

SOLAR INSOLATION-INDUCED DESTABILIZATION OF SUBSURFACE CLATHRATES ON MARS: IMPLICATIONS FOR THE MARTIAN ATMOSPHERIC METHANE. R. Ishimaru¹, G. Komatsu^{2,1}, and T. Matsui¹, ¹Planetary Exploration Research Center (PERC), Chiba Institute of Technology (Chitech), 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan (ishimaru@perc.it-chiba.ac.jp, ishimaru.ryo@gmail.com), ²International Research School of Planetary Sciences, Università d'Annunzio, Viale Pindaro 42, 65127 Pescara, Italy.

Introduction: Mars Express and ground based telescopes recently discovered CH₄ in the martian atmosphere [1, 2]. An expectation that it may have a biological origin brings renewed attention to Mars. The observed distribution of CH₄ is localized ones [1-5], which suggests existence of localized sources of CH₄ because the time required for global mixing in the martian atmosphere is very short. CH₄ release from subsurface clathrates has been proposed as a plausible source of CH₄ [6-8]. Since the region where clathrates are stable exists in the subsurface martian environment [7], CH₄ are expected to be stored as methane clathrates when CH₄ is delivered or produced in the subsurface. This is likely to occur because the origin of CH₄ on Mars could be subsurface biological or geochemical activities (volcanic or hydrothermal reactions such as serpentinization of basalt) [e.g., 2, 7]. Then, dissociation of such clathrates may release CH₄ into the atmosphere.

Destabilization of clathrates is required for dissociation of clathrates. Here, we show the possibility that solar insolation induces the destabilization of subsurface clathrates. Clathrates are destabilized via temperature increase. If solar heating can increase the temperature in the area of subsurface clathrates, a resultant CH₄ release may contribute to the presence of CH₄ in the martian atmosphere.

Two regions have been suggested as a source of martian CH₄: low-latitude region (roughly 30°S-30°N) [2] or northern polar cap [5]. Since destabilization of subsurface clathrates is controlled by surface temperature and subsurface environment as shown below, we consider these two regions in this study.

Model: In this study, we examine insolation-induced destabilization of clathrates considering stability conditions of clathrates and thermal conduction in subsurface materials. First, a clathrate-forming region (depth) is determined from stability conditions of clathrates. Second, an annual skin depth to which a seasonal temperature variation (due to insolation) of the surface propagates via conduction is estimated using thermal conductive properties of subsurface materials. If a seasonal temperature variation can propagate to a clathrate-forming depth, then destabilization of clathrates is assumed to occur.

Clathrate-forming region. In low temperature or high pressure conditions, H₂O in the presence of gases solidifies into a crystalline structure known as clathrate. Multiple gas species can occupy clathrate cavities to form multicomponent clathrates (the term binary clathrate is used when two gas species occupy the cavity) [7]. Since the major constituent in the martian atmosphere is CO₂, CO₂ is likely to be trapped as binary clathrates together with CH₄ on Mars. According to the calculations of Chastain and Chevrier [7], binary clathrates containing both CO₂ and CH₄ form at lower pressures than pure CH₄ clathrates; binary clathrate can form at shallower depths than CH₄ clathrates. This makes it easier for insolation to heat the subsurface clathrates, which would have an advantage in the destabilization of subsurface. To examine this effect, we consider clathrate compositions ranging from pure CH₄ clathrate to CO₂-rich binary clathrates. We use the Chastain and Chevrier (2007)'s values [7] as stability conditions (temperature and pressure) of each clathrate.

Annual skin depth. Seasonal variations of insolation induce seasonal variations in the temperature of the surface which would propagate to subsurface. The depth to which annual thermal variations propagate depends on the thermal parameters of subsurface materials and the time scale of the variation. The e-folding depth of subsurface temperature variations, annual skin depth, δ is estimated by

$$\delta = \sqrt{kP/\rho c \pi},$$

where P , k , ρ , and c are the time scale of the variation (one martian year), thermal conductivity, density, and specific heat of subsurface materials, respectively [9]. Since ~ 5 times an annual skin depth is a measure of depth to which temperature variations of the surface propagate [10, 11], we use the depth as the propagation depth of temperature variation. Three subsurface materials with different thermal properties are considered as possible materials in low-latitude regions on Mars: sandstone, ice-cemented soil, dry unconsolidated soil, and basaltic rock. Since a conductive contact between materials increases thermal conductivity, low-porosity sandstone, ice-cemented soil, and basaltic rock have higher thermal conductivity compared to unconsolidated soil. Thermal properties of these four materials are given by [9, 10, 12]. The polar cap is assumed to be composed of H₂O ice or CO₂ ice.

