



Martian zeolites as a source of atmospheric methane



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ABSTRACT

The origin of the martian methane is still poorly understood. A plausible explanation is that methane could have been produced either by hydrothermal alteration of basaltic crust or by serpentinization of ultramafic rocks producing hydrogen and reducing crustal carbon into methane. Once formed, methane storage on Mars is commonly associated with the presence of hidden clathrate reservoirs. Here, we alternatively suggest that chabazite and clinoptilolite, which belong to the family of zeolites, may form a plausible storage reservoir of methane in the martian subsurface. Because of the existence of many volcanic terrains, zeolites are expected to be widespread on Mars and their Global Equivalent Layer may range up to more than ~ 1 km, according to the most optimistic estimates. If the martian methane present in chabazite and clinoptilolite is directly sourced from an abiotic source in the subsurface, the destabilization of a localized layer of a few millimeters per year may be sufficient to explain the current observations. The sporadic release of methane from these zeolites requires that they also remained isolated from the atmosphere during its evolution. The methane release over the ages could be due to several mechanisms such as impacts, seismic activity or erosion. If the methane outgassing from excavated chabazite and/or clinoptilolite prevails on Mars, then the presence of these zeolites around Gale Crater could explain the variation of methane level observed by Mars Science Laboratory.

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1. Introduction

The origin of the martian methane (CH_4) is still poorly understood. Despite the fact that the presence of CH_4 remains under debate (Zahnle, 2015; Zahnle et al., 2011), detections have been claimed at the 10–60 parts per billion by volume (ppbv) level in Mars' atmosphere from space and ground-based observations at the end of the 90s and during the following decade (Fonti and Marzò, 2010; Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2009). Recent observations suggest a CH_4 atmospheric abundance of ~ 10 ppbv, and in some cases no or little CH_4 with an upper limit of ~ 7 ppbv in 2009–2010, during Mars' northern spring (Krasnopolsky, 2012; Villanueva et al., 2013). More

recent *in situ* measurements performed by Mars Science Laboratory (MSL) have evidenced variations in the methane detection at the location of Gale Crater. Despite a background level of methane remaining at 0.69 ± 0.25 ppbv, an elevated level of methane of 7.2 ± 2.1 ppbv was evidenced during a timespan of ~ 6 months (see Table 1 of Webster (2015)), a range of values comparable to the levels observed remotely during the last decade.

Because local methane enhancements such as those measured by MSL require CH_4 atmospheric lifetimes of less than 1 yr (Lefèvre and Forget, 2009), its release from a subsurface reservoir or an active primary source has widely been discussed in the literature. A plausible explanation is that CH_4 could have been produced either by hydrothermal alteration of basaltic crust (Lyons et al., 2005) or by serpentinization of ultramafic rocks producing H_2 and reducing crustal carbon into CH_4 (Atreya et al., 2007; Chassefière et al., 2013; Chassefière and Leblanc, 2011; Holm et al., 2015; Oze and Sharma, 2005). This hypothesis is supported by the

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Table 1

Adsorption enthalpies and Henry constants obtained from adsorption experiments of single components on chabazite and of binary mixtures on clinoptilolite.

		Chabazite			Clinoptilolite	
		150 K	200 K	300 K	150 K	300 K
ΔH (kJ mol ⁻¹)	CH ₄		-23 ^a		-12 ^b	
	CO ₂		-45 ^a		-21 ^b	
K_H (mol kg ⁻¹ kPa ⁻¹)	CH ₄	50	0.503	0.005	0.877	0.007
	CO ₂	2×10^6	256	0.031	345	0.076

^a Jensen et al. (2012).

^b Arefi Pour et al. (2015).

fact that ultramafic and serpentinized rocks have been observed on Mars, in particular in the Nili Fossae region (Brown et al., 2010; Ehlmann et al., 2010; Viviano et al., 2013). Once formed, methane storage on Mars is commonly associated with the presence of hidden clathrate reservoirs. Martian clathrates would form an intermediate storage reservoir in the subsurface that regularly releases methane into the atmosphere (Chastain and Chevrier, 2007; Gainey and Elwood Madden, 2012; Herri and Chassefière, 2012; Mousis, 2013, 2015; Prieto-Ballesteros et al., 2006; Thomas et al., 2009). However, because clathrates are more likely thermodynamically stable in the martian subsurface and at depths depending on the soil's porosity (Mousis, 2013), their existence has never been proven by remote or *in situ* observations. Interestingly, it has been recently proposed that halite or regolith could also sequester CH₄ on the martian surface (Fries et al., 2015; Hu et al., 2015), but these mechanisms still need to be thoroughly investigated.

Here, because of their ability to trap substantial amounts of gases, we suggest that zeolites may form an alternative plausible storage reservoir of methane in the martian subsurface. Spectral evidence for the presence of zeolite has been found on the martian surface (Carter et al., 2013; Ehlmann, 2009, 2014; Ruff, 2004) and there is strong geological case arguing for the presence of this aluminosilicate as part of the martian regolith. In Section 2, we explain why chabazite, analcime and clinoptilolite are good candidates to account for the widespread occurrence of zeolites on Mars. We also provide an estimate of the amount of zeolites potentially existing on the planet. Section 3 is dedicated to the description of the adsorption properties of chabazite, analcime and clinoptilolite. The amount of methane potentially trapped in these zeolites in martian conditions is estimated in Section 4. Section 5 is devoted to discussion.

