

AQUEOUS PERCHLORATE LIQUID SOLUTIONS AT THE PHOENIX LANDING SITE. J. Hanley, V. F. Chevrier, T. S. Altheide, Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR 72701, jhanley@uark.edu.

Introduction: The possibility of liquid water or brines on the surface of Mars is one of the most important topics in Mars research [1]. Recent results from NASA's polar lander, Phoenix, have indicated the presence of perchlorates (ClO_4^-) in the soil surrounding the landing site [2]. It is likely that these ions associate with either sodium or magnesium [3], which would make them ideal candidates for liquid brines on the surface [4, 5]. Very little is known regarding the behavior of these salts and their solutions in water, especially at low temperatures. Through evaporation experiments and geochemical modeling, we have studied the stability of perchlorates in a simulated Martian environment, and applied these results to Phoenix observations.

Experimental: Experiments were performed in a Martian simulation chamber using previously described methods [1]. Samples of NaClO_4 or $\text{Mg}(\text{ClO}_4)_2$ 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 and converted into evaporation rate.

Results: At temperatures between 256 and 269 K, evaporation rates of sodium perchlorate (Fig. 1A) range from 0.07 mm h^{-1} (55 wt% concentration at 258 K) to 0.49 mm h^{-1} (20 wt% concentration at 266 K). As seen in previous studies, evaporation rate is dependent on both temperature and concentration of the solution [1]. For instance, the evaporation rate of a 55 wt% solution ranges from 0.07 to 0.19 mm h^{-1} over a temperature range of 11 K. The evaporation rate is also dependent on perchlorate concentration: at 266 K, the 20 wt% sodium perchlorate evaporates at 0.49 mm h^{-1} , while the 55 wt% evaporates at 0.14 mm h^{-1} .

Magnesium perchlorate behaves in a similar manner (Fig. 1B). Evaporation rates range from 0.29 mm h^{-1} (20 wt% at 267 K) to 0.06 mm h^{-1} (49 wt% at 260 K). Again, evaporation rates are dependent on both temperature and concentration. For instance, at 264 K, the 20 wt% magnesium perchlorate evaporates at 0.29 mm h^{-1} , while a 49 wt% solution evaporates at 0.07 mm h^{-1} . In addition, temperature plays a suppressive role as seen in the 49 wt%: evaporation rates range from 0.17 mm h^{-1} (272 K) to 0.06 mm h^{-1} (260 K).

Experimental evaporation rates are slightly lower in magnesium perchlorate than for sodium perchlorate, due to lower water activity in magnesium perchlorate solutions (from stronger ionic interactions with Mg^{2+} and ClO_4^-), as demonstrated by the Pitzer model [6].

