

**CRYOVOLCANIC RELEASE OF METHANE ON TITAN: EXPERIMENTAL CONSTRAINTS FROM THE STABILITY OF METHANE CLATHRATES IN PRESENCE OF AMMONIA.** M. Choukroun<sup>1</sup>, O. Grasset<sup>2</sup>, C. Sotin<sup>1</sup>, G. Tobie<sup>2</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (MS 79-24, 4800 Oak Grove Dr., Pasadena, CA 91106, E-mail: [Mathieu.Choukroun@jpl.nasa.gov](mailto:Mathieu.Choukroun@jpl.nasa.gov), <sup>2</sup>UMR-CNRS 6112 Planétologie et Géodynamique, Université de Nantes, Nantes, France.

**Introduction:** The 1.4 – 5% CH<sub>4</sub> measured by the Gas Chromatograph and Mass Spectrometer (GCMS) instrument onboard the Huygens probe during its descent in Titan's thick nitrogen-dominated atmosphere [1] would disappear in less than 100 My owing to complex photochemical processes [2]. Methane clathrate hydrates are thermodynamically stable in the pressure-temperature conditions of Titan's interior. Dissociation of these icy structures containing trapped gas during cryovolcanic events is a likely replenishment process of the atmospheric methane [3], consistent with the observation of potential cryovolcanoes on Titan's surface by the Cassini spacecraft [4,5]. However, Titan's present-day internal structure and thermal profile [3,6] do not allow dissociation of methane clathrates at depth in the H<sub>2</sub>O-CH<sub>4</sub> system [7], thus questioning the effect of CH<sub>4</sub> content and of other compounds on the stability of methane clathrates. Ammonia must be considered, as Titan's N<sub>2</sub> probably originates from its conversion [1]. We have conducted new high pressure – low temperature (HP-LT) experiments at the Laboratoire de Planetologie et Geodynamique de Nantes, France, on the stability of methane clathrates to address these effects, and bring new insights into cryovolcanic processes on Titan.

#### Stability of methane clathrates under pressure:

The HP-LT experimental setup used in our study consists in a liquid nitrogen-cooled cryostat equipped with an optical sapphire-anvil cell [8]. Cell loading and sample characterization are as described in [9].

*Effect of low CH<sub>4</sub> amounts.* Several experiments have been conducted in the H<sub>2</sub>O-CH<sub>4</sub> system. The dissociation curves obtained [10] vary strongly from one experiment to another, with dissociation temperatures always lower than commonly admitted [e.g. 7]. A statistical thermodynamics model [11] has been used to investigate the potential effect of methane abundance in the samples on the dissociation curve. Experiments and thermodynamic modeling point out a very strong impact of low methane amounts on the dissociation temperature of methane clathrates: 0.1% CH<sub>4</sub> amounts lead to a decrease in dissociation temperature of ~40 K at pressure levels above 100 MPa.

*Effect of other compounds.* In one experiment, large amounts of nitrogen were mixed with methane in the sample as was detected by Raman spectroscopy.

The dissociation curve obtained is consistent with such a mixture, based on the dissociation curves of pure CH<sub>4</sub> [7] and pure N<sub>2</sub> [12] clathrates. Thus, our experiments show that presence of N<sub>2</sub> can decrease the dissociation temperature of CH<sub>4</sub> clathrates by up to 15 K.

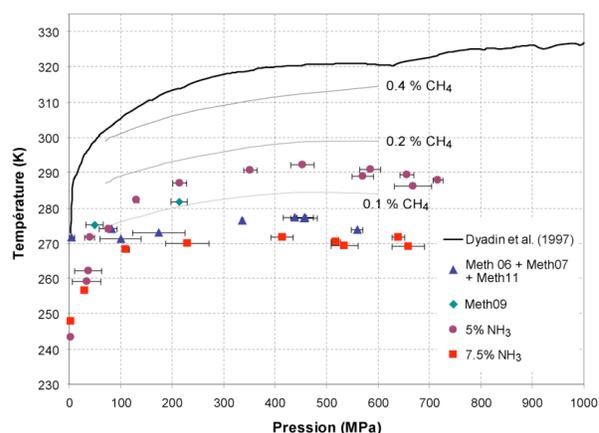


Figure 1. Synthetisis of the various results from this study.

