



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  $\sim 1.5$  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.

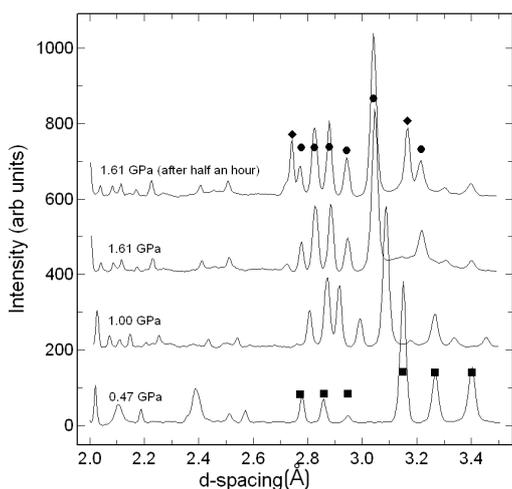


Figure 1-Diffraction patterns showing the progression of the sample from MHI (indicated by squares) towards MHII (circles) with solid methane I (diamonds) growing.

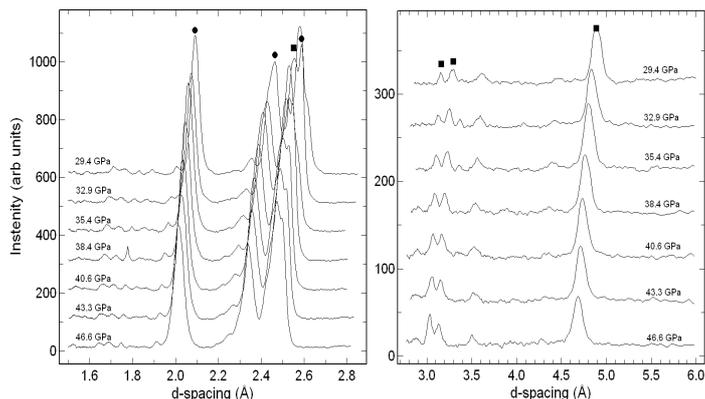


Figure 2 - The large methane peaks (indicated by circles) unfortunately obscure the weaker methane clathrate (squares) and prevented us from observing the possible phase transition that begins at  $\sim 40$  GPa. However, elsewhere in the pattern we see no discernable change (above background values)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

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