Atmospheric biomarkers of subsurface life on Mars

Michael E. Summers, B. Joseph Lieb, and Emily Chapman
School of Computational Sciences and Department of Physics and Astronomy, George Mason University, Fairfax, Virginia, USA

Yuk L. Yung
California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California, USA

Received 24 April 2002; revised 19 June 2002; accepted 18 July 2002; published 20 December 2002.

[1] If life exists beneath the Martian surface similar to terrestrial bacteria that rely upon chemical reactions involving H₂ and/or CO as energy sources, then it may be possible to infer its existence by observing metabolic by-products that would appear as trace gases in the Martian atmosphere. We have studied the fate of organic trace gases in the Martian atmosphere and find that most have very short chemical lifetimes, however CH₄ has a chemical lifetime of about 300 yrs and thus it will tend to be uniformly distributed in the Martian atmosphere. Using the current observational upper limit on atmospheric CH₄ we deduce that its flux, from all sources, into the Martian atmosphere must be at least 10⁵ times less than terrestrial bacteria that rely upon chemical reactions. Thus, if life exists, it is conceivable that subsurface life could persist to the warmer, and if supplied with liquid water and usable energy, life originated early in Martian history when the planet was liquid water also suggests that liquid water may be present at shallow depths at least at some locations on Mars [Malin and Edgett, 2000]. Furthermore, the geologically young volcanic features in the Tharsis region [Carr, 1996] suggest that geothermal energy may be available to maintain underground water in the liquid form.

[4] The Martian atmosphere is dominated by CO₂ (95.3%), N₂ (2.7%) and ⁴⁰Ar (1.6%) with a surface pressure ~6–10 mbar [Yung and DeMore, 1999]. The CO₂ partial pressure is controlled by vapor pressure equilibrium between the gas and solid phase at the poles [Carr, 1996]. Water vapor is present at a much lower level (0.03%) and is controlled by ice/gas equilibrium within the atmosphere and on or underneath the surface. Trace gases, such as O₂, O₃, CO, and H₂ are present in the Martian atmosphere and produced by solar driven photochemistry acting upon their source molecules CO₂ and H₂O [Nair et al., 1994]. In such an atmosphere, organic trace gases released from the subsurface would be rapidly oxidized.

2. Chemical Model

[5] In Figure 1 we show the vertical profiles of several trace gases in the Martian atmosphere obtained from a one-dimensional (vertical coordinate), globally averaged, photochemical-vertical transport model [Nair et al., 1994; Anbar et al., 1993]. An earlier version of this model has been used to simulate Earth-based observations of several atmospheric constituents in the Martian atmosphere, e.g., CO, O₂ and O₃ [Nair et al., 1994]. We have modified this model to include reducing photochemistry, in particular that of CH₄, H₂S, HCN and others discussed below. As far as we are aware this is the first model of the Martian atmosphere to include reducing chemistry. On Earth the simultaneous presence of both reducing and oxidizing gases, e.g. CH₄ and O₂, is a hallmark of life. Methane is rapidly oxidized in the Earth’s atmosphere and thus the persistence of this disequilibrium mix of gases is due directly to their biological sources. It is thus reasonable to look for disequilibrium mix of gases on Mars or other planets as potential signatures of life.

[6] Here we are concerned with how background trace gases react with and destroy putative organic molecules, so for this study we have fixed the model surface abundances of H₂, CO, and O₂ (which enter as model boundary conditions) to their observed/inferred values of 40 ppmv (parts per million by volume) [Krasnopolsky et al., 1998], 600 ppmv [Clancy et al., 1990] and 1300 ppmv [Yung and DeMore, 1999], respectively. We use a standard eddy mixing parameterization to characterize globally averaged vertical transport and integrate the model forward in time.
reactions with OH and O(1D). Above lifetimes of selected biogenic trace gases [lifetimes. The chemical loss of H2S (a product of terrestrial transport calculations in order to determine their chemical these constituents are independent of their actual atmos-
pheral loss. The loss of CH3COOH is due to reaction with OH. We also, shown is the tentative detection (70 ± 50 ppb) by Krasnopolsky et al. [1997], and the upper limit obtained by Lellouch et al. [2000].