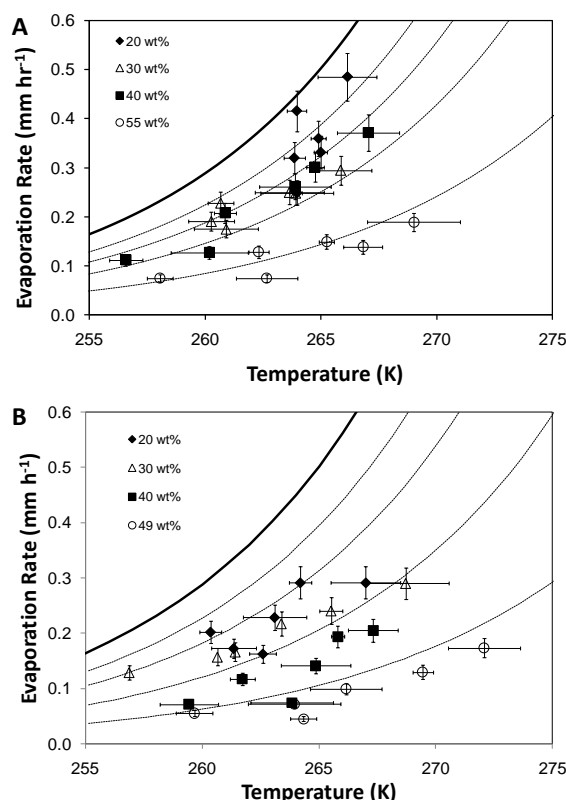


Figure 1. Evaporation rate of NaClO_4 (A) and $\text{Mg}(\text{ClO}_4)_2$ (B) as a function of sample temperature and concentration. Dashed lines are theoretical evaporation rates for each concentration, calculated from the Ingersoll (1970) equation and Pitzer model [1]. The solid line is for pure liquid water.

Discussion: From data collected from various sources [6, 7], and calculating the corresponding thermodynamic parameters, we determined the phase diagrams (Fig. 2). Three phases are known for sodium perchlorate: NaClO_4 (anhydrous), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$. The eutectic temperature was determined to be 236 K at a concentration of 52 wt%.

Less is known about the low-temperature properties of magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$. Calculated eutectic temperature was found to be 200 K at 43.9 wt% (Fig. 2B), close to previous measurements [8]. Mg -perchlorate has one of the lowest eutectic temperatures ever observed, allowing it to easily be liquid even at the Phoenix site. At low temperature, magnesium perchlorate has only one hydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. This hexa-hydrate is stable up to ~409 K, where it converts to $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ [9]. Thus the deliquescence property suggested before for magnesium perchlorate may not be valid on Mars,

since temperatures remain too low for the tetra-hydrate phase to form.

While temperatures are more favorable for liquid solutions on the warmest day, equilibrium vapor pressure values are also higher, and thus liquid perchlorate solutions are evaporating (Fig. 3). Paradoxically, on the coldest days, the atmospheric water vapor pressure crosses above the saturation value of eutectic $\text{Mg}(\text{ClO}_4)_2$ solutions, making the liquid thermodynamically stable for a few hours (Fig. 3A). This is not the case for NaClO_4 where a higher eutectic makes it evaporating or frozen, but never stable.

Using the Pitzer model to calculate the activity of liquid water in the solutions and our kinetic model of water evaporation [1], we extrapolated evaporation rates to the Phoenix landing site conditions. Input data included water vapor pressure and temperature measured by Phoenix's TECP [10] (Fig. 3A). We obtained the cumulated evaporated thickness over time (Fig. 3B). As previously demonstrated, the main control on the evaporation rate remains the temperature [1]. Liquid, if formed, could easily remain metastable for several days.

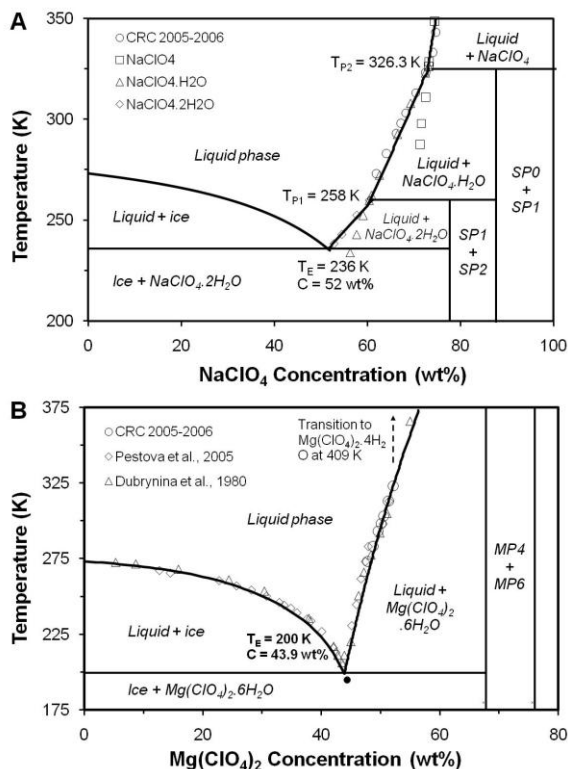


Figure 2. Phase diagram for (A) sodium and (B) magnesium perchlorates. Solid lines are determined by theoretical calculations based on data from various sources.

