MLF Experimental Report	提出日 Date of Report 2014.5.15
課題番号 Project No. 2013B0279 実験課題名 Title of experiment Hydroge's position, occupancy and chemistry in dense hydrous minerals in earth's interior 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 Toru Ishigaki 装置名 Name of Instrument/（BL No.） iMATERIA (BL20) 実施日 Date of Experiment 2014.3.20-21

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.

Hydrous magnesium silicate Mg_2SiO_4:xD_2O

iron-bearing hydrous magnesium silicate $(Mg,Fe)_2SiO_4$:xD_2O

brucite $Mg(OH,OD)_2$

TiZr: $Ti_{68}Zr_{32}$

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.

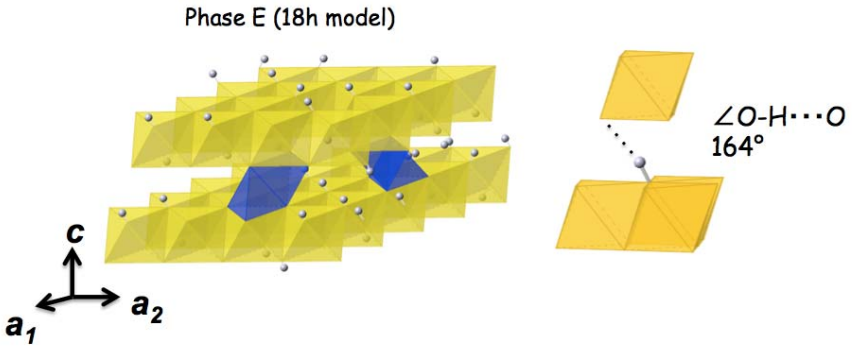
Phase E, which is one of the dense hydrous magnesium silicates with the composition of Mg_2SiO_4:xD_2O or Mg_2SiO_4:xH_2O, were synthesized by Kawai-type apparatus from the mixtures of synthetic $Mg(OD)_2$/$Mg(OH)_2$ and SiO_2 glass. The mixture sealed into a gold capsule was reacted at 15 GPa pressure and at 900-1100 °C. The recovered samples were initially evaluated by powder X-ray diffractometry (XRD) and Raman spectroscopy. The samples with Mg_2SiO_4:xD_2O composition do not have large amounts of additional phases and showed very weak OH stretching peak. Two representatives of the sample powders with ~50 mg in each weight, synthesized at two different temperatures, were separately enclosed into a vanadium container with 6 mm of inner diameter and their powder neutron diffraction (PND) patterns were collected at room temperature at iMATERIA. By normalization of the intensities using an incoherent scattering pattern of vanadium, diffraction profiles with low and flat background were successfully obtained. The Reitveld refinement on the PND patterns were performed using the “Z-Rietveld” code in order to

specify the deuterium positions and its site occupancy in the structure.

The crystal structure of phase E was known to contain brucite [$Mg(OH)_2$] -like layers which are crosslinked by SiO_4 tetrahedra and MgO_6 octahedra. Hydroxyl bonds have been thought to align normal to the octahedral layers, where hydrogen atoms are located at the 6c Wycoff positions, based on single crystal X-ray diffraction study of hydrogenated sample (Uchiyama *et al.*, 2011). However, the present Rietveld analyses propose that another possible hydrogen position of 18h. The table below shows the results of refined deuterium positions and site occupancies of a representative sample.

	Atom	Occupancy	X	Y	Z
6c model	D	0.47(1)	0	0	0.2026(7)
18h model	D	0.103(3)	-0.0666(8)	0.0666(8)	0.1979(5)

The *Rwp* factors of the 6c and 18h models are almost identical (~0.05), but isotropic temperature factor for the 18h model (B=1.6) is much more reliable than that of the 6h model (B=7.0). In the 18h model, hydroxyl bond in the phase E structure is tilted away from the direction normal to octahedral layers. The tilting of OD dipole is caused by the presence of hydrogen bond. The crystal structure model of deuterated phase E at the present study is described below:



We are also aiming at determination of hydrogen positions in the crystal structure of hydrogenated phase E, as well as some of the other hydrous phases. The PND patterns of these samples were also obtained additionally with the same scheme as the deuterated phase E samples. Its PND data are now under evaluation by the Rietveld method.