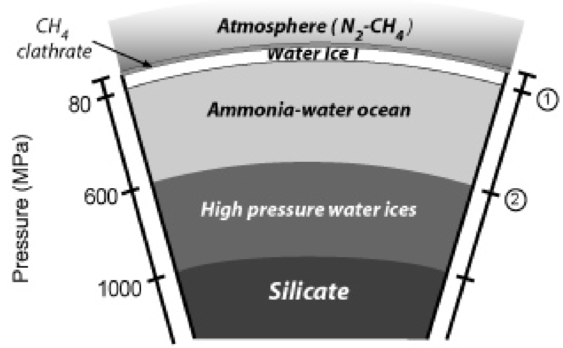
AMMONIA, A METHANE HYDRATE INHIBITOR – IMPLICATIONS FOR TITAN'S ATMOSPHERIC METHANE. M. Choukroun, G. Tobie, O. Grasset. LPG (UMR-CNRS 6112), 2 rue de la Houssiniere, BP 92208, 44322 Nantes Cedex 03, France. (corresp. author: mathieu.choukroun@univ-nantes.fr).

Introduction: Titan is surrounded by a thick atmosphere of N_2 and CH_4. As methane is irreversibly photodissociated over a short period of time (a few tens of Myrs [e.g. 1]), replenishing processes are required to explain its current abundance. Methane clathrate hydrates (MH) are inferred as an internal source of methane [e.g. 2-4]. Release of methane would occur through cryovolcanic processes, which is supported by recent observation from the Visual and Infrared Mapping Spectrometer (VIMS) onboard the Cassini spacecraft of a potential cryovolcano on Titan's surface [5]. However, the modalities of these processes are still poorly constrained. Titan's current thermal profile precludes dissociation of MH to occur at depth. Therefore, more studies are required to explain methane replenishment. The aim of the work presented here is to provide experimental constraints on MH stability in the ternary system H_2O-CH_4-NH_3. It also shows that not only one, but two MH structures can ascend to the surface. These new data will support Cassini results on Titan's surface composition and cryovolcanism.

Present-day understanding of the internal dynamics of Titan: The low density of Titan indicates that this satellite is mostly formed by H_2O (liquid water and ices) and silicates. Direct sampling by the Gas Chromatograph Mass Spectrometer onboard the Huygens probe provides substantial evidence that ammonia is the primordial source of Titan's atmospheric N_2 [6]. This implies NH_3 was brought during the accretion and must be still present within Titan's interior. Ammonia is known to decrease the melting point of ices [7,8], which has strong implications on Titan's current internal structure. Figure 1 shows the most probable structure for Titan [4,9,10]. The phase diagram presents the liquidus of ices in the pure H_2O and in the H_2O–NH_3 (95%-5%) systems. The current thermal profile within the icy layers of Titan is also shown in the 5% NH_3 case, according to [4]. Thicknesses of the icy crust, the ocean and the high-pressure ices layer strongly depend on the ammonia content of the H_2O mantle: considering a pure H_2O case, the icy crust and the internal ocean are about 100 km and 200 km thick respectively, whereas a primordial amount of 5% NH_3 induces thicknesses of the icy crust and an ocean of 50 km and 300 km, respectively [10]. In the latter case, ammonia would be stable as dihydrates or monohydrates within the icy crust of Titan, and the ocean would contain 10% NH_3.



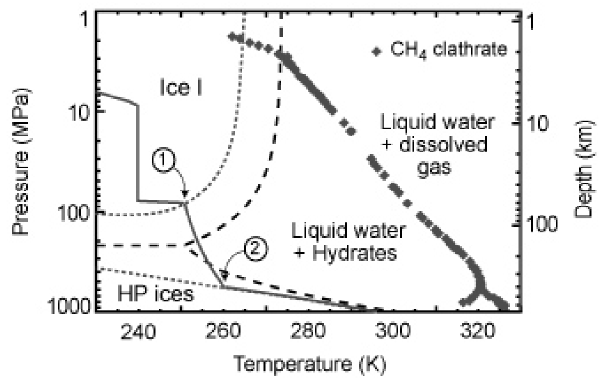


Figure 1: Above: *Schematic structure of Titan [4]. The MH reservoir could be located either above, or below the ice I crust.* Below: *Phase diagram of H_2O in the pure water case (dashed) and in presence of 5% NH_3 (dotted); MH dissociation curve and Titan's internal profile.*

Methane cryovolcanism: Dissociation of MH is the most likely internal process for atmospheric methane's replenishement. The dissociation curve of MH [11] is shown on Figure 1. Whether ammonia is present or not, Titan's present-day thermal profile precludes MH dissociation to occur at high pressure. Nonetheless, thermal convection in the ice I layer could locally induce MH dissociation within the icy crust at shallow depths [4,10]. However, the dissociation curve was established in the pure H_2O-CH_4 system, for the usually encountered structure I (sI) MH. Other MH structures could occur on Titan, and no experimental data present the inhibitory effect of ammonia on MH. This emphasizes the need for further experimental constraints on these two problems.

