EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

ESRF	**Experiment title:** **Methane hydrates and Titan's early differentiation.**	**Experiment number**: ES28
Beamline:	**Date of experiment**: from: 05/06/2013 to: 08/06/2013	**Date of report**: 04/09/2013
Shifts: 9	**Local contact(s)**: M. Mezouar	*Received at ESRF:*

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Report:

The origin of Titan's atmospheric methane has long been debated and its early differentiation is still highly discussed[1]. To assess these questions, we investigated the dissociation of methane hydrates (MH) at high pressure and high temperature. Indeed, methane is likely stored in the moon interior in the form of clathrate hydrates[2] and may have been progressively or abruptly released to the surface during the differentiation process[3,4]. This proposal aimed at confirming recent measurements on methane hydrates between 1.5 and 5 GPa obtained by our group with Raman spectroscopy, in particular at temperatures close to the dissociation curve of methane hydrate. As far as today, many studies have given results on the structure change in methane hydrates at high pressure, up to 86 GPa. However, most of the previous studies have been performed at room temperature, which is not representative of the temperature expected in Titan's interior. Using high pressure Raman spectroscopy, we have recently confirmed that methane hydrates remain stable after 2 GPa, but we also showed that they destabilize close to the melting curve of high-pressure water ice polymorphs (Bezacier et al. Submitted to PEPI) [5]. These results have important implications for the storage of methane in Titan's interior and its release during differentiation. In order to confirm these new results on the stability of methane hydrate, we determined the structure change in the vicinity of the dissociation curve by X-Rays using the ESRF facilities on ID27.

In a previous study, we have shown that methane hydrates have a different Raman signature than solid methane at high pressure and that the higher shift presented by methane hydrates is a key to follow the MH stability. We thus showed that MH-III (the high-pressure form of Methane Hydrate) is stable above 3 GPa[5] at room temperature and that it dissociates at temperatures close to the melting curve of ice (Fig. 1), which is the typical temperature expected in Titan's interior during differentiation. With X-rays we confirmed our previous observations and we tracked the **structural change occurring when approaching the dissociation curve**. X-rays allowed us to confirm that methane hydrates destabilize a few Kelvin below

the melting curve of ice VI and VII (Fig. 1). Thanks to the automatic pressure device, we also observed the total dissociation of MH-III into water and solid methane. Solid methane and methane hydrates have distinct powder patterns.

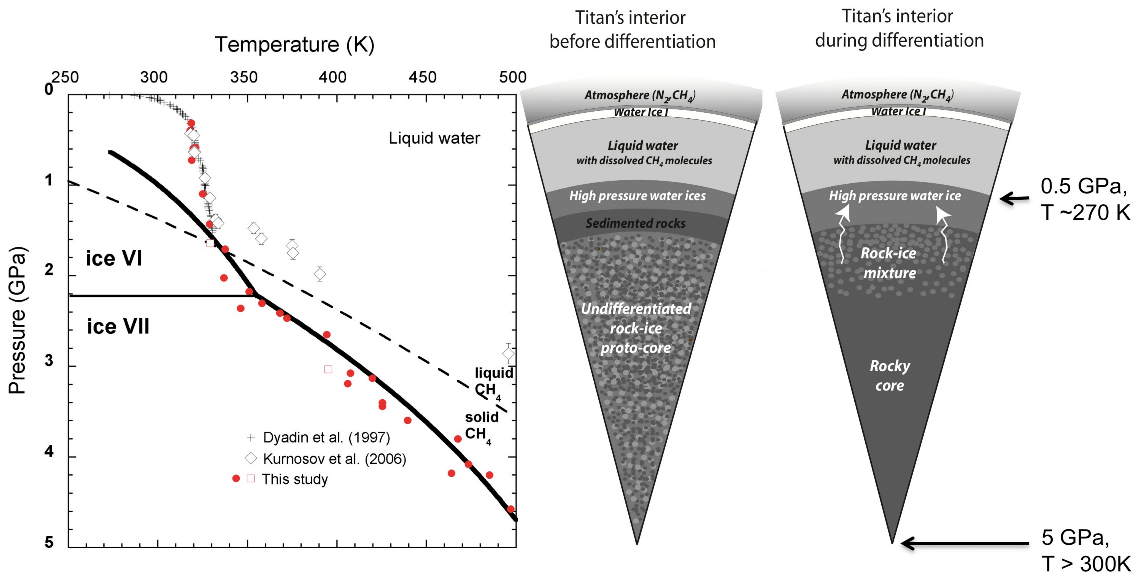

Figure 1. **Phase diagram of methane hydrates** Red rounds present observed dissociations with Raman spectroscopy. Red squares present observed dissociations with X-rays. Black diamonds present dissociations at high temperature of methane hydrates in a water-ammonia-methane medium[6].

This study was necessary to perfectly characterize the methane hydrate structure and evolution with pressure. It is also a first step in the study of gas hydrates at high-temperature and it will then be pursued with a mixture of methane and carbon dioxide hydrates.

From a general point of view, this study gives insight into the fate of methane in Titan's interior. Depending on the thermal state of the interior of Titan, methane hydrates could destabilize and form pure methane and ices and be re-clathrated under the liquid ocean (high temperatures) or stay stable as MH-III in the deep interior (low temperature). These last results have been combined with a previous Raman study and an article was submitted on September 4th to Physics of the Earth and Planetary Interiors.

Nevertheless, a P-V-T equation of state for methane hydrates is required to improve numerical modelling. That is why, we will need additional beamtime to determine the equation of state of methane hydrates at high-temperature.

References

[1]Tobie et al., p. 24-50 in *Titan: Interior, Surface, Atmosphere, and Space Environment*, Cambridge University Press (2012a), [2]Loveday et al., *Chem. Phys. Letters,* 350, 459-465 (2001), [3]Tobie et al., *Nature*, 441, 61-64 (2006), [4]Tobie et al. *ApJ*, **752**, 2, id 125 (2012b), [5]Bezacier et al., *submitted to PEPI Sept 2013*, [6]Kurnosov et al., *Journal of Chemical Science*, 61(12) (2006).