VOLUMETRIC AND OPTICAL STUDIES OF HIGH PRESSURE PHASES OF MgSO$_4$·H$_2$0 WITH APPLICATIONS TO EUROPA.
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Introduction: We report optical and volumetric measurements of a 17 wt.% sample of MgSO$_4$ in H$_2$O at high pressures using a volumetric cell with sapphire windows. Magnesium sulfate was chosen because it is a likely constituent of Europa's ocean and icy shell [1,2]. In addition, magnesium sulfate minerals are common terrestrial evaporite phases, and they also probably occur on Mars [3]. The 17wt.% composition is close to the eutectic composition at one atmosphere. Data runs at pressures from 0.2 MPa to 350 MPa, and temperatures from 230 K to 300 K were made. Eutectic melting points were measured, and visual movies of crystallization and melting were obtained over this pressure range.

Relation to previous work: This work extends our previous studies of MgSO$_4$·H$_2$O [4] to include optical imaging to identify phases and transitions more precisely, and to extend the pressure ranges over that reported previously [5]. This work also complements our work with the Na$_2$SO$_4$·H$_2$O system [6,7]. Experimental details are given in those references.

Experiments: This system has multiple hydrated states that must be considered. The two most important are MgSO$_4$·7H$_2$O (epsomite, indicated by MS7) and MgSO$_4$·11H$_2$O (MS11). (Historically, MS11 has been listed as MS12, but recent work by Peterson and Wang has identified the phase as MS11) [8]. At this concentration, MS11 is the stable state, but long-lived metastable states of MS7, and generally sluggish dynamics in the hydrated salt systems, make accurate measurements of phase boundaries challenging.

Results and Interpretation: Fig. 1 shows a plot of transducer voltage (approximately proportional to the sample volume) *vs*. temperature for a fairly typical data run at 50 MPa.

After pressurizing to 50 MPa with the sample a homogeneous liquid (point a, Fig. 1) we began cooling. After supercooling to 250 K (point b) a sharp increase in volume (voltage) indicated rapid crystallization of a low-density solid assemblage. Further cooling to point (c) produced the crystals shown in Fig. 2, which resemble images obtained by Fortes of pseudomorphs of MgSO$_4$·11H$_2$O (MS11) containing spherulitic needles of epsomite (MS7) [9]. The image is 2.0 mm across and has a resolution of about 1.5 μm/pixel. Further cooling to point (d) resulted in additional slow growth of those crystals, but no significant

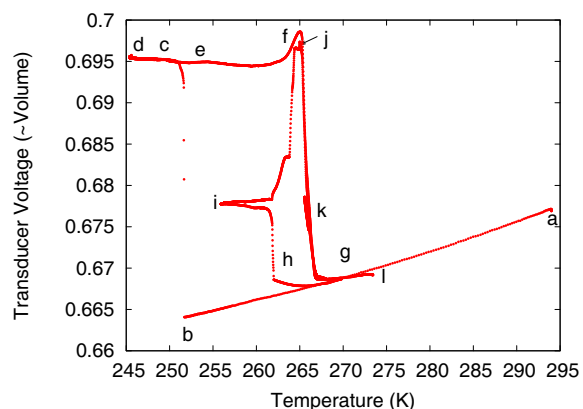changes. The upper portion of the image remained liquid throughout.
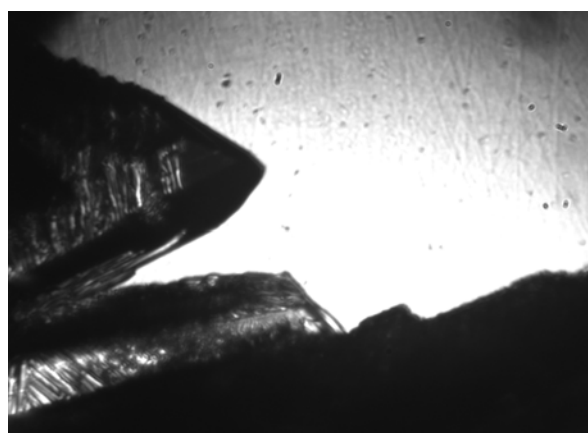

Figure 1: Experimental data run at 50 MPa

Figure 2: MgSO$_4$ hydrate crystals at 50 MPa.

At this point at least some portions of the sample were frozen solid so that the voltage and pressure transducers did not accurately reflect conditions inside the sample. Further warming brought the sample to point (f), where eutectic melting commenced with a large drop in voltage (volume). Eutectic melting ended with the voltage slightly above the original cooling curve due to a small residual mass of solid material. This dissolved on a liquidus curve at point (g) in Fig. 1, approaching the cooling curve from above. This part of the graph may suggest that pressure shifts the eutectic in the water-rich direction, as was ob-

served earlier[4]. If so, the residual material would be a sulfate hydrate, presumably MS7 or MS11. The solid material that is dissolving appears to slump downward, as expected for a solid that is denser than the ambient liquid.

