

**THE PHASE BEHAVIOR OF THE TERNARY  $\text{H}_2\text{O}$ -THF- $\text{NH}_3$  SYSTEM AT LOW TEMPERATURES: IMPLICATIONS FOR CLATHRATE HYDRATES AND METHANE OUTGASSING ON TITAN.** E. Gloesener<sup>1</sup>, M. Choukroun<sup>1</sup>, H. E. Maynard-Casely<sup>2</sup>, T. H. Vu<sup>1</sup>, A. G. Davies<sup>1</sup> and C. Sotin<sup>3</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA (elodie.d.gloesener@jpl.nasa.gov), <sup>2</sup>Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia, <sup>3</sup>Laboratoire de Planétologie et de Géodynamique, Université de Nantes, France.

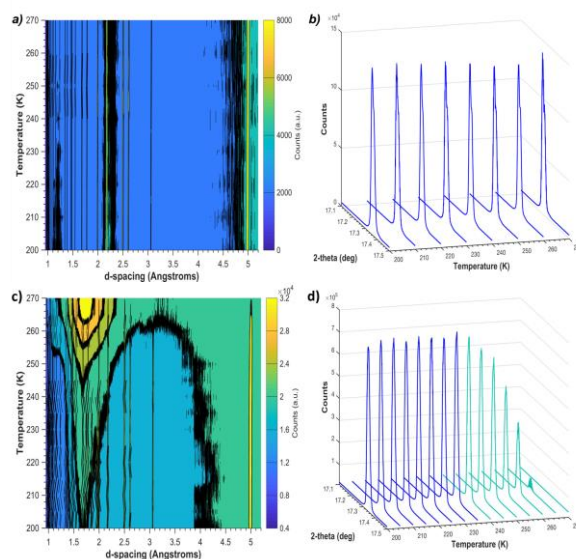
**Introduction:** Methane clathrate hydrates are thought to play a major role on Titan as their decomposition could contribute significantly to the replenishment of atmospheric methane. However, in the absence of inhibitors and/or thermal anomalies, methane clathrates in Titan's icy shell would remain stable all the way to the surface. Clathrate dissociation pathways involving interaction with ammonia, a strong antifreeze agent, have been proposed [1]. Ammonia, which would be available within the ice  $\text{I}_h$  layer in the form of ammonia hydrates, could cause partial melting of water ice between the eutectic point at 176 K (at 1 bar) and the liquidus temperature, and therefore potentially promote cryovolcanism through the decomposition of the surrounding clathrate hydrates.

Within that framework, low-temperature Raman experiments [2] have shown that tetrahydrofuran (THF) clathrates, an ambient-pressure analogue of methane clathrates, undergo partial dissociation in the presence of ammonia at temperature as low as 203.6 K. A subsequent study using differential scanning calorimetry and Raman spectroscopy [3] has confirmed this behavior and established that the ternary  $\text{H}_2\text{O}$ -THF- $\text{NH}_3$  system presents a great chemical complexity with the reported formation of multiple phases such as the expected THF-clathrates and ammonia hydrates as well as a more intriguing unknown THF- $\text{NH}_3$ -rich phase. Moreover, synchrotron X-ray diffraction (XRD) patterns for THF clathrates with and without the presence of ammonia (see Fig. 1) have shown clear evidence for partial dissociation when  $\text{NH}_3$  is present. Raman spectroscopy experiments in the ternary  $\text{H}_2\text{O}$ - $\text{CH}_4$ - $\text{NH}_3$  system [4] have also determined that ammonia affects the stability of  $\text{CH}_4$  clathrates in a similar way that it affects THF clathrates and water ice (see Fig. 2).

In this work, we go a step further in establishing  $\text{NH}_3$  effects on clathrate hydrates by conducting cryogenic X-ray diffraction studies. We focus on the ternary  $\text{H}_2\text{O}$ -THF- $\text{NH}_3$  system and the investigation of the reported unknown THF- $\text{NH}_3$ -rich phase.

**Method:** Our samples are prepared using ammonium hydroxide (28-30 wt% Certified ACS plus), tetrahydrofuran (Fisher Scientific, Certified), and water HPLC grade (Fisher Scientific, Certified). The desired ammonia concentrations relative to water are achieved

by simple dilution. Each solution obtained is deposited into an open-ended 0.7 mm diameter glass capillary, which is then sealed and mounted onto the goniometer. Sample temperature is lowered via a liquid nitrogen-cooled Oxford Cryosystems 800 cryostream. XRD patterns are acquired at 1 s per step ( $2\theta$  angular resolution of  $0.02^\circ$ ) at temperature intervals of 10 K over the temperature range between 90 and 270 K using a Bruker D8 DISCOVER DaVinci instrument equipped with a  $\text{Cu K}\alpha$  X-ray source ( $\lambda = 1.5406 \text{ \AA}$ ) and a linear energy-dispersive LynxEye XE-T 1D detector.

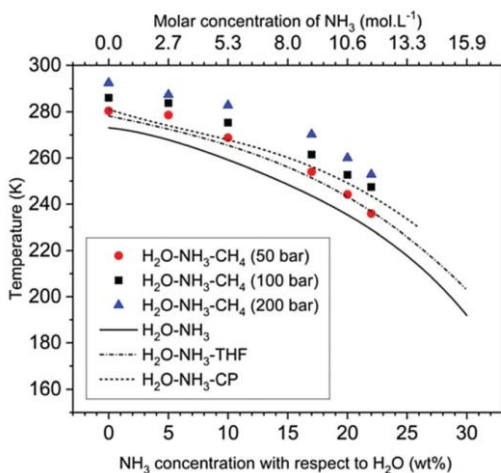


**Figure 1:** Synchrotron XRD patterns for THF clathrates (a-b) without ammonia and (c-d) with ammonia. In the presence of  $\text{NH}_3$ , THF clathrate peaks decrease progressively in the range 230-270 K.

**Preliminary results:** Our data are consistent with previous studies and show the partial dissociation of THF clathrates in the presence of  $\text{NH}_3$ . In addition, our XRD patterns exhibit double peaks for THF clathrates, which shows the presence of the new THF- $\text{NH}_3$ -rich phase. We will present our results and their interpretation for a range of ammonia concentrations relative to water up to 30 wt%.

The phase behavior of clathrates in the presence of ammonia has important implications for Titan and the outgassing of methane. The dissociation point of THF clathrates is decreased in a similar way as that of water

ice  $I_h$  in the presence of  $NH_3$ . Transposing this effect to  $CH_4$  clathrates implies that partial dissociation of clathrates in the icy crust of Titan may occur at temperatures as low as 200 K.



**Figure 2:** Phase diagram of the  $H_2O-NH_3-CH_4$  system at 50, 100 and 200 bar of  $CH_4$  in comparison with those of  $H_2O-NH_3-THF$  and  $H_2O-NH_3-CP$  [4].

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**References:** [1] Choukroun M. et al. (2010) *Icarus*, 205, 581-593. [2] Vu T. H. et al. (2014) *J. Phys. Chem. B*, 118, 13371-13377. [3] Muñoz Iglesias V. et al. (2018) *ACS Earth Space Chem.*, 2, 135-146. [4] Petuya C. et al. (2020) *Chem. Commun.*, 56, 12391-12394.