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The Search for Life on Mars

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Abstract

The abiotic and biological pathways for methanogenesis on Mars are surprisingly similar. Both mechanisms use CO₂ and H₂ as starting materials and result in the production of CH₄. However, the geochemical pathway has a high kinetic barrier and the reaction is slow. A biological pathway quickens this process. The total flux of 1.7×10^7 mol year⁻¹ that is needed to maintain the observed CH₄ in steady state in the atmosphere is examined in the context of fluxes of He from the interior of the planet and photochemical production of H₂ in the atmosphere. *In situ* analysis of the isotopologues of CH₄ and estimates of the relative abundances of members of the alkane family, as well as of CH₄:H₂ ratios and species such as acetic acid, could be used to discriminate between abiotic and biological sources on Mars. Discerning how methane generation emerged on the evolutionarily retarded Mars may open a window on how life originated so long ago on our own planet.

Keywords: life, mars, methanogenesis, biochemical vortex, geochemical siphon

‘Life is flux’ Heraclitus (c. 535–c. 475 BCE)

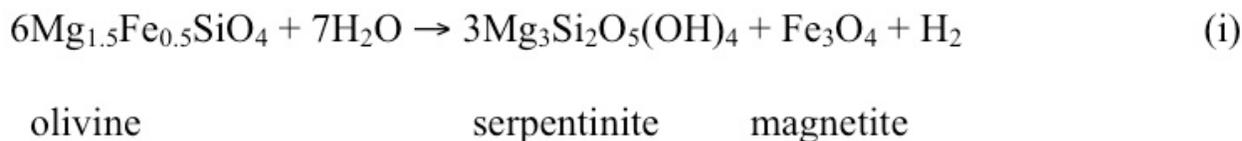
1. INTRODUCTION

That ‘Life is flux’ is clear from our present understanding of the terrestrial biosphere (e.g., Schlesinger 1997). Here we pursue this concept in our search for extraterrestrial life, focusing on Mars where the order of magnitude of the flux of organic carbon has been deduced from recent observations. It is a great challenge to determine whether the ~10 ppbv of methane (CH₄) on Mars is biogenic or not (Krasnopolsky, 2004; Formisano et al., 2004; Mumma et al., 2009). Since the lifetime of CH₄ on Mars is about 300 years (Summers et al., 2002; Wong et al., 2003) this indicates a source of 2.2×10^5 molecules cm⁻²s⁻¹, or 1.7×10^7 mol year⁻¹. For comparison, the CH₄ flux generated by the terrestrial biosphere is 3.3×10^{13} mol year⁻¹. As there is no evidence of life on the surface of Mars, any hypothetical microbes there must reside beneath the surface. The carbon flux cited above might serve as a link between a putative subterranean biosphere on Mars and what we can measure above the surface. The alternative of course is that the methane anomalies either relate to an inorganic origin or are being released from some occluded source.

This paper is divided in four sections. Section 2 gives an overview of the planetary environment and life. Section 3 discusses the possibility of life on Mars. Section 4 summarizes the conclusions.

2. PLANETARY ENVIRONMENT AND LIFE

At least in their early histories, wet rocky planets can be compared to single biological cells. The interiors of the planets are electron-rich and basic, comprising dense well structured ferrous iron- and alkaline earth-bearing minerals, while their exteriors are wet, somewhat oxidized, carbonic and mildly acidic. The insides of prokaryote cells are also crowded and well structured, consisting of relatively electron-rich organic molecules that render them slightly alkaline, whereas their exteriors are also generally more oxidized and acidic (Spitzer and Poolman, 2009). Aqueous geochemistry in the former and biochemistry in the latter are both vectorial (Harold, 2001; Russell, 2007). And the planets, as well as particular prokaryotes, can reduce the carbon dioxide that surrounds their exteriors to methane (Proskurowski et al., 2008; Brazelton et al., 2010), i.e., carbon dioxide is an electron acceptor in each case (Martin and Russell, 2007). The particular prokaryotic process that reduces carbon dioxide to methane is achieved by the methanogenic archaeobacteria, while the aqueous geochemical process achieving the same reduction, though at much lower yield, is known as serpentinization. The serpentinization process first allows electrons to be transferred from ferrous iron to hydrogen as ocean water, seeping down cracks in the crust, oxidizes the iron to magnetite (Abrajano et al. 1990; McCollom and Bach, 2009).



