

Have olivine, will gas: Serpentinization and the abiogenic production of methane on Mars

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[1] Spatial variability of methane (CH_4) on Mars suggests the presence of localized subsurface sources. Here, we show that olivine hydration in the Martian regolith and crust may be a major CH_4 source, which contributed significantly to the warming of early Mars. Methane production is kinetically and thermodynamically favored during low-T aqueous alteration of olivine-rich rocks. Sustained release of CH_4 on present-day Mars may come through the breakdown of ancient CH_4 hydrates and from springs driven by geothermal heat. **Citation:** Oze, C., and M. Sharma (2005), Have olivine, will gas: Serpentinization and the abiogenic production of methane on Mars, *Geophys. Res. Lett.*, *32*, L10203, doi:10.1029/2005GL022691.

1. Introduction

[2] Recent detection of CH_4 in the Martian atmosphere [Formisano *et al.*, 2004] has suggested that methanogenic microbes [Krasnopolsky *et al.*, 2004], thermal decomposition of buried organic material, comet and meteor impacts [Kress and McKay, 2004], mantle plumes, or hydrothermal alteration of basalt may be the greenhouse gas source. However, CH_4 abundance is spatially variable indicating localized sources in the Martian regolith. Given that the residence time of CH_4 in the Martian atmosphere is short (~ 340 yr) [Krasnopolsky *et al.*, 2004], comet and meteor impacts and/or magmatic activity are not likely to account for the current spatial variability of CH_4 . The bulk of CH_4 produced on Earth is generated by bacteria and it has been suggested that CH_4 could be a tracer of life on another planet. Here we propose that the entire inventory of CH_4 on Mars is abiogenic and related to the hydration of olivine and pyroxenes (serpentinization) close to the Martian surface. Serpentinization at depths, where $\text{H}_2\text{O}_{(l)}$ is potentially present, is a viable source of H_2 , which reacts with CO_2 to form CH_4 .

[3] Several Earth analogs demonstrate the potential of abiogenic methanogenesis. Methane has been discovered in vent fluids issuing from peridotite-hosted hydrothermal systems [Charlou *et al.*, 2002]. The formation of CH_4 from CO_2 bearing fluids has also been reported in experiments involving hydrothermal reactions at elevated T and P [Foustoukos and Seyfried, 2004; Horita and Berndt, 1999]. Methane formation is favorable at low Ts and Ps as evident by the pressure of CH_4 in springs originating from altering peridotites [Barnes *et al.*, 1978]. Here, we consider the reaction routes, their kinetic barriers, and the thermochemistry related to the formation of H_2 -rich fluids,

abiogenic methanogenesis, and the localization of H_2 or CH_4 into the Martian atmosphere.

2. Liquid Water and CO_2 in Martian Regolith

[4] Liquid water is unstable on the surface of Mars. The low surface T (220 K) and P (6 mbar) dictate that H_2O , if close to the surface, should be present in a layer of permafrost, which is potentially globally distributed. The Odyssey spacecraft has identified and mapped high concentrations of hydrogen (presumably as $\text{H}_2\text{O}_{(s)}$) in the top meter of the Martian surface [Feldman *et al.*, 2004]. With increasing depth, the current geothermal gradients predict a region where $\text{H}_2\text{O}_{(l)}$ should become stable under permafrost. This is illustrated in Figure 1 where four potential geotherms (5, 10, 15 and 20 K km^{-1}) for the upper 50 km of crust are shown [McGovern *et al.*, 2002]. Hellas Basin, an 8 km deep depression, is also shown in Figure 1 with the appropriate geotherms to demonstrate how topographic variations can significantly influence the occurrence of $\text{H}_2\text{O}_{(l)}$.

