EVAPORATION KINETICS OF LIQUID MAGNESIUM SULFATE BRINES UNDER SIMULATED MAR-TIAN SURFACE PRESSURE. T. S. Altheide[1], V. F. Chevrier[1], and J. Denson[2]. [1]W. M. Keck Laboratory for Space Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR, 72701, talthei@uark.edu. [2]Department of Biological Sciences, Science and Engineering 601, University of Arkansas, Fayetteville, AR, 72701.

Introduction: Despite the hostile surface conditions on Mars, various features have been observed which suggest the activity of liquid water [1,2]. In addition, abundant hydrated and water-related minerals have been detected on the surface which also speaks to a wet past [3,4]. It has been suggested that to account for such activity, liquid water could be stabilized at the surface by the presence of solutes, which would suppress the freezing point of liquid water [5]. Through simulated experiments, it has been shown that lower temperature brines may have significantly lower evaporation rates than that of pure liquid water [6].

Recent observations of the martian surface have detected large deposits of magnesium sulfate ($MgSO_4$) [7,8]. Also, experimental studies have reported have shown that $MgSO_4$ hydration states are quite complex and highly dependent on temperature and water vapor pressure, and that various phases should be expected on Mars [9,10]. However, no experiment so far has investigated the stability of magnesium sulfate solutions on the surface of Mars. Here, we present work on low pressure evaporation kinetics of magnesium sulfates.

Methods and Materials: Liquid magnesium sulfate solutions were prepared at 5, 10, 15, 20, and 25 wt %. Each concentrated solution was evaporated under 7 mbar of CO_2 pressure in the Andromeda Simulation Chamber, in either high or low humidity.

Andromeda Chamber Testing: The chamber was initially evacuated by lowering the pressure to about 0.50 torr (or 0.67 mbar). The chamber was then filled with 1 atm of pure CO_2 gas, and the temperature was lowered to below 0°C using a methanol/dry ice slurry circulated around the outside the chamber. The magnesium sulfate solution was then placed into the chamber, which is carefully pumped back down to 6 mbar. Twenty minutes after pressure was reached, data collection started.   During each experimental run, the pressure was maintained between 5 and 7 mbar.

Data Analysis: For high humidity experiments, the humidity in the chamber was allowed to build-up in order to test the model using the specific interaction theory (SIT). The evaporation rate of each solution (in mm h^{-1}) were determined using the mass lost from the surface of each sample during low pressure simulation and using the density of each brine. The Pitzer ion interaction model was used to determine the activity of water and the precipitation of salt in solution.

Results: Table 1 displays the testing data of $MgSO_4$ solutions, ranging from $5 - 25$ wt% sulfate, during low-pressure exposure in the chamber. Both high humidity and low humidity test solutions are shown. Mass lost was observed for each sulfate sample as it was exposed to ~7 mbar of CO_2 for approximately (Figure 1). From the mass loss, we determined the evaporation rate (mm h^{-1}) each solution tested. Figure 2 shows the determined evaporation rate of various low-humidity $MgSO_4$ solutions at the corresponding surface sample temperature during evaporation in the Andromeda Chamber. This demonstrates a clear view of the effect of sample temperature on the resulting evaporation rate.

Table 1: Characteristics of $MgSO_4$ solutions tested in low-pressure simulation chamber. Densities were measured before testing. Evaporation rate (in mm h^{-1}) was determined using slope of mass loss, density, and surface area from each sample.

Sample	Density (g/cm³)	Evaporation Rate (mm/hr)	Ave. Sample Temp. (°C)	Ave. Pressure (mbar)	Beginning Humidity	Ending Humidity
25% MgSO₄	1.27	0.056	0.76	5.24	7.97	23.19
25% MgSO₄	1.27	0.092	-1.39	5.24	10.39	15.79
25% MgSO₄	1.27	0.043	-1.22	5.22	0.69	0.05
25% MgSO₄	1.27	0.080	-0.84	5.23	3.55	0.25
20% MgSO₄	1.21	0.068	-3.28	5.25	7.87	15.68
20% MgSO₄	1.21	0.337	-5.43	5.23	5.38	1.89
20% MgSO₄	1.21	0.114	-4.80	5.27	28.77	19.47
20% MgSO₄	1.21	0.229	-7.53	5.22	17.66	42.37
20% MgSO₄	1.21	0.422	-4.60	5.22	27.3	0.80
15% MgSO₄	1.17	0.559	-7.99	5.23	3.46	0.61
15% MgSO₄	1.17	0.204	-6.45	5.26	10.41	18.49
15% MgSO₄	1.17	0.241	-8.45	5.24	20.08	19.44
15% MgSO₄	1.17	0.154	-10.09	5.24	16.24	34.4
10% MgSO₄	1.11	0.669	-6.77	5.20	28.20	37.88
10% MgSO₄	1.11	0.573	-11.04	5.24	6.26	2.17
5% MgSO₄	1.06	0.389	-5.82	5.24	8.59	9.04
5% MgSO₄	1.06	0.245	-4.98	5.25	16.64	47.08
5% MgSO₄	1.06	0.331	-5.67	5.23	43.34	53.34
5% MgSO₄	1.06	0.270	-5.85	5.24	15.09	49.84

