

## THE PHASE BEHAVIOUR OF EPSOMITE ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) TO 50 KBAR: PLANETARY

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**Introduction:** Hydrated sulfate salts are important evaporite minerals on the Earth, and on Mars too, as well as being a candidate rock-forming mineral inside the icy moons of the outer solar system [see Ref. 1 for a review]. Hydrated magnesium sulfate salts have been proposed as the origin of the low-latitude neutron absorption features on Mars [2]; certainly magnesium sulfate salts have been observed in abundance by the Opportunity rover in Meridiani Planum [3]. The dehydration of  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$  (which we call Fritzsche's salt, after its discoverer) to epsomite has been mooted as the origin of global rifting and cryovolcanism on Ganymede [4], and the spectral signature of hydrated sulfate salts has been detected by the NIMS instrument aboard the Galileo spacecraft [5].

In order to be able to model the interiors of these icy moons, we are carrying out a program of investigation of epsomite and its related hydrates at high pressure [6]. Previously, we have studied deuterated epsomite to 5.5 kbar in a gas pressure cell, and observed no phase changes. Here we report the results of work to extend that pressure range by an order of magnitude, to 50 kbar, using an opposed anvil press mounted on the high-pressure beamline (PEARL/HiPr) at the ISIS neutron spallation source in the U.K. Such pressures are applicable to the deep interiors of large icy moons (likely core-mantle pressures are 15-20 kbar, and core pressures in large undifferentiated objects would be 35-40 kbar. Such pressures are also in the lower range of expected due to impact shock. Our aim in this experiment was to investigate the possible high-pressure polymorphism and dehydration reported by earlier workers [7,8].

**Experimental method:** Single crystals (ca. 5mm long) of deuterated epsomite, grown for our previous work, were extracted from their mother liquor, dried and powdered under air. The powder was loaded into TiZr gaskets of the encapsulated type [9], with 4:1 MeOD/EtOD as the pressure transmitting fluid, and mounted between the anvils of a Paris-Edinburgh pressure cell. In two separate loadings (one at 200 K, and one at room temperature) the load on the cell was increased in 3 tons increments from 7 tons to 49 tons. The  $\sim 80 \text{ mm}^3$  sample was observed by the time-of-flight neutron diffraction method, with data being collected for two hours at each point. At 49 tons, 200 K, the sample was warmed to 280 K in 20 K steps. Pressure on the sample was determined using a Pb foil

calibrant and the equation of state parameterised in Ref. 10.

**Results:** Along the 200 K isotherm, we observed no phase transformations up to the highest load (pressure), 49 tons (52.5 kbar). The two hour data collection time was adequate for determination of the unit cell parameters of epsomite using GSAS [11]. The refined unit cell volume as a function of pressure was fitted with a 3<sup>rd</sup> order Birch-Murnaghan equation of state (Fig. 1), yielding zero-pressure volume,  $V_0 = 965(2) \text{ \AA}^3$ , zero-pressure bulk modulus,  $K_0 = 250(10)$  kbar, and the first pressure derivative of the bulk modulus,  $K' = 2.0(3)$ . This is in excellent agreement with the values determined at 200 K from the gas cell work up to 5.5 kbar [6].

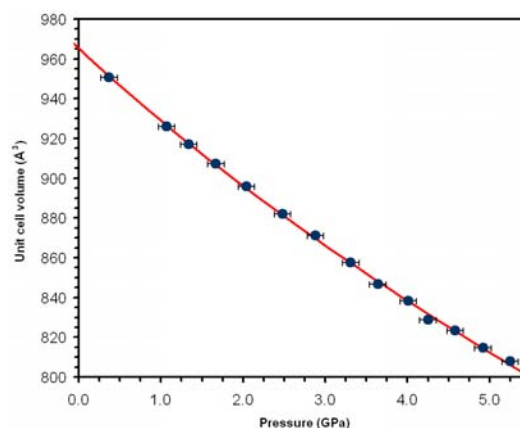


Figure 1. The refined unit cell volume of epsomite as a function of pressure at 200 K. The solid line is a 3<sup>rd</sup> order Birch-Murnaghan fit to the data with parameters quoted in the text.