Structure of methane hydrates on Titan: Three types of hydrate structures were identified at atmospheric pressure [13]: structure I (sI), structure II (sII) and structure H (sH). Gas hydrates adopt one of these structure depending on guest size. For instance, CH_4 and CO_2 hydrates are stable as sI, and heavy hydrocarbons (C_n with n>3) crystallize as sII or sH. However, experimental studies reported unexpected structures, such as transient sII CO_2 hydrates [14] and sII MH [15,16]. sII has lower water contents than sI [13], and solubility of water in methane is extremely low [17]. Therefore it has been suggested [16] that the typical sI MH structure is observed when the amounts of CH_4 available to clathration are low, whereas the sII MH structure occurs when CH_4 amounts are too high to allow sI MH crystallization. This result, further developed here, implies that in methane-rich zones in cryovolcanoes, sII MH could be present instead of the expected sI. Though it is assumed similar to that of sI MH, the dissociation curve of sII MH is not constrained. Experiments are currently conducted in the H_2O-CH_4 system to establish this dissociation curve; preliminary results will by presented at the meeting.

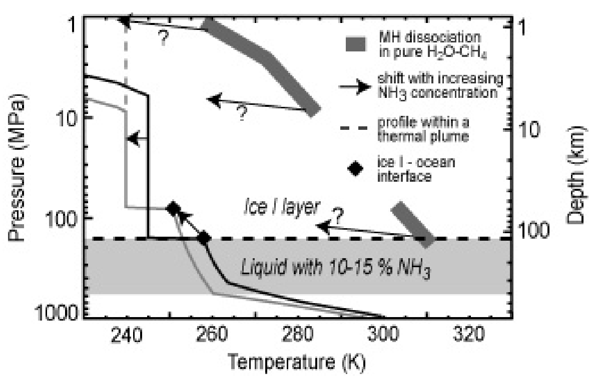


Figure 2: *Schematic P-T diagram presenting H_2O phases (dotted and dashed lines) and Titan's current thermal profile (plain lines) in the pure water case (black) and with a primordial 5% NH_3 concentration (grey).*

Influence of NH_3: Ammonia as a MH inhibitor is considered twice as effective as methanol [13]. It was thus estimated to decrease MH dissociation by about 12 K for a primordial 5% NH_3 concentration [10]. However, further experimental studies are required to confirm this effect in the pressure range that covers the icy crust: [0-100 MPa] and to constrain the temperature shift of the dissociation curve of MH (Figure 2). Two regions of Titan's H_2O mantle can be the location of MH accumulation and dissociation, see Figure 2: 1) the crust-ocean interface at ~100 MPa, and 2) the shallow region of the crust below 10 MPa (conductive lid of MH). The effect of ammonia on the crust-ocean interface and on the thermal profile within the convective layer of the crust is well-constrained [10] and shown in Figure 2. As for MH, two major questions remain. Can ammonia inhibition induce their dissociation at the crust-ocean interface? Within the crust, what is the maximum depth at which thermal plumes can dissociate MH in presence of ammonia?

Experiments on MH dissociation are currently performed in the H_2O-NH_3-CH_4 system within an optical sapphire-anvil cell to answer these questions. Figure 3 shows MH crystals (probably sII) generated in this system, with NH_3/H_2O ratio of 5%. First data acquired in this system will be shown.

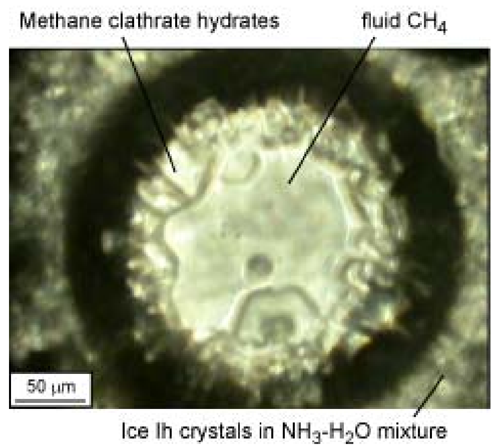


Figure 3: *Sample microphotograph taken during an experiment in the H_2O-NH_3-CH_4 system. This view shows MH crystals growing in fluid CH_4 at 25MPa and 340K, surrounded by a mixture of very small sized ice Ih crystals, liquid water and ammonia. Phases were identified using in-situ Raman spectroscopy. Conditions are ~25 MPa and 240 K.*

References: [1] Yung Y. L. et al. (1984) *Astrophys. J. Suppl. Ser., 55*, 465-506. [2] Lunine J. I. and Stevenson D. J. (1987). *Icarus, 70*, 61-77. [3] Loveday J. S. et al. (2001) *Nature, 410*, 661-663. [4] Tobie G. et al. (2006) *Nature*, in press. [5] Sotin C. et al. (2005) *Nature, 435*, 786-789. [6] Niemann H. B. et al. (2005) *Nature,* doi:10.1038/nature04122. [7] Hogenbloom D. L. et al. (1997) *Icarus*, *128 (1)*, 171-180. [8] Leliwa-Kopystynski J. et al. (2002) *Icarus*, *159 (2)*, 518-528. [9] Sohl F. et al. (2003) *J. Geophys. Res*., *108 (E12)*, 4-1. [10] Grasset O. and Pargamin J. (2005) *Planet. Space Sci., 53*, 371-384. [11] Dyadin Y.A. et al. (1997) *Mendeleev Commun.*, *7*, 34-35. [12] Tobie, G. et al. (2006) *LPSC*, this meeting. [13] Sloan E. D. (1998) Marcel Dekker : New York. [14] Staykova D. K. et al. (2003) *J. Phys. Chem. B*, *107*, 10299-10311. [15] Schicks J. M. and Ripmeester J. A. (2004) *Angew. Chem. Int. Ed.*, *43*, 3310-3313. [16] Choukroun M. et al., submitted to *J. Phys. Chem. B*. [17] Chapoy A. et al. (2004) *Fluid Phase Equil.*, *214*, 101-117.