DO CLATHRATE HYDRATES HAVE ANY INFLUENCE ON THE ATMOSPHERE OF MARS?

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Abstract.   Recent observations have evidenced traces of methane heterogeneously distributed in the Martian atmosphere (Krasnopolsky et al. 2004). However, because the lifetime of CH_4 in the atmosphere of Mars is estimated to be around 250-430 years on the basis of gas-phase chemistry (Krasnopolsky et al. 2004), its actual sources on Mars remain controversial. Among other assumptions, it has been proposed (Chastain & Chevrier 2007) that clathrate hydrates located in the subsurface of Mars could be at the origin of the small quantities of CH_4 detected. In the present work, we have calculated the relative abundance of CH_4 in clathrate hydrates on Mars, using a statistical model based on the theory of van der Waals and Platteeuw (1959). The results show that methane enriched clathrate hydrates could be stable in the subsurface of Mars only if a primitive methane-rich atmosphere has existed or if a subsurface source of CH_4 has been (or is still) present.

1   Introduction

Recently, a small quantity of methane (~ 10 ppbv) has been detected in the atmosphere of Mars by the Planetary Fourier Spectrometer (PFS) onboard the *Mars Express* spacecraft (Formisano et al. 2004). The photochemical mean lifetime of the martian atmospheric methane is $\sim$ 300-600 years (Krasnopolsky et al. 2004; Formisano et al. 2004), and so it should not still exist today. To explain its presence, several scenarios have been invoked, like the release of methane from a subsurface reservoir, or the existence of an active biological (organisms living in the near subsurface of the planet; Formisano et al. 2004; Krasnopolsky et al. 2004; Krasnopolsky 2006) or geological (e.g. olivine hydratation in the martian regolith or crust; Oze & Sharma 2005) primary source of methane. The martian atmospheric methane could also come from the decomposition of possible methane clathrate hydrates in the near-subsurface (Prieto-Ballesteros et al. 2006; Chastain & Chevrier 2007). Indeed, because they can trap methane over large timescales, clathrate hydrates could be a secondary reservoir, filled either by ancient or by current methane sources (Prieto-Ballesteros et al. 2006; Chastain & Chevrier 2007).

Such a mechanism has recently been studied by Chastain & Chevrier (2007) with the program CSMHYD developed by Sloan (1998), and for a model of an atmosphere containing only CO_2 and CH_4. We reinvestigate here this work, by using a statistical thermodynamic model based on experimental data and on the original work of van der Waals & Platteeuw (1959). This model enables calculations at lower temperatures than the CSMHYD, and for an initial gas phase containing more species. It is thus possible to study the composition of clathrate hydrates formed from the martian atmosphere, at temperatures even as lower as the extreme ones measured in the polar caps ($\sim$ 130 K; Kieffer et al. 2001)

2   Model

To carry out this study, we have used the same approach as in our previous studies devoted to the trapping of noble gases by clathrate hydrates on Titan (Thomas et al. 2007, 2008), based on the statistical model proposed by van der Waals & Platteuw (1959). In such an approach the relative abundance f_K of a guest species K in a clathrate hydrate (of structure I or II) is defined as the ratio of the average number of guest molecules of species K in the clathrate hydrate over the average total number of incorporated molecules, as :

$$f_K = \frac{b_L y_{K,L} + b_S y_{K,S}}{b_L \sum_J y_{J,L} + b_S \sum_J y_{J,S}}, \tag{2.1}$$

where the sums in the denominator run over all species present in the system, and b_S and b_L are the number of small and large cages per unit cell, respectively. This statistical approach relies on the representation of the interactions between the guest species K and the water molecules forming the surrounding cage by a spherically averaged Kihara potential. As a consequence, the calculations of the relative abundances of a guest species trapped in clathrate hydrate strongly depend on the accurate determination of the interaction parameters.

In this study, we have used the set of parameters for the Kihara potential determined by Parrish & Prausnitz (1972) from experimentally measured clathrate hydrate properties. Unfortunately this set does not provide the complete list of Kihara parameters required by the molecules studied in our system. As a consequence, for the CO molecule, we have used the parameters given by Diaz Peña et al. (1982). The parameters used in this study are given in Table 1.

Table 1. Kihara parameters used in the present study. σ is the Lennard-Jones diameter, ϵ is the depth of the potential well, and a is the radius of the impenetrable core. These parameters derive from [a] Parrish & Prausnitz (1972), [b] Jager (2001), [c] Diaz Peña et al. (1982).