until a steady state is reached. The model will thus simulate the long-term chemical conditions of the atmosphere. Atmospheric constituents that have long chemical lifetimes (e-folding timescale for concentration changes) compared to the vertical transport timescale (due to vertical eddy mixing), e.g., O2 and H2, exhibit quasi-uniform mixing ratio profiles as seen in Figure 1. Other species that have chemical lifetimes shorter than the transport timescale, e.g. OH and O3, have equilibrium concentration profiles that reflect the local balance between chemical production and loss.

[7] From the model results we have calculated chemical lifetimes of selected biogenic trace gases [Weiss et al., 2000] that we show in Figure 2. Note that the chemical lifetimes of these constituents are independent of their actual atmospheric concentrations, thus it is not necessary to perform transport calculations in order to determine their chemical lifetimes. The chemical loss of H2S (a product of terrestrial cyanobacteria metabolism) and CH2O are dominated by reaction with OH below ~40 km altitude. Above that level both photolysis and the reaction with O contribute to their loss. The loss of CH2COOH is due to reaction with OH. We find that methane has a chemical lifetime near the Martian surface of ~300 yrs, and its chemical loss is controlled by reactions with OH and O(1D). Above ~60 km altitude solar photolysis, mostly at 121.56 nm wavelength (Lyman α), begins to dominate CH4 loss, and above ~100 km additional loss is by ion-molecule reactions.

[8] Near the surface, the lifetimes of CH2O, H2S, and CH2COOH are roughly 2 weeks, 3 months, and 1 year, respectively. Given a vertical eddy mixing timescale of order 3 months near the Martian surface, and a horizontal transport timescale of order of several days, we would expect CH2O to have an abundance that decreases rapidly with distance from its source region. Thus observations of the geographic distributions of such short-lived biogenic trace gases could be used to map their source regions. For the other molecules, and in particular CH4 with its very long chemical lifetime, their mixing ratios will be more uniform on a global scale.

[9] There are several types of terrestrial bacteria that utilize H2 (4H2 + CO2 → CH4 + 2H2O) or CO (3CO + 2H2O → CH4 + 2CO2) as energy sources, the energy for metabolism being extracted from the molecular bonds [Stevens and McKinley, 1995; Weiss et al., 2000; Chapelle et al., 2002]. On Mars both H2 and CO are readily produced in the atmosphere by the photochemical breakdown of H2O and CO2, respectively. Diffusion of H2 and CO downward into the Martian regolith could provide a subsurface biosphere with a continual source of energy for metabolism [Boston et al., 1992; Weiss et al., 2000]. On Earth, anaerobic methanogens utilize H2 and CO in metabolism and release CH4 as a by-product. Recent laboratory studies of hydrogen consumption by Methanobacterium wolfei, Methanobacterium formicicum and Methanosarcina barkeri, under conditions that mimic those expected in Martian subsurface habitats [Kral et al., 1998, 2000], have shown that these bacteria can indeed metabolize as long as the H2 concentration is above 15 ppmv (see Figure 1). On Mars, the CH4 produced from such a terrestrial-type form of life would remain in the gas phase, diffuse upward and into the atmosphere, where it would be oxidized by OH and O(1D).

[10] We assume that the energy source for Martian subsurface life is provided by photochemically produced CO and H2, i.e., the atmospheric production rate of CO and H2 thus limits metabolism and thus organic production of CH4. The globally averaged atmospheric production rate for CO is φCO = 8.6 × 108 cm2 s−1 and for H2 is φH2 = 8.8 × 109 cm2 s−1 respectively. In addition, we assume a global coverage factor α, and a CO/H2 to CH4 conversion efficiency ε. Thus, in the case of CO, the upward flux of CH4 into the atmosphere will be given by αεφCO. We assume an ad hoc value for αε = 10−4, which can be interpreted as, e.g. a 1% coverage of subsurface life with a 1% conversion efficiency, i.e. only 10−4 of the global atmospheric production of CO is utilized by subsurface life.

