

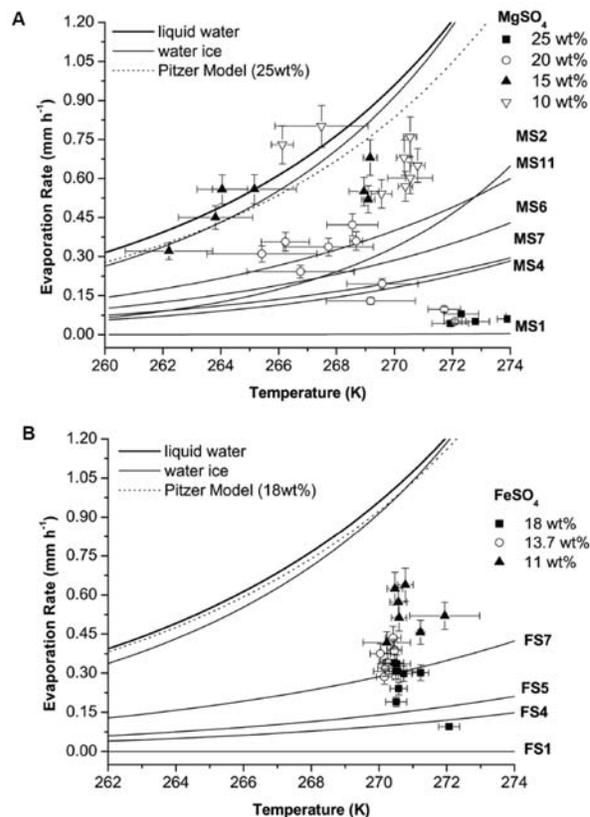
**EVAPORATION OF SULFATE AND CHLORIDE BRINES ON THE SURFACE OF MARS.** T. S. Altheide<sup>1</sup>, V. F. Chevrier<sup>1</sup>, J. Denson<sup>2</sup>, and C. Nicholson<sup>3</sup>. <sup>1</sup>W. M. Keck Laboratory for Space Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR, 72701, [talthei@uark.edu](mailto:talthei@uark.edu). <sup>2</sup>Department of Biological Sciences, Science and Engineering 601, University of Arkansas, Fayetteville, AR, 72701. <sup>3</sup>Department of Chemistry, University of Arkansas, Fayetteville, AR, 72701.

**Introduction:** Despite the low temperature and pressure surface conditions on Mars, various features have been observed which suggest the activity of liquid water [1]. 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 [2]. Through simulated experiments, it has been shown that lower temperature brines may have significantly lower evaporation rates than that of pure liquid water [1, 3]

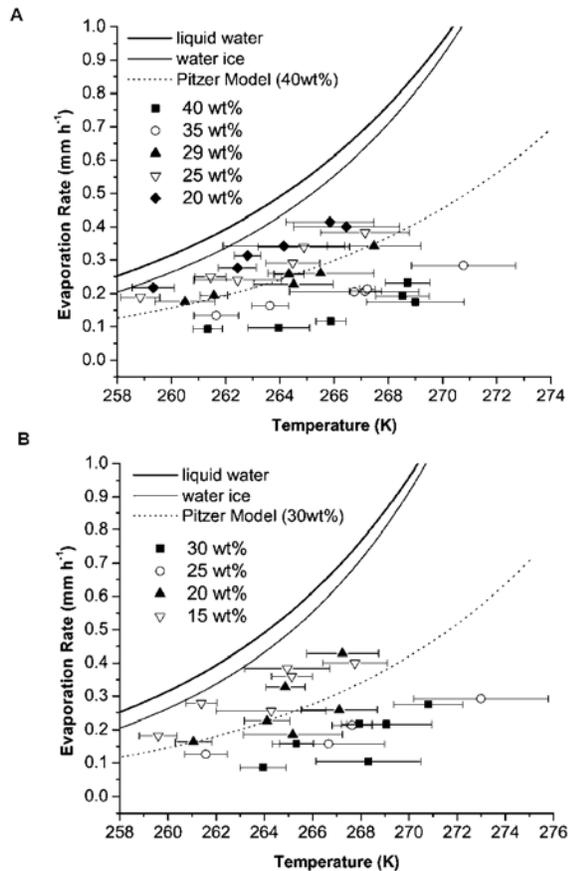
Recent observations of the martian surface have detected large deposits of sulfates, as well as those of chlorides [4, 5]. Also, experimental studies have shown that  $\text{MgSO}_4$  hydration states are quite complex and highly dependent on temperature and water vapor pressure, and that various phases should be expected on Mars [6]. 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 sulfate and chloride solutions.

**Methods and Materials:** Liquid magnesium and ferrous sulfate, and ferric and magnesium chloride solutions were prepared and then evaporated under 7 mbar of  $\text{CO}_2$  pressure in the Andromeda Simulation Chamber. The chamber was initially evacuated by lowering the pressure to about 0.50 torr s. The chamber was then filled with 1 atm of pure  $\text{CO}_2$  gas, and the temperature was lowered to below  $0^\circ\text{C}$  using a methanol/dry ice slurry circulated around the outside the chamber. The salt solution was then placed into the chamber, which was 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.