Then a portion of this hydrogen reduces all the carbon dioxide remaining in solution after the precipitation of calcium carbonate to methane as well as C₂ to C₄ hydrocarbons (Griffith and Shock, 1995; Proskurowski et al., 2008).



The methane, along with the unspent hydrogen, is exhaled in hydrothermal fluids at submarine springs. But can we be sure that carbon dioxide would always be there in the atmospheres of all wet rocky planets to accept electrons from hydrogen and thus act as the ultimate source of organic carbon, both biogenic and chemical? Thermodynamic calculations, as well as empirical observations, do suggest that the stable state of carbon in volcanic magmas and their exhalations is essentially carbon dioxide with negligible methane, not only on Earth (Shock, 1992; Craddock and Greeley, 2009) but also on early Mars (Hirschmann and Withers, 2008). Even the now dry planet Venus presently has a 92 bar atmosphere that is predominantly composed of CO_2 , with subordinate nitrogen and sulfur dioxide (Kasting et al., 1988; Yung and DeMore, 1999; Bullock and Grinspoon, 2001). Thus, given a source of CO_2 and H_2 , as we have seen, it is possible to form CH_4 . First, there was (and still is) the geochemical pathway as shown in Fig. 1a, which has to overcome kinetic barriers (comprising the intermediates: formate, HCOO^- , and formaldehyde HCHO) and is therefore slow. That it works at all is because once a little formaldehyde has been generated, then there is more energy to be discharged ‘downhill’ to a methyl group and thence to the stable methane molecule, than there is in the back reaction to formate and CO_2 (Fig. 1a). In other words, the hydrogenation reactions are ‘pulled’ toward methane in a process that can be likened geochemically to a siphon (Russell and Hall, 2009). The biological pathway quickens the process by way of the acetyl coenzyme-A pathway, the most ancient of biochemical pathways (Fuchs, 1989). In this case, the same kinetic impediments to methanogenesis are cleared, though much more rapidly, with the energy provided by the protonmotive force (Fig. 1b). Is there a clue here as to how life would be induced to emerge on any wet, rocky world?

