20, 30, 40, and 50 ppbv (violet curves) of methane, compared with the PFS average spectrum (black curve). The synthetic spectra have been computed for 6.7 millibars of CO_2, including 350 ppm of H_2O, along with dust and water ice clouds. The temperature profile obtained from simultaneous measurements in the thermal radiation was used. (**B**) Same as (A), with the PFS mean spectrum shown in Fig. 1B.

the 10 ppbv measured with the PFS. However, the estimated necessary micrometeoritic source of methane is much greater than what could realistically be produced, because carbonaceous chondritic material is not representative of most meteorites, which are actually depleted in carbon, and whatever organics enter the martian atmosphere would most likely not be converted to methane in the planet's oxidizing environment.

Comets are potentially the largest exogenous source of methane at Mars. From observations of eight Oort cloud comets (*26*), we conclude that the CH_4/H_2O mixing ratio lies in the 0.15 to 1.5% range, with most comets showing >0.5% and one as high as 2.3%. For our estimate, we assume a cometary CH_4 value of 1% and that most of the mass of the comet consists of water ice. Taking an average impact rate of 1.6×10^{-8} year^{-1} for the ecliptic comets at Mars (*27*) and a typical cometary radius of 1 km, the amount of methane delivered to Mars by the comets would be on the order of 1 ton year^{-1} on average; that is, less than 1% of that needed to maintain a steady-state mixing ratio of 10 ppbv of methane on Mars. Because the lifetime of methane is only a few hundred years, the "average" flux from the comets is not a very meaningful quantity, considering the above rate of one impact every 62 million years. We have therefore considered the possibility that the methane on Mars is constantly declining and that the quantity measured today may simply be a relic of a cometary impact that occurred in the past several hundred to thousands of years. We have calculated the size of that comet, with the constraint that the impactor supplied enough methane (about three times the current abundance if the impact occurred one methane lifetime ago) that 2.2×10^{15} cm^{-2} CH_4 molecules (10 ppbv) remain today on Mars. Our calculations (*28*) show that this requires an impact by a comet with a radius ranging from as small as ~130 m, which struck Mars as recently as 100 years ago, to a radius as large as ~360 m, which struck it as long ago as 2000 years. The observed variability of methane over Mars may favor a recent impact, younger than one methane lifetime, unless some localized surface sinks are present to effciently scavenge methane from the atmosphere. It is not presently known whether a single impact event of this type did actually take place, but it appears promising enough to warrant further investigation.

On the other hand, methane could have been formed by magmatic processes or stored in methane hydrates for later release to the atmosphere. Terrestrial volcanoes are not a big source of methane, and large-scale volcanism has not taken place on Mars for over 100 million years. However, small-scale outgassing of methane cannot be ruled out. A potentially larger source of methane than volcanism may come from the alteration of basalt at a temperature <150°C, a process that also results in the wet-phase conversion of original CO_2 into CH_4 in a subpermafrost aquifer. In their chemical equilibrium computer model, Wallendahl *et al*. (*3*) calculate that as much as 0.2 bar, or ~10^{15} tons, of CH_4 could have been produced if the only source of C in this region was the CO_2 initially present in the crustal pores. Methane could have been sequestered in stable methane hydrate and gradually risen to the planet's surface (*4*). The rate of release to the atmosphere is unknown, but if one assumes that leaking has been taking place at a uniform rate over time, it would amount to ~200,000 tons year^{-1}, which is much greater than the 100 tons or so per year needed to maintain a steady-state mixing ratio of 10 ppbv of CH_4 on Mars today. Even if methane from the hydrate is being released at a rate that is a factor of 1000 slower, it would still be sufficient to account for the observations. Finally, recent laboratory experiments confirm abiogenic generation of methane in mineral-catalyzed hydrothermal reactions of CO_2 and H_2O at 390°C and 400 bars (*29*),

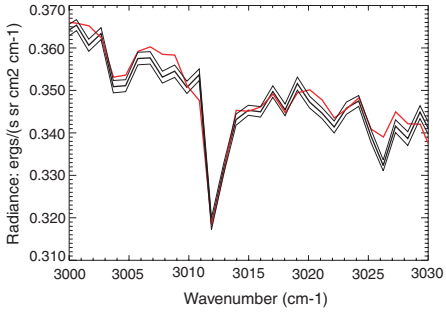


Fig. 3. Average of 121 PFS spectra (black curve) and synthetic spectra with 35 ppbv of methane (red line) for orbit 145 of Mars Express (inertial attitude). The error on the measurements is shown as ±1σ confidence lines. The water vapor mixing ratio used for the synthetic spectrum is 600 ppmv.