The results obtained on the stability of methane clathrates in the H<sub>2</sub>O-NH<sub>3</sub>-CH<sub>4</sub> system are presented in Figure 1. Because of the strong influence of methane contents and presence of other compounds on the stability of methane clathrate hydrates, quantification of the effect of ammonia on the dissociation curve is difficult to achieve. Nonetheless, the two experiments with 5% and 7.5% NH<sub>3</sub> contained similar amounts of methane, estimated at ~0.2%. Considering no or little N<sub>2</sub> was present in these experiments, it appears that ammonia has a very significant effect on the dissociation of methane clathrates. A 7.5% NH<sub>3</sub> concentration could decrease the dissociation curve by up to 20 K.

**Implications for cryovolcanism on Titan:** Methane clathrates are most likely stored in the upper crust of Titan, due to their low density. Horizontally averaged temperature profiles predicted for a convective ice I outer layer in the conductive lid regime for a 3 km-thick crust enriched in thermally insulating hydrates [3] are reported in Figure 2. They lie within the stability field of methane clathrates. Our experiments suggest that the dissociation temperature is decreased by NH<sub>3</sub> but not to a sufficient extent as to cause dissociation along the average temperature profile. How-

ever, the temperature profile within an upwelling plume might allow dissociation at a few kilometers depth. A concentration of  $\sim 10\text{-}15\%$   $\text{NH}_3$  appears necessary to decrease the dissociation temperature by 30 K in a clathrate-rich [3] upper crust of Titan. In Figure 2, a similar inhibition of methane clathrates can be seen for 5%  $\text{NH}_3$  because of the combined influence of  $\text{NH}_3$  and low methane contents. This curve corresponds to  $\sim 15\text{-}20\%$   $\text{NH}_3$  in a  $\text{CH}_4$ -rich environment.

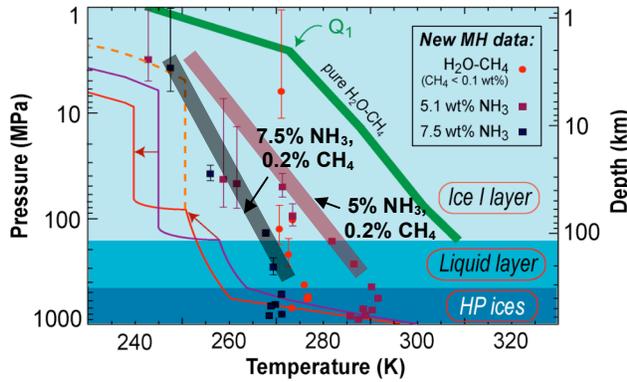


Figure 2: Pressure-temperature diagram comparing possible Titan's present-day thermal profiles at equilibrium (purple: 0%  $\text{NH}_3$ ; red: 5% primordial  $\text{NH}_3$ ), and within a thermal plume (orange), with new experimental data and methane clathrates dissociation curve in  $\text{H}_2\text{O-CH}_4$  [7].

It seems unlikely that cryomagmas originate from Titan's putative internal liquid layer, containing a maximum of 15%  $\text{NH}_3$  [e.g. 3,6], since such liquids are much denser than crust-forming materials. A crustal origin of cryomagmas, such as a near-eutectic  $\text{H}_2\text{O-NH}_3$  composition produced by the melting of ammonia hydrates is favored. Nonetheless, a 35%  $\text{NH}_3$  cryomagma would continuously induce melting of the ice I layer, hence decreasing  $\text{NH}_3$  concentration.