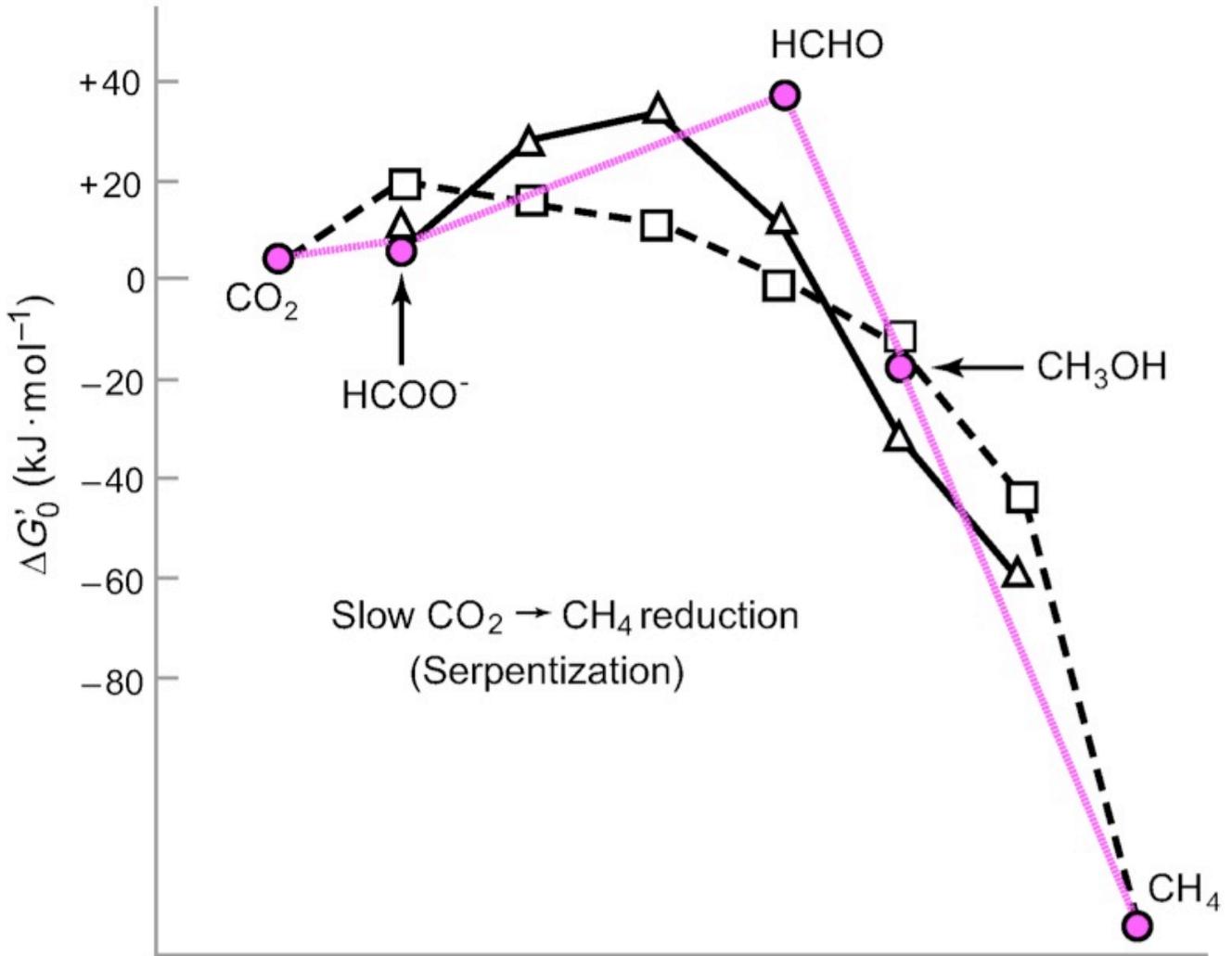


Figure 1a. Free-energy profile of the geochemical pathway (in purple) to methane (Seewald et al., 2006) is contrasted with the reduction profiles of the acetogenic bacteria (triangles) and methanogenic archaea (squares) that both use the acetyl coenzyme-A pathway. We can think of the geochemical pathway as a chemical siphon while the much more rapid biochemical pathways are driven by chemiosmosis over the intermediates, formate and formaldehyde. Adapted from Maden (2000).

