

DESTABILIZATION OF ZEOLITES ON MARS: POSSIBLE SOURCE OF ITS ATMOSPHERIC METHANE. O. Mosis¹, J.-M. Simon², J.-P. Bellat², S. Bouley³, E. Chassefière³, F. Schmidt³, V. Sautter⁴, Y. Quesnel⁵, S. Picaut⁶ and S. Lectez⁷, ¹Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille) UMR 7326, 13388, Marseille, France, olivier.mosis@lam.fr, ²Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303, CNRS-Université de Bourgogne Franche Comté, Dijon, France, ³Laboratoire GEOPS (Géosciences Paris Sud), Bat. 509, Université Paris Sud, 91405 Orsay Cedex, France, ⁴Muséum d'Histoire Naturelle, Paris, France, ⁵Aix-Marseille Université, CNRS, IRD, CEREGE UM34, 13545 Aix-en-Provence, France, ⁶Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, Besançon Cedex, France, ⁷Leeds University, School of Earth and Environment, Leeds, United Kingdom.

Introduction: The origin of the martian methane is still poorly understood. 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 [1], 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 [2], 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 [3] or by serpentinization of ultramafic rocks producing H_2 and reducing crustal carbon into CH_4 [4-8]. Once formed, methane storage on Mars is commonly associated to the presence of hidden clathrate reservoirs. Martian clathrates would form an intermediate storage reservoir in the subsurface that regularly releases methane into the atmosphere

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 [9-12] and there is strong geological case arguing for the presence of this aluminosilicate as part of the martian regolite.

Adsorption properties of the chabazite zeolite:

Because chabazite is the end product of weathering sequences in a wide range of chemical context ranging from silica-rich to silica-poor volcanic rocks, we estimate that this mineral is a good candidate to account for the widespread occurrence of zeolites on Mars.

The common chemical formula of a hydrated chabazite is $[\text{Ca}_6\text{Al}_{12}\text{Si}_{24}\text{O}_{72}]\cdot(\text{H}_2\text{O})_{40}$. There exists several forms of chabazite zeolites that differ from their Si/Al ratio and the nature of cations, which counterbalance the electric charges. The framework structure of cha-

basite is composed of SiO_4 and AlO_4 tetrahedrons joined by their oxygen atoms. This arrangement forms primary building units interconnected by secondary building units, as shown in Fig. 1. The unit cell of chabazite thus contains one large ellipsoidal cavity accessed by six 8-ring windows [13].

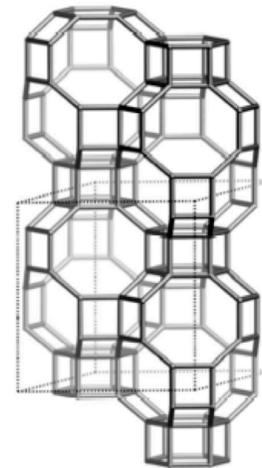


Fig. 1: Structural arrangement of chabazite unit cells viewed along [001] [14]. For clarity reason the silicon, aluminium, oxygen and alkali atoms are not represented.

The chabazite zeolite gets specific adsorption properties for various molecules having a size smaller than the 8-ring apertures, which gives them access to the ellipsoidal cages. Owing to the presence of compensation alkali cations, the chabazite is a hydrophilic material. This zeolite is also able to adsorb CO_2 and CH_4 , two molecules of interest for the martian atmosphere. Figure 2 represents the evolution of the CH_4/CO_2 ratio in chabazite as a function of the CH_4/CO_2 ratio in the coexisting gas at three temperatures of interest, namely the coldest winter temperature reached in the south pole region (150 K), and the average night (200 K) and day (300 K) surface temperatures at mid-latitudes. It shows that the CH_4/CO_2 ratio must be in the $\sim 10^{-5}$ - 3×10^{-4} range at 150 K in the coexisting gas phase to give a ratio in chabazite matching the values measured

by MSL (between ~ 0.25 and 7.2 ppbv). On the other hand, CH_4/CO_2 ratios exceeding ~ 0.1 and 4 ppmv in gas give ratios in chabazite that are always higher than the MSL values at 300 and 200 K, respectively.

