

## From micrometer scale to planet size - $\ensuremath{\text{CO}}_2$ Hydrates on Mars

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From a thermodynamic point of view there is no argument against the existence  $CO_2$ -hydrates in the Martian regolith close to the surface. It was postulated, that  $CO_2$ -hydrates may occur in the ice layers of the north and the south polar caps. On this basis, many suggestions linking decomposition of  $CO_2$ -hydrates to morphological features like chaotic terrains, gullies, some outflow channels or pancake-dome structures have been put forward. However, the discussions in a large number of publications about such a possibility did not reach any final conclusion because of the lack of elementary knowledge about the formation and decomposition kinetics of this particular gas hydrates. Our investigations are filling this gap.

As it is established,  $CO_2$  and  $H_2O$  are abundant in Martian regolith. At present days p-T conditions the most likely formation reaction to take place is between gaseous  $CO_2$ and water ice. To provide a physicochemical basis for these ideas, we performed a series of  $CO_2$ -hydrate formation and decomposition experiments at Martian surface and sub-surface conditions, using p-V-T methods as well as in-situ neutron diffraction at ILL Grenoble. The experiments indicate that the time for formation is directly related to the accessible surface area of the ice grains, temperature and  $CO_2$  pressure. At p-T conditions close to the Martian poles  $CO_2$ -hydrates are thermodynamically stable at the surface. Despite this fact our results show that at these low temperatures the very slow kinetics prevent any significant formation of clathrates. In addition, seasonal temperature changes are likely to destroy minute amounts, which had been formed. However, there is still a fair chance to find  $CO_2$ -hydrates deeper in the regolith at different latitudes (given a pressure sealing of the overburden layers e.g. by water ice). Higher temperatures and pressures, which are likely to exist at various places, create much more favorable conditions. Additionally, climate variations on longer time-scales provide a conceivable scenario for hydrate formation and decomposition cycles. Upon decomposition, in a temperature interval from about 240 to 273 K, we have firmly established a behavior, called "self-preservation" (or "anomalous preservation"), which may preserve CO<sub>2</sub>-hydrates for geologically long time scales. Self-preservation is a complex micro-structural process related to changes on the surface of decomposing hydrates. Small (up to  $20\mu$ m) ice crystals formed upon decomposition create a layer, which due to annealing of ice defects and Ostwald ripening drastically slow down the out-diffusion of gas molecules, thus preventing decomposition. Below this temperature regime the "self-preservation" also occurs in the narrow p-T range. The sealing is less effective and it is governed by the speed of decomposition. The destruction of this fragile state achieved mechanically or by reaching the ice melting temperature may lead to the rapid decomposition leading to the formation of various geomorphologic features at the Martian surface.