Conclusions: Thermodynamic calculations show that magnesium perchlorate remains liquid at much lower temperatures than sodium perchlorate. In these

conditions, the combination of a larger stability field for liquid and lower evaporation rates show that magnesium perchlorate should be the dominant liquid phase at the Phoenix landing site. While there are short periods of time when $\text{Mg}(\text{ClO}_4)_2$ is stable on the surface, the majority of the time it is either evaporating or frozen (and likely sublimating). Thus, there must be an efficient mechanism to replenish the lost water for a solution to remain stable over long timescales.

References: [1] Chevrier, V. F., and T. S. Altheide (2008), *GRL*, 35, L22101, doi:10.1029/2008GL035489. [2] Hecht, M. H. et al (2009) *LPS XL*, Abstract #2420. [3] Marion, G.M. et al (2009) *LPS XL*, Abstract #1959. [4] Hanley, J. et al (2009) *LPS XL*, Abstract #1380 [5] Renno, N.O. et al (2009) *LPS XL*, Abstract #1440. [6] Pitzer, K. S. (1991), Ch. 3. *Activity coefficients in Electrolyte Solutions. 2nd Edition*, 75-154, CRC Press. [7] Chretien, A., and R. Kohlmuller (1966), *Nouveau Traite de Chim. Min., Vol 2 (#1), Sodium and Lithium*, 344-354. [8] Pestova, O. N. et al. (2005), *Rus. J. App Chem*, 78, 409-413. [9] Dobrynina, T.A. et al. (1980), *Rus. J. Inorg. Chem.*, 25, 1237-1239. [10] Hudson, T.L. et al. (2009), *LPS XL*, Abstract #1804.

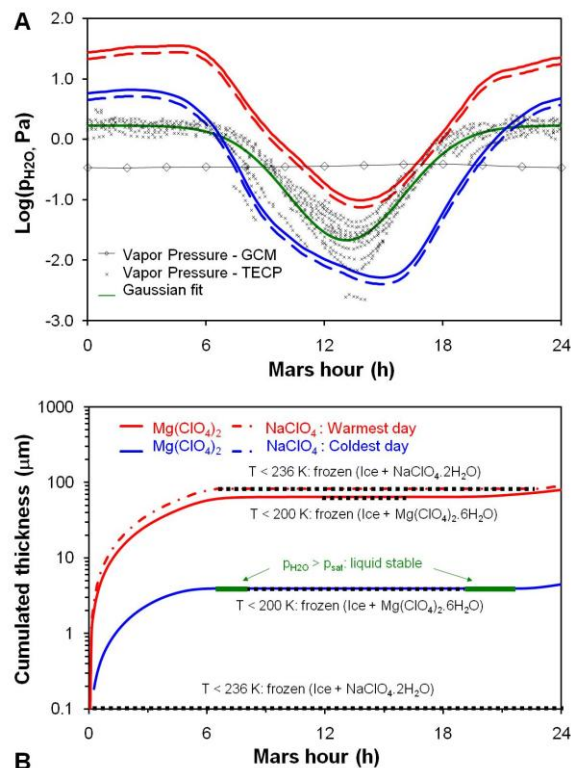


Figure 3. (A) Water vapor pressures. Blue and red curves are equilibrium pressure above eutectic solutions of NaClO_4 (dashed) and $\text{Mg}(\text{ClO}_4)_2$ (plain) for the coldest and warmest days, respectively. (B) Integrated evaporation curves over time after noon for $\text{Mg}(\text{ClO}_4)_2$ (plain lines) and NaClO_4 (dashed lines). Red is for the warmest day, blue for the coldest. Thick dotted black lines represent frozen periods. Green areas represent thermodynamically stable periods for liquid $\text{Mg}(\text{ClO}_4)_2$ eutectic solutions.