Icarus 260 (2015) 205–214

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Methane storage capacity of the early martian cryosphere

Jeremie Lasue [a,b,*], Yoann Quesnel [c], Benoit Langlais [d], Eric Chassefière [e]

[a] Université de Toulouse; UPS-OMP; IRAP, Toulouse, France
[b] CNRS; IRAP, 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France
[c] Aix-Marseille Université, CNRS, IRD, CEREGE UM34, Aix-en-Provence, France
[d] Université de Nantes, Laboratoire de Planétologie et Géodynamique, CNRS UMR 6112, Nantes, France
[e] Univ. Paris-Sud, GEOPS-CNRS, UMR8148, Orsay, France

ARTICLE INFO

Article history:
Received 18 March 2015
Revised 17 June 2015
Accepted 13 July 2015
Available online 20 July 2015

Keywords:
Mars
Mars, surface
Mars, interior

ABSTRACT

Methane is a key molecule to understand the habitability of Mars due to its possible biological origin and short atmospheric lifetime. Recent methane detections on Mars present a large variability that is probably due to relatively localized sources and sink processes yet unknown. In this study, we determine how much methane could have been abiotically produced by early Mars serpentinization processes that could also explain the observed martian remanent magnetic field. Under the assumption of a cold early Mars environment, a cryosphere could trap such methane as clathrates in stable form at depth. The extent and spatial distribution of these methane reservoirs have been calculated with respect to the magnetization distribution and other factors. We calculate that the maximum storage capacity of such a clathrate cryosphere is about 2.1×10^{19}–2.2×10^{20} moles of CH_4, which can explain sporadic releases of methane that have been observed on the surface of the planet during the past decade ($\sim 1.2 \times 10^9$ moles). This amount of trapped methane is sufficient for similar sized releases to have happened yearly during the history of the planet. While the stability of such reservoirs depends on many factors that are poorly constrained, it is possible that they have remained trapped at depth until the present day. Due to the possible implications of methane detection for life and its influence on the atmospheric and climate processes on the planet, confirming the sporadic release of methane on Mars and the global distribution of its sources is one of the major goals of the current and next space missions to Mars.

1. Introduction

The detection of methane on Mars from orbit and from the ground has proven elusive. During the year 2003, it reached up to 10 ppb (parts per billion) globally with local abundances up to 30 ppb as detected from space with the Planetary Fourier Spectrometer onboard the Mars Express spacecraft (Formisano et al., 2004) as well as from the ground using the Fourier Transform Spectrometer at the Canada–France–Hawaii Telescope (Krasnopolsky et al., 2004). Using infrared spectrometers from CSHELL/IRTF (Hawaii) and NIRSPEC/Keck-2 (Hawaii), Mumma et al. (2009) detected methane abundances over a span of three martian years and generated maps of the methane abundances on the surface of the planet showing spatial and temporal variations of the signal, indicating strongly localized source with a methane flux estimated to be $\geqslant 0.6$ kg per second. Such high values were not replicated by later studies and an upper limit of 8 ppb has been obtained from telescopic observations surveys between 2006 and 2010 (Villanueva et al., 2013).

The Mars Science Laboratory (MSL) rover at Gale Crater includes a very sensitive Sample at Mars (SAM) laboratory designed to detect and analyze complex carbonaceous molecules on samples collected on the planet as well as the atmosphere (Mahaffy et al., 2012). The Tunable Laser Spectrometer (TLS) of the instrument is specifically designed to detect and quantify isotopes and is particularly well suited to detect methane down to the ppb by volume (ppbv) level. In the initial part of the mission during the year 2012, a measured value of 0.18 ± 0.67 ppbv with an upper limit of 1.3 ppbv of methane was obtained indicating an almost complete absence of the gas in the surroundings of Gale Crater at the time (Webster et al., 2013a).

However, recent in situ measurements by TLS are showing variations in the methane detection at Gale Crater over the 8 km traverse to Mount Sharp during the two terrestrial years of the nominal MSL mission. While the background level of methane remains around 0.69 ± 0.25 ppbv, an elevated level of

---

[*] Corresponding author at: Institut de Recherche en Astrophysique et Planétologie, Observatoire Midi-Pyrénées, 9 Avenue Colonel Roche, BP 44346, Toulouse FR-31028, France. Fax: +33 (0)632664554.

E-mail address: jlasue@irap.omp.eu (J. Lasue).

http://dx.doi.org/10.1016/j.icarus.2015.07.010

methane of 7.2 ± 2.1 ppbv was detected during approximately 2 months, implying that Mars is episodically producing methane from an additional unknown source (Webster et al., 2014). Such variations could be the result of local sporadic methane release combined with specific meteorological phenomena linked to the topography around Gale Crater, but the exact processes by which methane is released and destroyed on such short timescales remains to be determined. The fact that the evolution of minor species in the martian atmosphere is not exhaustively understood is also reflected by the analysis of atmospheric O_2 by Chemcam passive spectroscopy on-board MSL showing that over the 2 years of nominal mission, the level of O_2 does not follow the seasonal patterns that were expected (McConnochie et al., 2014).

Current conditions on Mars favor the formation and stability of methane clathrates at depth (Fisk and Giovannoni, 1999; Max and Clifford, 2000), serving as a potential source for the observed releases of atmospheric methane (Chastain and Chevrier, 2007). On Earth, methane is produced by both biotic and abiotic processes. While 95% of this terrestrial production is due to biological activity, on Mars, no evidence of current biological activity as yet been demonstrated.

