（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。）

MLF Experimental Report	提出日 Date of Report 11 May 2013
課題番号 Project No. 2012B0223 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 Shigeo Sasaki 所属 Affiliation Dept. of Materials Science and Technology, Gifu University	装置責任者 Name of responsible person Kazuya Aizawa, Stefanus Harjo 装置名 Name of Instrument/（BL No.） TAKUMI/BL19 実施日 Date of Experiment 28 Nov. 2012 – 1 Dec. 2012

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.

1. Fully deuterated methane hydrate, CD_4-nD_2O in sapphire anvil cell
2. Methane deuterohydrate, CH_4-nD_2O in sapphire anvil cell
3. Vanadium rod, V
4. NIST alumina powder in V can, Al_2O_3

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.

The aim of this continuing proposal is to measure the neurton diffraction of the structure H of methane deuterohydrate (CH_4-nD_2O) and fully deuterated methane hydrate (CD_4-nD_2O) in order to find out the possible structural difference (especially for the guest methane storage capacity in large cages) between the two methane hydrate species by fully utilizing the advantages of high resolution and low background of BL19 “TAKUMI”.

Two kinds of methane hydrates were prepared by the following procedure. D_2O ice powder with ~5 μm in diameter was made by spraying water into a cooled chamber. This powder ice was put into a high pressure vessel where CH_4 or CD_4 gas at 8 MPa was filled at 263 K. After ~20 hours, the powder ice almost transformed into structure I hydrate (CH_4-5.75 D_2O or CD_4-5.75 D_2O). Then it was loaded into large sample chamber (1.5 mmϕ x 2.0 mm) of the anvil cell cooled at 80 K in order to prevent the grain growth. Structure H hydrate suitable for powder diffraction was obtained by quick compression of the structure I hydrate into above the structure I - structure H phase transformation pressure of 0.9 GPa while keeping the cell at low temperature. Due to increase of methane capacity in dense hydrate, some D_2O is segregated to form ice VI phase, which means that the specimen of structure H methane hydrate is coexistent with ice VI.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Neutron diffraction measurements were performed for the two structure H methane hydrate samples (fully deuterated methane hydrate: CD_4-nD_2O, methane deuterohydrate: CH_4-nD_2O) in the sapphire anvil cell prepared by the above procedure (Fig. 1), and we successfully obtained their powder diffraction patterns. Figures 2a and 2b show the obtained raw diffraction patterns as a function of TOF for fully deuterated methane hydrate (CD_4-nD_2O) at P = 1.46 GPa, and methane deuterohydrate (CH_4-nD_2O) at P = 1.23 GPa, respectively. These diffraction patterns show the very strong and sharp peaks of target methane hydrate samples. These peaks are obviously distinguishable from those of surrounding ice VI and aluminum gasket. In addition, the quality of these powder diffraction patterns were confirmed by mapping spectra (Intensity-TOF-pixel). Although the incoherent scattering from ^1H of CH_4 (Fig. 2b) affects the diffraction pattern of methane deuterohydrate, these fine diffraction patterns are thought to be able to analyze the guest methane (CD_4 or CH_4) storage capacity in large cage of the structure H.

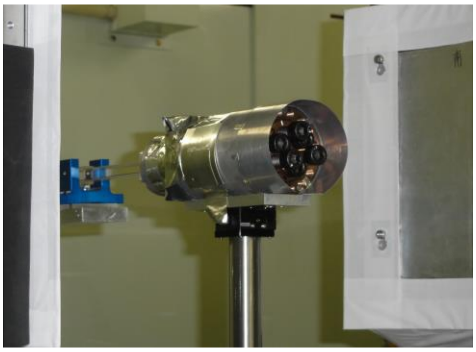

Fig. 1. Sapphire anvil cell including methane hydrate sample at TAKUMI.

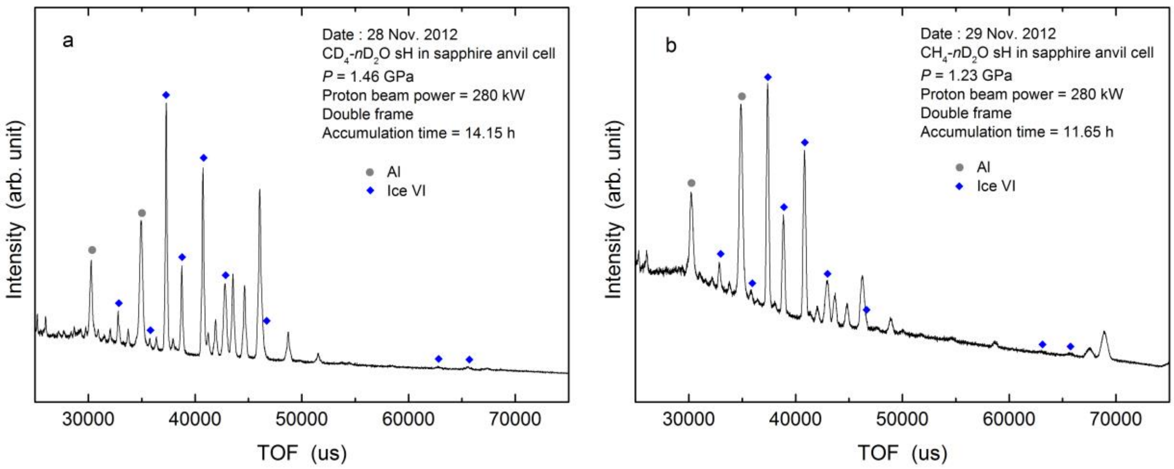

Fig. 2. Neutron powder diffraction patterns for a. fully deuterated methane hydrate (CD_4-nD_2O) at P = 1.46 GPa and b. methane deuterohydrate (CH_4-nD_2O) at P = 1.23 GPa. Solid circles and solid diamonds stand for the peaks from aluminum gasket and ice VI, respectively.

Moreover, the neutron diffraction for a vanadium rod, NIST alumina powder in V can, and empty anvil cells were also measured for normalizing the intensity of diffraction patterns, the *d*-value calibration, and the absorption and background corrections for anvils, gaskets, and other surroundings. The Rietveld analysis of guest methane storage capacity in large cages of the two kinds of structure H methane hydrates are now in progress, taking account of the above calibrations.