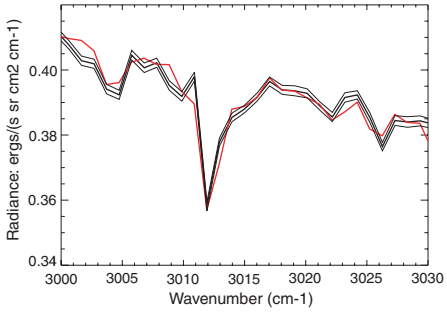


Fig. 4. Average PFS spectrum (black curve) for orbit 72 of Mars Express (inertial attitude, airmass factor 2.1). The error on the measurements is shown as ±1σ confidence lines. The PFS spectrum is an average over 120 measurements. A synthetic spectrum with 0 ppbv is shown, in good agreement with the measurements. The water mixing ratio is 400 ppb.

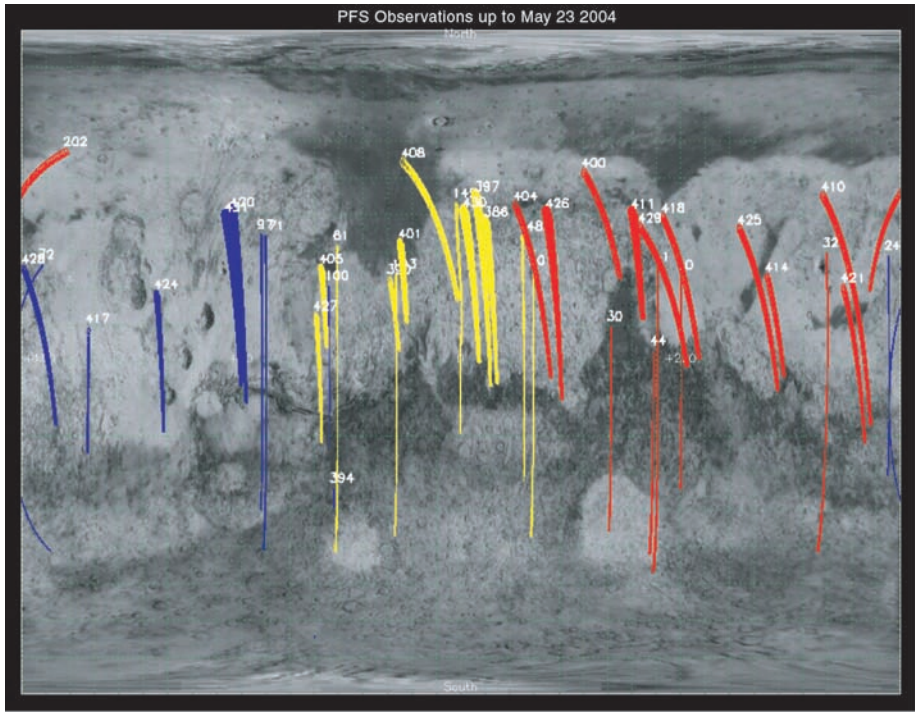


Fig. 5. Geographical distribution of the orbits considered: red (high methane mixing ratio), yellow (medium methane mixing ratio), and blue (low methane mixing ratio). Strong fluctuations occur in each of the three categories, indicating the possible presence of localized sources.

conditions that are likely to be encountered in subpermafrost aquifers or deep under the polar ice on Mars. Moreover, the catalyst used in the experiment—Fe-Cr oxide—is also believed to be present in the martian rocks.

If the source is biogenic and current, methanogens that use CO or H_2 for energy are candidate sources. Chemolithotrophic microbial ecosystems are common deep in Earth's subsurface, and they release methane as a product of metabolism, as in $4CO + 2H_2O \rightarrow CH_4 + 3CO_2$, and $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ (*30*–*32*). There exists a distinct possibility that in the subpermafrost aquifer environment of Mars, one or several microbial colonies may exist, where microorganisms utilize CO and/or H_2 and produce methane in turn (*1*, *2*). The martian atmosphere provides a ready source of CO [~700 ppm (*33*)] and H_2 [40 to 50 ppm of H_2, based on models and observations (*34*–*37*)]. These gases are expected to diffuse through the regolith to the subsurface aquifers. Abundant H_2 may also be made available locally via the hydration of ultramafic silicates. It has been suggested that the source of methane need not be current. If microorganisms existed on Mars only in the past during its (possible) warm and wet phase and produced methane, that methane could have been stored in methane hydrates for later release, as discussed above. A comparison of the CH_4 source strength at Mars (4 g s^{-1}) with that on Earth [1.67×10^7 g s^{-1}(*38*)] indicates that if methane on Mars is microbial in origin, the microbe population must be tiny. This is because nearly all of the 1700 ppbv of CH_4 in Earth's atmosphere has its ultimate origin in living things, and the martian source pales in comparison. It is important to point out that if microorganisms are or were present on Mars, the subpermafrost region is their most likely abode, because the presence of hydrogen peroxide, intense ultraviolet (UV) radiation, and the low temperature and low pressure at the surface of Mars would render the surface hostile to life as we know it.