[5] The stability of H_2O in the Martian crust ranges from 4 km to 15 km. At 4 km and using the 20 K km^{-1} geotherm, the T will be 270 K allowing for the stability of $\text{H}_2\text{O}_{(l)}$. Liquid water possibly exists as a eutectic brine [Burns, 1993; Knauth and Burt, 2002] implying that it should be present at depths shallower than 4 km and deeper than 15 km. As rock fractures anneal with depth, $\text{H}_2\text{O}_{(l)}$ would cease to flow at ~ 10 km. Deep hydrothermal systems resulting solely from geothermal heating have been observed in the Canadian High Arctic where perennial 279 K springs are found coming through 600 m of permafrost [Andersen *et al.*, 2002]. The Martian regolith and crust appear to be sufficiently permeable to setup hydrothermal convection systems driven solely by geothermal heat [Travis *et al.*, 2003]. Deep depressions such as Hellas Basin (Figure 1) and Valles Marineris could potentially tap deeper geothermal systems. Additionally, rock stratification would permit lateral movement of H_2O or melted permafrost from its source manifesting as liquid flows at cliff faces [Malin and Edgett, 2000].

[6] Although the conditions for hydrothermal circulation and the aqueous alteration of the rocks appear to exist on Mars, the main issue is whether H_2O is present at the depths indicated in Figure 1. Also, is there a source of CO_2 in the Martian regolith and crust? Currently, there are no details available on the Martian subsurface hydrosphere. If the Martian hydrosphere evolved at the end of the Noachian period, through the development of a global layer of permafrost, which grew at the expense of a global groundwater system fed by the melting of ice-rich polar deposits,

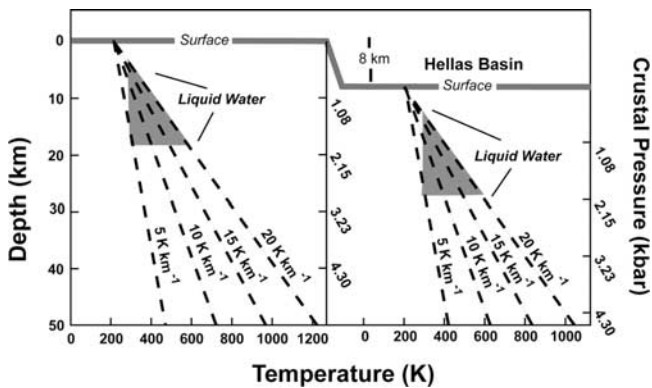


Figure 1. Geotherms of 5, 10, 15, and 20 K km⁻¹ are shown on a T-P-depth diagram where the surface of Mars in relation to Hellas Basin is noted. The depth and T at which H₂O_(l) can be present is shown with a grey polygon. Crustal Ps were calculated using a Martian crust density of 2900 kg m⁻³ and the gravity of Mars (3.71 m s⁻²).

H₂O_(l) should be present at depths below the permafrost [Travis *et al.*, 2003]. If basal melting still occurs at the Martian south pole and provides H₂O to a deep aquifer, this H₂O may contain atmospheric CO₂ initially trapped as bubbles in H₂O ice. On the other hand, the Martian regolith may potentially host an aquifer with ancient H₂O from which all CO₂ has been lost by reacting with silicates. Magmatic or metamorphic sources of CO₂ in Martian crust are likely insignificant.

3. Olivine Geochemistry and Serpentinization

[7] Spectral, mineralogic and chemical investigations by orbiters and landers and studies of Shergottite-Nakhilite-Chassigny (SNC) meteorites demonstrate that the Martian surface is covered by mafic to ultramafic rocks [e.g., Gellert *et al.*, 2004; Hoefen *et al.*, 2003; Wiens *et al.*, 1986]. The SNC meteorites indicate that olivine (~Fa₃₃Fe₆₇), low-Ca pyroxene (pigeonite, Fs₃₀En₅₇Wo₁₃), and high-Ca pyroxene (augite, Fs₂₅En₃₅Wo₄₀) are the predominant Fe-Mg silicates on Mars [Burns, 1993]. Olivine (Fa₇₀Fe₃₀-Fa₃₀Fe₇₀) is distributed globally between 60°S and 60°N with the largest surface exposure occurring in the Nili Fossae region [Hoefen *et al.*, 2003]. It follows that abundant olivine-bearing lithologies (picrite/dunite) are present at shallow depths and readily accessible to react with fluids within the Martian subsurface.

