CHARACTERISTICS AND STABILITY OF CHLORATE SALT SOLUTIONS WITH APPLICATIONS TO MARS. D. Berget[1], J. Hanley[2], and V. F. Chevrier[2], [1]Drake University, 2507 University Ave, Des Moines, IA 50311, djb002@drake.edu, [2]Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701.

Introduction: Although there has been little evidence for water on the surface of Mars [1], there is indirect evidence for liquid water that comes from recent gully formation, which suggests the presence of liquid water processes near the surface [2, 3]. However, pure water is unstable in its liquid form due to the low pressures and temperatures associated with the Martian surface, so water is likely to be kept frozen and sublimating, or evaporating if liquid [4]. Brines or salt-rich solutions composed of $Mg(ClO_4)_2$ or other chlorate salts have been suggested since they are known to lower the freezing point and evaporation rates [5].

Recent results from NASA's polar lander Phoenix have suggested the presence of perchlorates in the soil surrounding the landing site [6]. It is likely that these ions associate with either sodium or magnesium [7]. Between chloride (Cl oxidation state of -1) and perchlorate (oxidation state +7), three other ions exist: hypochlorite ClO^- (+1), chlorite ClO_2^- (+3) and chlorate ClO_3^- (+5). These ions may be present (and undetected) at the Phoenix landing site as intermediate species of the processes leading to perchlorates. Very little is known regarding the behavior of these salts in solution, especially at low temperatures. Through evaporation experiments and determination of the eutectic temperatures, we have studied the stability of chlorates in a simulated Martian environment.

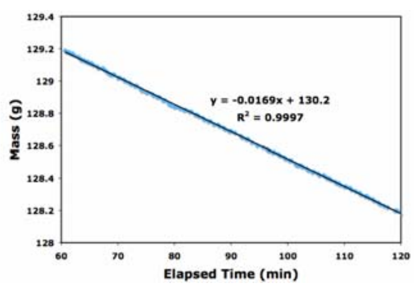

Figure 1. Mass loss of 50 wt% $NaClO_3$ at 265 K. A regression equation gives the slope of mass loss over time, which is then used to calculate the evaporation rate.

Experimental: *Evaporation Experiments.* Evaporation experiments were performed in a Martian simulation chamber using previously described methods [8]. Samples of $NaClO_3$ solutions at various concentrations (~20 to 50 wt%) are placed into a chilled CO_2 atmosphere (~263 K), which is then pumped down to Martian pressure (7 mbar). Using a precision balance, the mass loss rate was then measured (Fig. 1) and converted into evaporation rate (mm h^{-1}) using the following formula:

$$E = \frac{\Delta m / \Delta t \, S}{\rho_{sol}}$$

where $\Delta m/\Delta t$ is the mass loss rate, S is the surface area of the sample and ρ_{sol} is the density of the solution.

Eutectic Experiments. Eutectic temperatures were determined by freezing a small amount (~2-3 mL) of the solution between two copper plates enclosed in a polystyrene cell. As the solution melted, we monitored the resistivity and conductivity between the copper plates, watching for a discontinuity in the rate of change. Knowing the frozen solution will have high resistivity that will decrease as the solution melts, the discontinuity represents a phase change, and the temperature at which the discontinuity occurs is taken to be the eutectic temperature.

Results: *Evaporation Experiments.* At temperatures between 256 and 267 K, evaporation rates of sodium chlorate (Fig. 2) range from 0.141 mm h^{-1} (50 wt% concentration at 258 K) to 0.443 mm h^{-1} (20 wt% concentration at 264 K). As seen in previous studies, evaporation rate is dependent both directly on the temperature and inversely on the concentration of the solution [5, 8]. For instance, the evaporation rate of a 50 wt% solution ranges from 0.141 to 0.325 mm h^{-1} over a temperature range of 9 K. The evaporation rate is also dependent on chlorate concentration: at 265 K, the 20 wt% sodium chlorate evaporates at 0.443 mm h^{-1} while the 50 wt% evaporates at 0.284 mm h^{-1}.

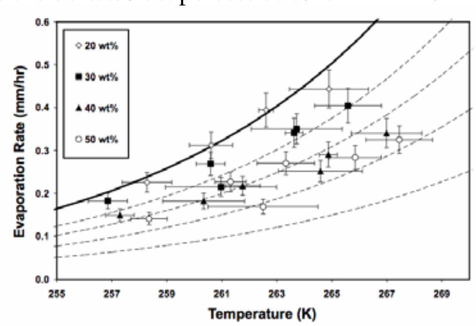

Figure 2. Evaporation rate of $NaClO_3$ as a function of sample temperature and concentration. Dashed lines are theoretical evaporation rates for each concentration, calculated from a modified Ingersoll [4] equation and Pitzer model. The solid line is for pure supercooled liquid water.

Eutectic Experiments. Eutectic temperatures of the salts in question have been determined theoretically, making experimental validation necessary for this study. We have found the following eutectic points from the conductivity of the melting solutions (Fig. 3): 219 K for 44 wt% $Mg(ClO_4)_2$; 240 K for 52 wt% $NaClO_4$; 247 K for 39 wt% $NaClO_3$; 232 K for 40 wt% $NaClO_2$; and ~ 252 K for 13 wt% NaClO.

