EARLY MARS SERPENTINIZATION DERIVED CH_4 RESERVOIRS AND H_2 INDUCED WARMING. E. Chassefière[1], J. Lasue[2], B. Langlais[3], Y. Quesnel[4] [1]GEOPS, Université Paris-Sud, CNRS, France (eric.chassefiere@u-psud.fr), [2]IRAP-OMP, CNRS-UPS, Toulouse, France, [3]LPG-CNRS, Université de Nantes, Nantes, France, [4]Aix-Marseille Université, CNRS, IRD, CEREGE UM34, Aix-en-Provence, France.

Introduction: The detection of CH_4 on Mars from orbit and from the ground has proven elusive. During the year 2003, it reached up to 10 ppb globally with local abundances up to 30 ppb [1, 2]. Such high values were not replicated by later studies and an upper limit of 8 ppb has been obtained from telescopic observations between 2006 and 2010 [3], while a local low upper limit of 1.3 ppb has been obtained more recently in situ by the Mars Science Laboratory rover at Gale Crater in 2013 [4]. Due to the possible implications of CH_4 detection for life and its influence on atmospheric processes on the planet [e.g. 3], confirming whether the release of CH_4 on Mars can be sporadic will be one of the goals of the next missions to study Mars.

Recent greenhouse calculations suggest that, unlike on Earth, CH_4 is not an efficient greenhouse gas on Mars and has not played a significant role in raising the surface temperature above the water freezing point [5]. The collision-induced absorption caused by H_2 could have been much more efficient provided the mixing ratio of H_2 in the atmosphere when valley networks formed was larger than ~5% [5]. Both CH_4 and H_2 are produced (indirectly for CH_4) by serpentinization, which is assumed in our study to be the main process having formed CH_4 abiotically on early Mars. To understand if serpentinization may have had an influence on Mars' climate through the release of large amounts of H_2 to the atmosphere is of significant interest to solve the enigma of valley network formation. First, we assess whether abiotic production of CH_4 on early Mars could have created large CH_4 clathrate reservoirs in the cryosphere of the planet. Second, we provide a preliminary assessment of the ability of H_2 released by early serpentinization to have heated Mars surface above the water freezing point.

The remanent magnetic field of Mars and early Mars CH_4 production by serpentinization

One of the main ways to produce CH_4 abiotically is through serpentinization, a metamorphic process by which low-silica mafic rocks are hydrothermally altered to store water, produce magnetite and release dihydrogen. While this process may still be occurring today at depth, it must have been more frequent on early Mars for which conditions included higher rates of volcanic activity and impact cratering together with liquid water on the surface. This could have proven a major process to trap a large fraction of the water of the planet during the Noachian in altered minerals at depth and at the same time release a significant amount of CH_4 in the atmosphere [6].

As serpentinization increases the crustal volume and creates a large number of magnetite, it has been hypothesized to explain both the crustal dichotomy of the planet and the strong remanent magnetic field of the old southern terrains [7]. Thus, assuming that the remanent magnetic field is due to serpentinization, it is possible – deriving the crustal magnetization from magnetic field data – to estimate the amount of water trapped in altered minerals as well as the CH_4 released during the alteration. A typical serpentinization reaction can be expressed as:

$$Mg_{1.5}Fe_{0.5}SiO_4 + 7/6H_2O \rightarrow 1/2Mg_3Si_2O_5(OH)_4 + 1/6Fe_3O_4 + 1/6H_2$$

for which on average, every H_2O molecule used for iron oxidation involves 6 H_2O molecules for the hydration of olivine to be trapped in serpentine. At the same time 1 molecule of H_2 or equivalently ¼ molecule of CH_4 are released in the atmosphere [8].

Based on a global model of the magnetization of the crust using an Equivalent Source Dipole (ESD) method [9], the total volume necessary to explain the remanent magnetization is ~3.6 10^8 km^3 [6, 10]. This is equivalent to a GEL of ~2.5 km of serpentinized material. Using more conservative assumptions, this value becomes ~1.5 km serpentinized GEL, which can be considered as a lower range. These values in turn indicate that the formation of chrysotile over ~2.5 km GEL is equivalent to ~0.8 km GEL of trapped water and the release of 2.75 10^{20} moles of CH_4. Respectively, the conservative estimate gives a ~1.5 km serpentine GEL equivalent to a ~0.5 km GEL of trapped water and the release of 1.75 10^{20} moles of CH_4. These values are obtained by assuming that all H_2 molecules formed through serpentinization are converted to CH_4 by Fischer-Tropsch reactions. As summarized by [11], the average volume mixing ratio of CH_4 in vents above deep sea hydrothermal systems on Earth is ~0.1, the main released species being H_2, and is rather in the range from 0.01-0.1 for continental systems. The total release rate of CH_4 produced by serpentinization could be therefore one order of magnitude lower than estimated above, typically a few 10^{19} moles of CH_4.

