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 serpentinization, 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: 0.2x10⁻⁴ 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).
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:**