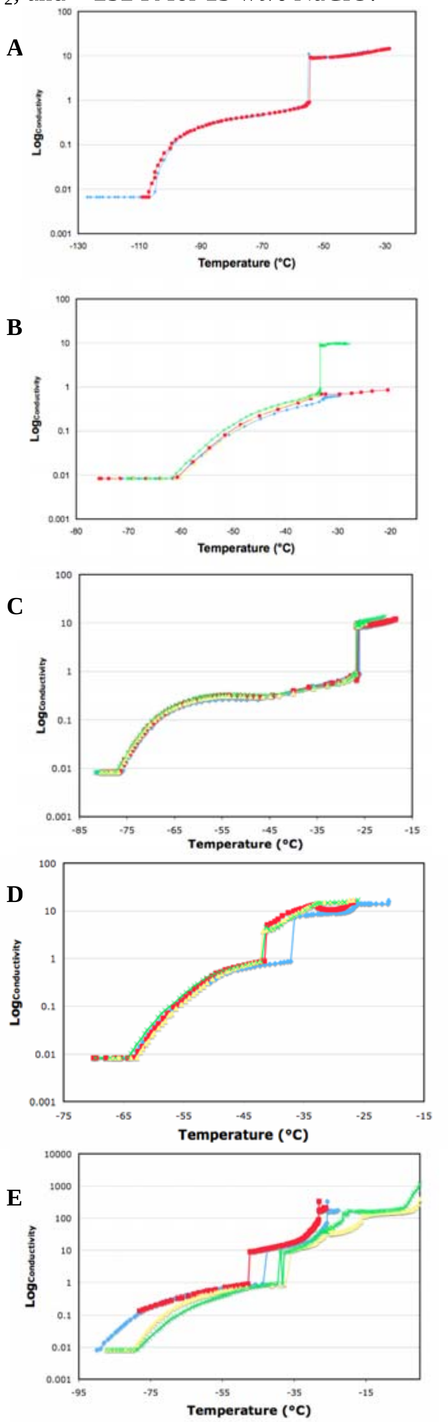

Figure 3. Logarithmic plot of conductivity of (A) $Mg(ClO_4)_2$, (B) $NaClO_4$, (C) $NaClO_3$, (D) $NaClO_2$, and (E) NaClO as a function of sample temperature.

Discussion: *Sodium Chlorate Evaporation.* The results of our evaporation experiments have shown that evaporation rates have a direct relationship with the temperature of the solution and an inverse relationship with the concentration. These results also indicate that $NaClO_3$ in a liquid water solution with a depth of 1 m could last approximately 222 sols at 256 K and 125 sols at 267 K on Mars, assuming the atmospheric conditions remained relatively consistent.

Eutectic Experiments. Few data are available from low-temperature experiments with chlorate salts. Previous calculations have concluded that the eutectic temperature for $Mg(ClO_4)_2$ is much closer to 206 K than we have experimentally found [5]. The consistency of our results suggests that either theoretical determinations of the eutectic temperature were incorrect, or there is a phase change at this temperature that no study has predicted. Calculated eutectic temperatures for the $NaClO_4$ and $NaClO_3$ solutions seem to be in good agreement with the experimental data we have obtained, and the consistency of the results reinforces their credibility.

The results from the $NaClO_2$ and NaClO tests are complicated by purity of the salts. Because the hypochlorite melting point is at room temperature, the salt must be kept in solution with water, sodium chloride, and possibly sodium chlorite and chlorate. The sodium chlorite is only 80% pure, and mixed with NaCl and other compounds. Determining the exact make-up of these salt solutions would be a great step in the direction toward solidifying their properties and stability.

Conclusions: The evaporation rates of $NaClO_3$ are similar to that of $NaClO_4$, but higher than those of $Mg(ClO_4)_2$. The magnesium perchlorate also has a much lower eutectic temperature, which, along with its low evaporation rates, suggests that it should be the dominant liquid phase at the Phoenix landing site. The $NaClO_2$ and NaClO solutions require further study, as both have intermediate eutectic temperatures and could also be interesting avenues upon which to pursue this research further.

References: [1] Smith, P. H. et al. (2009), *Science, 325*, 58-61. [2] Malin, M. C., and K. S. Edgett (2000), *Science, 288*, 2330– 2335. [3] Malin, M. C., et al. (2006), *Science, 314*, 1573–1577. [4] Ingersoll, A. P. (1970), *Science, 168*, 972-973. [5] Chevrier, V. F. et al. (2009), *GRL, 36*, L10202, doi:10.1029/2009GL037497. [6] Hecht, M. H. et al. (2009*) Science* **325**, 5936, pp. 64-67. [7] Kounaves, S. P. et al (2009), *J. Geophys. Res., 114*, E00A19, doi:10.1029/2008JE003084. [8] Chevrier, V. F., and T. S. Altheide (2008), *GRL, 35,* L22101, doi:10.1029/2008GL035489.