[8] Olivine hydration leading to its dissolution is controlled (pH < 8) by the decomposition of a silica-rich/metal deficient protonated precursor complex followed by SiO₄ tetrahedra polymerization [Pokrovsky and Schott, 2000]. The variables governing the dissolution rate are temperature (T), pH, Eh, CO₃²⁻ and silica activity in water, and the Fe/Mg ratio of olivine. The reported dissolution rate of olivine in pure H₂O ranges from ~10⁻¹¹ to ~10⁻¹⁷ mol cm⁻² s⁻¹ at 298.15 K due to compositional and pH changes [Wogelius and Walther, 1992; Pokrovsky and Schott, 2000]. Olivine dissolution decreases with increasing pH and is minimized at a neutral pH. It is further reduced in alkaline solutions by high activities of CO₃²⁻ and silica. In deoxygenated environments, fayalitic olivine dissolution is accelerated compared

to its forsteritic counterpart. The dissolution rates of low-Ca pyroxenes are similar to those of olivine; however, high-Ca pyroxenes dissolve about a factor of ten slower than olivine [Burns, 1993; Lasaga *et al.*, 1994]. In this paper, we will calculate pH dependent rates for olivine dissolution at 298.15 K (r_{298.15}) after Wogelius and Walther [1992]. The dissolution rate (r_T) at a T would then be estimated using the Arrhenius relation: $r_T = r_{298.15} \times e^{[\frac{-E_a}{R}(\frac{1}{T} - \frac{1}{298.15})]}$. Here E_a is the activation energy of olivine dissolution (~70 kJ mol⁻¹) [Lasaga *et al.*, 1994] and R is the gas constant.

[9] The dissolution rate for the Chassigny olivine (Fa₃₃Fe₆₇) at a pH of 7 (worst-case scenario) is given by: $-\log r = 3656.4/T + 1.375$, where r is in mol cm⁻² s⁻¹ and T is in K [Wogelius and Walther, 1992]. The dissolution rate at a depth of 5 km using the geotherms in Figure 1 should vary from 1.6 × 10⁻¹³ to 5 × 10⁻¹⁷ mol cm⁻² s⁻¹. This corresponds to a lifetime of 74 years to 2.4 × 10⁵ years for a 1 mm diameter grain of olivine. Olivine dissolution (and low-Ca pyroxenes) is, therefore, a kinetically favorable and geologically rapid process in low-T aqueous environments such as those shown in Figure 1. Moreover, Fe-rich olivine and low-Ca pyroxene appear to be abundant at the surface supporting their potential large-scale alteration with subsurface fluids.

[10] Olivine reacts with water to form hydrous Mg and Fe²⁺ silicates and hydroxides as well as H₂ at Ts < 600 K and at low SiO_{2(aq)} concentrations [Allen and Seyfried, 2003]. The relevant reactions involving olivine and water ±CO₂ are given in Table 1. The corresponding Gibbs free energy of reaction values of the reactions are listed in Table 2 and were calculated using SUPCRT92 [Johnson *et al.*, 1992] and the slop98.dat database. Hydration of fayalitic olivine in the system FeO-SiO₂-H₂O and the formation of magnetite results in the production of H_{2(aq)} (R1-3). Fayalite hydration is favorable when Fe-chrysotile (R4) is formed (applicable for < 600 K) compared to reactions that form quartz (R1), amorphous silica (R2), and aqueous silica (R3), which are relevant at > 600 K. Forsterite hydration in the system MgO-SiO₂-H₂O results in brucite and Mg-chrysotile (R5) and is favorable at Ts less than 570 K and 500 bar due to the stability of forsterite at higher Ps and Ts [Wegner and Ernst, 1983]. The Mg₂SiO₄-Fe₂SiO₄ solid solution is commonly treated as an ideal solid solution

