Influence of subsurface properties on ice and methane clathrate stability on Mars

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Introduction: Thermodynamic conditions prevailing on Mars favour clathrate formation from near subsurface to deep down in the cryosphere (until several kilometers deep) [5] and kinetics experiments [4] showed that their dissociation, initiated by a change in temperature, pressure or composition of the reservoir, is a feasible mechanism for near-surface methane release on Mars. The depth and thickness of clathrate stability zone (CSZ) in the subsurface depend on many factors such as thermal state and composition of the crust, heat flow, average surface temperature, confining pressure and salinity of the water involved in clathrate formation.

Water diffusion from the regolith plays a role in clathrate destabilization. Indeed, loss of shallow ice eliminates overburden pressure and initiates clathrate dissociation and the release of the trapped gas. In addition, the presence of water ice in the pores affects gas diffusion through the regolith.

In this work, the water vapour transport in the martian subsurface and near-surface ice evolution (ice redistribution and porosity changes) are investigated using a 1D diffusive model and the different subsurface properties that influence water ice and methane clathrate stability such as thermal inertia or local heat flow are discussed.

Model: To determine clathrate stability conditions, we follow an approach similar to [8] based on the work of [9] and on available experimental dissociation curves. This model is coupled to a 1D thermal model to obtain clathrate stability zone variations in the subsurface of Mars as a function of pressure in pore spaces, thermal properties of the soil, local heat flow, fraction of CH_4 trapped in clathrates and the presence of perchlorates in the water involved in clathrate formation. The diffusive model used to study water vapour exchanges and ice stability is based on the work of [7] but, in addition, it takes into account the different diffusion regimes (Fickian and Knudsen diffusion), the influence of ice redistribution on the effective diffusion coefficient and diffusion advection.

Results: Methane clathrate stability zone can significantly vary depending on the subsurface composition as can be seen in Fig.1 where the stability zone is calculated using mean annual surface temperatures [2] and assuming a surface heat flow of 19 mW m^{-2}, the present-day average value [6] . Material with high thermal conductivity evacuates heat more efficiently and thus maintains lower temperatures, which allows methane clathrate formation with a stability zone of several kilometers thick. For example, in ice-cemented soil (Fig.1A) CH_4 CSZ extends from about 45.5m to 11.8 km deep at the equator and from about 60 cm to near 22 km deep at the pole. On the contrary, material with low thermal conductivity acts as a thermal insulator and therefore methane clathrate in such a soil can only exist at high latitudes and their stability zone has a thickness of several tens to several hundreds of meters. For example, CH_4 clathrate in dry unconsolidated soil (Fig.1D) is stable from about 62.6 cm to 214 m deep at the pole.

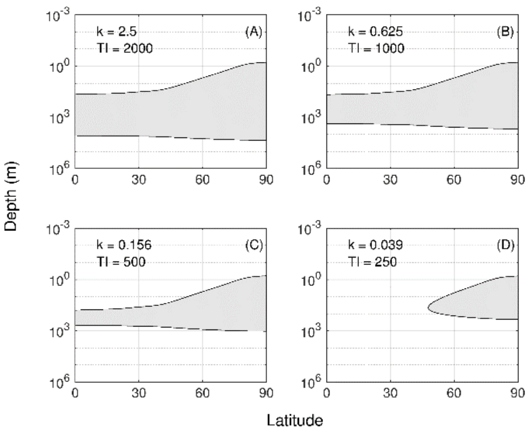

Figure 1: Methane clathrate stability zone in the martian subsurface for different thermal properties in the subsurface thermal model corresponding to thermal inertia (TI) ranging from 250 to 2000 J m^{-2} K^{-1} s$^{-1/2}$. The volumetric heat capacity is kept constant (1.6 x 10^{6} J K^{-1} m^{-3}) while the thermal conductivity (*k*) is changed to 2.5 (A), 0.625 (B), 0.156 (C) and 0.039 W m^{-1} K^{-1} (D) respectively.

The depth of ice table also notably vary with subsurface composition. For higher values of the thermal conductivity, the temperature oscillations due to seasonal variations reach a greater depth. These temperature variations affect the amount of ice and the ice table depth that is located deeper with increasing thermal conductivity.

The presence of salts in the system is important in the determination of CSZ as it affects the activity of water which affects both the freezing point of pure water and the clathrate stability conditions. Increasing salinity induces an upward shift of the base of CSZ and therefore reduces its thickness [3]. Magnesium perchlorate ($Mg(ClO_4)_2$) exhibits one of the lowest eutectic temperature of all salts, 206K [1], and its presence, in addition to shift the base of CSZ, significantly affects the top of CSZ at low latitudes. At the equator, CH_4 clathrates are stable deeper than 300 m in the presence of eutectic $Mg(ClO_4)_2$ brine and their stability zone has a thickness of a few hundred meters.

Regarding the effect of adsorption on water vapour transport, results show that the temporal change in the surface flux of water vapour and in the total mass of ice in the subsurface has a larger amplitude when this process is taken into account. The vertical profile of water vapour density and the quantity of water exchanged periodically are strongly affected by adsorption. However, there is the same net accumulation of ice with and without adsorption. The density of adsorbed water depends on the specific surface area of the soil. Simulations including adsorption showed that the amount of ice increases with the specific surface area.

In addition to these results, those related to other subsurface properties such as the local heat flow as well as their implications will be presented at the meeting. The results have strong implications on subsurface gas transport and methane outgassing scenarios on Mars that is among the main objectives of ExoMars Trace Gas Orbiter.

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