METHANE CLATHRATE HYDRATES STABILITY DURING CRYOVOLCANIC PROCESSES : EVIDENCE FROM THEIR EXPERIMENTAL STUDY IN THE H_2O-NH_3-CH_4 SYSTEM.

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Introduction: Intense photochemical processes take place in Titan's thick atmosphere, which preclude persistence of methane in the atmosphere over a period exceeding a few tens of Myrs [e.g. 1]. Dissociation of methane clathrate hydrates (MH) trapped within Titan's interior is a likely process for methane outgassing [e.g. 2-4], which could occur in cryovolcanoes such as those suggested by the Visual and Infrared Mapping Spectrometer (VIMS) and the Radar instrument onboard the Cassini spacecraft [5,6]. However, Titan's current thermal profile precludes dissociation of MH to occur at depth. In absence of inhibitors such as ammonia, MH could remain stable during intrusive ascent through the upper crust, up to the surface. In this case, two molecular structures of MH could be present on Titan's surface. Nonetheless, the possible presence of ammonia hydrates in Titan's ice layer may affect the stability of MH, resulting in their dissociation. The inhibiting effect of ammonia in Titan's conditions on MH stability remains unexplored. The work presented here provides new experimental constraints on MH structure and stability in the ternary system H_2O-CH_4-NH_3.

Titan's internal structure and dynamics: Direct sampling by the Gas Chromatograph Mass Spectrometer (GCMS) onboard the Huygens probe provides substantial evidence that ammonia is the primordial source of Titan's atmospheric N_2 [7]. This implies NH_3 was brought during the accretion and must be still present within Titan's interior. Ammonia decreases strongly the melting point of ices [e.g. 8]. Figure 1 shows the structure inferred for Titan, taking this effect into account [4, 9, 10]. Thicknesses of the icy crust, the ocean and the high-pressure ices layer depend on the ammonia content of the H_2O mantle: in 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 the 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 up to 10% NH_3. Due to their low density, MH can be located from the surface down to the crust – ocean interface. Their dissociation curve has been previously established [11]. Titan's present-day thermal profile precludes MH dissociation to occur at high pressure [2]. Thermal convection in the ice I layer and intrusion of warm ice in the cold upper crust could eventually induce MH dissociation at shallow depths [4,10]. However, without reliable experimental data, the dissociation process remains uncertain.

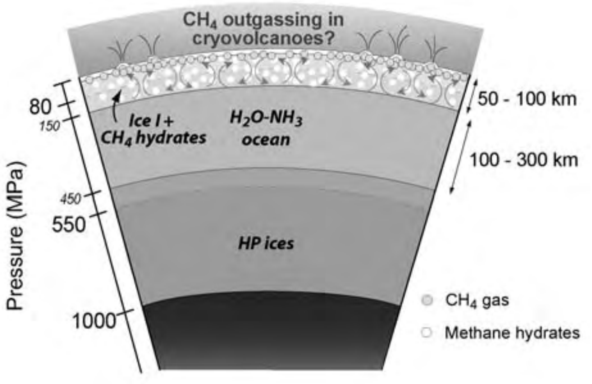

Figure 1: *Schematic structure of Titan [after 4]. The MH reservoir could be located either above, or within the ice I crust. Layer interfaces are indicated in two cases: pure H_2O (solid lines); and 5% primordial NH_3 (dashed lines). The latter case is the most probable. See text for details.*

Stability of MH in presence of NH_3: Ammonia as a MH inhibitor is considered twice as effective as methanol [12]. It was estimated to decrease MH dissociation by about 12 K for a primordial 5% NH_3 concentration [10]. Further experiments on MH dissociation are currently performed in the H_2O-NH_3-CH_4 system within an optical sapphire-anvil cell 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. Preliminary experiments point out a stronger inhibiting effect than expected, see dissociation curve on Fig. 2.

Nonetheless, the decrease in dissociation temperature does not allow MH dissociation in presence of 10% NH_3. Thus it seems likely that MH are stable on Titan, even during convective motions of the icy crust and cryovolcanic events (scenario 1 in Fig. 2). This result raises the problem of MH detection on Titan using Cassini's instruments such as VIMS and the Radar. Nonetheless, non-equilibrium processes involving ammonia-water cryomagma transport [16] in the crust could induce MH dissociation and outgassing.

