

**ANALYZING HYDRATED SALT SOLUTIONS AT THE PHOENIX LANDING SITE.** H. Farris<sup>1,2</sup>, J. Hanley<sup>2</sup>, and V. Chevrier<sup>2</sup>, <sup>1</sup>Department of Physics, Albion College, 611 E. Porter Street, Albion, Michigan 49224, hf11@albion.edu, <sup>2</sup>Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, Arkansas 72701.

**Introduction:** In 2008, NASA’s Phoenix lander arrived in the northern arctic plain of Mars. Its objective was to perform analyses on the subsurface water ice, ultimately characterizing the geology, climate, and habitability of the Martian polar regions. Two of the instruments on board were TECP (Thermal Electric Conductivity Probe), which recorded temperature and relative humidity measurements, and WCL (Wet Chemistry Lab), which deposited soil into a leaching solution and recorded the resulting ion concentrations.

The most interesting of these ions were perchlorate salts ( $\text{ClO}_4^-$ ) [1]. The presence of salt significantly lowers the eutectic temperature of water, or the lowest possible temperature to have any remaining liquid. While perchlorates have some of the lowest documented eutectic temperatures, some are dramatically lower than others [2].  $\text{NaClO}_4$  for example has a eutectic temperature of 236 K (Fig. 1A), while  $\text{Mg}(\text{ClO}_4)_2$  can be liquid down to 206 K (Fig. 1B).

Relative humidity (RH) also affects the stability of liquid water. When the water vapor pressure of the salt is less than that of the air, deliquescence occurs. Deliquescence is when the salt reacts with adsorbed water from the air to create a solution. The temperature and RH at which this happens are important properties of

each salt and has important implications for the stability of liquid water on Mars. In fact, based on measured temperatures and RH at the Phoenix landing site, liquid water can be stable for short periods of time in the presence of  $\text{Mg}(\text{ClO}_4)_2$  [2].

**Methods:** The research was divided into two parts, a modeling component and an experimental component. Ion concentrations reported from WCL were put into Geochemist’s Workbench in an attempt to understand what minerals may have been present in the soil analyzed by Phoenix. The minerals which precipitated last and with the highest concentrations were focused on for the experimental component. Inside the humidity chamber, the relative humidity was fixed using the humidity buffer technique [5]. The buffers used were  $\text{MgCl}_2$  and  $\text{NaCl}$ . Temperature was increased until deliquescence was observed through spectral and photographic analysis of the sample.

*Geochemical Modeling.* Evaporation models were conducted in Geochemist’s Workbench, essentially running WCL experiments in reverse. Starting with specific ion concentrations dissolved in 1kg of water (Table 1), the water was evaporated and minerals precipitated as a result. The initial conditions for the model included a pH of 7.7, a charge balance on  $\text{SO}_4^{2-}$  to account for a lack of anions in solution, temperature of 7°C, and the flow through setting on. Flow through keeps the minerals which have already precipitated from reacting with each other.

The minerals which precipitated last are the most soluble and of those, the ones that are of the highest concentrations are thus the most important to study. Here, those minerals are  $\text{Mg}(\text{ClO}_4)_2$  hydrates (Fig. 2). Again, perchlorates are interesting because of their low eutectic temperatures, therefore these were the first salts to test in the humidity experiments.

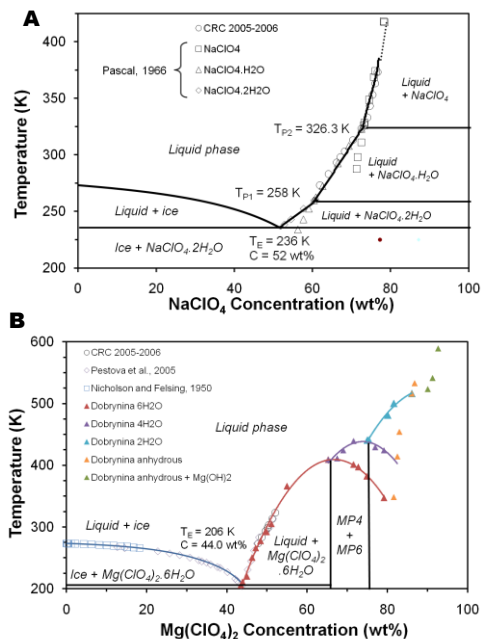


Figure 1. Stability diagram of (A)  $\text{NaClO}_4$  and (B)  $\text{Mg}(\text{ClO}_4)_2$  as a function of concentration [2, 3].

Ion	Concentration
$\text{Na}^+$	1.4 mmol
$\text{K}^+$	0.38 mmol
$\text{Ca}^{2+}$	0.58 mmol
$\text{Mg}^{2+}$	3.3 mmol
$\text{SO}_4^{2-}$	1 mmol
$\text{Cl}^-$	0.54 mmol
$\text{ClO}_4^-$	2.4 mmol
$\text{HCO}_3^-$	Swapped for Calcite: 4.5 wt%

Table 1. Initial ion concentrations for the evaporation model [1, 4]

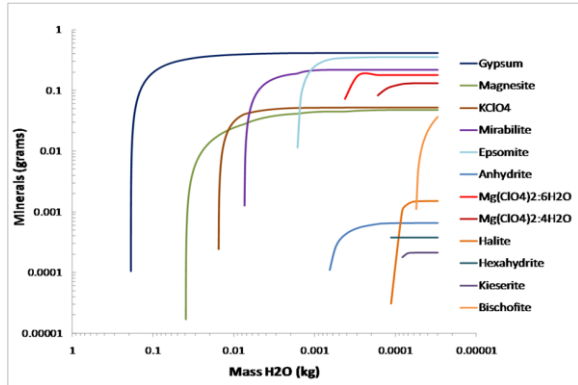


Figure 2. Minerals that precipitated upon evaporation from a solution with initial concentrations given in Table 1 [1].