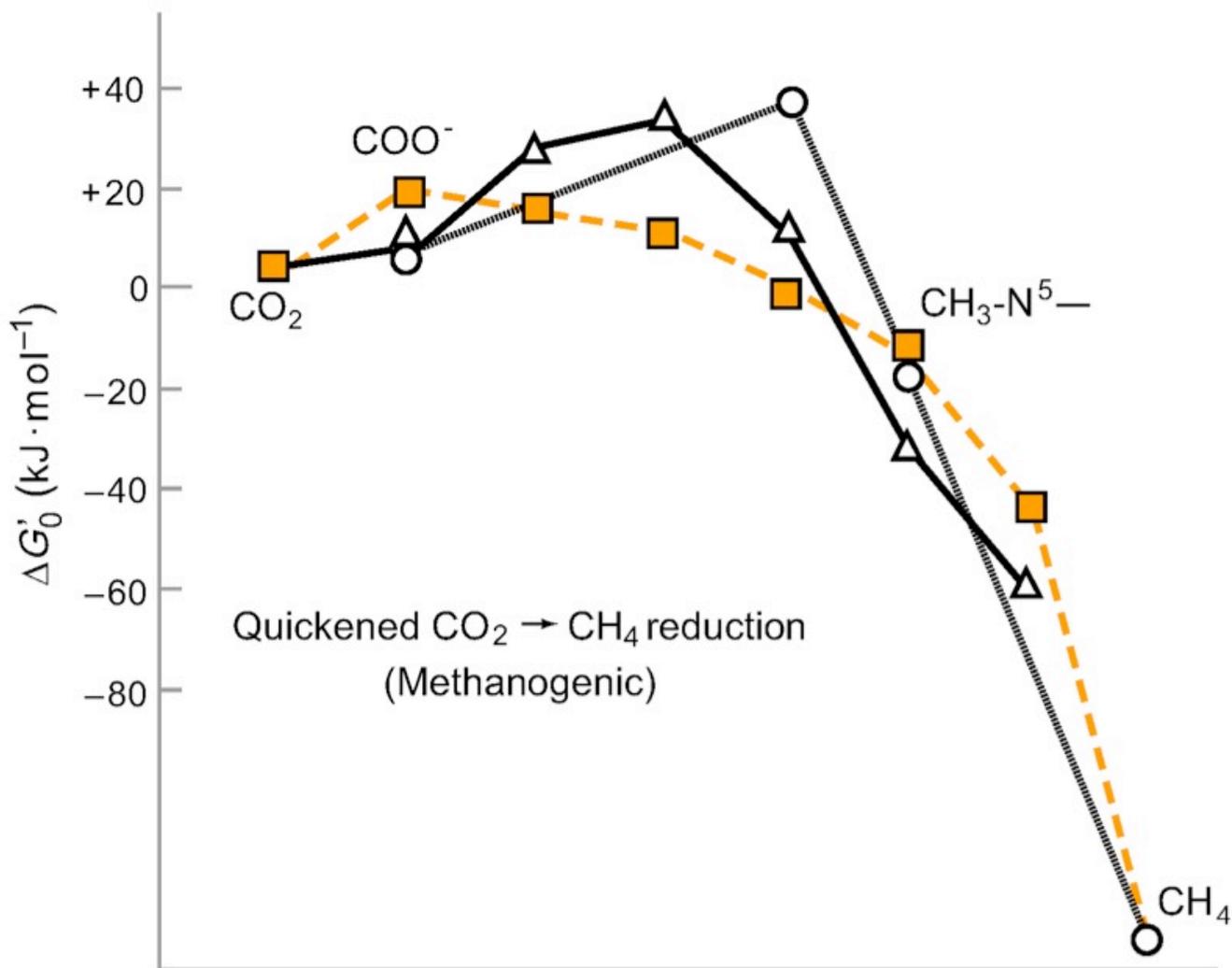


Figure 1b. Free-energy profile of the methanogenic reduction pathway (in orange) taken by the methanoarchaea compared to the sluggish geochemical pathway (open circles) and the acetogenic pathway (triangles). H₄Folate is tetrahydrofolate and H₄MPT is tetrahydromethanopterin. Adapted from Maden (2000).

We can imagine that alkaline hydrothermal fluid would be prevented from mixing with a carbonic ocean by the precipitation of inorganic materials that agglomerate into a porous submarine hydrothermal mound. The physical boundaries of the pore spaces would have the effect of damming protons on the outside of the mound while hydrogen is partially pooled in compartments constituting the inside of the mound. It is argued here that the proton pressure will be tapped through the semi-permeable barriers while the electron pressure, derived from hydrogen by iron-nickel and molybdenum sulfide clusters acting as catalysts, will find outlet to electron acceptors such as carbon dioxide and nitrate in the ambient carbonic fluid (Ducluzeau et al., 2009). The thermodynamic barriers are lowered sufficiently by these sulfide catalysts so that the proton and electron pressures can now more quickly drive the hydrogenation reactions to methane—a first step in the emergence of metabolism by way of a natural chemiosmotic process (Russell et al., 1994). This heralds the organic-takeover of the inorganic compartments with molecules produced as by-products of the overall hydrogenation reactions. Once an organic membrane and/or cell wall has evolved from peptidic products for example (Childers et al., 2009), then the coupling of proton with electron transport could be facilitated by quinone (strictly methanophenazine) chemistry (Nitschke and Russell,