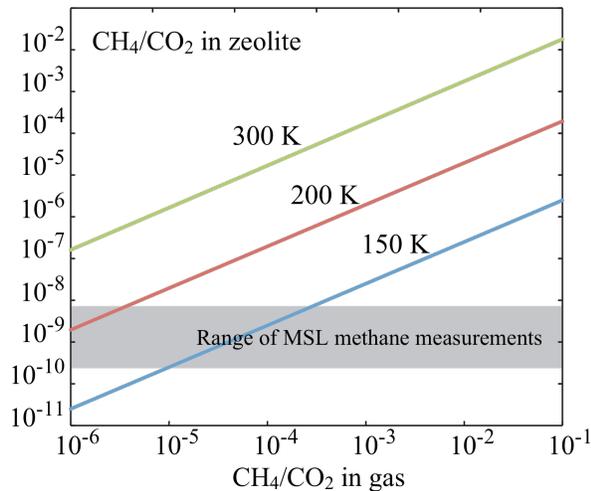


Fig. 2: CH_4/CO_2 ratio in zeolite as a function of its ratio in coexisting gas represented at $T = 150, 200$ and 300 K and 0.6 KPa of total pressure. The grey area corresponds to the range of CH_4 measurements made so far by MSL in the martian atmosphere.

Discussion: Comparison with models depicting the composition of clathrates potentially existing in the martian subsurface shows that zeolite can be a comparable methane sink at significantly higher temperatures. For example, the CH_4/CO_2 ratio in chabazite is at least 10% the value in the coexisting gas at temperatures exceeding 285 K. Similar selectivities are achieved in clathrates for CH_4 mole fractions in the 10^{-4} - 10^{-2} range but the existence of these structures requires temperatures lower than ~ 150 K at 0.6 kPa of atmospheric pressure [15], namely the coldest temperature reached during winter in the south pole region. Therefore, scenarios advocating a substantial trapping of volatiles in martian clathrates argue that these ices are buried in the soil at sufficient depth, allowing them to be isolated from the atmosphere and remain stable over long time periods [7, 15-18]. This scenario also applies to martian zeolites, allowing CH_4 to be extracted either from a potentially methane-rich ancient atmosphere or directly from an abiotic source localized in the crust. Because of their burial in the soil, zeolites could have preserved the trapped methane over long time periods and create the sporadic releases observed

in the atmosphere over the last decade due to impacts, seismic activity or erosion.

References: [1] Webster, C.-R., and 29 colleagues (2015), *Science*, 347, 415-417. [2] Lefèvre, F., Forget, F. (2009), *Nature*, 460, 720-723. [3] Lyons, J. R., Manning, C., Nimmo, F. (2005), *GRL*, 32, L13201. [4] Oze, C., Sharma, M. (2005), *GRL*, 32, L10203. [5] Atreya, S. K., Mahaffy, P. R., Wong, A.-S. (2007), *PSS*, 55, 358-369. [6] Chassefière, E., Leblanc, F. (2011), *EPSL*, 310, 262-271. [7] Chassefière, E., Dartois, E., Herri, J.-M., Tian, F., Schmidt, F., Mousis, O., Lakhlifi, A. (2013), *Icarus*, 223, 878-891. [8] Holm, N. G., Oze, C., Mousis, O., Waite, J. H., Guilbert-Lepoutre, A. (2015), *Astrobiology*, 15, 587-600. [9] Ruff, S. W. (2004), *Icarus*, 168, 131-143. [10] Ehlmann, B. L., and 11 colleagues (2009), *JGR (Planets)*, 114, E00D08. [11] Carter, J., Poulet, F., Bibring, J.-P., Mangold, N., Murchie, S. (2013), *JGR (Planets)*, 118, 831-858. [12] Ehlmann, B. L. (2014), Eighth International Conference on Mars, 1791, 1245. [13] Pascale, F., Ugliengo, P., Civalleri, B., Orlando, R., D'Arco, P., Dovesi, R. (2002), *Journal of Chemical Physics*, 117, 5337-5346. [14] Baerlocher, C., Meier, W. M., Olson, D. H. (2001), *Atlas of zeolite framework types*, Elsevier. [15] Mousis, O., and 10 colleagues (2013), *SSRv*, 174, 213-250. [16] Chastain, B. K., Chevrier, V. (2007), 55, 1246-1256. [17] Thomas, C., Mousis, O., Picaud, S., Ballenegger, V. (2009), *PSS*, 57, 42-47. [18] Herri, J.-M., Chassefière, E. (2012), *PSS*, 73, 376-386.