Because methane has such an important influence on the atmosphere and climate of Mars, and because it is also a potential byproduct of a subsurface biosphere, determining or constraining its rate of release is a major goal of current and future Mars missions (see e.g. Atreya et al., 2007; Villanueva et al., 2013). Here, we assess whether abiotic production of methane on early Mars could be linked to large methane clathrate reservoirs in the cryosphere of the planet that could have been stable over time to generate the current localized, sporadic release of gas. One of this abiotic process is related to serpentinization, a metamorphic process which hydrothermally alters mafic and ultramafic minerals into serpentine and magnetite (e.g., Oze and Sharma, 2007). Water can be trapped and dihydrogen may be released through that process. In this work we discuss this hypothesis and postulate about the amount of CH_4 which could be produced today via this ancient process.

2. Remanent magnetic field of Mars and early Mars methane production by serpentinization

2.1. Serpentinization, crustal magnetization and H_2 release

The planet Mars lacks, today, a planetary, global, dynamic magnetic field. Instead there are only relics of a past global magnetic field, which left imprints in the martian lithosphere through magnetization and demagnetization processes. The Mars Global Surveyor magnetic field experiment (MAG/ER) detected very intense and localized magnetic fields of lithospheric origin, up to 1500 nanotesla (nT) at 90-km altitude, which is one to two orders of magnitude larger than the terrestrial lithospheric field. At 200-km and 400-km constant altitudes, the intensity of the magnetic field reaches up to 650 nT and 200 nT respectively (Langlais et al., 2004). The magnetized areas are mostly located in the southern hemisphere (Acuna et al., 1999; Langlais et al., 2004), and the largest volcanic provinces, as well as the largest impact basins, are mostly devoid of significant magnetic anomalies.

As illustrated in Fig. 1, the global distribution of the remanent magnetic field on Mars as detected by MGS, shown by the 10-nT contour plot to identify the magnetized areas (after Langlais et al., 2004) also shows a broad-scale correlation with (see Fig. 1):

- the Noachian surface (shaded MOLA topography, Smith et al., 2001),
- the valley networks distribution (blue lines, Hynek et al., 2010),
- some serpentine surface occurrences detected by CRISM (dark green triangles, Ehlmann et al., 2010).

In addition, pyroxene free outcrops (Koeppen and Hamilton, 2008; Ody et al., 2012) and hydrated minerals (Poulet et al., 2007; Carter et al., 2013) were broadly detected over the same areas. Serpentinization is a metamorphic process by which low-silica mafic rocks are hydrothermally altered to store water, eventually produce magnetite and release dihydrogen. When occurring in the presence of a global magnetic field, the newly-formed magnetite records a remanent magnetization (Langlais and Quesnel, 2008; Quesnel et al., 2009). 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 relatively abundant liquid water on the surface and in the near subsurface.

Indeed, all the necessary conditions for active serpentinization to occur on early Mars were present as evidenced by:

- the presence of olivine and pyroxene on the surface of Noachian to Hesperian outcrops on Mars (McSween et al., 2006; Koeppen and Hamilton, 2008; Edwards and Christensen, 2011; Ody et al., 2012, 2013),
- water flowing at the surface is demonstrated by the extent of valley networks (more extensive maps of valley networks, with potential evidence for water cycle on the surface of Mars were generated by Luo and Stepinski (2009) and Hynek et al. (2010)), the presence of ice in the near subsurface at later times as shown by the extent of the cryosphere (e.g. Lasue et al., 2013), and also the numerous observations of clay minerals on Noachian surfaces (Ehlmann et al., 2011). Furthermore, recent observations by Mars Science Laboratory have shown the sustained presence of a fluvio-lacustrine environment at the bottom of Gale Crater on Mars (Grotzinger et al., 2014),
- hydrothermal alteration of martian crust potentially efficient from geochemical models (Griffith and Shock, 1997),
- hydrothermalism, triggered by intrusive volcanism within the cryosphere, potentially active at recent epochs (Dohm et al., 2008), as well as at much earlier times due to internal heating or impacts (Stevenson, 2001; Breuer and Spohn, 2006; Schwenzer et al., 2012),
- the detection of serpentine surface occurrences by CRISM showing that the reactions necessary to generate this mineral did occur on or close to the surface of the planet. Though some detections correlate with the remanent magnetic field, few others do not. This may be explained by the potential large depth of such outcrops, making orbital detection challenging. Moreover, the serpentine outcrops may be weathered with time, reducing their surface occurrences, with preferential alteration into other products (oxides and smectites) as discussed in Ehlmann et al. (2010). Therefore, the current distribution of serpentine detections does not necessarily rule out a potential link between deep serpentine reservoirs and the remanent magnetic field.

Thus, using crustal magnetized volumes derived from magnetic field data, Chassefière et al. (2013) estimated the amount of water trapped in altered minerals as well as the dihydrogen released during the alteration. They particularly investigated how the trapped water could influence the water reservoirs and modify the D/H ratio of the planet. Indeed, the H atoms released to the atmosphere are lost to space through thermal escape, increasing the D/H ratio in water reservoirs exchanging with atmosphere. They concluded