Table 1. Generation of H₂ and CH₄ Related to Serpentinization of Olivine and Pyroxene

	Reactions
R1	3Fe ₂ SiO ₄ + 2H ₂ O = 3SiO _{2[quartz]} + 2Fe ₃ O ₄ + 2H _{2(aq)}
R2	3Fe ₂ SiO ₄ + 2H ₂ O = 3SiO _{2[Amorph-Silica]} + 2Fe ₃ O ₄ + 2H _{2(aq)}
R3	3Fe ₂ SiO ₄ + 2H ₂ O = 3SiO _{2(aq)} + 2Fe ₃ O ₄ + 2H _{2(aq)}
R4	6Fe ₂ SiO ₄ + 7H ₂ O = 3Fe ₃ Si ₂ O ₅ (OH) ₄ ^a + Fe ₃ O ₄ + H _{2(aq)}
R5	2Mg ₂ SiO ₄ + 3H ₂ O = Mg(OH) ₂ + Mg ₃ Si ₂ O ₅ (OH) ₄
R6	6Fe ₂ SiO ₄ + CO _{2(aq)} + 2H ₂ O = 6SiO _{2[Quartz]} + 4Fe ₃ O ₄ + CH ₄
R7	24Fe ₂ SiO ₄ + 26H ₂ O + CO _{2(aq)} = 12Fe ₃ Si ₂ O ₅ (OH) ₄ ^a + 4Fe ₃ O ₄ + CH ₄
R8	3FeSiO ₃ + H ₂ O = Fe ₃ O ₄ + H _{2(aq)} + 3SiO _{2(aq)}
R9	3FeSiO ₃ + H ₂ O = Fe ₃ O ₄ + H _{2(aq)} + 3SiO _{2[Amorph-Silica]}
R10	12FeSiO ₃ + 2H ₂ O + CO _{2(aq)} = 4Fe ₃ O ₄ + CH ₄ + 12SiO _{2(aq)}
R11	12FeSiO ₃ + 2H ₂ O + CO _{2(aq)} = 4Fe ₃ O ₄ + CH ₄ + 12SiO _{2[Amorph-Silica]}
R12	4H ₂ + CO ₂ = CH ₄ + 2H ₂ O
R13	H ₂ + SO ₂ = H ₂ S + O ₂

^aThermodynamic properties for Fe-chrysotile was computed based on an exchange reaction involving chrysotile, ferrous-oxide, and periclase using the slop98.dat database.

Table 2. Gibbs Free Energy of Reaction (kJ mol^{-1}) Values for Reactions in Table 1

Letter	298 K, 1 bar kJ mol^{-1} Aqueous	323 K, 1 bar kJ mol^{-1} Aqueous	323 K, 500 bar kJ mol^{-1} Aqueous	573 K, 500 bar kJ mol^{-1} Aqueous
R1	56.3	57.5	59.2	54.3
R2	78.2	78.1	80.9	68.3
R3	124	124	124	118
R4	-2204	-2198	-2199	-2138
R5	-47.4	-44.4	-44.81	-7.17
R6	-4226 (-4242 ^a)	-4232 (-4250 ^a)	-4225 (-4245 ^a)	-4321 (-4347 ^a)
R7	-9010 (-9026 ^a)	-8986(-9004 ^a)	-8990 (-9011 ^a)	-8675 (-8702 ^a)
R8	98.5	97.1	97.0	90.5
R9	52.0	51.1	53.1	40.8
R10	200 (184 ^a)	198 (180 ^a)	194 (174 ^a)	237 (210 ^a)
R11	14.4 (-1.85 ^a)	14.1 (-4.43 ^a)	19.0 (-1.39 ^a)	38.0 (11.1 ^a)

