実験報告書様式（一般利用課題・成果公開利用）

（ ※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 2014/9/3 承認者 Approver Takanori HATTORI 提出日 Date of Report 2014/9/3
課題番号 Project No. 2014A0004 実験課題名 Title of experiment Low-Temperature and High-Pressure transformation of sulfuric acid hydrates 実験責任者名 Name of principal investigator Helen Maynard-Casely 所属 Affiliation Bragg Institute, ANSTO	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 9th-16th June 2014

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.

During the experiment we attempted four experimental runs. For each of these sample runs a solution of dueterated sulfuric acid and dueterated water was sealed with 0.03 g of lead, to act as an internal pressure calibrant, into a TiZr sealed gasket. This gasket was supported by an aluminimum ring, and the assembly was placed into the Mito pressure cell, mounted onto the PLANET beamline. The first run, with a sample of 35 wt% $D_2SO_4.D_2O$ solution was not successful as the gasket did not seal properly at 7 tonnes of load. For runs 2-4, the sample was sealed with 11 tonnes of load, which was sufficent to seal the TiZr gasket but did not apply too much pressure to the sample intially. For samples 2 to 4 a common experimental temperature and pressure path was followed, designed to maximise the area of phase space explored, and data collected to chart this. The samples were cooled to 100 K (this was undertaken to freeze the sample into an glass/amorphous state) then the sampes were warmed to 180 K to crystallise (this behvaiour has been noted in previous studies by the principal investigator). Upon crystallisation at 180 K the samples were cooled to 100 K where they were compressed to ~2 GPa. Once reaching this pressure the samples were heated to 300 K. The action of heating also increased the pressure, an affect that was expected. Each sample rose to ~3.5 GPa upon heating to 300 K. From this point the load applied to the sample was lowered and data was taken in stages until the sample melted where each run was finished.

Run	Sample	First data run #	Last data run #
Calibration	Emply and Vanadium in Mito pressure cell	12931	12939
1	35 wt% $D_2SO_4.D_2O$	12940	12971
2	35 wt% $D_2SO_4.D_2O$	12972	13033
3	45 wt % $D_2SO_4.D_2O$	13034	13096
4	25 wt% $D_2SO_4.D_2O$	13097	13131

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.

Aims of the experiment

The aim of the proposed experiment was to establish the high-pressure and low temperature behaviour of water-rich sulfuric acid hydrates. Sulfuric acid hydrates are thought to form readily on the surfaces of the ice moons of Jupiter; Europa, Ganymede and Callisto. After forming these materials, which are denser than the surrounding water ice, would potentially sink into the ice crust of these moons and be subjected to the high pressures of these environments. Hence, understanding the high-pressure and low temperature behaviour of sulfuric acid hydrates could vastly impact on the interior models of the icy moons of Jupiter.

Preliminary results from data

The sample crystallised at the expected temperature, 180 K, but not to any known forms of sulfuric acid hydrate. Hence from the very beginning of the experiment we were probing new behaviour of this planetary ice material.

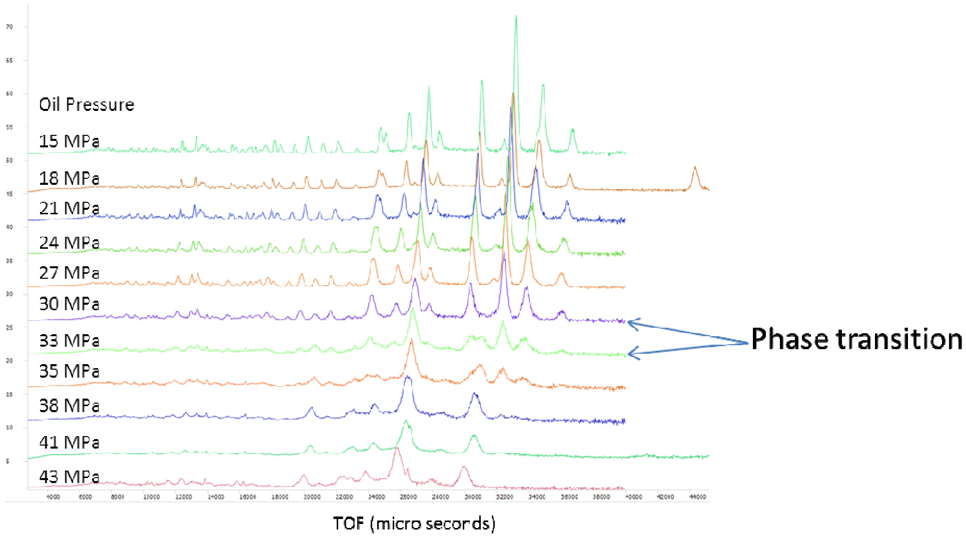

Figure 1 – Compression of 35 wt. % $D_2SO_4.D_2O$ sample at 100 K during Run 2. The pattern collected at 15 MPa is at this point belivieved to be a mixture of a new form of sulfruic acid hydrate and a high pressure ice phase. During the collection we undertook a two measurements in ‘double frame’ mode, which allowed observations of peaks at TOF higer than (4000 micro seconds). As is shown in the Figure, this hydrate underwent a phase transition between 30 MPa and 33 MPa of oli pressure applied to the pressure cell.

