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Laboratory study on the kinetics of CO_2 hydrates in a broad p-T range relevant to Mars

A. Falenty, W. F. Kuhs

Geowissenschaftliches Zentrum, Abteilung Kristallographie, Universität Göttingen,
Goldschmidtstr.1, 37077 Göttingen, Germany (afalent@gwdg.de / Fax: +49-551-39-9521 /
Phone: +49-551-2137)

Although recent investigations revealed that liquid water was indeed actively reshaping Mars in a distant past, the present cold climate is not favorable for the stability of liquid water at the planet surface or close to it. The discovery of geologically young structures (e.g chaotic terrains, gullies) pushed many authors to search for alternative scenarios to liquid water [1]. Among others a rapid decomposition of CO_2 hydrates (CO_2 clathrates) formed in the not too distant past has been suggested as a possible source for their formation. CO_2 clathrates appear also in considerations about the composition of polar caps and regolith [2]. In contrary to water and CO_2 systems that are well established in Martian p-T conditions, CO_2 hydrates still carry many unknowns. Only few experimental data exist for the water-CO_2-hydrate system below the melting point of water and kinetic data of formation and decomposition did not exist, which motivated our laboratory work.

We have performed systematic laboratory formation [3-5] and decomposition studies [6] on CO_2 hydrates mimicking Martian surface and sub-surface conditions using in-situ neutron diffraction at ILL Grenoble as well as an in-house p-V-T method combined with x-ray diffraction and ex-situ cryo FE-SEM observations. Hexagonal water ice (I_h) and CO_2 gas have been chosen for the experiments as the most probable constituents in the formation reaction. The size of ice particles, temperature and excess of free gas has proven to influence strongly the reaction speed. At p-T conditions close to the Martian poles CO_2 hydrates are thermodynamically stable at the surface. Despite of this fact our results show that at these low temperatures the very slow kinetics prevents any significant formation of clathrates. This finding is in agreement with the unsuccessful efforts to detect clathrates by orbital IR spectroscopy. The formation process within the regolith is also limited, as a number of serious difficulties have to be overcome (e.g. sufficient amount of water ice, constant supply of CO_2, increased gas pressure). Yet, our studies indicate reasonably short times of transformation for ice particles of sub-μ size suspended in the atmosphere.

A number of authors assume that substantial amount of hydrates might have been formed in the planets subsurface. This possibility is confirmed in our work. In further studies, we have investigated possible scenarios for hydrate decomposition and their possible influence on the planet surface and atmosphere. Surprisingly, we have found that ice formed upon clathrate decomposition below 190K is not hexagonal but crystallizes in its "cubic" form (ice I_c). At higher temperatures a defective ice I_h is formed [7]. Ice I_c with its higher specific surface is not only decreasing the time needed for any transformation reaction but also carries other important consequences. The chemical reactivity of ice I_c surfaces differs from the one of ordinary hexagonal ice and should be taken into consideration in surface and atmospheric chemistry processes.

In a temperature interval from about 240 to 273 K, we have firmly established a behavior, called "self-preservation" (or "anomalous preservation") [7], that is capable of preservation of CO_2hydrates in semi-stable state for geologically long time scales making them an excellent gas storage. This complex micro-structural process is governed by changes on the surface of decomposing hydrates. A layer of small ice crystals [8] (up to 20μm) formed upon decomposition drastically slow down the out-diffusion of gas molecules, thus preventing further decomposition due to annealing and some coarsening processes. Its effect rapidly decreases with the particle size. The destruction of this fragile state above the melting point of water, as speculated, indeed leads to the very rapid, catastrophic decomposition known also from terrestrial examples. Yet, a similar effect below the freezing point of water cannot be expected. Instead, temporary gas outbursts are conceivable.

Between 190K and 240K neither annealing of defective ice I_h nor the crystal regrowth is fast enough to effectively slow down outward diffusing gas molecules. In such a scenario slow decomposition is to be expected and therefore the impact on the surface will be very limited. Surprisingly we also have found "self preservation" in a narrow pressure range. The sealing effect is, however, less pronounced as the preservation mechanism differs from the higher temperature one. Therefore only large agglomerations of CO_2 hydrates may be effectively saved from further decomposition.

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