At room temperature, we observed a series of polymorphic phase transitions upon compression (Fig. 2), broadly in agreement with existing piston-cylinder observations. Epsomite appears to undergo a very sluggish transition (or series of transitions) below 15 kbar; the diffraction patterns from the first and second hours of data collection at 10 and 13 tons are different. However, at 16 tons (14.7 kbar) the diffraction pattern has ceased to change, and remains stable up to 28 tons (28.1 kbar). This phase is probably the phase IV reported by Livshits *et al.* [8] and the phase seen from 15 – 25 kbar by Bridgman [7]. We have indexed the phase IV powder pattern with a monoclinic unit cell of

dimensions  $a = 5.9231 \text{ \AA}$ ,  $b = 5.6815 \text{ \AA}$ ,  $c = 6.1044 \text{ \AA}$ ,  $\beta = 90.769^\circ$ ,  $V = 205.41 \text{ \AA}^3$  (thus  $Z = 1$ , yielding  $V/V_0 = 0.84$  consistent with Bridgman's values [7]. Molecular symmetry limits the likely space-groups to P2 or Pm, and work is in progress to solve the structure.

It is apparent from the 10 ton and 13 ton data that at least one, and possibly two, intermediate phases exist, which would correspond to phases II and III of Livshits *et al.*, [8].

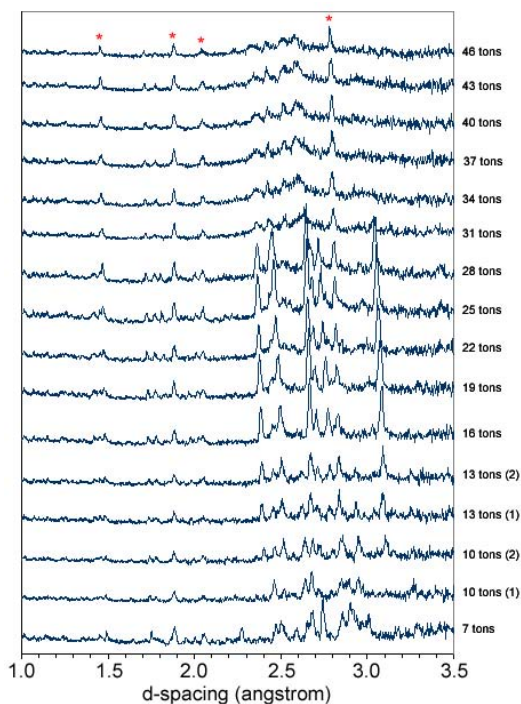


Figure 2. Neutron powder diffraction patterns from deuterated epsomite at room temperature as a function of the applied load on the pressure cell. Peaks marked with asterisks are due to the Pb pressure calibrant, and due to parasitic scattering from the anvils of the pressure cell (composed of tungsten carbide with a nickel binder).

The diffraction patterns from 31 – 46 tons exhibit a marked amorphous hump with some residual Bragg peaks. We interpret this as dehydration of the crystal with a lower hydrate (hexahydrate?) sitting in a liquid or glassy brine.

**Planetary implications:** The sluggish nature of the phase transitions, even at room temperature, leads us to believe that the high-pressure phases can be recovered metastably to ambient pressure at relatively high temperatures (probably  $\gg 200 \text{ K}$ ). If this is the case, then impact metamorphosed epsomite on Mars might be able to persist for long periods, providing a

useful shock pressure barometer. Similarly, on the surfaces of icy moons, there would seem to be no impediment to the survival of high-pressure phases in the very cold near-surface regolith. Since epsomite becomes dehydrated at a relatively low pressure of roughly 30 kbar, it is likely that the bedrock and highly shocked ejecta of impact craters on the icy Galilean moons will have been completely dehydrated: one should therefore expect to find the spectral signature of lower hydrates (the monohydrate, kieserite, or even anhydrous  $\text{MgSO}_4$ ) in the vicinity of impact craters.

If epsomite constitutes a major component of the mantles of the icy Galilean moons, then we would expect there to be phase transitions from the ambient pressure phase of epsomite to phases II and III at depths of  $\sim 450 \text{ km}$  and  $\sim 700 \text{ km}$ , respectively, based on the transition pressures reported by Livshits *et al.* [8]; we will be carrying out further work to study these phases in the near future. The higher-pressure phase IV would become stable at depths of  $\sim 900 \text{ km}$ . The work we have done provides the framework for further study of the high pressure polymorphs of epsomite, and determination of the volume change from the dehydration of Fritzsche's salt.

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