CH_4-RICH CLATHRATE HYDRATE STABILITY ZONE IN THE PRESENT MARTIAN SUBSURFACE.

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Introduction

Since 2003, several detections of methane in the atmosphere of Mars were reported from Earth-based and Mars orbit instruments [1–5] with abundances up to tens of parts per billion by volume (ppbv). Recently, the Curiosity rover detected methane with background levels of 0.7 ppbv and episodic releases of 7 ppbv [6]. Although the methane sources are still unknown, this gas may have been stored in reservoirs of clathrate hydrate in the martian subsurface where thermodynamics conditions are favourable to their presence [7]. Clathrate hydrates are crystalline compounds constituted by cages formed by hydrogen-bonded water molecules inside of which guest gas molecules are trapped. In this study, the fraction of methane trapped in clathrate hydrates from a gas phase including the Mars'atmosphere main components is investigated. Present-day maps of CH_4-rich clathrate stability zone variations are then determined by coupling the stability conditions of methane clathrate with a subsurface model whose near-surface layers properties are changed at locations studied to fit with the thermal inertia derived from TES MGS observations [8].

Methane abundance in clathrate hydrates

In presence of CO_2, clathrate hydrates can efficiently trap methane only if the gas phase is strongly enriched in CH_4 [7, 9]. We calculated the relative abundances of methane in mixed CO_2-CH_4-N_2-Ar clathrates by considering several initial abundances of CH_4 in the gas phase (see Table 1). For cases 1, 3 and 5, we assume that the ratios between CO_2, N_2 and Ar are similar to those measured in the present martian atmosphere. In cases 2, 4 and 6, the gas phase is enriched in N_2 compared to the previous cases, which is thought to be more representative of Early Mars atmosphere. To determine the fraction of methane trapped in clathrates from a specific gas phase at given temperature and pressure, we follow the method described by [10, 11]. This approach is based on the statistical thermodynamics model of [12] but uses experimentally determined dissociation curves instead of calculated dissociation pressures [11]. The calculations have been performed using temperature and pressure conditions of clathrate formation. The Kihara parameters, the constants to determine the dissociation pressure and the parameters for the clathrate cavities have been taken from [13].
The evolution with temperature of the methane fraction trapped in mixed clathrate hydrates (structure I) from the various initial compositions considered in this study is shown in Fig. 1. The relative abundance of CH_4 in clathrates slightly increases with the formation temperature and depends on the composition of the initial gas phase. When the abundance of methane in the initial gas phase is low, the fraction of trapped CH_4 is small and the clathrates contain mainly CO_2. On the contrary, when the initial gas phase is enriched in methane, the trapping of CH_4 is efficient. In addition, in the same initial concentration of methane and temperature conditions, the relative abundance of CH_4 is larger in clathrate hydrates formed from an initial gas phase richer in N_2.

Table 1
The different compositions considered for the initial gas phase

	CH_4 (%)	CO_2 (%)	N_2 (%)	Ar (%)
case 1	1.0	94.7	2.7	1.6
case 2	1.0	81.2	16.2	1.6
case 3	20.0	76.5	2.2	1.3
case 4	20.0	65.6	13.1	1.3
case 5	90.0	9.57	0.27	0.16
case 6	90.0	8.2	1.64	0.16

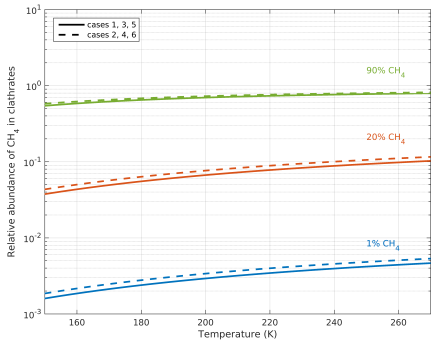

Fig.1. Fraction of CH_4 incorporated in clathrate hydrates from a gas phase with different CH_4-CO_2-N_2-Ar mixture ratios (see Table 1) as a function of temperature.