Before all the crystals had dissolved, the sample was cooled again, and by point (h) large faceted crystals were observed. These appear to be a sulfate hydrate, MS11, MS7, or perhaps a different one. After point (h), there was again rapid crystallization, presumably involving considerable Ice I. At times, the Ice I grew as dendrites out ahead of the faceted crystals. Upon warming, the eutectic transition occurred at the same temperature as before. To confirm the reversible nature of the transition, we cooled slightly and re-warmed, generating a loop at point (k). Final melting on the liquidus was also duplicated.

Other runs at pressures of 200 MPa and below, for which ice I is the stable ice phase, showed many similarities and some differences when compared with this run at 50 MPa. In most cases the initial supercooling led to a very rapid transition that turned the camera image from clear to black in one time step and prevented us from seeing any structure such as that in Fig. 2 in the rapidly growing solid. In other runs, dendrites that we hypothesized to be ice I are seen to be engulfed by a rapidly growing fine-grained solid that may be a eutectic mixture of hydrate and ice crystals. In all the data runs from 50 to 200 MPa, the last solid phase dissolved along a liquidus in the same fashion as described above for the 50 MPa run.

Preliminary results for the eutectic temperature as a function of pressure are shown in Fig. 3.
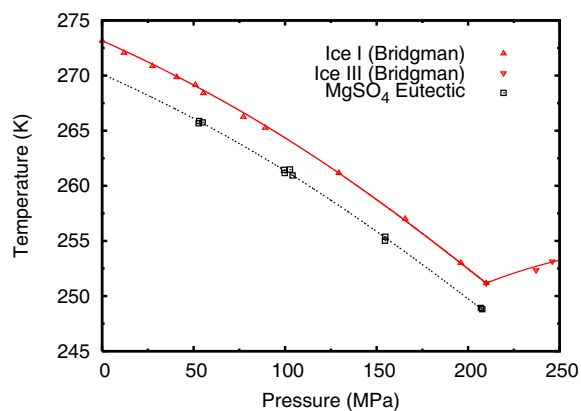

Figure 3: Eutectic temperatures for 17wt.% solutions of magnesium sulfate. Shown for comparison are the Ice I and Ice III data of Bridgman [10].

Discussion: The freezing point depressions of the eutectic in this chemical system are generally larger than those observed for sodium sulfate. The difference
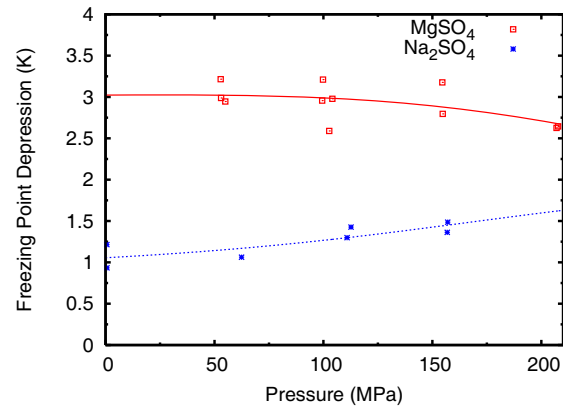

Figure 4: Freezing point depression as a function of pressure for magnesium sulfate. Shown for comparison are our earlier results for sodium sulfate [7].

between the ice and eutectic temperatures increases with increasing pressure for the sodium sulfate, but it does not appear to do so for magnesium sulfate. Additional data are needed to confirm the apparent decrease in Fig. 4; however, a slight decrease in freezing point depression would be consistent with the observation above that the eutectic composition appears to shift slightly in the water-rich direction with increasing pressure. Thus, eutectic melt compositions will be sensitive to pressure and depth of origin, just as basaltic melt compositions on Earth depend on pressure and depth of partial melting. In the ternary system, H_2O-Na_2SO_4-$MgSO_4$, we expect that the combined effect of these pressure-induced shifts in the binaries will be to increase the ternary eutectic's abundance of sodium sulfate, and decrease that of magnesium sulfate, as pressure increases. Hence, eutectic melts in this system will be pressure and depth sensitive. Ocean compositions, for example, may be dependent on the pressure and depth of the ocean.

Finally, within a given satellite, the ascent of ternary sulfate brines in dikes or diapirs will tend to precipitate sodium sulfates first and the liquid will evolve toward more magnesian compositions as cooling and freezing progressively takes place during ascent.

References: [1] McCord, T.B. *et al*. (1998) *Science, 280*, 1242. [2] Kargel, J.S. *et al*. (2000) *Icarus 148,* 226-265. [3] Squyres, S.W. *et al*. (2004) *Science, 306*. [4] Hogenboom, D.L. *et al*. (1995) *Icarus 115*: 258-277. [5] Hogenboom, D.L. *et al*. *LPS XXXVI*, Abstract #1825. [6] Hogenboom, D.L. *et al*. *LPS XXX*, Abstract #1793. [7] Dougherty, A. J. *et al*. *LPS XXXVII*, Abstract #1732. [8] Peterson, R.C. and Wang, R. (2006) *Geology 34*, 957-960. [9] Fortes, A. D., private communication. [10] Bridgman, P.W. (1911) *Proc. Amer. Acad. Arts Sci. 47*, 441.