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Martian methane and link with clathrates in the crust of Mars

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The recent detection of methane in the Martian atmosphere (Krasnopolsky et al., 2004; Formisano et al., 2004; Geminale et al., 2008; Mumma et al., 2009; Fonti and Marzo, 2010) generated a large interest among the scientific community in particular because the source of this gas is still unknown and because it is a potential biomarker. Methane, observed at a level of 10 parts per billion and per volume, has a non-uniform distribution involving a photochemical lifetime of 200 days (Lefevre and Forget, 2009), smaller than the 300 years calculated by photochemical models. In addition, there is a correlation between the mixing ratio of water vapor and methane (Geminale et al., 2008). In order to explain this phenomenon, the existence of metastable clathrates decomposing in the atmosphere and releasing CH4 has been suggested (Chassefière, 2009). Clathrates are chemical compounds formed by the inclusion of gas molecules in the cavities of a water molecules network and are stable at high pressure and low temperature.

In addition to the biological origin, often invoked to explain most of the methane on Earth, the Martian methane may also have been produced by hydrogeochemical or volcanic processes or may be the last traces of an amount brought by a meteoritic impact a few hundred or thousands years (Atreya et al., 2007). Methane could also come from the exposure to ultraviolet of meteorites falling continuously on the surface of Mars (Keppler et al., 2012). Although the process is very likely to occur on Mars, it does not produce all the expected amount of methane currently measured. Moreover, conditions in the Martian crust are favorable to the stability of methane clathrates. So CH4 emissions observed may also be due to the dissociation of the clathrates due to a change in temperature, pressure or composition. Current conditions of Mars do not allow them to be stable on the surface but they can remain stable in the crust if they were formed below a certain depth depending on the surface temperature conditions. For a temperature change diffusion inside the crust (skin depth) depending on the timescale involved it is though possible to obtain destabilization of clathrates.

We have calculated the distribution of methane, carbon dioxide and mixed clathrates (CH4-CO_2) in the Martian crust, assuming that the latter was constituted of basalt with pores filled with ice. The results showed that the clathrate stability zone approaches the surface with increasing latitude (therefore increasing the possibility to have methane degassing near the pole) and that CO_2 clathrates were formed at shallower depth than methane clathrates (therefore increasing the possibility to have methane if methane is mixed with CO_2). We also studied the destabilization of clathrates due to seasonal variations in temperature, change in obliquity and an increase of the water salinity. The thermal oscillations caused by the variation of the obliquity could have destabilized clathrates on all latitudes while the thermal oscillations due to the succession of the seasons destabilize clathrates at high latitude only.