Figure 1 shows the compression of the sample in experimental Run 2 at 100 K. The first pattern collected in this sequence, it is believed at this time, is a mixed pattern of a new sulfric acid hydrate and a high pressure water ice. Upon compression, at a pressure of ~1.5 GPa determined from the internal lead calibrant, the sample underwent a transistion to a further new phase of sulfuric acid hydrate. The pattern of this new hydrate was distinctly strained, and co-existed with large broad feature in the pattern, which was interpreted to be a form of amorphous ice.

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

On warming the pattern fully amorphised at 200 K, which is very unusual behaviour. On further warming it crystallised to a pattern that has been interpreted to be a mixture of a further new sulfruric acid hydrate and Ice VII. On decompression at 300 K the high-pressure ice phases did not behave as expected. Indeed, Ice VII was observed in Run 2 to transform to ice VI at 1.8 GPa – much higher than the boundary in pure deuterated water at 0.9 GPa. Additionally on compression it was noted that the ice phases melted at much higher pressures than in pure ice. Across the three solutions studied, this effect was very variable and indicates that the presence of sulfuric acid, as well as forming hydrate phases at high-pressures, also has a sigificant effect on the water ice phases formed.

Intial conclusions

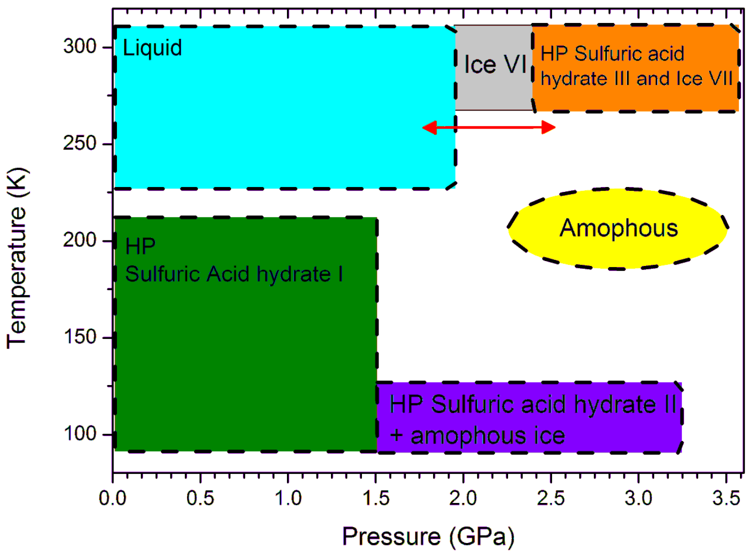

Figure 2 – Preliminary phase diagram of sulfuric acid hydrates under pressure. The red arrows indicated that the Ice VI to liquid and Ice VI to a mixture of High Pressure sulfuric acid hydrates and Ice VII is very dependent on the wt. % of sulfuric acid in the sample. The dotted lines indicated that, at this stage in the analysis, these boundaries are only for guidance and will be confirmed at a later stage.

The initial conclusions are summarised in Figure 2, but additionally the following points can be made from the prelimary analysis.

1) Hydrates of sulfuric acid do exist at high-pressure, but are distinctly different from the seven forms that are observed at ambient pressures. Hence, sulfuirc acid hydrate do have to be considered as materials for the interors of the ice moons of Jupiter.
2) At present, preliminary data analysis suggests that three new phases of sulfuric acid hydrate were observed during the experiment. Of these, the data quality of two is sufficent for indexing and potential

structure solution. It is possible that these patterns (especially those from initial compression at 100 K) are in fact from two hydrate phases – this will be determined from closer inspection of the data.

3) The full amorphisation of the pattern on warming from 100 K to 300 K at 2.5 GPa is very strange behaviour in a sytem of this kind. Further study will be needed to investigate this mechanism and to see if there is a precident for this behaviour in the litereature.
4) The presence of sulfuric acid distinctly changes the melting and phase boundaries of the high-pressure ice phases VII and VI. For instance Ice VI was observed existing at a much higher pressure (greater than 2 GPa) than observed in pure D_2O. Charting this modification of phase boundaries as a function of pressure and acid content is an essential input for interior models of Jupiter's ice moons.

Further work and publication outlook

To date, because of time contraints and the complexity of the observed behvaiour, only very preliminary analysis has been undertaken on this data set. However, the data set obtained from this experiment will be the starting point for the principal investigator's (Helen Maynard-Casely) JSPS fellowship at Univeristy of Tokyo, commencing in November 2014. During this three month fellowship Dr Maynard-Casely will be working in the lab of Assoc/Prof Komatsu and be able to undertake a number of complimentary measurments to the data collected at the PLANET beamline. Hence, an exact plan for publication of this work would be unrealistic at this time. But, we anticipate that at least two peer-reviewed papers could result from this work and it is hoped that the work will be presented at the American Geophysical Union conference in 2015.