2009). This complexification and evolution of the methanogenic process eventually results in the microbiologic invention of a proton pump allowing emerging life to free itself from an external proton gradient and begin to search for commensurate energies beyond the hydrothermal/water interface and so build what is known as the deep biosphere (Russell and Arndt, 2005; Martin and Russell, 2007).

3. THE MARTIAN ENVIRONMENT

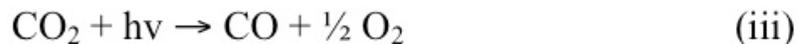
Bulk Composition and Fluxes: The chemical composition of the Martian atmosphere is well understood, thanks to earlier studies [McElroy and Donahue, 1972; Parkinson and Hunten, 1972; see also Chapter 7, Yung and DeMore, 1999]. The atmosphere consists primarily of CO₂ with trace amounts of H₂ O, CO, O₂, O₃, H₂O₂ and H₂, as summarized in Table 1a, along with model predictions in Table 1b. N₂ has been detected in the atmosphere with mole fraction of 0.027. The oxides of nitrogen do not play important roles in atmospheric chemistry.

Table 1 (a) Abundances of selected trace species in the Martian atmosphere, (b) Model predictions (unless otherwise stated, all data are from Nair et al. 1994, with updates)

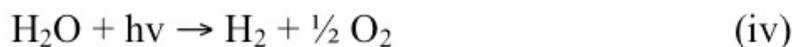
Species	Observed Abundance	References
H ₂ O	8.8 pr- μ m (variable)	
CO	$6-8 \times 10^{-4}$	
O ₂	1.2×10^{-3}	
O ₃	$(4-20) \times 10^{-8}$ (variable)	
H ₂ O ₂	1.8×10^{-8} (variable)	Clancy <i>et al.</i> (2004)
H ₂	1.5×10^{-5}	Krasnopolsky and Feldman (2001)
He	1×10^{-5}	Krasnopolsky and Gladstone (2005)

Species	Model Abundance
CO	4.6×10^{-4}
O ₂	1.2×10^{-3}
O ₃	1.9×10^{-8}
H ₂ O ₂	9.4×10^{-9}
H ₂	3.8×10^{-5}

It is somewhat surprising that the atmosphere of Mars contains oxidants, e.g., O₂, O₃ and H₂ O₂, as well as reductants, e.g., CO and H₂. It is the greatest triumph of photochemical models that we are able to account for the composition of the atmosphere from first principles. If CO and O₂ were derived from CO₂ photolysis in a pure CO₂ atmosphere, we should have



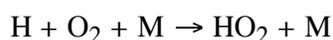
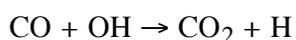
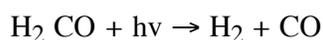
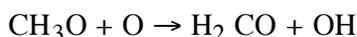
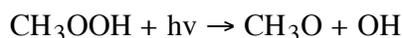
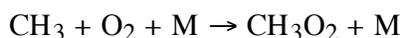
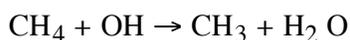
In this case, the ratio CO/O₂ should be 2. However, the observations suggest that the value of this ratio is about 1/2. Hence, there must be another source of O₂. This source has been identified to be the photolysis of H₂O



The model predicts an escape flux of $H_{\text{tot}} = H + 2H_2$ equal to 2.4×10^8 atoms $\text{cm}^{-2}\text{s}^{-1}$. The loss of hydrogen must be accompanied by an accumulation of O_2 in the atmosphere at the rate of 1.2×10^8 molecules $\text{cm}^{-2}\text{s}^{-1}$, or 9×10^9 mol year^{-1} . Eventually oxygen atoms also escape from the top of the atmosphere via a non-thermal mechanism (McElroy, 1972), so that over a long time period the oxidation state of the atmosphere remains constant.

