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PHASE EQUILIBRIA OF THE MAGNESIUM SULFATE-WATER SYSTEM TO 4 KBARS

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Introduction. Magnesium sulfate is the most abundant salt in carbonaceous chondrites [1], and may be important in the low-temperature igneous evolution and aqueous differentiation of icy satellites and large chondritic asteroids [2]. Accordingly, we are investigating high-pressure phase equilibria in $\text{MgSO}_4\text{-H}_2\text{O}$ solutions under pressures up to four kbars. An initial report was presented two years ago [3]. This abstract summarizes our results to date including studies of solutions containing 15.3%, 17%, and 22% MgSO_4 . Briefly, these results demonstrate (1) that increasing pressure causes the eutectic and peritectic compositions to shift to much lower concentrations of magnesium sulfate, and (2) the existence of a new low-density phase of magnesium sulfate hydrate.

Experimental. The experiment was conducted with the same apparatus and techniques described previously [3]. The pressure vessel and ~ 2.6 ml of enclosed sample were pressurized by additional sample through small-bore tubing which connected the vessel to a mercury u-tube maintained at 30°C . The sample was cooled to the desired temperatures using a liquid nitrogen bath. Volume changes of the sample were measured by a sensitive transducer that produced a voltage proportional to the displacement of mercury in the u-tube. The temperature of the sample was measured by a thermometer strapped to the outside of the vessel. Recent improvements in the experiment will allow the subsolidus region to be explored in future runs. A deformable sample cell has been developed to go inside a new pressure vessel surrounded by a pressure transmitting fluid. This should eliminate the problem of the vessel "locking up" when the sample freezes [3]. A new thermometer in an armored probe will permit the temperature of the sample to be measured directly with greater sensitivity and more rapid response.

Results. Fig. 1 illustrates the phase diagram of the system $\text{H}_2\text{O-MgSO}_4$ system at 1 atm (from [2]). This system exhibits four magnesium sulfate hydrates, of which dodecahydrate (hereafter, MS12) and epsomite (MS7), plus an unidentified new hydrate, occur in these experiments. These experiments also have encountered a eutectic and a peritectic which, at 1 atm, occur near 17% and 21.1% MgSO_4 , respectively. Our earlier report showed two examples of experimental runs, one for a 15.3% solution at 2000 bars (below the ice transition pressure) and the other for a 17% solution at 3460 bars (above the transition). Figs. 2 and 3 of this report show two more runs, including a 17% mixture at 3800 bars and a 22% mixture at 2950 bars. The voltages plotted in these figures are almost linearly related to sample volume. The runs shown in Figs. 2 and 3 were conducted above the ice I / ice II transition pressure, so that the frozen samples apparently consist of ice II and MS12. Both frozen mixtures are denser than their equivalent liquids, as indicated in Figs. 2 and 3.

The 17% sample melts in four stages at 3800 bars including two nearly temperature-invariant transitions and two univariant stages (Fig. 2). The invariant transitions are equated with the eutectic and peritectic, designated 'E' and 'P1', respectively, in Fig. 1. The fact that the 17% sample seems to undergo peritectic melting indicates that the peritectic shifts to the water-rich side of 17% MgSO_4 at 3800 bars. In [3] we indicated a similar compositional shift for the eutectic. These compositional shifts result from pressure-induced depression of the ice liquidus temperature and an elevation of the liquidus of the denser phases, MS12 and MS7. The sloping curve between the eutectic and peritectic in Fig. 2 apparently corresponds to MS12 melting along the liquidus between 'E' and 'P1' in Fig. 1. MS 7 appears to be the final, high-temperature liquidus phase.

Fig. 3, in addition to showing the eutectic, also shows that the last solid to melt has a density lower than the liquid's density. This phase cannot be ice II because it completely melts above 275 K. A hitherto unknown magnesium sulfate hydrate, containing over twelve molecules of water, is the only alternative because MS7 and MS12 are denser than the liquid. This phase has been observed on several runs. There are indications that this phase either is metastable or has a very restricted stability.

Fig. 4 shows the eutectic and peritectic temperatures for MgSO_4 solutions. The eutectic curve apparently represents pressure melting of mixtures of MS12 and ice I or ice II. The short-dashed curve represents the peritectic reaction (P1 in Fig. 1), and the long-dashed 'metaeutectic' curve probably represents melting of metastable mixtures of MS7 and ice; the metaeutectic often is encountered at 1 atm when melting rapidly-frozen MgSO_4 solutions.

