

# ISIS Experimental Report

## Rutherford Appleton Laboratory

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**Title of Experiment:** The effect of pressure on the structure of meridianiite ( $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$ )

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**Instrument:** PEARL/HiPr

**Experimental Team:** A. D. Fortes, I. G. Wood, M. G. Tucker

**Date of Experiment:** 12 - 15/06/2009

**Introduction:** During RB820064, carried out on PEARL/HiPr in September 2008, we were able to collect some preliminary data from  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$  (meridianiite) up  $\sim 1$  GPa. We showed that one or more phase changes occur at  $\sim 1$  GPa when meridianiite is compressed at 240 K, and then warmed to room temperature at 1 GPa. We could not ascertain positively the identity of the new phases or phase mixtures; several peaks could be attributed to ice VI, suggesting that meridianiite has undergone a dehydration reaction to ice +  $\text{MgSO}_4 \cdot n\text{D}_2\text{O}$ , where  $n$  signifies a lower hydrate (possibly, but not necessarily epsomite or a high-pressure polymorph of epsomite). The purpose of the present study was to confirm the observations of RB820064 and to collect diffraction data with a larger signal to noise ratio; to spend longer counting at each P,T point. In the earlier experiment, dry packing of the gaskets resulted in a very slow take-up of the load which used a significant portion of the allotted beamtime.

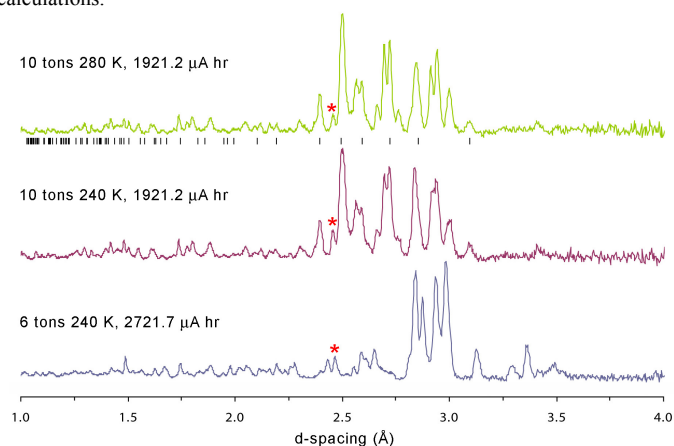
**Experimental:** As before, we had to bring a loading jig and a set of anvils back to UCL to carry out the loading in our cold rooms, since the ISIS cold rooms were not useable. Powdered deuterated meridianiite was loaded into encapsulated gaskets along with a small pellet of Pb to act as the pressure calibrant, and fluorinert to act as the pressure-transmitting medium. The experience of the previous loading meant that a very rapid assembly of the P-E cell was achieved on return to ISIS without risking melting of the specimen.

The cell was sealed under a load of 6 tons and equilibrated at a temperature of 240 K. Inspection of the diffraction pattern revealed strong Bragg peaks from  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$  and data were collected at this P,T point for 17 hours (2722  $\mu\text{A hr}$ ) in order to provide a high-quality reference pattern. Later refinement revealed the presence of accessory ice V in the specimen, which is consistent (at this temperature) with the pressure of  $5.6 \pm 0.6$  kbar obtained from the Pb pellet. The load was increased first to 8 tons and then to 10 tons at 240 K. Due to the tight packing of the gaskets, and the use of fluorinert, pressure was taken up immediately; the expected phase transition occurred at 10 tons ( $\sim 9$  kbar). Data were subsequently collected at this P,T point for 12 hours (1921  $\mu\text{A hr}$ ). Subsequent warming to 260 K and 280 K at a load of 10 tons resulted in no change in the diffraction pattern. Another long integration (12 hr, 1921  $\mu\text{A hr}$ ) was acquired at 10 tons 280 K. Finally, the specimen was compressed, at 280 K, under loads of 15 t, 20 t, and 25 t, with no significant change being observed. The low-noise datasets collected at 6 tons 240 K, 10 tons 240 K, and 10 tons 280 K, are shown in Figure 1.