2. Zeolites on Mars

Zeolites have been first detected by Ruff (2004) on martian dust using the Mars Global Surveyor (MGS) TES spectroscopic observations. Fialips et al. (2005) then suggested that the water-equivalent hydrogen observed by Mars Odyssey could be partially stored by zeolite minerals present in the first meters in the martian regolith. Indeed, Dickinson and Rosen (2003) observed up to 18 wt% of authigenic chabazite in frozen soils of Antarctica (equivalent to martian conditions). Recently, both OMEGA and CRISM instruments onboard the ESA Mars Express and NASA Mars Reconnaissance Orbiter (MRO) detected zeolite minerals on the rocky outcrops of several places on Mars (Carter et al., 2013; Ehlmann, 2009, 2014). While the first observations on dust and soils suggested a grossly zeolite mineral distribution at mid-latitude, we now have detailed observations revealing the geological/morphological context of zeolite outcrops (152 occurrences were detected by Carter et al. (2013)). For instance, Ehlmann (2009) claimed the identification of pure analcime (Si–Al–Na form) in the deposits in and around the central peaks of two 25-km impact craters nearby Nili Fossae and Isidis. These peaks would then reflect post-impact hydrothermal

alteration (Osinski and Pierazzo, 2013). Carter et al. (2013) had a detailed discussion of the issue of their timing of formation and concluded that most hydrous minerals, including zeolites, were formed during the Noachian period. However, they also noticed the presence of zeolites in the younger northern lowlands, probably resulting from ice-volcano interaction.

In summary, both TES and OMEGA instruments were able to remotely differentiate zeolite spectra from other alteration minerals, namely opal A and saponite formed under similar conditions. Such secondary zeolites result from low temperature aqueous alteration by alkaline brines (or ice) of volcanic glass included in pyroclastic or volcanic sedimentary rocks and form authigenic cements in volcanoclastic sandstone. Note that volcanic ash and tephra, the common contributor to sedimentary material on Mars, should be widespread, as explosive volcanism on Mars is the rule rather than the exception (Grott, 2013). However, the resolution of existing infrared spectra remains insufficient to constrain the variety of zeolites that really crystallized on Mars.

Among the possible zeolites, chabazite is a good candidate to account for their widespread occurrence on Mars. This mineral is the end product of weathering sequences in a wide range of chemical context ranging from silica-rich to silica-poor volcanic rocks. Chabazite typically forms in chemically open systems, in which transports of soluble ions take place efficiently by flowing vadose water or near-surface ground water (Sheppard and Hay, 2001). On the other hand, in the closed systems in the martian subsurface, more alkali analcime and clinoptilolite should be the major zeolites due to limitation of transports of soluble ions. Also, there are several terrestrial locations where nearly pure analcimes form thick bedding (several tens of meters) with wide spatial extent (hundreds of kilometers) (Deer et al., 2004; Sheppard and Gude, 1973; Whateley et al., 1996).

One can provide an estimate of the amount of zeolites potentially existing on Mars. Using Noachian estimates for the martian crustal thermal flux (12–20 °C/km) and thermodynamic data of low-grade metamorphic facies (~160–220 °C and from 0 to 3×10^5 kPa), zeolites may be formed at depths ranging from approximately 8 to 15–20 km (e.g. McSween et al. (2015)). This estimate is confirmed by the detection of zeolites near central peaks, independently suggesting that those minerals are indeed present at depths of several kilometers in the crust. Assuming this depth range (8–15 km), it corresponds to a global volume of 10^9 km³ and a Global Equivalent Layer (GEL) reaching ~7 km of martian zeolites. However, the maps of Carter et al. (2013) show that the area where zeolites (and all hydrous minerals) were detected by remote sensing is equivalent to the surface of the 0–45°S latitudinal band, i.e. about 35% of the surface of Mars. If we do not consider temperature constraints but only different thicknesses (0.001–10 km) of a 100% zeolite layer at all 0–45 °S latitudes, the total volume and GEL are in the $\sim 5 \times 10^4$ – 5×10^8 km³ and ~0.35–3500 m ranges, respectively. The smallest values may be considered as reasonable estimates (in the range of ~1% of zeolite in crystal clays; Ehlmann et al. (2011)), but other geological settings or models can be considered. For instance, the total volume of possible isolated cylindrical zeolite layers located beneath ~150 impact craters (Carter et al., 2013) ranging from 5 to 200 km of diameter (zeolite layer thickness from 0.1 km to unrealistic 20 km) may reach $\sim 10^3$ to 10^8 km³ (0.07–700 m GEL). These isolated layers may correspond to zeolite minerals formed by post-impact hydrothermal alteration (Osinski and Pierazzo, 2013). Therefore, it seems that any scenario of zeolite geological generation (sparse post-impact hydrothermal alteration or crustal global alteration) can lead to important ranges of volumes/GEL. These values, in particular the most optimistic ones, should not be taken as true quantities, but only as starting reasonable estimates. Indeed crustal porosity and fluids surely decrease the efficiency of zeolite

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