



	Experiment title: High pressure studies of methane-hydrates	Experiment number: HS-2983
Beamline: ID09A	Date of experiment: from:08/04/06 to:11/04/06	Date of report: 21/09/06
Shifts: 6	Local contact(s): Monica Amboage	<i>Received at ESRF:</i>
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Report: Like many simple gases, methane combines with water to form a clathrate hydrate. In these compounds guest methane molecules fill cages formed from H-bonded host water molecules. These cages are believed to be stabilised by repulsive hydrocarbon-water interactions and so methane hydrate is a model system for the study of these repulsive interactions. In addition, methane hydrate is common in nature and its properties and behaviour are crucial to modelling of bodies in the outer solar system. For example, the high pressure properties of methane hydrate are central to models of the origin of the methane in the atmosphere of Saturn's largest moon, Titan.

Modelling and preliminary high-pressure diffraction studies suggested that methane hydrate would decompose into water (high-pressure ice), and methane between 1 and 2 GPa [3, 2]. However, our studies showed this view to be incorrect and that cubic methane clathrate hydrate loses water and transforms to first to an hexagonal structure, methane hydrate II (MHII) [5], and then at 2 GPa to a dihydrate (MH-III) whose hydrogen bond network is closely related to ice Ih [4]. The structure of MHIII is extremely stable and has yet to be observed to decompose under pressure [1, 6], though it is calculated to do so at pressures approaching 100 GPa [7]. In their study of methane hydrate to 86 GPa, Hirai's group found evidence that MH-III undergoes a structural phase transition at 40 GPa. However, because this group used MH-I with a methane:water ratio of 5.6:1 as a starting sample, the quality of the data obtained from MH-III were not sufficient to solve the structure or to carry out structure refinements.

In this experiment, we aimed to overcome this limitation by loading a sample of approximately the desired 2:1 water methane composition and growing samples of MH-III in-situ with only minimal contamination from other phases. This procedure was only partially successful. In order to grow the desired phase, fine control of pressure (on the order

of a kilobar) is imperative. In our DAC such control at pressures below 10 kbar is very difficult and because of that we lost several samples brought to the ESRF. However, we were able to grow samples of methane hydrate-II, which has a 3.5:1 water methane composition at ~ 1.5 GPa (see Fig 1) and to transform this into MH-III by increasing pressure to 2.1 GPa. But at the transformation to MH-III the water expelled from the MH-II structure did not react with the excess of methane and we were left with a sample containing methane, ice VII and MH-III. Figure 2 shows the diffraction patterns collected from this sample with increasing pressure up to the maximum of 46.6 GPa achieved. As can be seen, methane undergoes at least three phase transitions and its diffraction pattern becomes increasingly complex. Thus while we are able to confirm Hirai's group finding that MH-III has a very wide range of stability, we were not able to study the structural pressure dependence of MH-III or its transition behaviour.

This experiment marks a significant breakthrough, for the first time we were able to load methane and water and to grow the hydrate in-situ in the diamond cell. In subsequent tests we have found that it will be possible to grow MH-III directly by modest heating of the cell to melt the methane and water. Using this procedure it will be possible to grow a sample which is almost completely MH-III and to carry out measurements of the structural pressure dependence and of the phase transition at 40 GPa.

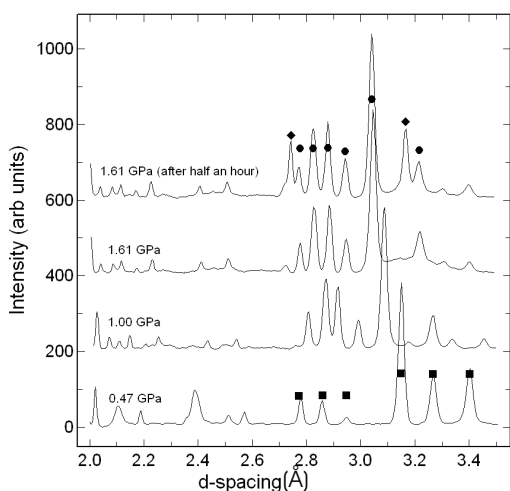


Figure 1-Diffraction patterns showing the progression of the sample from MHI (indicated by squares) towards MHIII (circles) with solid methane I (diamonds) growing.

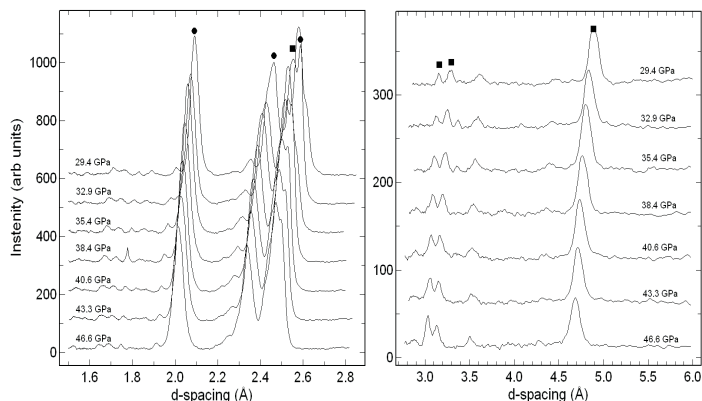


Figure 2 - The large methane peaks (indicated by circles) unfortunately obscure the weaker methane clathrate (squares) and prevented us from observing the possible phase transition that begins at ~ 40 GPa. However, elsewhere in the pattern we see no discernable change (above background values) like the ones reported in Machida's paper

References

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