ESRF	**Experiment title:** **Binary hydrates (carbon dioxide and methane) for Titan's early differentiation.**	**Experiment number**: ES83
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Report:

The origin of Titan's atmosphere has long been debated and its early differentiation is still highly discussed[1]. In particular, in Titan's conditions, CO_2, the principal carbon species[2] can combine with CH_4 to form multi-guest clathrates. To confirm these multi-guest clathrates, the structural changes in binary hydrates should be investigated at high pressure and high temperature. Indeed, methane and carbon dioxide are likely stored in the moon interior in the form of clathrate hydrates[3] and may be progressively or abruptly released to the surface during the differentiation processes[2,4]. As a first step to fully understand the behaviour of mixed hydrates, an X-ray investigation is necessary to get the precise crystallographic structures of single-crystals of hydrates at high-pressure. This proposal aims to get the crystallographic structures at high-pressure of single-crystals of mixed hydrates between 0 and 5 GPa. Our preliminary results obtained with Raman spectroscopy show that mixed hydrates form easily but Raman characterization is not sufficient to assess the occupancy of cages and the phase transition occurring with pressure. As far as today, many studies have been carried out on the structure changes in methane hydrates[5] or carbon dioxide hydrates at high pressure. However, no study on binary hydrates of methane and carbon dioxide at high-pressure has been performed lately. Only one study on methane and ethane hydrates has been performed[6] and shows that they destabilize above 2.1 GPa. Using high pressure Raman spectroscopy, we have recently confirmed that methane and carbon dioxide hydrates remain stable above 2 GPa and up to 1 GPa, respectively, and that a binary clathrate structure exists above 1 GPa. These results have important implications for the storage of methane and carbon dioxide in Titan's interior or other icy satellites and their release during differentiation. In order to get better knowledge on the stability of binary hydrates, we propose to establish the equation of state of single-crystals of mixed methane and carbon dioxide hydrates by X-Rays using the ESRF facilities, and particularly ID09A for single-crystal crystallography.

Many studies at high pressure with X-rays and Raman spectroscopy have been carried out lately and determined the crystallography of methane and carbon dioxide hydrates between 0.2 and 5 GPa and 0 and 1 GPa, respectively. But there is still a lack of data concerning the binary hydrates. Indeed, in Titan's conditions, CO_2, the principal carbon species[2] can combine with CH_4 to form multi-guest clathrate. In this context, we propose also to perform preliminary investigations on the stability and structure of CO_2-CH_4 clathrate hydrates. Recent results on methane and ethane hydrates show a high stability with pressure.

With X-rays we observed the progressive changes occuring in the structures. We have observed the structure sI, the structure sII and then the structure sH. We observed these structures at different temperature levels. The evolution was progressive and took a lot of time but we were able to get PVT data for three temperatures. X-ray powder diffraction patterns of high-quality were collected. We decided to give up the melting curves because it was not possible during 3 days. Dissociation data will be performed in the Laboratory in Nantes. Thus we expect to be able to get many informations from these new data. It was the first time that we were able to catch the sII and sH phase.

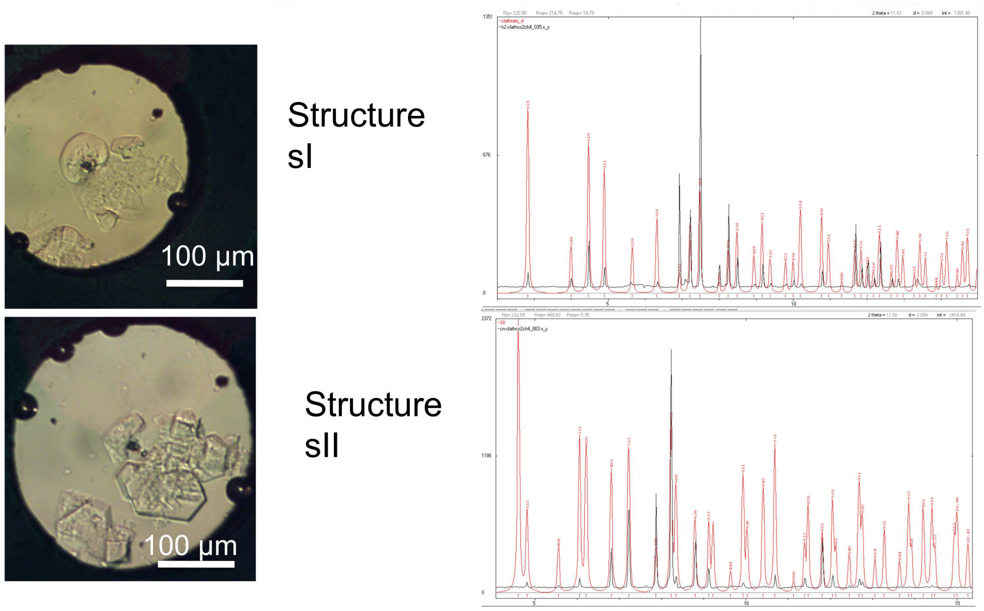

Figure 1. Observed (black) and modeled (red) structures sI and sII of binary hydrates..

This study was important and permitted to perfectly characterize the binary hydrate structure and evolution with pressure. It is also a first step in the study of binary hydrates.

With these data, we should be able to get the equation of state of binary hydrates. It will be useful for modelling the interior of Titan or other icy bodies.

References

[1]Tobie et al., p. 24-50 in *Titan: Interior, Surface, Atmosphere, and Space Environment*, Cambridge University Press (2012a), [2]Tobie et al. *ApJ*, **752**, 2, id 125 (2012b), [3]Loveday et al., *Chem. Phys. Letters*, 350, 459-465 (2001), [4]Tobie et al., *Nature*, 441, 61-64 (2006), , [5]Bezacier et al., *Physics of the Earth and Planetary Interiors* (2014), [6]Hirai et al., J. Chem. Phys., (2010).