MLF Experimental Report	提出日 Date of Report 2012.8.16
課題番号 Project No. 2012A0059 実験課題名 Title of experiment Guest storage capacity into dense methane hydrate 実験責任者名 Name of principal investigator Takuo Okuchi 所属 Affiliation Okayama University	装置責任者 Name of responsible person Kazuya Aizawa 装置名 Name of Instrument/（BL No.） TAKUMI（BL 19） 実施日 Date of Experiment 2012.6.5 – 6.9

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

fully-deuterated methane hydrate (CD_4:5.75 D_2O) powder
partially-deuterated methane hydrate (CD_4:5.75 H_2O) powder
vanadium (V) pellet
magnesium deuteroxide ($Mg(OD)_2$) powder
olivine $(Mg,Fe)_2SiO_4$ powder
grycerine-d8 ($C_3D_5OD_3$) liquid

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Three methane hydrate samples were loaded into high-pressure cells prior to the experiment. Structure H hydrate powder was successfully prepared by quick compression of the sample above the phase transition pressure of 0.9 GPa while keeping the cell at low temperature. After the arrival, the state of the sample is checked again by optical microscope. The neutron beam is shielded and collimated by the combination of cadmium foil surrounding the cell, sintered ^{6}LiF collimator at beam entrance of the cell (to reduce gamma ray into detectors), Gd plate and/or hBN (boron nitride) rod with collimation holes fit to the exit path from the focusing device. We used 2 mm-gauge volume radial collimator to cut the spurious diffraction peaks from the cell body, sample gasket, anvils, etc. We also used neutron focusing device to enhance the beam intensity at larger wavelength. The sample dimensions were 2 to 2.5 mm in height and also in diameter, so that their uses were very effective to improve the signal to background ratio (see Figure). Diffrction patterns were obtained for up to 16 hours accumulation time at 210 kW of beam power. The obtained patterns were then corrected for intensity distribution against wavelength using scattering

profiles of vanadium pellet standard and air, both of which were separately measured at the same optical conditions with the sample measurements.

Figure shows the corrected diffraction pattern of fully deuterated structure H methane hydrate at 1.2 GPa, including our ongoing Rietveld refinement fitting results using FULLPROF software. We have prepared peak-pattern simulations of plausible structure H hydrates with multiple methane occupancy in the large cage, which have suggested that the number of methane molecules in this cage will be unambiguously determined as long as large d-value (>3 A) peaks were detected with enough intensity and resolution to conduct the Rietveld refinement. As shown by black line in the Figure, these large-d peaks were successfully observed with excellent quality. Although the observed pattern is proved to be different from any simulation results those we obtained previously, the answer for cage occupancy will be given rather soon by further improvement of the structure model.

We note that some preliminary experiments for other high pressure samples than the methane hydrate have been made using a small part of the experimental time, while most of the time is used for methane hydrate and wavelength/intensity standard samples. We report that the given 3-and-half day beamtime has been quite efficiently used. As the necessary consequence, five high-pressure cells are exposed to the neutron beams, and two cells of large remaining activity should be left at the beamline after the experiments. Two months after that, these cells have been finally recovered, and now all the cells are ready for use for the next experiments.