**Results:** Mass loss was observed for each sample as it was exposed to  $\sim 7$  mbar of  $\text{CO}_2$ . From the mass loss, we determined the evaporation rate ( $\text{mm h}^{-1}$ ) for each solution tested. Figure 1 shows the determined evaporation rate of magnesium and ferrous sulfate solutions, while Figure 2 displays the evaporation rates of ferric and magnesium chloride brines, at the corresponding surface sample temperature during evaporation in the Andromeda Chamber.



**Figure 1.** Evaporation rates (in  $\text{mm h}^{-1}$ ) of (A)  $\text{MgSO}_4$  and (B)  $\text{FeSO}_4$  brines as a function of sample temperature. Error on the evaporation rate is 10%, supported from previous evaporation studies [1]. The thick black lines in each graph are the theoretical evaporation curves for pure liquid water [2]. The thin black lines are the modeled sublimation curve of water ice [2, 7]. The dotted lines are the theoretical evaporation rates of the highest concentration tested, 25 wt% for  $\text{MgSO}_4$  and 18 wt% for  $\text{FeSO}_4$ , calculated using the Pitzer model [8]. The other labeled black lines in each graph represent the theoretical evaporation rates of various magnesium and ferrous sulfate phases during crystallization of hydrates, depending on the hydration of the salt. Thermodynamic reaction constants for  $\text{FeSO}_4$  and  $\text{MgSO}_4$  were calculated from literature values [9-11]. MS = magnesium sulfate and FS = ferrous sulfate

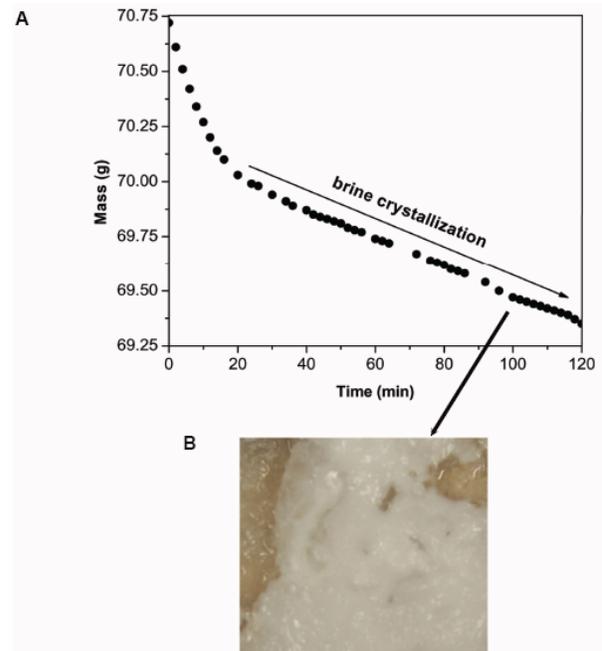


**Figure 2.** Evaporation rates (in  $\text{mm hr}^{-1}$ ) of (A)  $\text{FeCl}_3$  and (B)  $\text{MgCl}_2$  solutions as a function of sample temperature. Error on the evaporation rate is 10%, supported from previous evaporation studies [1]. The thick black lines are the theoretical evaporation of pure liquid water [2]. The thin black lines are the modeled sublimation rate of water ice [2, 7]. The dotted lines in each graph are the theoretical evaporation of the highest concentration tested, 40 wt% for  $\text{FeCl}_3$  and 30 wt% for  $\text{MgCl}_2$ , calculated using the Pitzer model [8].

**Discussion:** The data show that sulfate and chloride 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 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 (Figures 1 and 2).

For the sulfate brines tested, saturated samples displayed salt crystallization during evaporation. The effect of salt precipitation on the mass loss of a sample can be seen in Figure 3A. An image of the resultant precipitated salt is shown in Figure 3B. When a brine

crystallizes, the evaporation rate of the solution is lowered because the phase which precipitates out is hydrated.



**Figure 3.** (A) Observed mass loss of 20 wt% magnesium sulfate solution during two hours of exposure to 7 mbar of  $\text{CO}_2$ . The slope change at 20 min is attributed to the onset of sulfate crystallization. (B) Image of white sulfate crust formed during the 20 wt% magnesium sulfate experiment.

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

**References:** [1] Chevrier, V. and T. Altheide, (2008) *GRL* 35, L22101. [2] Ingersoll, A. P., (1970) *Science* 168, 972-973. [3] Sears, D. W. G. and S. R. Moore, (2005) *GRL* 32, . [4] Gendrin, A., *et al.*, (2005) *Science* 307, 1587-1591. [5] Osterloo, M. M., *et al.*, (2008) *Science* 319, 1651-1654. [6] Chipera, S. J. and D. T. Vaniman, (2007) *GCA* 71, 241-250. [7] Murphy, D. M. and T. Koop, (2005) *Quart. J. R. Meteor. Soc.* 131, 1539-1565. [8] Pitzer, K.S., (1991). [9] Chou, I.-M. and R. R. Seal, (2007) *JGR* 112, E11004. [10] DeKock, C. W., (1986) *U.S. Dept. of the Interior, Bureau of Mines* 59 p. [11] Hemingway, B. S., *et al.*, (2002) *U.S. Geological Survey Open-File Report 02-161* .