Molecule	σ(Å)	ϵ/k_B(K)	a(Å)
CH_4[a]	3.2398	153.17	0.300
O_2[a]	2.7673	166.37	0.360
CO[c]	3.101	134.95	0.284
N_2[a]	3.2199	127.95	0.350
CO_2[a]	2.9681	169.09	0.6805[b]
Xe[a]	3.1906	201.34	0.280
Ar[a]	2.9434	170.50	0.184
Kr[a]	2.9739	198.34	0.230

3 Results

This model has been used to calculate the composition of clathrate hydrates formed in the near subsurface of Mars as a function of the temperature and of the gas phase composition, from a martian atmosphere containing CO_2, N_2, O_2, CO, Kr, Xe and Ar[1], together with CH_4. Three different initial gas phase abundances of CH_4 have been studied. In each case, the ratios between CO_2, N_2, O_2, CO, Kr, Xe and Ar are taken equal to those measured in the present martian atmosphere, and the sum of all initial gas phase abundances is equal to 1. The largest value of CH_4 initial gas phase abundance (50%) is typical of methane-rich conditions in which CH_4 is supplied from below by microbial or geological processes or from above from ancient atmospheres. In contrast, the lowest values (0.01% and 1%) are more typical of recent atmospheric compositions.

The figure 1 shows the evolution with temperature of the relative abundances f_K in clathrate hydrates of all the species initially present, and for the three different abundances of CH_4 considered. For each case, the relative abundances of Ar, N_2, O_2, CO, Kr and CH_4 slightly increase with the formation temperature, whereas that of CO_2 and Xe slightly decrease, irrespective of the initial gas phase abundances. However, the trapping of Ar, N_2, O_2, CO, Kr and Xe is always weak, whereas the incorporation of CH_4 and CO_2 in clathrate hydrates strongly depends on their initial gas phase abundances. Indeed, Figs. 1.a and 1.b show that CH_4 is poorly trapped when its initial gas phase abundance is lower than a few percent, whereas in such a situation, CO_2 fills almost entirely the clathrate hydrates. On the contrary, considering a methane-rich initial gas phase leads to a strong competition between the trapping of CO_2 and that of CH_4 (Fig. 1.c).

To show the trapping efficiency, we have calculated the ratio between the relative abundance f_K of a given gas in the multiple guest clathrate hydrate and its initial gas phase abundance x_K (Thomas et al. 2007, 2008).

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[1]The present martian atmosphere contains 95% of CO_2, 2.7% of N_2, 0.13% of O_2, 0.07% of CO, 2.10^{-5}% of Kr, 8.10^{-6}% of Xe and 1.6% of Ar (Moroz 1998).
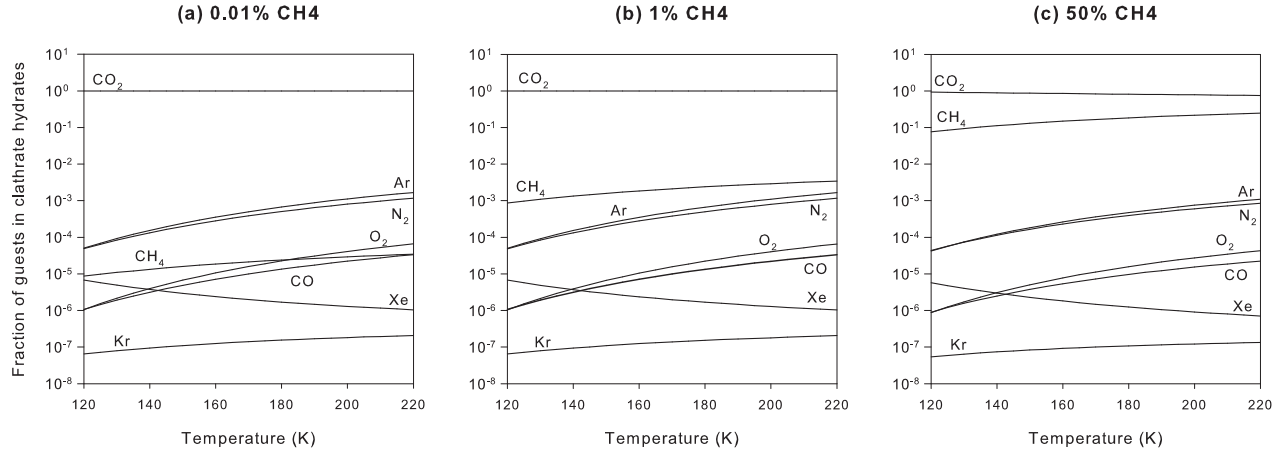
Fig. 1. Relative abundances of CH_4, CO_2, CO, O_2, N_2, Ar, Kr and Xe in clathrate hydrates as a function of temperature for the different methane abundances considered in the present work.

