



Laboratory studies on the formation kinetics of gas hydrates at pressures and temperatures of planetary interest

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Gas hydrates (clathrate hydrates) have been suggested to be of major importance in planetary bodies like Mars (as CO₂ hydrate) [1] or Titan (as methane hydrate) [2]. Recently, decomposition of gas hydrates into vacuum has been proposed as a mechanism of Enceladus' plume formation [3]. We will report on laboratory work related to composition and stability as well as the formation and decomposition kinetics of gas hydrates with a focus on CO₂, methane and neon hydrates and covering a temperature range from ~120 K up to the ice melting point. In-situ neutron diffraction, Raman spectroscopy and electron microscopy are used to establish a general model for hydrate formation and decomposition including the effect of anomalous preservation; the latter is explained in terms of an ice shielding effect [4], which depends on the ice microstructure [5] and varies with guest type and the p-T conditions during the initial decomposition step. Our work [6] clearly establishes the importance of exposed surface area for the formation and decomposition of gas hydrates. Furthermore, the crystallographic nature of the water ices (amorphous ice, ice Ic and normal ice Ih) involved appears to play some role for the kinetics. It turns out that "cubic" ice (Ice Ic) well known from small icy bodies may be of particular importance also in planetary settings. Our studies give clear indications on the still unresolved question whether or not CO₂ hydrates play any major role in terra-forming processes on Mars. The seasonal near-surface formation of CO₂ hydrates in polar regions of Mars is considered to be unlikely due to very slow reaction kinetics. Also, the experimentally established cage fillings contradict earlier speculations for planetary noble gas reservoirs in the

form of mixed CO₂ hydrates.

- [1] J.S.Kargel *Mars: A Warmer Wetter Planet*, Springer Berlin, 2004.
- [2] G. Tobie, J.I. Lunine and C. Sotin (2006), Episodic outgassing as the origin of atmospheric methane on Titan, *Nature* **440**, 61-64
- [3] S. Kieffer, X. Lu, C. M. Bethke, J. R. Spencer, S. Marshak and A. Navrotsky (2006), A clathrate reservoir hypothesis for Enceladus' south polar plume, *Science* **314**, 1764-1766
- [4] A. Falenty, G. Genov and W. F. Kuhs (2007) From ice to CO₂ hydrates and back-study of nucleation and initial growth using scanning electron microscopy. In: *Physics and Chemistry of Ice* (ed. W. F. Kuhs), RSC Publishing, Cambridge, 2007, pp. 171-179
- [5] W. F. Kuhs, G. Genov, D. K. Staykova, and T. Hansen (2004), Ice perfection and onset of anomalous preservation of gas hydrates, *Phys. Chem. Chem. Phys.* **6**, 4917-4920
- [6] G. Genov, W. F. Kuhs, D. K. Staykova, E. Goreshnik, and A. N. Salamatin (2004), Experimental studies on the formation of porous gas hydrates, *Am. Miner.* **89**, 1228-1239