Helium (primarily ^4He) has been detected in the atmosphere of Mars (Krasnopolsky and Gladstone, 2005). As He readily escapes from Mars, there must be a steady source of He from the interior of the planet. This has been estimated to be 2×10^5 atoms $\text{cm}^{-2}\text{s}^{-1}$ or 1.5×10^7 mol year^{-1} . This value should be compared with the terrestrial flux of 4.1×10^5 atoms $\text{cm}^{-2}\text{s}^{-1}$ or 1.1×10^8 mol year^{-1} (Sano, 1986). If we scale the terrestrial He flux to that of Mars by the mass of planets, the value is $0.11 \times 1.1 \times 10^8 = 1.2 \times 10^7$ mol year^{-1} , which is within a factor of 2 of the Martian flux (and the uncertainties in the estimates of He fluxes are greater than a factor of 2). Thus Mars, like Earth, has an internal source of He that is approximately the same per unit mass of the planet. In addition, this interior source readily communicates with the surface of the planet. A relation between CH_4 and He fluxes on Mars has been studied by analogy with terrestrial analogs by Onstott et al. (2006).

The Lifetime of CH_4 on Mars: The primary fate of CH_4 on Mars is oxidation to CO_2 and H_2O ,



There are other similar branches not listed here, but the net result is oxidation to CO_2 , H_2O and H_2 . The last species either escapes or is oxidized to H_2O . The first reaction listed in the above oxidation scheme has a high activation energy, resulting in a long lifetime of ~ 300 years for CH_4 . In order to explain the rapid changes in CH_4 as reported by Mumma et al. (2009), the lifetime has to be shorter than 1 year (Lefevre and Forget, 2009), which is incompatible with the standard chemistry of the Martian atmosphere summarized in this paper. Non-standard chemistry (e.g., Atreya et al., 2007) is unlikely because the hypothetical oxidants will also oxidize CO and H_2 in the Martian atmosphere, and there is currently no evidence for additional destruction mechanisms for these species. We believe that the most likely explanation for the observed variability of CH_4 on Mars is physical adsorption in the soil (Gough et al., 2009). In this case, the CH_4 from the atmosphere is temporarily sequestered in the soil during the cold season, and is released to the atmosphere as the warm season returns. There is no net chemical

destruction or production of CH_4 . If we accept this interpretation, the flux needed to maintain the observed amount of CH_4 is on the order of $1.7 \times 10^7 \text{ mol year}^{-1}$. Otherwise, it would have to be 100-1000 times higher. In this paper, we assume that the smaller flux is correct.

Abiotic versus Biotic Methanogenesis: Both hydrothermal convective systems and life are fluxes. Indeed convective and metabolic cycles are coupled on Earth and life probably emerged here closely coupled to a submarine hydrothermal system of moderate temperature (Russell and Arndt, 2005). Plate tectonics brings new material and heat from the interior, while faulting associated with this motion offers fresh mineral surfaces to invasive surface waters, resulting in a hydrothermal nutrient supply to the surface. For example, ferrous iron in olivine-rich ocean crust is oxidized by ocean water involved in hydrothermal convection cells, releasing hydrogen in an abiotic process known as serpentinization (i). Up to a tenth of this hydrogen goes on to reduce dissolved carbon dioxide to methane in the same convective cell, catalyzed by iron-nickel sulfides and fine nickel-iron filaments in the ocean crust (ii) (Russell and Hall, 1997).