In Figure 3, we propose a new model of cryovolcanism, in which ammonia hydrates would be mixed with the upper clathrate-rich crust. A warm ice intrusion rising through the upper crust (orange thermal profile in Figure 2) induces melting of ammonia hydrates, see Figure 3a. Produced  $\text{NH}_3$ -rich cryomagmas then dissociate surrounding methane clathrates, thus releasing water and methane gas. The large gas volume induces the over-pressure required for creating cracks and allowing methane to escape (Figure 3b). We predict that this release would be accompanied by explosive deposition of fine-grained ice.

A pure methane clathrates upper crust of  $\sim 3\text{-km}$  thickness [3] contains more than 100 times the current amounts of atmospheric methane of  $3 \times 10^{20}\text{g}$  [13], which seems sufficient to replenish the atmospheric

methane on Titan. However, this study has shown that cryovolcanism can only occur at a local scale. Also, only a few potentially cryovolcanic features have been detected on Titan's surface. If a 5-km diameter plume triggers cryovolcanism that dissociates all the overlying clathrate-rich crust, the maximum amount of methane outgassed is  $\sim 10^{15}\text{g}$ , which is less than 1/100000 of the total atmospheric  $\text{CH}_4$  amounts. As such a small amount would be photochemically destroyed within 1000 years, similar cryovolcanic events should occur at least every thousand years to sustain few percents of methane in the atmosphere. We are currently improving on this crude calculation to see whether or not cryovolcanism alone could replenish Titan's atmospheric methane.

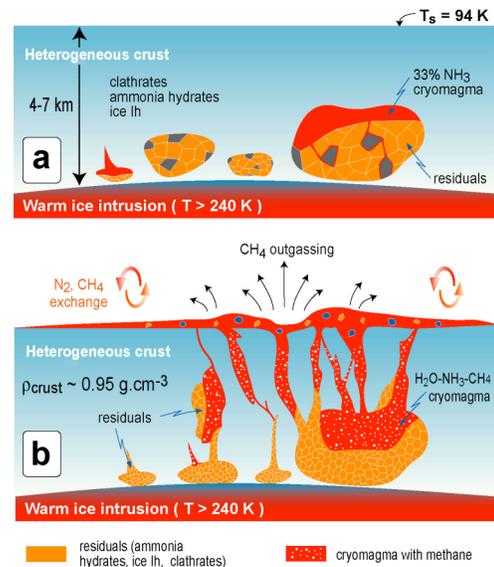


Figure 3: New model for cryovolcanic release of methane on Titan, associated with: a) melting of  $\text{NH}_3$  hydrates, b) clathrates dissociation, cryomagma ascent and methane release.

**References:** [1] Niemann H. B. et al. (2005), *Nature* 438, 779-784. [2] Yung Y. L. et al. (1984), *Astrophys. J. Suppl. Series* 55, 465-506. [3] Tobie G. et al. (2006), *Nature* 440, 61-64. [4] Sotin C. et al (2005), *Nature* 435, 786-789. [5] Lopes R. M. C. et al. (2007), *Icarus* 186(2), 395-412. [6] Grasset O. and Pargamin J. (2005), *Planet. Space Sci.* 53, 371-384. [7] Dyadin Y. A. et al. (1997), *Mendeleev Comm.* 7, 34-35. [8] Grasset O. et al. (2005), *High Press. Res.* 25(4), 255-265. [9] Choukroun M. et al. (2007), *J. Raman Spectrosc.* 38, 440-451. [10] Choukroun M. (2007), *PhD Thesis*, Universite de Nantes. [11] Sloan E. D. (1998), *Ed: Marcel Dekker, N.Y.* [12] Marshall D. R. et al. (1964), *AIChE J.* 10(2), 202-205. [13] Lunine J. I. and Stevenson D. J. (1987), *Icarus* 70, 61-77.