[11] Note that αεφ is an absolute upper limit, i.e., the subsurface ecology would in this case be utilizing all CO and/or H2 that is photochemically produced in the Martian

Figure 1. Model calculation of the vertical mixing ratios of trace gases in the Martian atmosphere using the Caltech photochemical-vertical transport model [Nair et al., 1994]. Shown are the CH4 mixing ratios for two cases where the upward flux of CH4 is a consequence of subsurface metabolism. Also, shown is the tentative detection (70 ± 50 ppb) by Krasnopolsky et al. [1997], and the upper limit obtained by Lellouch et al. [2000].

Figure 2. Diurnal average of chemical lifetimes of selected biogenic molecules in the Martian atmosphere are shown in comparison with the vertical eddy mixing timescale.
atmosphere. We calculate the atmospheric CH₄ abundance profiles for two cases: one case where H₂ and the other where CO is the energy source. As on Earth, it is unlikely that a single type of bacteria could simultaneously use both for metabolism. For simplicity we consider them separately, although it is possible that multiple forms of chemisynthesizers have evolved on Mars. With a surface source of CH₄ given by $\omega_\text{CH}_4$, the model CH₄ abundance reaches a steady state distribution within less than a thousand years.

[12] As seen in Figure 1, the CH₄ mixing ratio for the H₂ (CO) case is approximately $1.5 \times 10^{-9}$ ($1.4 \times 10^{-9}$) at the surface and its vertical profile is quasi-constant below ~60 km altitude, but begins to decrease above that altitude due to photolysis. Above ~110 km altitude the CH₄ mixing ratio increases with altitude as a consequence of diffusive separation, in spite of its rapid loss by photolysis and ion-molecule charge exchange reactions in the Martian upper atmosphere. The long chemical lifetime of CH₄ in the Martian atmosphere has an important consequence for the possibility of remote detection of this potential biomarker of subsurface life. Because the lifetime is substantially longer than transport timescales, CH₄ will be uniformly distributed globally (both horizontally and vertically) by various transport mechanisms even if its source is very localized. This will facilitate its remote detection, possibly even from Earth.

[13] The calculated atmospheric mixing ratio of CH₄ will scale roughly with the assumed value for $\omega_\text{CH}_4$, as long as CH₄ is a minor constituent such that it does not affect the thermal or dynamical state of the atmosphere. For example, $\omega_\text{CH}_4 = 10^{-5}$ (with an H₂ energy source) would imply a CH₄ mixing ratio of $1.5 \times 10^{-9}$. Although a tentative detection of CH₄ in the Martian atmosphere of $70 \pm 50$ ppbv (parts per billion by volume) has been reported [Krasnopolsky et al., 1997], more recent ISO (Infrared Space Observatory) Mars observations in the 3–8 μm wavelength region give a CH₄ upper limit of 50 ppbv [Lellouch et al., 2000]. Using the latter upper limit, we infer that $\omega_\text{CH}_4 < 3.3 \times 10^{-6}$. Thus if subsurface chemisynthesizers as discussed above exist on Mars, they must be regionally very restricted, have small H₂/CO conversion efficiencies, or both.

