Atmospheric biomarkers of subsurface life on Mars

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[1] If life exists beneath the Martian surface similar to terrestrial bacteria that rely upon chemical reactions involving H_2 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 CH_4 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 CH_4 we deduce that its flux, from all sources, into the Martian atmosphere must be at least 10^5 times less than terrestrial value. If there are abiotic sources of CH_4 on Mars then the biological component of the CH_4 must be even less. *INDEX TERMS:* 5405 Planetology: Solid Surface Planets: Atmospheres—composition and chemistry; 6225 Planetology: Solar System Objects: Mars. **Citation:** Summers, M. E., B. J. Lieb, E. Chapman, and Y. L. Yung, Atmospheric biomarkers of subsurface life on Mars, *Geophys. Res. Lett.*, *29*(24), 2171, doi:10.1029/2002GL015377, 2002.

1. Introduction

[2] Given the highly oxidizing nature of the Martian surface and atmosphere it would be difficult for life, as we know it, to survive there [*Jakosky*, 1998]. However, if life originated early in Martian history when the planet was warmer, and if supplied with liquid water and usable energy, it is conceivable that subsurface life could persist to the present [*McKay and Stoker*, 1989]. The recognition of terrestrial extremeophiles thriving deep underground and in the deep ocean, also provides motivation to seriously consider the possibility of an extant subsurface biosphere on Mars.

[3] There is substantial evidence that liquid water was ubiquitous on the early Mars. This evidence includes the numerous fluvial features [*Carr*, 1996; *Phillips et al.*, 2001], the massive erosion of the Northern regions [*Hynek and Phillips*, 2001], and the existence of carbonates in ALH84001 [*McKay et al.*, 1996]. Some of this water might still be present as ice and/or liquid in the subsurface regolith [*Mellon and Jakosky*, 1993]. Recent Mars Orbiter Surveyor MOC images of geologically young (possibly thousands of years or less) gullies that were likely formed by the action of 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 CO_2 (95.3%), N_2 (2.7%) and ^{40}Ar (1.6%) with a surface pressure $\sim$6–10 mbar [*Yung and DeMore*, 1999]. The CO_2 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 O, O_2, O_3, CO, and H_2, are present in the Martian atmosphere and produced by solar driven photochemistry acting upon their source molecules CO_2 and H_2O [*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, O_2 and O_3 [*Nair et al.*, 1994]. We have modified this model to include reducing photochemistry, in particular that of CH_4, H_2S, 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. CH_4 and O_2, 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 mixes 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 H_2, CO, and O_2 (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
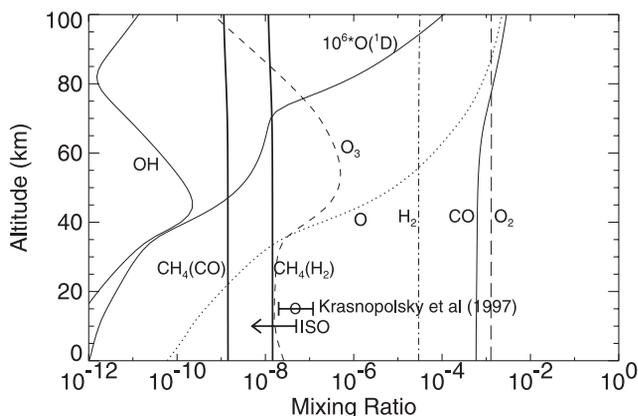
Figure 1. Model calculation of the vertical mixing ratios of trace gases in the Martian atmosphere using the Caltech photochemical-vertical transport model [*Nair et al.*, 1994]. Shown are the CH_4 mixing ratios for two cases where the upward flux of CH_4 is a consequence of subsurface metabolism. Also, shown is the tentative detection (70 ± 50 ppb) by *Krasnopolsky et al.* [1997], and the upper limit obtained by *Lellouch et al.* [2000].

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., O_2 and H_2, 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 O_3, 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 H_2S (a product of terrestrial cyanobacteria metabolism) and CH_2O 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 CH_3COOH 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 CH_4 loss, and above ~100 km additional loss is by ion-molecule reactions.

[8] Near the surface, the lifetimes of CH_2O, H_2S, and CH_3COOH 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 CH_2O 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 CH_4 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 H_2 ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$) or CO ($3CO + 2H_2O \rightarrow CH_4 + 2CO_2$) 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 H_2 and CO are readily produced in the atmosphere by the photochemical breakup of H_2O and CO_2, respectively. Diffusion of H_2 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 H_2 and CO in metabolism and release CH_4 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 H_2 concentration is above 15 ppmv (see Figure 1). On Mars, the CH_4 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 H_2, i.e., the atmospheric production rate of CO and H_2 thus limits metabolism and thus organic production of CH_4. The globally averaged atmospheric production rate for CO is $\phi_{co} = 8.6 \times 10^8$ cm^{-2} s^{-1} and for H_2 is $\phi_{H2} = 8.8 \times 10^9$ cm^{-2} s^{-1} respectively. In addition, we assume a global coverage factor α, and a CO/H_2 to CH_4 conversion efficiency ε. Thus, in the case of CO, the upward flux of CH_4 into the atmosphere will be given by $\alpha\varepsilon\phi_{co}$. We assume an ad hoc value for $\alpha\varepsilon = 10^{-4}$, 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 $\alpha\varepsilon\phi$ is an absolute upper limit, i.e., the subsurface ecology would in this case be utilizing all CO and/or H_2 that is photochemically produced in the Martian
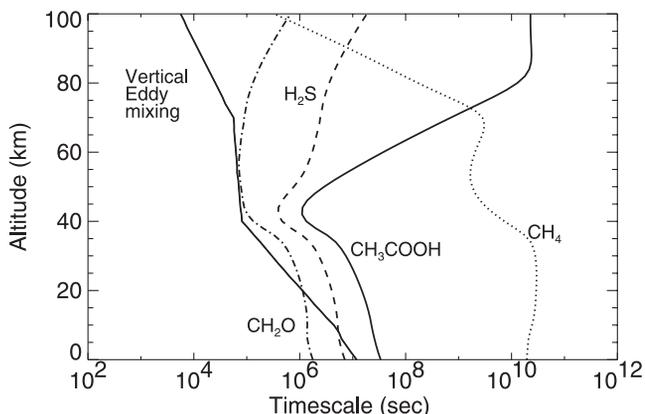

