（ ※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 2017/10/13 承認者 Approver Takanori Hattori 提出日 Date of Report 2017/9/14
課題番号 Project No. 2016A0194 実験課題名 Title of experiment In situ Neutron diffraction study of fundamental phase diagram of benzene at pressures to 10 GPa and temperatures to 1200 K 実験責任者名 Name of principal investigator Konstantin Litasov 所属 Affiliation VS Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia	装置責任者 Name of Instrument scientist Takanori Hattori 装置名 Name of Instrument/(BL No.) BL11 PLANET 実施日 Date of Experiment 06-2016

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.

Benzene, C6H6;

Deuterated benzene, C6D6

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.

During experiments, we used about 0.5 of beam time due to significant problems with beam down. However, with significant help from beam line scientists we performed most significant experiments as was planned.

We performed several experiments on heating of deuterated and normal benzene at pressures up to 9 GPa (Fig.1). Detailed analysis of the experimental results revealed following major conclusions presented in the paper submitted to Phys Chem Chem Phys.

The high-temperature structural properties of solid benzene were studied at 1.5–8.2 GPa up to melting or decomposition using multianvil apparatus and *in situ* neutron and X-ray diffraction. The crystal structure of deuterated benzene phase II ($P2_1/c$ unit cell) was refined at these parameters (Fig.2). Our data show minor temperature effect on the compression behavior of deuterated benzene at 7.8–8.2 GPa indicating low temperature expansion of organic compounds at high pressures.

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

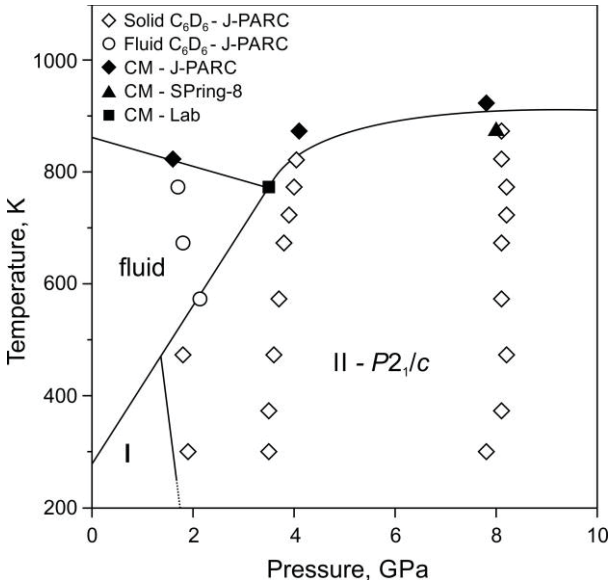

Figure 1. The phase diagram of benzene constrained from the present results. The melting line and the I–II phase boundary are from (Akella and Kennedy, 1971). CM – carbonaceous material.

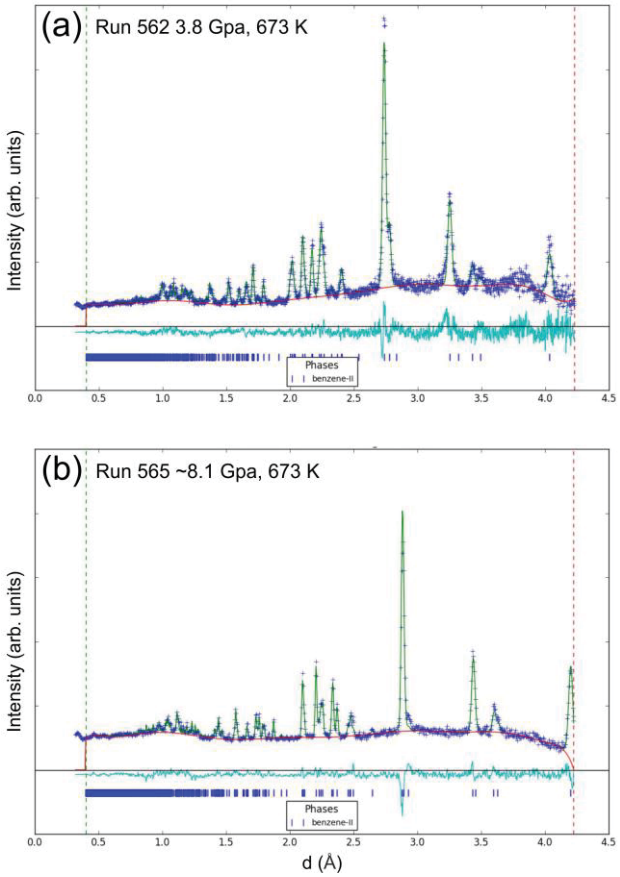

Figure 2. Rietveld refinement of neutron diffraction patterns of C6D6 acquired at (a) 3.8 GPa and 673 K and (b) 8.1 GPa and 673 K.

In the crystal structure analysis at 3.5–4.0 GPa we observed the deviation of D4 from ring plane with rising temperature caused by the displacement of benzene molecules and decrease of intermolecular van der Waals bond of π–conjuncted carbon skeleton and the deuterium atom of adjacent molecule. The part of C···D interactions between the molecules decreases from 42.4 % at 298 K and 3.5 GPa to 41.3 % at 723 K and 3.9 GPa that promotes the reaction of oligomers formation at the crystals boundaries. In the pressure range of 1.5–8.2 GPa benzene decomposition was defined between 773–923 K. Melting was identified at 2.2 GPa and 573 K. Quenched products analyzed by Raman spectroscopy consist of carbonaceous material containing up to 10 % of sp^3 carbon. The defined benzene phase diagram is consistent with naphthalene, pyrene and coronene phase diagrams at 1.5–8 GPa, which we determined previously (Chanyshev et al., 2015; 2017).