**Humidity Experiments.** In preparation for an experiment, the sample is ground to a powder consistency and laid down in a petri dish. The sample is then heated to eliminate any excess water and placed into the humidity chamber on a hot plate with temperature control. The humidity buffers, or saturated salt solutions, are placed in the chamber as well. The chamber is closed, a vacuum is pulled and then replaced with nitrogen, to remove any H<sub>2</sub>O already present. Nitrogen will not react with our sample or buffer and is also spectrally neutral in the near-infrared (NIR), making it the optimal choice for these experiments. The fiber optic cable runs from the chamber to an FTIR Spectrometer with a Iridium Antimonide (InSb) detector that is cooled with liquid nitrogen. The sample is observed in the NIR range of 11,000-2300 cm<sup>-1</sup> (0.9-4.3μm). Spectra were taken over the course of the run as a means of identifying the presence of water, and therefore deliquescence of the sample (Fig. 4). The webcam and digital microscope were used to image the sample and take time-lapse videos. Experiments were generally run overnight to ensure complete equilibration with the humidity buffer and thus, a constant humidity within the chamber.

**Results and Discussion:** Due to a high relative humidity at room temperature, when NaCl was used as a humidity buffer, it caused the sample to completely deliquesce (Fig. 3). When MgCl<sub>2</sub> is used, the temperature started at room temperature and then was gradually increased until the point where the MgCl<sub>2</sub> line crossed the Mg(ClO<sub>4</sub>)<sub>2</sub> line changing from the solid to liquid phase. Although deliquescence never occurred, we confirmed that hexahydrate is the stable phase of the Mg(ClO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O system at ~30% relative humidity and temperatures ranging from 295 K to 333 K. There are currently calibration issues with the hygrometer and difficulties controlling the temperature gradient throughout the chamber.

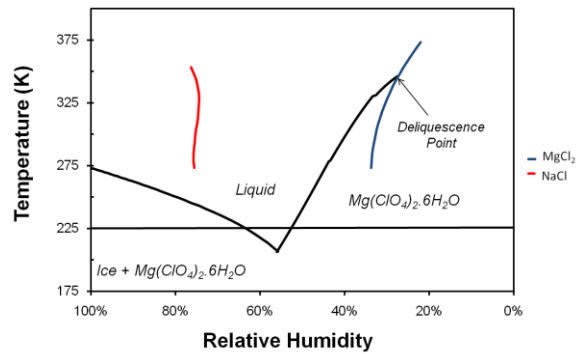


Figure 3. Stability diagram of Mg(ClO<sub>4</sub>)<sub>2</sub> hexahydrate as a function of relative humidity. MgCl<sub>2</sub> and NaCl humidity buffer stability lines are overlaid, showing deliquescence points.

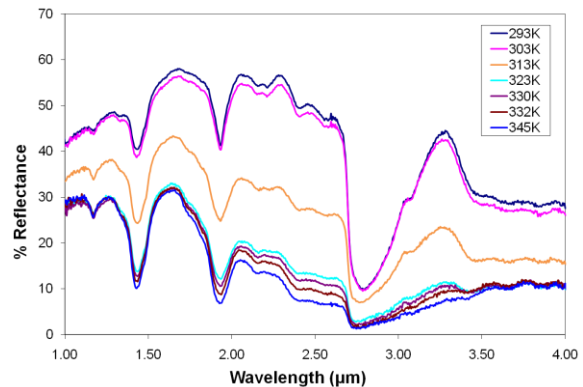


Figure 4. Spectra of Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O upon heating at 30% relative humidity. Water bands at 1.4μm and 1.9μm appear to broaden and deepen as temperature is increased. This could be because it is nearing the transition to liquid water.

These problems are in the process of being resolved and will allow for the testing of other salts at various humidities and temperatures.

**Conclusions and Future Work:** From the modeling, it is concluded that Mg(ClO<sub>4</sub>)<sub>2</sub> is the most interesting mineral to precipitate because of its solubility, abundance and relevance to Mars. Once the humidity chamber is fully functional, more experiments will continue to be run at lower humidities that better simulate conditions on the Martian surface.

#### References and Acknowledgements:

- [1] Hecht, M. H. et al. (2009) *Science*, 325, 64-67 [2] Chevrier, et al. (2009) *GRL*, 36, L10202. [3] Pestova et al. (2005) *RUSJ App. Chem*, 78, 409-413. [4] Kounaves, S. P. et al. (2010), *GRL*, 90, L09201 [5] Greenspan (1977) *J. Res. NBS-A Phys Chem*, 81A, 89-96.

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