Clathrate hydrate stability zone

The region of the crust that meets the thermodynamic criteria of clathrates stability is called hydrate stability zone (HSZ) and its thickness is determined by the local geothermal gradient. In practice, its determination is complex and depends on many factors including salinity and nature of dissolved solids in the groundwater, the local geothermal gradient, the pressure, the average surface temperature, the recent thermal history of the crust and the subsurface heterogeneity. To obtain the variations of the hydrate stability zone within the martian subsurface, we coupled the stability conditions of clathrates with a 1D subsurface thermal model. Fig. 2 represents the stability conditions of the mixed CO_2-CH_4-N_2-Ar clathrates formed from the different gas compositions considered in this work. The addition of methane in clathrates increases the dissociation pressure in the same temperature conditions. Therefore CH_4-rich clathrates form at larger depth in the martian crust than clathrate hydrates with a low relative abundance of methane. The dissociation pressure is also more important for mixed clathrate hydrates formed from a gas phase richer in N_2.

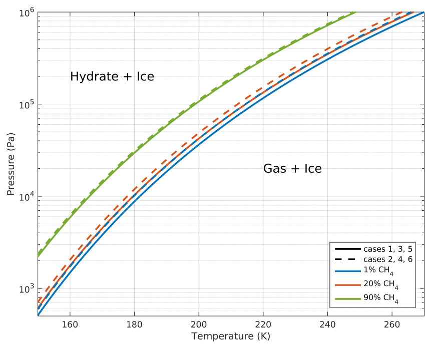

Fig.2. Phase diagram of mixed CO_2-CH_4-N_2-Ar clathrates for different abundances of methane in the initial gas phase.

The thermal properties of the subsurface model are set to fit with the thermal inertia derived from TES MGS observations [8] until 1m deep and then the thermal inertia is increased to 2290 J m^{-2} K^{-1} $s^{-1/2}$ to correspond to ice-cemented soil. The heat equation is solved at each time step with the Crank-Nicolson algorithm. The boundary condition at the bottom is given by the heat flux and the change in surface temperature and pressure over the year is given by the Mars Climate Database (MCD) [14]. The depth from which CH_4-rich clathrates (case 5 in Table 1) are stable within the martian subsurface at present-day is represented in Fig.3. Results show that CH_4-rich clathrates are stable close to the surface with a stability zone strongly dependent on the average annual surface temperature and approaching the surface with increasing latitude.

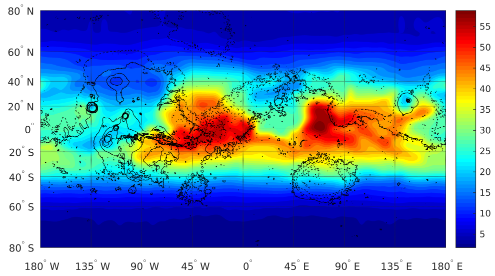

Fig.3. Depth (m) of the beginning of hydrate stability zone in present-day martian subsurface for CH_4-rich clathrates formed from a gas phase with 90% of methane (case 5 in Table 1).

Regarding the crust composition, the type of soil directly controls the geothermal conditions and therefore the depth of clathrate formation. We tested different subsurface composition with representative thermophysical properties for typical martian materials. Unconsolidated soil acts as a thermal insulator and prevents the clathrate formation in the crust except on a small part of a few tens of meters thick. The stability zone of methane clathrates in unconsolidated soil can only exist at high latitudes and has a thickness of several tens to several hundreds of meters. In contrast, sandstone or ice-cemented soil allows the clathrate formation with a stability zone of several kilometers. This is explained by the fact that they evacuate heat more efficiently and thus maintain lower temperatures. The heat flux also controls the depth of hydrate stability zone and mainly affects its base.

Discussion and conclusion

Given the very low abundance of methane on Mars, CH_4-rich clathrate hydrates cannot be formed from the current planet's atmosphere. If they are present in the martian crust, CH_4-rich clathrates should have been formed in contact with a subsurface source or an early martian atmosphere, richer in methane. While the presence of CH_4-rich clathrates on Mars depends on many factors (the obliquity variations, the thermal history and the composition of the crust, the dissociation rate of clathrates, the amounts of methane available in the subsurface or in the early martian atmosphere), it is possible that these methane reservoirs have remained trapped at depth until the present day. The current stability zone of CH_4-rich clathrate hydrates is close to the surface and the methane release from these reservoirs could explain transient CH_4 plumes that have been observed on the surface during the past years [4]. The *ExoMars Trace Gas Orbiter* will provide valuable measurements to understand the volatile reservoirs on Mars and particularly the sources and the sinks of methane.

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