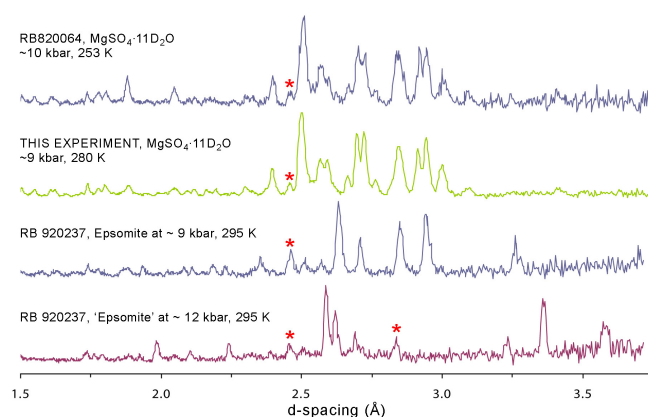
**Results:** The sequence of phase changes we observed agree quantitatively with the observations made in RB820064 despite the use of a pressure medium in this experiment. It is clear that  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$  experiences a phase transformation at a pressure of 8-10 kbar at 240 K. It is also clearer now that this transformation involves the expulsion of water of hydration from the crystal structure to form high-pressure ice VI. We found that the unit-cell parameters derived from the 002 and 200 reflections of the exsolved ice VI agree very well with the expected unit-cell dimensions corresponding to a pressure of 9 kbar. The identity of the non-ice component remains unknown. As shown in Figure 2, we cannot attribute any of the residual Bragg peaks to the low-pressure  $\text{P}2_12_12_1$  phase of epsomite ( $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$ ) or to the phase which is formed by compression of epsomite to 12 kbar. Therefore, the unknown phase may be a new polymorph of  $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$  or else it is another hydrate with an as-yet undetermined hydration number. A very crude

argument based on the individual phase scale factors suggests to us that (accounting for the pre-existing ice V) the post-transition ice VI represents the loss of 4 – 5 water molecules from  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$ . Hence, the unknown phase probably has a hydration number of 6 or 7 but further work is necessary to establish its identity.

**Figure 1.** The three long integrations collected during this experiment; red asterisks mark one of the strong Bragg peaks of Pb; tick marks report the locations of Bragg peaks from ice VI. The lowermost pattern has been used to refine the unit-cell of  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$  at 5.6 kbar,  $a = 6.7234(4)$  Å,  $b = 6.7250(4)$  Å,  $c = 17.2238(11)$  Å,  $\alpha = 88.733(5)^\circ$ ,  $\beta = 89.578(6)^\circ$ ,  $\gamma = 62.339(5)^\circ$ ,  $V = 689.59(5)$  Å<sup>3</sup>. The evolution of the unit-cell shape (increase of  $\alpha$  and  $\beta$ , decrease of  $\gamma$ , reduction in difference between  $a$  and  $b$ ) agree very well indeed with *ab initio* calculations (Brand, 2009). The incompressibility of  $\text{MgSO}_4 \cdot 11\text{D}_2\text{O}$  found from these results and the zero-pressure unit-cell at 240 K (Fortes *et al.* 2008) is 24 GPa, also in excellent agreement with *ab initio* calculations.



**Figure 2.** A comparison of the high-pressure mixed-phase data obtained in this study with, (i) the same material formed in RB820064 (top two diffraction patterns); (ii) the  $\text{P}2_12_12_1$  phase of epsomite at a similar pressure; (iii) the phase formed by compression of epsomite to 12 kbar. Clearly, the phase mixture we have produced,  $\text{MgSO}_4 \cdot n\text{D}_2\text{O}$  + ice VI does not contain any previously recognised phase of epsomite or high-pressure hydrate formed therefrom. Again, the red asterisk indicate the strongest peaks due to the Pb pressure calibrant.



### References

- Brand, H. E. A. (2009): Ph.D Thesis, University College London.  
Fortes *et al.* (2008): *Phys. Chem. Min.* **35**(4), 207-221.