（ ※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。 ）

CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2015/8/17 承認者 Approver Takanori Hattori 提出日 Date of Report 2015/8/11
課題番号 Project No. 2014B10188 実験課題名 Title of experiment 単層カーボンナノチューブのナノ空間内の水の常温付近での高圧下における相変化挙動解析 実験責任者名 Name of principal investigator Katsumi Kaneko 所属 Affiliation Center for Energy and Environmental Science, Shinshu Univ.	装置責任者 Name of Instrument scientist Takanori Hattori 装置名 Name of Instrument/(BL No.) PLANET/(BL11) 実施日 Date of Experiment 15/03/06-15/03/10

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.

We used Nano-CPT100 (Nano-C, Inc.) as a single wall carbon nanotube (SWCNT) sample. For opening cups of the end of nanotubes, we oxidized it in an electrical furnace at 380 ℃ (+1 ℃/min) for 1h in air flow (300 ml/min). We conducted neutron scattering measurement of SWCNT with and without heavy water under ambient pressure and under 0.3 GPa. For the ambient pressure measurements, we prepared 2 samples; oxidized SWCNT (0.29 g) and oxidized SWCNT containing 440 mg/g of heavy water (0.25 g). Each measurement on the ambient pressure was accumulated for 4.5h. For the high pressure measurements, we prepared 2 samples; oxidized SWCNT containing 440 mg/g of heavy water (33 mg) and unoxidized SWCNT containing 440 mg /g of heavy water (28 mg). The samples under high pressure were pelletized under 980 N to fit the size of high pressure anvil cells. Each measurement on the high pressure was accumulated for 9.5h

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.

At first, we measured neutron scattering of oxidized SWCNT containing heavy water at ambient condition (Figure 1(a)).For a comparison, we also show the neutron scattering profile of oxidized SWCNT itself in Fig. 1(a). In the neutron scattering profile of SWCNT itself, we can see Bragg peaks of (10) and (11) of graphene structure of carbon nanotube. The peak at 1.8 $Å^{-1}$ is attributed to the (002) diffraction of graphite structure of graphitic impurities in SWCNT samples. In the profile of oxidized SWCNT containing heavy water, we can see the intensity increase of the 1.83 $Å^{-1}$ peak compare with that of SWCNT itself.

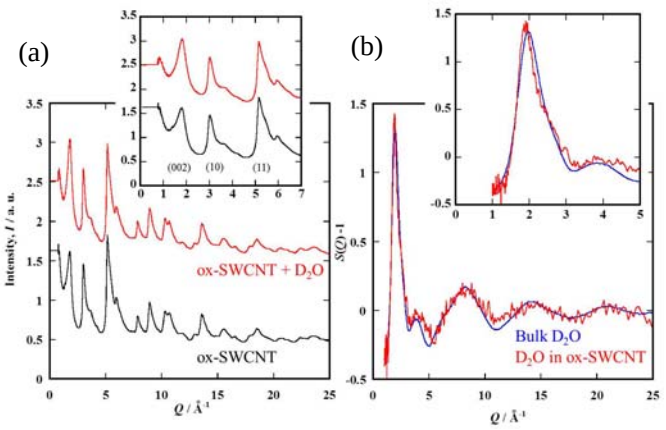

Figure 1 (a)ND profiles and (b)structure factors

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

It is attributed to the water assembly structure inside carbon nanotube and we can obtain the structure function $S(Q)$ by subtraction of the profiles of SWCNT itself from that of SWCNT containing heavy water. Figure 1 (b) shows the $S(Q)$-1 of D_2O inside of the oxidized SWCNT. For a comparison, we also plotted that of the bulk D_2O in Fig. 1(b). The 1st peak intensity becomes large and the position shifts to the low Q in SWCNT. To understand more detailed structural change of heavy water inside of the SWCNT, we obtained radial distribution functions (RDFs) by Fourier transformation, as shown in Figure 2.The peak position of 1st, 2nd and 3rd neighbors of heavy water inside SWCNT pores shift to larger distance. Furthermore, the peak intensity of 2nd and 3rd peaks becomes larger than that of bulk heavy water although that of first peak is opposite situation. The relatively longer ordered structure of D_2O inside SWCNT could be attributed to the ice like hydrogen bond formation in carbon nanospaces.

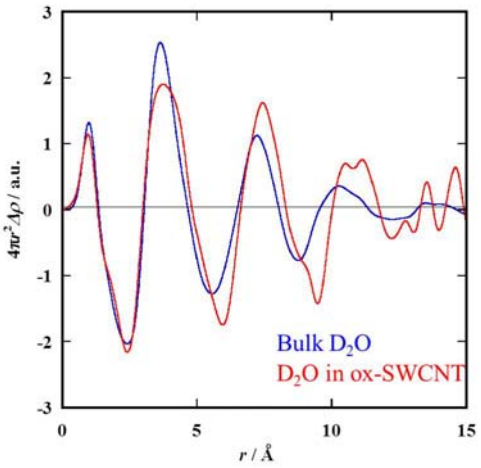

Figure 2 Radial distribution function of heavy water inside carbon nanotube.

Finally, we measured the neutron scattering of oxidized SWCNT containing heavy water under high pressure and low temperature condition (0.3 GPa, -70 ºC) as shown in Figure 3. We also showed the neutron scattering profile of oxidized SWCNT containing heavy water under ambient condition, that of ice II and that of ice I_h in the same Figure. The sharp peaks in red line mainly relevant to those of the bulk ice II which exists outside of SWCNT. It confirmed that we succeeded to measure under high pressure and low temperature conditions. For the confined heavy water, we can see the broad peak located at 1.95 $Å^{-1}$, as shown broken line. The peak position is larger than that of ambient condition. These facts imply two interesting feature; i) water could not form long range ordered phase (i.e. like a crystal) in carbon nanospaces because of the spatial limitation even at high pressure and low temperature condition, but ii) water inter-molecular distance would be contracted (ca. 6%) under high pressure and low temperature condition.

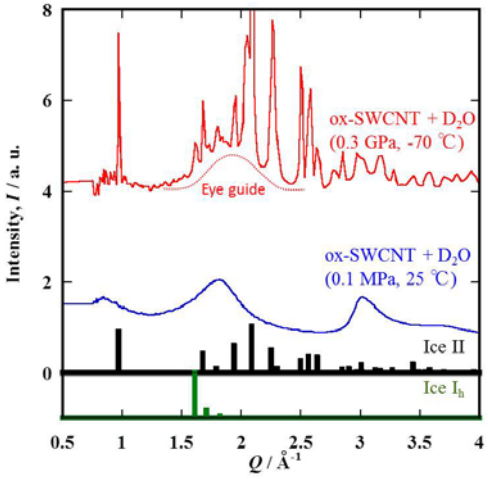

Figure 3 ND profiles of heavy water confined in SWCNT under high pressure and low temperature condition.

It is difficult to evaluate RDF of confined heavy water under high pressure and low temperature conditions because of the presence of many peaks of bulk ice II. However, we are now trying to analyze the anomaly on water structure using revers Monte Carlo simulation which can selectively simulate the molecular structure of confined phase. Our results would shed new light on anomaly of water properties inside nanospaces and our further studies would be required because of the importance from scientific fields as well as the applications.