Figure 2. Diurnal average of chemical lifetimes of selected biogenic molecules in the Martian atmosphere are shown in comparison with the vertical eddy mixing timescale.

atmosphere. We calculate the atmospheric CH_4 abundance profiles for two cases: one case where H_2 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 chemisysthesizers have evolved on Mars. With a surface source of CH_4 given by $\alpha\varepsilon\phi$, the model CH_4 abundance reaches a steady state distribution within less than a thousand years.

[12] As seen in Figure 1, the CH_4 mixing ratio for the H_2 (CO) case is approximately 1.5×10^{-8} (1.4×10^{-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 CH_4 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 CH_4 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, CH_4 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 CH_4 will scale roughly with the assumed value for $\alpha\varepsilon$, as long as CH_4 is a minor constituent such that it does not affect the thermal or dynamical state of the atmosphere. For example, $\alpha\varepsilon = 10^{-5}$ (with an H_2 energy source) would imply a CH_4 mixing ratio of 1.5×10^{-9}. Although a tentative detection of CH_4 in the Martian atmosphere of 70 ± 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 CH_4 upper limit of 50 ppbv [*Lellouch et al.*, 2000]. Using the latter upper limit, we infer that $\alpha\varepsilon < 3.3 \times 10^{-4}$. Thus if subsurface chemisynthesizers as discussed above exist on Mars, they must be regionally very restricted, have small H_2/CO conversion efficiencies, or both.

[14] From the observed upper limit of 50 ppbv, we can also calculate the maximum upward surface flux of CH_4 on Mars, independent of assumptions about biology and $\alpha\varepsilon$. From our model simulations we find that the globally averaged upward flux of CH_4 into the Martian atmosphere must be $<3 \times 10^6$ cm^{-2} s^{-1} in order for the steady state atmospheric abundance of CH_4 to be <50 ppbv. This equates to global source of <110 gm s^{-1}, which is about 6.4×10^{-6} times the terrestrial value of 1.7×10^7 gm s^{-1} [*Yung and DeMore*, 1999]. This upper limit will pertain regardless of the source of the CH_4, i.e., whether or not the source is due to chemisynthesizers using H_2 and CO as power sources, lithophiles using water-rock reactions for energy, or even if the CH_4 is due to abiotic processes. If there are significant abiotic sources of CH_4 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 CH_4 in the Martian atmosphere is a mixing ratio of 1.4×10^{-10} (Toon, G.C., private communication). Thus compared to the Earth we should be able to detect, with current techniques, a Martian subsurface CH_4 source that is on the order of 1.8×10^{-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 CH_4 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 H_2.

[17] The CH_3-H 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 H_2 in the Martian atmosphere is similar to that of CH_4. An estimate of the potential loss of H_2, other than via atmospheric chemistry, has recently been made [*Weiss et al.*, 2000]. The photochemical model of Mars predicts an H_2 concentration of 37 ppmv [*Nair et al.*, 1994]. The observational constraint on H_2 is 40 ± 10 ppmv [*Krasnopolsky et al.*, 1998]. Thus if there were a large additional surface sink for H_2 on Mars, the observed H_2 abundance would be too small compared with the model prediction. The fact that it is not indicates that surface oxidization has little effect on H_2. Because of their similar chemical properties surface oxidization is thus expected to have little effect on the atmospheric abundance of CH_4. In addition we have performed model simulations where we assume that every CH_4 molecule that hits the surface is lost via oxidation. Even in this case the atmospheric mixing ratio of CH_4 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(^{1}D) occurs.)

[18] The possibility of consumption of H_2 by bacteria on Mars has been recently studied by *Kral et al.* [2000]. They determined the minimum value of the concentration of H_2 at which uptake by bacteria was observed. The lowest value reported was 15 ppmv of H_2. Thus, it is unlikely that H_2 is of use to the biosphere unless it is significantly above above ~ 1 ppmv. Similar experiments have not been done for CH_4, but again CH_4 and H_2 have similar chemical bonds and similar results would be expected. The upper limit of CH_4 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 H_2 than CH_4 in the Martian atmosphere, which would strongly favor the evolution of methane producers over consumers.

[19] Detection of CH_4 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 CH_4 and other organic molecules that will provide a transient source of atmospheric gases. It is also possible that CH_4 could be released from the Martian

interior and is thus primordial in origin. If CH_4 is detected on Mars, then the next step would be to determine the isotopic fractionation of $^{13}CH_4$ and CH_3D relative to CO_2 and HDO, respectively. This may offer a possible discrimination between biological and geochemical sources [*Yung and DeMore*, 1999].

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