Conclusions. The eutectic and peritectic ('E' and 'P1' in Fig. 1) shift to substantially lower salinities under increasing pressures up to four kbars. This indicates that magnesium sulfate would be more likely to

MAGNESIUM SULFATE-WATER SYSTEM: Hogenboom, D.L., et al.

remain as a residual solid in the interiors of icy satellites, contrary to predictions of models based on phase equilibria at 1 atm [2]. Therefore, all briny lavas should be saturated with $MgSO_4$. These experiments have also detected a relatively low density magnesium sulfate hydrate, but the stoichiometry, stability limits, and other properties of this phase have not yet been determined.

References. [1] Fredriksson, K. and J.F. Kerridge 1988, *Meteoritics* 23, 35-44. [2] Kargel, J.S. 1991, *Icarus* 94, 368-390. [3] Hogenboom, D.L. et al., 1991, *Lun. Planet. Sci.* XXII, 581-582.

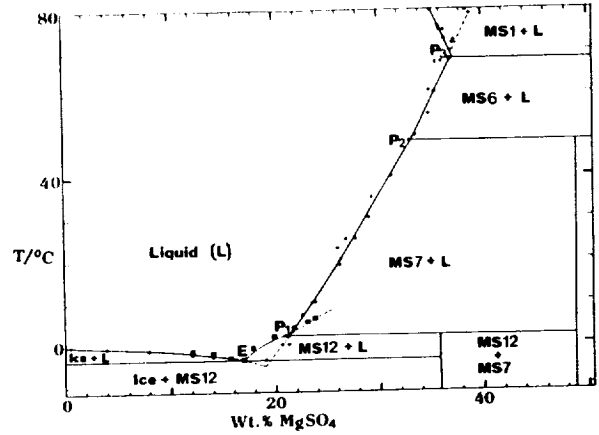


Figure 1. Phase diagram of the magnesium sulfate-water system at 1 atm (from [2]). MS1 refers to $MgSO_4 \cdot 1H_2O$; MS6, $MgSO_4 \cdot 6H_2O$; MS7, $MgSO_4 \cdot 7H_2O$; and MS12, $MgSO_4 \cdot 12H_2O$.

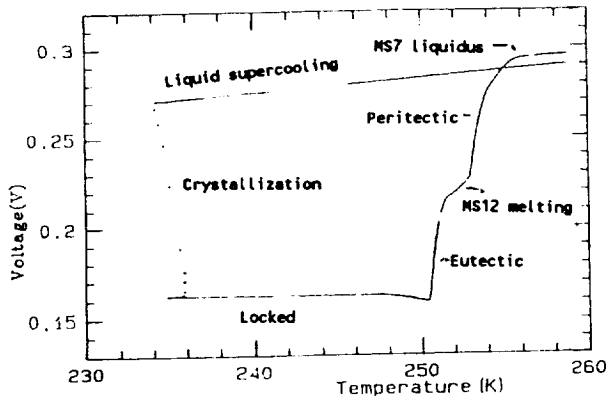


Figure 2. Experimental run at 3800 bars and 17% $MgSO_4$ solution.

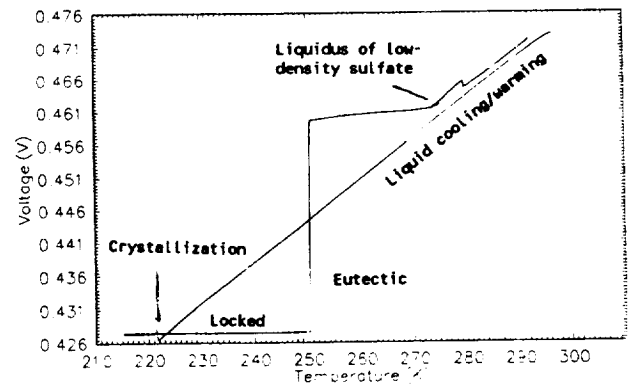


Figure 3. Experimental run at 2950 bars and 22% $MgSO_4$ solution.

Figure 4. Melting points of magnesium sulfate mixtures.