[14] From the observed upper limit of 50 ppbv, we can also calculate the maximum upward surface flux of CH₄ on Mars, independent of assumptions about biology and $\omega_\text{CH}_4$. From our model simulations we find that the globally averaged upward flux of CH₄ into the Martian atmosphere must be $<3 \times 10^6$ cm⁻² s⁻¹ in order for the steady state atmospheric abundance of CH₄ to be $<50$ ppbv. This equates to a global source of <110 gm s⁻¹, which is about $6.4 \times 10^{-6}$ times the terrestrial value of $1.7 \times 10^7$ gm s⁻¹ [Yung and DeMore, 1999]. This upper limit will pertain regardless of the source of the CH₄, i.e., whether or not the source is due to chemisynthesizers using H₂ and CO as power sources, lithophiles using water-rock reactions for energy, or even if the CH₄ is due to abiotic processes. If there are significant abiotic sources of CH₄ on Mars, e.g., methane production in hydrothermal systems, then the biological component must be even less. Because of methane's long chemical lifetime in the atmosphere, a global averaged measurement of its abundance or a single measurement at any location (far from its source region) would be sufficient to quantitative its global flux from the subsurface into the atmosphere.

[15] We note that the precision of current FTIR occultation measurements for CH₄ in the Martian atmosphere is a mixing ratio of $1.4 \times 10^{-10}$ (Toon, G.C., private communication). Thus compared to the Earth we should be able to detect, with current techniques, a Martian subsurface CH₄ source that is on the order of $1.8 \times 10^{-8}$ times that of the terrestrial source. This can provide the strictest test that we are aware of for a hypothetical subsurface biosphere of Mars.

3. Discussion

[16] The atmospheric lifetime of CH₄ in the atmosphere of Mars is ~300 yrs. What are the processes that can shorten this lifetime? There are two possibilities. One is oxidation on the surface via heterogeneous reactions, and the other is consumption by Martian bacteria. We shall argue that neither is likely on the basis of analogy with H₂.

[17] The CH₃H bond and H-H bond are 105 and 104 kcal/mole, respectively. Consequently, the chemical reactivity of these two molecules is similar. For example, the lifetime of H₂ in the Martian atmosphere is similar to that of CH₄. An estimate of the potential loss of H₂, other than via atmospheric chemistry, has recently been made [Weiss et al., 2000]. The photochemical model of Mars predicts an H₂ concentration of 37 ppmv [Nair et al., 1994]. The observational constraint on H₂ is 40 ± 10 ppmv [Krasnopolsky et al., 1998]. Thus if there were a large additional surface sink for H₂ on Mars, the observed H₂ abundance would be too small compared with the model prediction. The fact that it is not indicates that surface oxidation has little effect on H₂. Because of their similar chemical properties surface oxidation is thus expected to have little effect on the atmospheric abundance of CH₄. In addition we have performed model simulations where we assume that every CH₄ molecule that hits the surface is lost via oxidation. Even in this case the atmospheric mixing ratio of CH₄ is decreased by at most 30%. The reason is due to the fact that vertical transport by eddy mixing transports trace gases predominantly from source regions (the surface) to sink regions (higher in the atmosphere where oxidation by OH and O(1D) occurs.)

[18] The possibility of consumption of H₂ by bacteria on Mars has been recently studied by Kral et al. [2000]. They determined the minimum value of the concentration of H₂ at which uptake by bacteria was observed. The lowest value reported was 15 ppmv of H₂. Thus, it is unlikely that H₂ is of use to the biosphere unless it is significantly above above ~1 ppmv. Similar experiments have not been done for CH₄, but again CH₄ and H₂ have similar chemical bonds and similar results would be expected. The upper limit of CH₄ on Mars is 0.05 ppmv and hence it is unlikely to be usable by the subsurface biosphere. Furthermore, there is at least 800 times more H₂ than CH₄ in the Martian atmosphere, which would strongly favor the evolution of methane producers over consumers.

[19] Detection of CH₄ or any other of these organic molecules in the Martian atmosphere will not in itself prove the existence of sub-surface life on Mars. Cometary impacts have most likely released CH₄ and other organic molecules that will provide a transient source of atmospheric gases. It is also possible that CH₄ could be released from the Martian
interior and is thus primordial in origin. If CH₄ is detected on Mars, then the next step would be to determine the isotopic fractionation of $^{13}$CH₄ and CH₃D relative to CO₂ and HDO, respectively. This may offer a possible discrimination between biological and geochemical sources [Yung and DeMore, 1999].

References