Result and Discussion: First, we consider low-latitude regions. Figure 1 shows a stability diagram of clathrates for sandstone as an example. 5 times the annual skin depth is also shown. A vertical axis of depths is used instead of pressures. Properties of subsurface materials, such as density, are assumed constant with depth. The regions deeper than solid lines on the figure are clathrate stability zones (or clathrate-forming zones). Figure 1 shows that CO_2 -rich clathrates form at depths shallower than those of CH_4 -rich ones.

Here, unless temperature variations of the surface propagate, subsurface temperatures at depths of up to several tens of meters is assumed to be a constant value and the same as the mean annual surface temperature. This is because the effect of the geothermal heat flow at such depths can be neglected [10]. Since the mean annual surface temperature of low-latitude regions where CH_4 has been detected is ~ 210 K [11], the subsurface temperature is set to 210 K. As seen in Figure 1, at 210 K 5 times the annual skin depth can reach clathrate stability zones for binary clathrates containing CO_2 . In other words, the temperature of clathrates oscillates seasonally. This induces a cycle of destabilization and stabilization of clathrates, suggestive of CH_4 release. Since CO_2 -rich clathrates are deficient in CH_4 , CH_4 release from them may be consistent with the small quantity of CH_4 observed in the atmosphere [1, 2].

For ice-cemented soil and basaltic rock, we obtained results similar to those of sandstone. Meanwhile, we found that destabilization of clathrates does not occur in unconsolidated soil because low thermal conductivity of unconsolidated soil results in small skin depth. Not only the clathrate composition but also the thermal property of subsurface materials is important for destabilization of clathrates.

Here, the effects of local slopes also need to be considered. Specifically, poleward facing slopes experience a geometrically-reduced incident solar radiation, resulting in lower surface temperature [10]. This would allow formation of clathrates at shallower depths capable of gaining large amplitude of temperature oscillations, which raise the probability of CH_4 release.

Second, in the case of polar cap, we found that clathrate-forming regions is very shallow (< 2.5 m) because of low temperatures of the polar cap (155 K). Then, an annual skin depth is larger than clathrate-forming depth regardless of the clathrate composition. Thus, an anticipated large temperature increase may lead to the CH_4 release via dissociation of clathrates.

It is to be noted that it could take time for CH_4 to be released into the atmosphere through the destabilization of clathrates: the reaction time for dissociation of clathrates and the required time for the CH_4 to seep upward into the atmosphere, are not well known. In addition, the effect of temperature oscillation phase shifting with depth due to the finite time required for the thermal wave to diffuse downward [9] needs to be taken into account: the timing of CH_4 release is not necessarily synchronized with warm seasons at low latitudes, but CH_4 release at the polar cap may occur during warm seasons owing to very shallow clathrates. Further observations of CH_4 release is expected to impose constraints on our model, providing a clue to understanding the origin and release mechanism of CH_4 on Mars.

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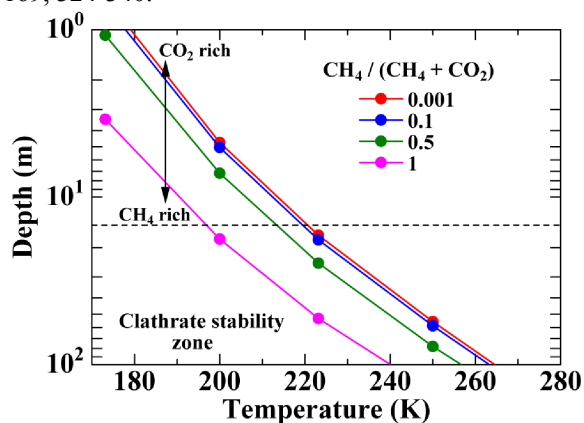


Figure 1. Stability diagram of clathrates (solid lines) and 5 times the annual skin depth (dashed line) for sandstone. Clathrate stability conditions for four different methane molar fraction ($\text{CH}_4 / (\text{CH}_4 + \text{CO}_2)$) in the initial gas phase before clathrate formation are shown as 0.001, 0.1, 0.5, and 1.