^aMethane: ($\text{CH}_{4(g)}$).

due the structure showing no preference for either Mg or Fe^{2+} . Minimal substitution of Mg into fayalite and the formation of serpentine will result in a rapid and exoergic route towards hydration and ultimately in higher yields of H_2 to be consumed by CH_4 . Serpentinization of fayalite at higher Ps and Ts when considering the dissolved SiO_2 species in R6 is energetically more favorable with the presence of $\text{CO}_{2(aq)}$ and the formation of CH_4 . The same reaction involving the formation of Fe-chrysotile (R7) is equally if not more favorable. An important hydration reaction to consider besides olivine for H_2 production is ferrosilite hydrolysis; yet, equilibrium calculations demonstrate that this reaction is not a favorable pathway leading to the production of CH_4 (R8–11). The thermochemistry of olivine hydration indicates that aqueous alteration of this mineral will lead to substantial production of H_2 and ultimately when coupled with CO_2 , toward CH_4 .

4. Martian Methanogenesis

[11] The production of CH_4 is fundamentally based on R12 (Table 1), which is exothermic and thermodynamically favorable at Ts < 600 K and over a variety of crustal Ps ranging from 0.5 to 500 bar (Figure 2). The Gibbs free energy of reaction (R12) increases as the T increases for gaseous H_2 , CO_2 , and CH_4 in $\text{H}_2\text{O}_{\text{liquid}}$ and $\text{H}_2\text{O}_{\text{vapor}}$. The analogous aqueous reaction is even more thermodynamically favorable up to 770 K at 500 bar; however, as P decreases the range of T where this reaction is favorable also decreases. Clearly, the reaction is limited by the presence of $\text{CO}_{2(aq)}$, which may be in short supply below the permafrost. Additionally, the abiogenic formation of CH_4 , although favorable, is slow (days) due to kinetic inhibition by high activation barriers [Sackett and Chung, 1979]. Chromium-spinels, Fe-Ni alloys, Ni-Fe sulfides, and magnetite are catalysts for methanogenesis (R12) and the presence of even small amounts of these catalysts are capable of rapidly accelerating this process (seconds) [Berndt et al., 1996; Foustoukos and Seyfried, 2004; Horita and Berndt, 1999; Sleep et al., 2004]. These catalysts are abundant in ultramafic and serpentinized rocks indicating that the rapid formation of CH_4 should occur in the regolith.

[12] Another limiting factor with regards to methanogenesis is related to the chemistry and abundance of sulfur (S) in the system. The SNC meteorites contain traces of reduced (FeS , Fe_{1-x}S) and oxidized S ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$) [Gooding, 1992]; the latter contains anomalous ^{17}O and is likely produced from low-T aqueous alteration of sulfides

[Thiemens et al., 2001]. Formation of H_2S (R13, Table 1) is more favorable than the formation of CH_4 from CO_2 at equivalent Ps and Ts. It follows that if oxidized S is present in the fluid, CH_4 will not be produced unless the supply of oxidized S is exhausted, reduced, or mineralized. Methanogenesis reactions are conducive during alteration of ultramafic rocks such as Nakhilites and Chassigny (with low-S). However, fluids derived from near-surface processes such as the weathering of basalt or fluids with oxidized S species may interact with geothermal fluids derived from serpentinization. Without knowing more about the mineralogy and hydrology related to S, the relevance of S in relation to methanogenesis on Mars is difficult to assess.