The remainder of the hydrogen is returned to the ocean floor and emanates at hot submarine springs. Here, some of this hydrogen is used by microbes—the methanoarchaea—to reduce carbon dioxide dissolved in the ocean to more methane, though in this convoluted biotic case, at rates much faster than does abiotic serpentinization (Proskurowski et al., 2006; Brazelton et al., 2010). The detritus and effluent from other microbes can also serve as a substrate for methane production. It follows that in the absence of life the methane flux would be subordinate to the hydrogen flux, whereas in its presence the overall flux of methane would dominate as on our Earth today.

When Mars was a young wet and hotter planet, convective mass transfer of heat would have operated as the main cooling mechanism. Knowing this, many have argued that life must have emerged on early Mars (Russell and Hall, 1999). However, Mars probably ran out of energy to drive large-scale convection at least 500 million years ago (Franck et al., 2000). By the same reckoning, Earth will be habitable for another 1.5 billion years. Nevertheless, liquid water permitting, residual energy from organic detritus in an ancient deep biosphere on Mars (Hartman and McKay, 1995) could still be accessed as a heterotrophic source, while there is enough atmospheric carbon monoxide and hydrogen to drive an autotrophic metabolism (Weiss et al., 2000). However, in the absence of large-scale convection, biological effluent from the planet, particularly of methane and acetate, would be small. Caveats to this would be the kind of resuscitation of hydrothermal convection one might expect through ephemeral thermal inputs contingent upon minor magmatic intrusions (Schultz-Makuch et al., 2007) and meteorite impacts (Cockell, 2006). Such structures would be obvious sites for further investigation. But supposing a deep biosphere in the putative northern ocean sediments lying beneath the weathered basaltic lava cap (Fairén et al., 2003), then methane seeps might be expected around its periphery.

We will summarize the major differences between abiotic versus biotic methanogenesis on Mars.

Efficiency: The primary serpentinization reaction (ii) provides a source of H_2 . An alternative source is the atmosphere (iv). As shown in Figs. 1a and b, the geochemical path to CH_4 formation is slow, whereas the biotic pathway is highly efficient. Therefore, a key question is the yield of CH_4 , which could be very low for the former (<10%) but very high for the latter (approaching 100%).

By-products: Apart from methane, the characteristic effluents of microbial metabolism include acetate or acetic acid (CH_3COOH) and hydrogen sulfide (from the reduction of sulfate) and negligible hydrogen. For comparison, the serpentinization reaction produces hydrogen and a subordinate quantity of methane.

4. CONCLUSIONS

We have examined the planetary environment of Mars and the abiotic and microbiological mechanisms for

producing CH_4 . The main ideas are summarized in Fig. 2. He and H fluxes show that Mars is an active planet geochemically and photochemically. The serpentinization reaction produces hydrogen, which together with atmospheric or geochemical CO_2 , provides the feedstock for methanogenesis.