CH_4 trapping capacity of the early cryosphere

A first estimate of how much CH_4 can be trapped in the cryosphere of Mars and what the lifetime of such deep underground reservoirs may be has been provided by [10]. Considering its size, early Mars could have gotten cold quite rapidly, leading to a developing underground cryosphere that would have increased in size with time, filling up all the volume available for it [12, 13]. A line of recent evidence even suggests that early Mars may have been only intermittently warm (e.g. [14]). The depth reached by a developing cryosphere during the Noachian depends on the surface temperature conditions of the planet, its geothermal heat flux, Q_g, as well as the thermal properties of the upper martian crust and its porosity at depth. [10] used the martian cryosphere univariate finite difference models developed in [13, 15] for a cryosphere saturated by clathrates. The Noachian geothermal heat flux was most probably larger than 50 mW.m^{-2}. The depth of the cryosphere would range from about 2 km below the equator and up to 5 km below the poles for Q_g = 50 mW.m^{-2}. It is found that the quantity of CH_4 necessary to explain the remanent magnetic field of the planet by serpentinization is of the same order of magnitude or larger than the trapping capacity of any cryosphere with Q_g > 50 mW.m^{-2} [10]. Nevertheless, if CH_4 represents only 10% of the outgassed hydrogen in volume [11], the capacity of the cryosphere definitely exceeds the amount of CH_4 produced. It is therefore likely that the whole trapping capacity of the early cryosphere of Mars was used to catch any CH_4 released through early serpentinization processes. If this was the case, then the quantity of CH_4 that could have survived in the subsurface of the planet to this day would be more that 10^{10} the quantity necessary to generate the strong CH_4 plume described in [2] (~1.2 10^9 moles).

These calculations show the maximum trapping capacity of the martian cryosphere determined by thermal modelling. The ability for a clathrate saturated cryosphere to survive to the present day will be highly dependent on the orbital, thermal and atmospheric history of the planet together with the diffusion and dissociation kinetics of CH_4 clathrates. The theoretical and experimental studies of CH_4 clathrates kinetics remain consistent with the possibility for deep underground martian clathrates to have remained stable over the history of the planet, but such values are poorly constrained and need to be better studied [16].

Release of H_2 to the atmosphere

Once formed, H_2 is expected to be rapidly released to the atmosphere. If most of the released hydrogen is under the form of H_2, the total amount of H_2 released is close to ~1.75 10^{20} moles multiplied by 4, that is ~7 10^{20} moles. This value can be translated into a H_2 column density of ~7 10^{26} molecules per square centimeter. According to [5], the value of the H_2 flux to the atmosphere required to maintain an atmospheric H_2 mixing ratio of 5%, assuming that hydrogen escaped at the diffusion limit, is ~10^{12} cm^{-2} s^{-1}. At this rate, the total amount of released H_2 is consumed in a typical time of ~7 $10^{26}/10^{12}$ = 7 10^{14} s, that is 2 10^7 yr. If most of serpentinization has been concentrated in a total period shorter than 2 10^7 yr, the required level of H_2 could have been reached in the atmosphere (possibly during several distinct episodes, with intermittently warm periods). Geomorphological analysis and hydrological modelling show that the ancient Martian valley network formed in a time range from 10^5-10^7 yr [17], lower than 2 10^7 yr. The hypothesis that H_2 produced by serpentinization has heated the surface above water freezing point during the whole duration of valley networks formation cannot be ruled out. If so, some of the CH_4 trapped in the cryosphere has been released to the atmosphere during warm episodes, in particular at equatorial latitudes. If H_2 release has been more regular and extended in time, e.g. over 10^8 yr or more, the H_2 level never reached the required level and no warm episode due to H_2 release is expected. This question deserves to be more thoroughly studied.

Conclusion: We have demonstrated that the CH_4 trapping capacity of the early martian cryosphere is larger than the quantity of CH_4 possibly released by early serpentinization processes that would have been necessary to generate the observed martian remanent magnetic field. The presence of such clathrate reservoirs could explain the sporadic release of CH_4 at the surface of the planet to this day. Once formed, H_2 has been rapidly released to the atmosphere, where it could have increased surface temperature above water freezing point during a time up to 2 10^7 yr, provided most of serpentinization has been concentrated in one or several periods of total duration lower than this value. This time is large enough to allow the formation of valley networks. If so, serpentinization could have played a significant role in the climate history of Mars.

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