

QUANTIFYING LOW TEMPERATURE PRODUCTION OF METHANE ON MARS. S. P. Schwenzer^{1,2}, CEPSTAR, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom; s.p.schwenzer@open.ac.uk, ²Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058, USA.

Introduction: Methane was first detected in the Martian atmosphere in 2003 [1-3], and its implications have been widely debated [e.g., 4-8]. Methane can be generated in terrestrial biological systems, and so is a potential indicator for past or present life (see e.g., [4,5]). However, methane can be produced anorganically (without intervention of life) in several sorts of terrestrial environments, some of which are relevant for Mars [4-7,9-13]. On Earth, anorganic methane can be produced by redox reactions associated with high- and low-temperature alteration of Fe-bearing rocks, so long as carbon is present. Methane production is common in mid-ocean ridge hydrothermal systems, and wherever serpentine is forming [6,7]. In fact, the anorganic production of methane on Earth is estimated to be 50–70 Mt y^{-1} [15]. Methane-producing reactions, including serpentinitization, can also provide significant energy that can be utilized by living organisms [14].

Thermochemical modeling of rock-water chemical reactions shows that, in addition to methane, molecular hydrogen and other reduced gas species can be produced. The alteration phases formed by those processes include hydrous silicates. Here, I quantify methane production and alteration minerals from three Martian rock compositions and pure olivine and compare them to the amounts released and observed in 2003.

Method: The CHILLER code [16] is used to evaluate gas phases and mineral assemblages that are likely to form from Martian rocks in low-temperature alteration environments. Earlier, Schwenzer and Kring [17,18] modeled LEW 88516 whole rock composition, LEW 88516 olivine and Chassigny at 1 °C at 1 bar (= near Mars' surface); here I add models with the composition of the Martian rock Fastball [19] at those conditions and at 13 °C and 110 bar (~ 1 km depth [20]). CO₂ concentration in the solution is adjusted to that in equilibrium with current Martian atmosphere: 0.2×10^{-4} mole/L. The system is closed to atmosphere and no further supply of C-species is available during consumption of CO₂ through the reaction. For comparison, I ran a model with higher CO₂ concentration to explore the effects of a potentially denser atmosphere on early Mars or subsurface CO₂ sources. Results are in Figure 1-4, and Table 1.

Fig. 1 (right): Alteration minerals (bar chart) and gas (pie chart; H₂ (yellow), H₂O (red)) formed upon alteration of LEW 88516 whole rock and olivine, Chassigny, and Fastball composition. Note, that the amount of CH₄ produced is directly dependent on the amount of C-species in the system (see text).

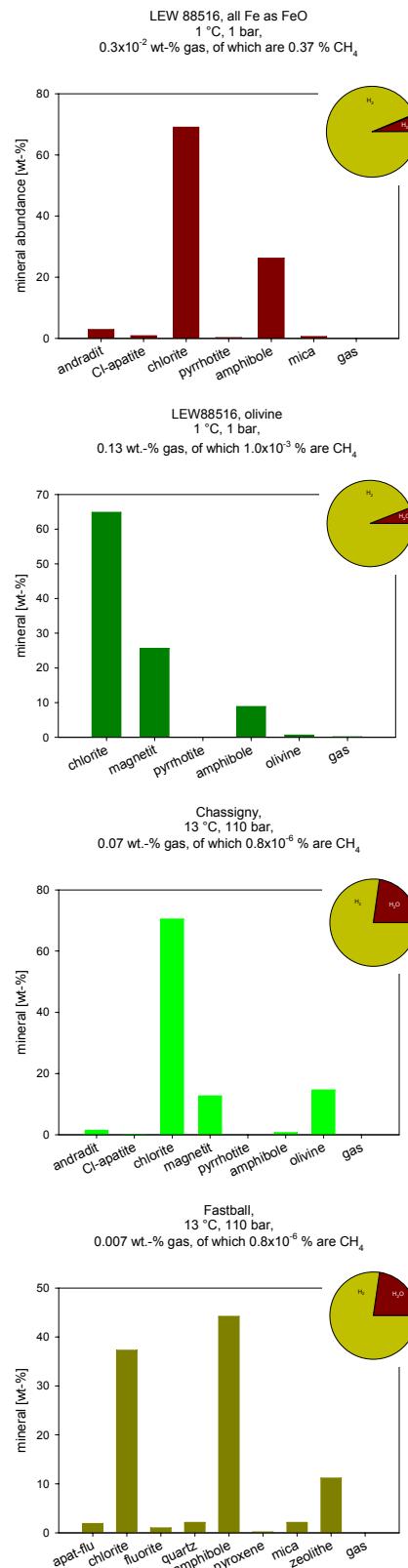


Table 1. Amount of gas produced and concentrations of main gases. Gas amount is in wt.-% of total products and equals to the production from 1 kg of host rock; individual gases are given as wt.-% of the amount of total gas. Mole CO₂ in the Fastball models refer to CO₂ in the fluid; LEW 88516 and Chassigny models were done with 0.2x10⁻⁴ mole CO₂.