Finally, the relatively long lifetime of CH_4 implies that the CH_4 distribution is expected to be uniform over the planet once a steady state is reached. The observed nonuniform distribution of CH_4 is indicative of either localized source(s) or localized sink(s), or both. Diffusion of CH_4 through the regolith into the interior of Mars is a distinct possibility. The surface loss could result in a nonuniform distribution of methane on Mars only if the process is more efficient than the time it takes for methane to become uniform, which is on the order of a few weeks or faster in the martian atmosphere. If the local surface sink, such as a sink due to varying mineralogy including surface oxidants, is not as rapid, a cometary source for methane on Mars would be less viable. We want to stress that the detection of methane does not imply the presence of life on Mars, now or in the past. It is one possibility, but as shown above, other sources are at least as plausible (*39*).

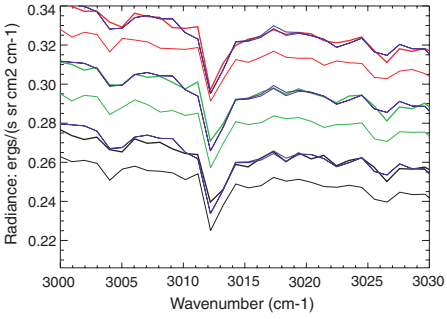


Fig. 6. Methane variation with longitude. Average PFS spectra for the January period (thick lines) and for the May period (thin lines) are shown. Curves have been vertically displaced for clarity. Corresponding SNRs range between 900 and 1040. For the 55° to 170° longitude case of January (thick black line), synthetic spectra with 20 and 30 ppbv of CH_4 are shown. The best fit result is 25 ± 5 ppbv of CH_4. Similarly, for the green curve, synthetic spectra with 10 and 20 ppbv of CH_4 are shown, and the best fit is with 15 ± 5 ppbv of CH_4. The red curve is shown with the 0 and 10 ppbv synthetic spectrum; the best fit is with slightly less than 10 ppbv of methane. The thin curves (spectra obtained in May) show the same behavior; fits are omitted for clarity.

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8. V. Formisano, in preparation.
9. M. Giuranna, in preparation.
10. See the discussion on the SNR and NER in the supporting online material (SOM).
11. The data cover the period from January 2004 through early February 2004 (areocentric longitude of the Sun = 330° to 350°) and the May 2004 period. This period is long compared with the average transport period in the atmosphere (less than 1 week for global dust storms), and it is short with respect to the martian year and a martian season.
12. See the discussion in the SOM on the computation of synthetic spectra.
13. N. I. Ignatiev, in preparation.
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22. The CH_4 lifetime used in the calculations (~2×10^{10} s near the surface) is taken from (*5*). It also agrees with the value for the lower atmosphere shown in figure 2 of (*39*). Because the photochemical loss of CH_4 is due to oxidation by OH and $O(^1D)$ near the surface and by solar UV above ~70 km, its lifetime can vary depending on the solar UV flux and the actual atmospheric water vapor and ozone distributions. The lifetime used in our calculations is based on average solar and martian conditions (150 ppm of H_2O at the surface), and it represents an e-folding time, or the time over which the concentration drops by a factor of exp(1) or 2.7, not by a factor of 2. For a methane lifetime that is shorter by a factor of 2, the required methane flux would be roughly twice as large.
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40. The PFS was built at the Istituto di Fisica dello Spazio Interplanetario of the Istituto Nazionale di Astrofisica, and the investigation is being funded by the Italian Space Agency (ASI) in the context of the Italian participation in the Mars Express mission of the European Space Agency. S.A. acknowledges support from NASA/Jet Propulsion Laboratory for participation in the Mars Express project. We are grateful to V. Cottini for a number of synthetic spectra computations and to A. Maturilli for the mapping figure.

Supporting Online Material

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References and Notes

21 June 2004; accepted 18 October 2004
Published online 28 October 2004;
10.1126/science.1101732
Include this information when citing this paper.