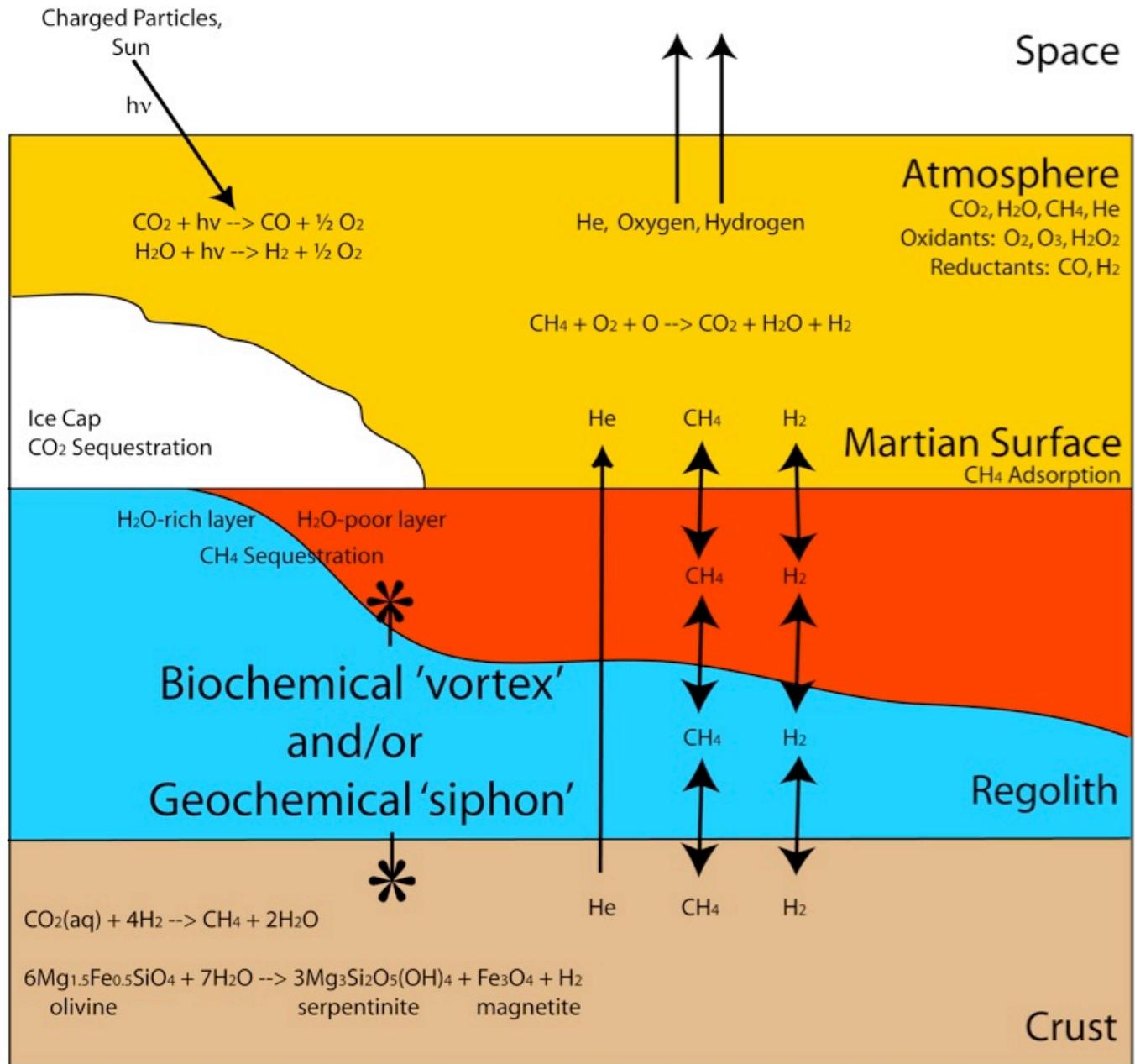


Figure 2. Schematic diagram for geochemical and/or microbiological methane generation and flow of other chemical species on Mars described in the text.

How could we distinguish between the abiotic and biological origins of CH_4 on Mars? Allen et al. (2006) suggest the use of isotopologues in the family of alkanes, as well as their relative abundances, to discriminate between competing sources. Corrections due to isotopic fractionation by atmospheric chemistry must be taken into account (Nair et al., 2005). We point out the two key discriminants: efficiency and by-products. The former could be tested by the measurements of H_2 and CH_4 fluxes. The products of microbial metabolism associated with CH_4 synthesis

include acetate, acetic acid and H₂ S, which should be absent in the abiotic process. Perhaps the most exciting implication of CH₄ on Mars is that it is the 'hydrogen atom' for the study of origin of life, whereas on Earth the pristine conditions have long ago been modified by the emergence and evolution of life. The Martian chemical environment is simple, and methanogenesis is among the simplest of biological processes. How far Mars has progressed from abiotic to microbiological synthesis of CH₄ has profound implications for the existence of extraterrestrial life in our solar system and extrasolar systems.

To find a planet or moon where microbes had evolved just beyond what might be termed 'the last universal common ancestor', and if found, determine the microbes' chirality, would be one major goal for future space exploration.

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