ISIS Experimental Report

Rutherford Appleton Laboratory

RB Number:			1010008
Date of Report:			12/08/2010
Title of Experiment:	Recovery and characterisation of high-pressure phases in the systems H_2O – NH_3, H_2O – H_2SO_4, and H_2O – $MgSO_4$.	**Local Contact:**	M. G. Tucker
Principal Proposer:	A.D. Fortes	**Instrument:**	PEARL/HiPr
Affiliation:	University College London		
Experimental Team:	A.D. Fortes, I. G. Wood, G. Sclater, M. G. Tucker	**Date of Experiment:**	28/04 – 03/05/2010

Introduction: The objective of this experiment is to synthesise four particular high-pressure polymorphs of various hydrates discovered by us in recent years during work carried out using the Paris-Edinburgh cell on PEARL/HiPr (see Fortes *et al.*, 2009 and experiment reports for RB 820064, 920226, 920237, 920238. At present, the crystal structures of these materials are unknown. We proposed to synthesise: (*i*) ADH IV; (*ii*) SAT-III; (*iii*) the high-pressure phase formed by compression of epsomite to 12 kbar at 295 K; and (*iv*) the phase mixture formed by compression of meridianiite to 9 kbar at 240 K. After synthesis in the P-E press, each phase was to be quenched to 100 K, decompressed, and then recovered for analysis using the GEM diffractometer.

Experimental method: Individual details pertaining to each of the four specimens are outlined below. In each case, quenching and recovery was achieved by first cooling the entire press to 100 K by spraying with liquid nitrogen until the bottom of the frame was immersed. The press was craned out of the cryotank and the breech was loosened, whereupon the gasketted sample dropped free into a jug of liquid nitrogen. The samples were stored in a large pool of liquid nitrogen in a spare cryotank.

(i) Stoichiometric $D_2SO_4{\cdot}4D_2O$ liquid was loaded into the P-E cell gaskets, and sealed by compression under a load of 7 tons at room T. The load was increased to 25 tons at room temperature, after which the specimen was then rapidly cooled to 190 K offline. The cell was mounted on the PEARL/HiPr beamline to confirm the SAT-III had been formed. Additional data were collected whilst cooling from 190 K to 130 K under loads of 25-28 tons, under loads of 12t, 7t, 4t, and 2.4t at 130 K, and under zero load (with the breech loose) at 130 K (Figure 1).

(ii) Stoichiometric $ND_3{\cdot}2D_2O$ liquid was loaded into the P-E cell gaskets by saturating a ball of silica wool, and sealed by compression under a load of 7 tons at room T. The load was increased to 16.5 tons and the specimen was cooled to 190 K offline. After 24 hr the P-E cell was mounted on the PEARL/HiPr beamline, where we discovered that the specimen had not crystallised. Attempts to form ADH IV by further compression failed, and a reload of the sample was done. ADH IV was subsequently formed at 180 K under a load of 15 tons, cooled to 120 K under zero load and recovered.

(iii) Powdered deuterated epsomite was packed into the P-E cell gaskets with fluorinert and sealed under a load of 6 tons at room T. The press was mounted on the PEARL/HiPr beamline in order to monitor the progress of compression from 6 – 15 tons. Due to the constraints posed by the amount of time required to prepare the previous two samples, we had to cut the integration time at each 1 ton load increment to 15 minutes. This time is too short; as a result, we missed the desired high-pressure phase (seen only in RB920237) and instead formed the high-pressure phase (or phase mixture) which occurs subsequently (Figure 2). Whilst this was not the outcome we wished for, we nonetheless successfully quenched this specimen to liquid nitrogen temperatures under zero load and recovered the gasketted specimen.

(iv) Powdered deuterated meridianiite was packed into the P-E cell gaskets with fluorinert in the UCL cold rooms. After transfer back to ISIS, the cold anvil assembly was stored in dry ice. *Due to time constraints, this specimen was not used.*

Figure 1: Comparison of data collected from SAT-III under load and under no load. The sample has clearly persisted in the high-pressure phase, but the peaks have shifted to longer times (longer d-spacings) as one would expect from the large reduction in pressure (~ 1 GPa). The strong reflection at ~ 8.8 ms, which does not shift, is from the tungsten carbide anvils of the P-E cell.

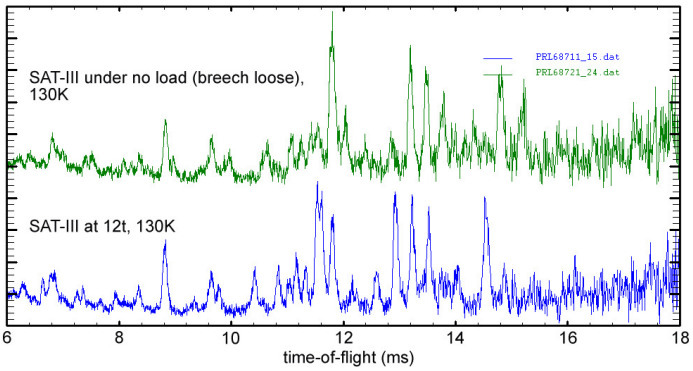
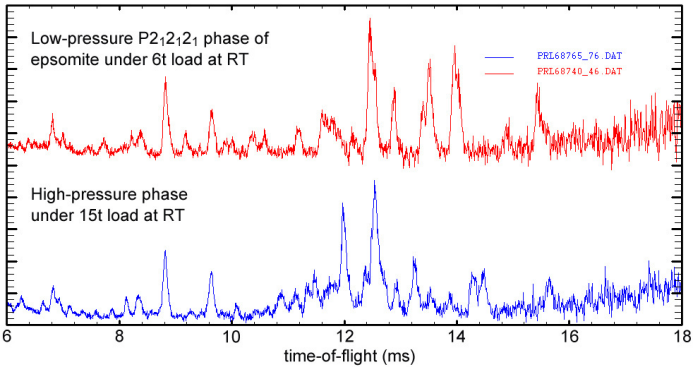


Figure 2: Comparison of the diffraction patterns from $MgSO_4{\cdot}7D_2O$ under loads of 6 tons (RT) and under 15 tons, after transformation to the high-pressure phase.



The further analysis of recovered samples carried out on GEM is described in the report RB 1010009.

References: Fortes *et al.* (2009b): *J. Appl. Cryst.* **42**(5), 846-866.