	LEW 88516	LEW 88516 Ol	Chas- signy
T[°C]/P[bar]	1/1	1/1	13/110
Gas amount [%]	3.5x10 ⁻³	0.131	0.065
H ₂	93.68	94.02	77.22
H ₂ O	5.95	5.97	22.78
CH ₄	0.37	1.0x10 ⁻³	0.8x10 ⁻⁶
	Fastball 0.2x10⁻⁴ mole CO₂	Fastball 0.2x10⁻⁴ mole CO₂	Fastball 0.01 mole CO₂
T[°C]/P[bar]	1/1	13/110	1/1
Gas amount [%]	0.021	6.8x10 ⁻³	0.007
H ₂	94.01	77.30	0.21
H ₂ O	5.92	22.70	0.76
CH ₄	0.07	0.8x10 ⁻⁶	99.03

Comparison to the observed “plume” release: The models show that, in fluids of 0.2x10⁻⁴ mole/L CO₂, between 1.5x10⁻⁵, and 5.2x10⁻¹⁰ g methane are produced from the alteration of one kg of the above rocks and minerals. Methane production is limited by the limited availability of CO₂/CO, and is therefore a minimum estimate. To maintain the observed concentrations of methane in the modern Martian atmosphere, a source of 1.26x10⁵ kg yr⁻¹ is required [4]. In this CO₂/CO limited scenario, to match this or the largest observed plume (2003, ~1.86x10⁷ kg [3]) requires the complete alteration of 8.4x10¹¹ kg or 1.2x10¹² kg (0.2 or 0.4 km³) of rock, respectively (taking the Fastball composition at 1 °C and 1 bar). If additional CO₂ is available, more methane can be produced (Tab. 1). This conservative estimate demonstrates that a comparably small volume of rock is needed to produce the methane required to match the measured concentrations.

Age of the methane and potential storage processes: An interesting question is, whether this methane is ancient (Noachian or Hesperian), or produced today. Ancient production on Mars during the Noachian is easily possible, because high-temperature environments in volcanic and impact generated hydrothermal systems were ubiquitous. If the observed methane is of Noachian age, the question remains, how this methane has been stored. Max and Clifford [13] suggested methane-clathrate formation during the Noachian, which could bind CH₄, and release it at any later time.

Our calculations show that anorganic methane production is possible on today’s Mars. With a geothermal gradient of 13 °C [20] and subsurface water, a considerable amount of methane could theoretically be produced at depth. Caution has to be exercised about production rates, because the formation of CH₄ from CO or CO₂ and H₂ may be kinetically inhibited or very slow [21]. Therefore, methane production at high temperatures, such as in hydrothermal systems, might have been the dominant process; and thus Noachian anorganic methane could be the source for the methane observed today. The methane plume of 2003 was centered over the Syrtis Major shield volcano and the adjacent Noachian terrane of Nili Fossae, which lead Mumma et al. [3] to suggest that the methane was either related to the volcano or to the abundant clays found in the Nili Fossae area [3].

If the methane is Noachian in age, impact craters could be significant in two ways. First, the heat released during crater formation could have driven both high- and low-temperature alteration of rocks ([17], Tab. 1) that produced methane. Second, impact craters can produce several sorts of reservoir structures for retention of methane: structural traps like faults, and stratigraphic caps like sheets of impact melt [22,23]. Thus, impact craters could promote generation of methane, and trap it against escape to the atmosphere. Disruption of these traps, as by temperature changes, mass movement, or marsquake could lead to the sudden release of stored methane.

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References: [1] Formisano V. et al. (2004) *Science*, **306**, 1758–1761. [2] Krasnopolski V.A. et al. (2004) *Icarus* **172**, 537–547. [3] Mumma M.J. et al. (2009) *Science*, **323**, 1041–1045. [4] Atreya S.K. et al. (2007) *Planet. Space Sci.*, **55**, 358–369. [5] Atreya et al. (2010) *Planet Space Sci.*, doi: 10.1016/j.pss.2010.10.008. [6] Oze C. & Sharma, M. (2005) *GRL*, **32**, doi: 10.1029/2005GL022691. [7] Oze C. & Sharma, M. (2007) *Icarus*, **186**, 557–561. [8] Parnell J. et al. (2010) *Int. J. Astrobiol.*, **9**, 193–200. [9] Wallendahl A. & Treiman A.H. (1997) *LPSC XXX*, #1268. [10] Zahnle K. et al. (2007) *Space Sci. Rev.*, **129**, 35–78. [11] Nisbet E.G. & Nisbet E.R. (2008) *Phil. Trans. R. Soc. B*, **363**, 2745–2754. [12] Nisbet et al. (2007) *Space Sci. Rev.*, **129**, 79–121. [13] Max M.D. & Clifford S.M. (2000) *JGR*, **105**, 4165–4171. [14] Varnes E.S. et al. (2003) *Astrobiology*, **3**, 407–414. [15] Etiope G. & Klusman R.W. (2002) *Chemosphere*, **49**, 777–789. [16] Reed M.H. & Spycher, N.F. (2006) Users Guide for CHILLER: A Program for Computing Water-Rock Reactions, Boiling, Mixing and Other Reaction Processes in Aqueous-Mineral-Gas systems and Minplot Guide. 67 p. (Univ. Oregon). [17] Schwenger S.P. & Kring D.A. (2009) *Geology*, **37**, 1091–1094. [18] Schwenger S.P. & Kring D.A. (2009) *LPSC XL*, #1421. [19] Gellert R. et al. (2006) *JGR*, **111**, doi:10.1029/2005JE002555. [20] Babeyko A.Yu. & Zharkov V.N. (2000) *Physics Earth Planet. Interiors*, **117**, 421–435. [21] Zolotov M. & Shock E. (1999) *JGR*, **104**, 14033–14049. [22] Donofrio R.R. (1998) *Oil & Gas Journal*, May 11, 1998, 69–83. [23] Grajales-Nishimura J.M. (2000) *Geology*, **28**, 307–310.