These abundance ratios have been calculated at the particular point on the dissociation curves corresponding to the present average atmospheric pressure on Mars, i.e. $P = 7$ mbar, and they are given in Table 2 together with the x_K and f_K values.

Table 2. Relative abundances of CH_4, CO_2, CO, O_2, N_2, Ar, Kr and Xe in the initial gas phase (x_G) and in clathrates (f_G), and abundance ratios. These ratios are calculated at $P = 7$ mbar, and at the corresponding temperature on the dissociation curves.

gaz	x_G	f_G	abundance ratio	gaz	x_G	f_G	abundance ratio
CH_4	1×10^{-4}	1.66×10^{-5}	0.166	Ar	1.61×10^{-2}	2.71×10^{-4}	1.68×10^{-2}
	0.1	1.77×10^{-2}	0.177		1.50×10^{-2}	2.62×10^{-4}	1.75×10^{-2}
	0.5	0.127	0.254		0.81×10^{-2}	1.69×10^{-4}	2.11×10^{-2}
CO_2	0.957	0.999	1.046	N_2	2.72×10^{-2}	2.20×10^{-4}	0.81×10^{-2}
	0.861	0.982	1.143		2.40×10^{-2}	2.05×10^{-4}	0.85×10^{-2}
	0.478	0.873	1.829		1.36×10^{-2}	1.54×10^{-4}	1.13×10^{-2}
Xe	8.04×10^{-8}	2.75×10^{-6}	34.27	CO	7.03×10^{-4}	5.45×10^{-6}	0.77×10^{-2}
	7.24×10^{-8}	2.71×10^{-6}	37.51		6.33×10^{-4}	5.11×10^{-6}	0.81×10^{-2}
	4.02×10^{-8}	2.42×10^{-6}	60.20		3.52×10^{-4}	3.48×10^{-6}	0.99×10^{-2}
Kr	2.01×10^{-7}	1.14×10^{-7}	0.568	O_2	1.31×10^{-3}	7.71×10^{-6}	0.59×10^{-2}
	1.81×10^{-7}	1.09×10^{-7}	0.603		1.18×10^{-3}	7.17×10^{-6}	0.61×10^{-2}
	1.01×10^{-7}	8.14×10^{-8}	0.810		0.65×10^{-3}	4.60×10^{-6}	0.70×10^{-2}

Table 2 shows that in such conditions, the abundance ratio of CH_4 increases with its initial gas phase abundance, but it remains lower than 1 in all situations, indicating that the trapping efficiency of CH_4 in the multiple guest clathrate hydrates considered here is quite low. On the contrary, with an abundance ratio always larger than 1, CO_2 is trapped in clathrate hydrates with a high efficiency. Thus, although the trapping of CH_4 becomes more and more efficient when its initial gas phase abundance increases, it remains much less efficient than the trapping of CO_2. Note that Table 2 also shows that the trapping of Xe (and in a lesser extent that of Kr) by clathrate hydrates is very efficient. However, Xe, Kr, Ar, CO, N_2 and O_2 have abundances almost negligible in the multiple guest clathrate hydrates considered in the present study.

4 Conclusion

Our calculations show that CO_2 and, in a lesser extent CH_4, are strongly trapped in the multiple guest clathrate hydrates considered here, even when additional gases such as Ar, Kr, Xe, CO, O_2 and N_2 are present in the

initial gas phase. Indeed, these latter gases do not influence the composition of the corresponding clathrate hydrate, although some of them are strongly trapped (Xe and Kr).

Although we have considered an initial gas phase containing more species than the one studied by Chastain & Chevrier (2007), our results are mostly similar to those they obtained, that is in presence of CO_2, a methane-rich clathrate hydrate can be thermodynamically stable only if the gas phase is itself strongly enriched in CH_4.

As a consequence, if methane-rich clathrate hydrates exist on Mars, they cannot have been formed from the present martian atmosphere (poor in methane; Mumma et al. 2003; Formisano et al. 2004; Krasnopolsky et al. 2004; Geminale et al. 2008), but only from an early martian atmosphere, richer in CH_4 than the present one.

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