[13] As shown above, methanogenesis via olivine hydration is kinetically and thermodynamically favorable at low Ts. Thus, a strong correlation is proposed between hydrothermally-induced CO_2 reduction by H_2 toward CH_4 within the crust and the observed abundance of 10 ppb of CH_4 in

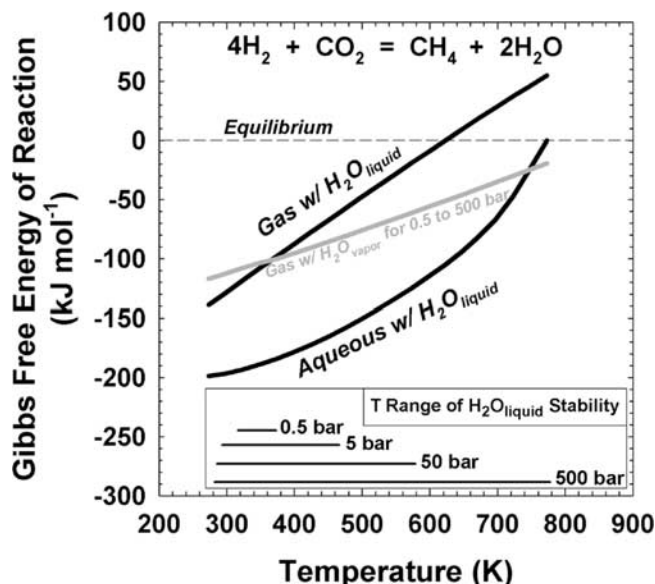


Figure 2. Gibbs free energy of reaction (kJ mol^{-1}) for gas and aqueous phase methanogenesis reactions (R12, Table 1) as a function of T in K at Ps of 500, 50, 5 and 0.5 bar. Temperature ranges for $\text{H}_2\text{O}_{\text{liquid}}$ stability at 0.5, 5, 50, and 500 bar (isobaric) are shown. Projection of the isobaric lines onto the reaction curves yields the Gibbs free energy of reaction.

the Martian atmosphere. It is important to note that if CH₄ were to be released in a single event, reactions R6–7 would require a mass of $\sim 10^{10}$ kg olivine to be altered in order to account for the total atmospheric CH₄. If CH₄ abundance in the atmosphere is in steady-state with a removal flux of 3.6×10^{-19} mol cm⁻² s⁻¹ [Krasnopolsky *et al.*, 2004], the reactions indicate that up to 8×10^8 kg olivine is needed per year to maintain the required flux. That is, $\sim 3.6 \times 10^{17}$ kg olivine is needed if the present-day flux is to be maintained throughout the history of Mars; this weight is equivalent to a 50 cm global olivine layer. This calculation suggests that copious quantities of H₂ and CH₄ are likely produced due to serpentinization reactions in the Martian crust. This further implies that substantially more CH₄ may have been present in the atmosphere of early Mars.

5. Concluding Remarks

[14] Following the first occurrence of H₂O_(l) on the Martian surface (>4 Ga), it is likely that extensive hydrothermal alteration was a major route for dissipative heat transfer. Serpentinization during this time would have released substantial quantities of CH₄ into the early Martian atmosphere. Kasting [1997] has estimated that a CH₄ mixing ratio of 0.01 for several bars of CO₂ pressure, supported by a CH₄ flux of 6.6×10^{-14} mol m⁻² s⁻¹ [Pavlov *et al.*, 2000], would be needed to raise the Martian surface T to support H₂O_(l). We estimate that abiogenic methanogenesis was very efficient on early Mars primarily due to a higher global heat flow leading to intense hydrothermal circulation. This would have resulted in an atmosphere with very high CH₄/CO₂ (>0.01). As the geothermal gradient declined, the CH₄/CO₂ ratio became too low to support H₂O_(l) on the surface. A growing layer of permafrost may then have sequestered some of the CH₄ [Pellenberg *et al.*, 2003], which is released occasionally. The observed atmospheric CH₄ variability could, therefore, result from either serpentinization reactions and/or decomposition of ancient gas hydrate. Carbon isotopic compositions of CH₄ and CO₂ in the Martian atmosphere and permafrost could potentially edify the origin of CH₄.

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