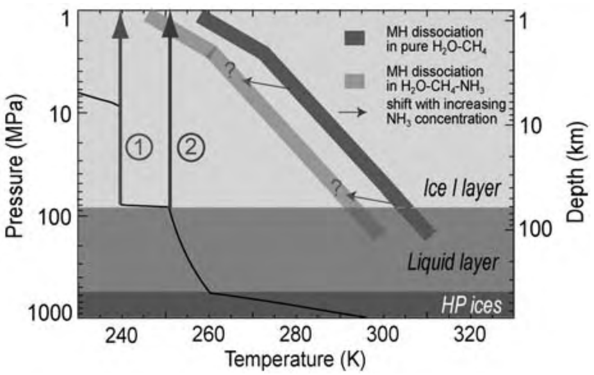

Figure 2: *Phase diagram showing the dissociation curve of MH in H_2O-CH_4 [11], the inferred dissociation curve in presence of 10% NH_3, Titan's thermal profile, and the interfaces depth. Two scenarios are schemed: 1) no dissociation of MH occurs; 2) melting of ammonia hydrates triggers dissociation (arrow at higher temperatures and no change in position of the dissociation curve for legibility of the figure).*

Methane hydrates structures on Titan: Three types of hydrate structures were identified at atmospheric pressure [12]: 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. However, experimental studies reported unexpected structures, such as transient sII CO_2 hydrates [13] and sII MH [14,15]. SII has lower water contents than sI [12], and solubility of water in methane is extremely low. Our experiments have shown [15] that the initial composition and distribution of H_2O and CH_4 determines crystallization of typical sI MH structure (low CH_4 amounts), or of transient sII MH structure (high CH_4 amounts, large methane-rich zones). Fig. 3 shows the aspect and Raman spectra of these two structures, as well as gaseous CH_4 and high-pressure MH phase. The results of this study [15] imply that in methane-rich zones in cryovolcanoes, sII MH could be present instead of or in addition to the expected sI. A remaining problem is the stability of sII relatively to sI MH.

Conclusions and prospects: Preliminary high pressure – low temperature experiments conducted in the H_2O-NH_3-CH_4 system show that MH dissociation cannot occur in thermodynamical equilibrium on Titan. Two molecular structures could then ascend up to the surface. Infrared measurements on MH signature are being conducted to help the detection of sI and/or sII MH on Titan's surface. Non-equilibrium processes, involving ammonia hydrates melting within the crust might achieve conditions for methane outgassing during cryovolcanic episodes.

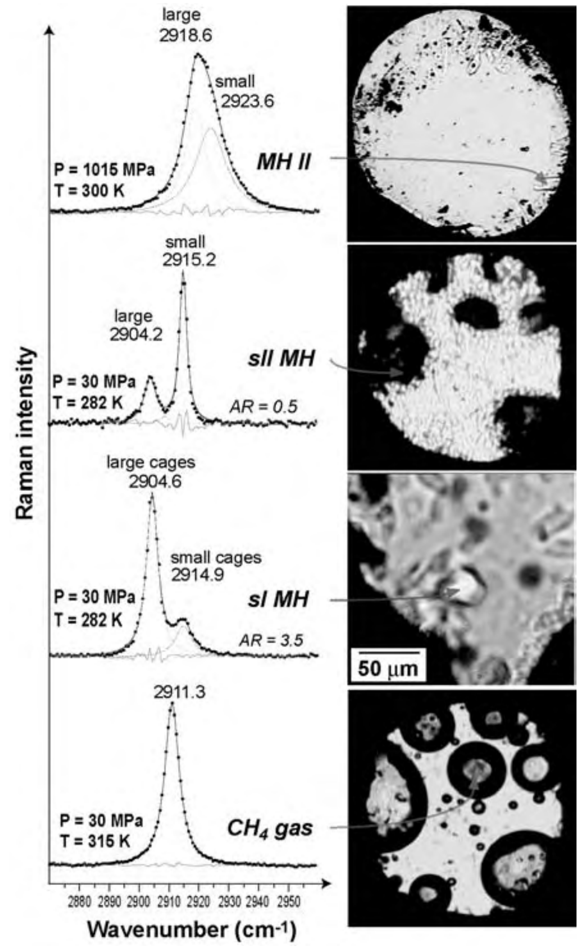

Figure 3: *Sample images and corresponding Raman spectra (left). Hole diameter is 1 mm. Raman spectroscopy allows characterization of the gas phase and of the various MH structures using peak positions and large cages over small cages peak area ratio (AR).*

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