Discussion and Conclusions: Observation of the data shows that sulfate concentration has a marked effect on the subsequent evaporation rate of solution at martian surface pressure, at least at higher concentrations (Figures 1 and 2). The effect of sulfate concentration, i.e. ion concentration, may be explained through use of the Pitzer ion interaction model, which

is used to describe interactions involving more than one ion in solution. In addition, the Pitzer model may be used to calculate water activities in solution and the resulting evaporation rates at any temperature (Figure 3). This then can be applied to the evaporation data obtained for the magnesium sulfates to determine water activity in the brine solution.
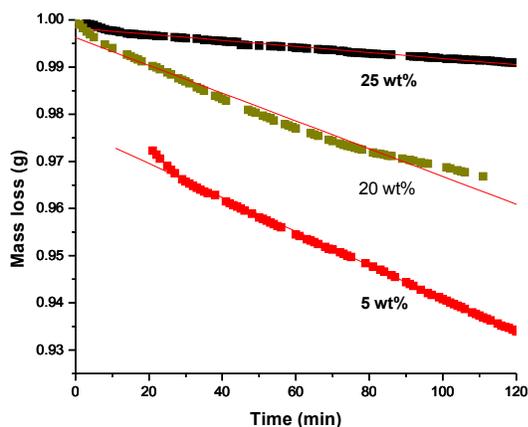

Figure 1: Mass loss slopes of 25, 20, and 5 wt% sulfate solutions under approximately 7 mbar of pressure.
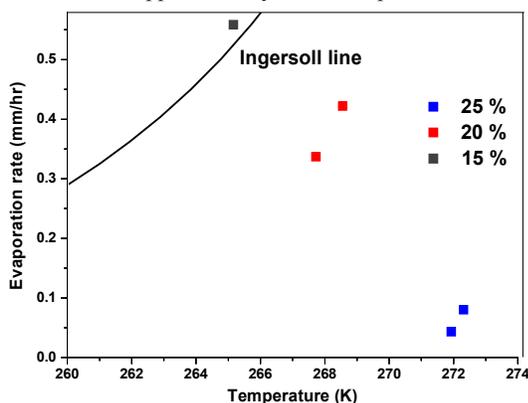

Figure 2: Evaporation of 10 – 25 wt% $MgSO_4$ solutions as a function of each solutions surface temperature. During testing, the humidity inside the chamber was kept at approximately 5% and below (see Table 1). The black line is the Ingersoll line for pure water.

The precipitation of salt, i.e. $MgSO_4 \cdot 7H_2O$ (epsomite, MS7) or $MgSO_4 \cdot 12H_2O$ (MS12) was also considered in the Pitzer model. When cooling a solution at appropriate concentration the first phase to crystallize is MS7. At the first peritectic point (T = 1.8°C) MS12 should crystallize. However, for kinetics reasons due to the higher difficulty to incorporate 12 molecules of water rather than 7 in the crystalline structure, MS7 continues to crystallize until the metastable eutectic point E' [11]. As the starting composition is at the metastable eutectic, the solution does not contain any

solid. During the evaporation of water, both MS7 and MS12 are susceptible to crystallize. Therefore, we considered both phases in the calculations. Their main effect is to decrease the amount of water available for evaporation, as each mole of crystallizing MS7 or MS12 takes 7 or 12 moles of water, respectively. The result is a lower apparent molality of water than the real molality of water if only $MgSO_4$ is considered. Calculations of both MS7 and MS12 for a 20 wt% solution give good fit of the data during the first 130 mn, even if the MS12 curve shows a slightly better fit than MS7 (Figure 3). MS12 may then be the main crystallizing phase during the first 130 minutes of evaporation.
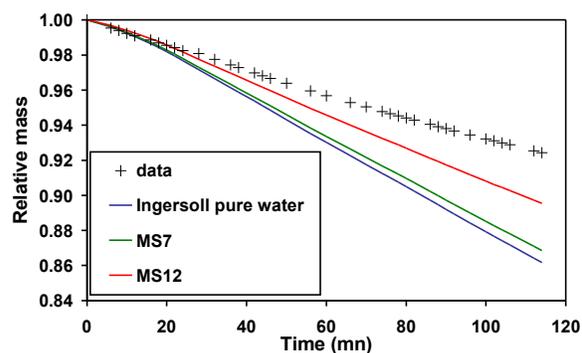

Figure 3: Relative mass loss of a 20 wt% brine solution, with calculated rates for both epsomite (MS7) and $MgSO_4 \cdot 12H_2O$.

Conclusions: Our results suggest that thermodynamics and phase transitions are important parameters for the evaporation of water. Also, formation of crusts during crystallization provides also a very efficient barrier to water evaporation, contributing significantly to the stabilization of brines. Therefore, martian ponds highly enriched in sulfate brines could last for much longer than previously thought, even in the highly unfavourable present day conditions.

References: [1] Heldmann, J.L. et al. *JGR 110*, 2005. [2] Malin, M.C. and Edgett, K.S. *Science 288*, 2000. [3] Bibring, J.P et al. *Science 312*, 2006. [4] Squyres, S.W. et al. *Science 306*, 2004. [5] Brass, G.W. *Icarus 42*, 1980. [6] Sears, D.W.G. and Chittenden, J.D. *GRL 32*, 2005. [7] Gendrin, A. et al. *Science 307*, 2005. [8] Rieder, R. et al. *Science 306*, 2004. [9] Chipera, S.J. and Vaniman, D.T. *GCA 71*, 2007. [10] Chou, I.M. and Seal, R.R. *JGR 112*, 2007. [11] Kargel, J.S. *Icarus 94,* 1991.