

ANALYSIS OF THE SALT ASSEMBLAGE FROM WCL AT THE PHOENIX LANDING SITE. J. Hanley¹, A. El Senousy¹, V. F. Chevrier¹, H. Farris², ¹Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR 72701; jhanley@uark.edu, ²Albion College, Albion, MI 49224.

Introduction: NASA's Phoenix lander provided a unique insight into the regolith of the north polar region of Mars through its Wet Chemistry Lab (WCL) analysis. Ions in solution were measured by a sensor array of electrochemically based ion-selective electrodes (ISE). WCL detected a variety of ions, some of which were expected (Cl^- and SO_4^{2-}), while others came as a surprise (ClO_4^-) [1-3]; however, one drawback to this method of wet analysis is that while we know the ionic composition of the soluble part of the regolith, we do not know the original salt paragenesis. Careful analysis and modeling is needed to determine how these ions will behave with respect to liquid water [1, 4, 5].

Additionally, though each ISE is selective, it is not specific, and modeling must also be utilized to rule out interference from other ions. In particular, the sensor used to detect ClO_4^- is also sensitive to ClO_3^- , as described by the Hofmeister series. This leaves the possibility that other ions may be present at the Phoenix landing site, but remained undetected. For instance, the formation pathway between chloride (Cl^-) and perchlorate (ClO_4^-) contains many forms of oxidized chlorine, such as ClO^- (hypochlorite) and ClO_2^- (chlorite), which are both quite unstable [4] and thus unlikely to be present, while the most stable of the intermediate phases is chlorate (ClO_3^-) [5]. In fact, it is almost as stable as perchlorate, and given the slow kinetics at Martian temperature, it is certainly possible that this ion may be present in conjunction with perchlorate. There is a lack of thermodynamic data for the various species of oxidized chlorine, especially those associated with magnesium. From the literature and our own data, we have constructed stability diagrams for KClO_3 , NaClO_3 , $\text{Ca}(\text{ClO}_3)_2$ and $\text{Mg}(\text{ClO}_3)_2$ [6], which allowed us to extract the Pitzer parameters and utilize them in our modeling.

After determining thermodynamic properties for each probable salt pair, we have begun to study the salt solution obtained by WCL to determine which salt phases would be present today. We have focused on chlorate (ClO_3^-) as an additional salt that is also likely present at the Phoenix landing site [7].

Methods: NaClO_3 and $\text{Mg}(\text{ClO}_3)_2$ salts were studied to understand their behavior with water at low temperatures. In particular, we wanted to obtain the Pitzer parameters that would allow us to add these salts to our model. First, evaporation rates were measured in our Mars simulation chamber. From these values we were able to extrapolate the activity of water and create a temperature stability diagram for each salt with

liquid water (Fig. 1). From these diagrams, the Pitzer parameters for each salt were calculated (see [7] for further explanation).

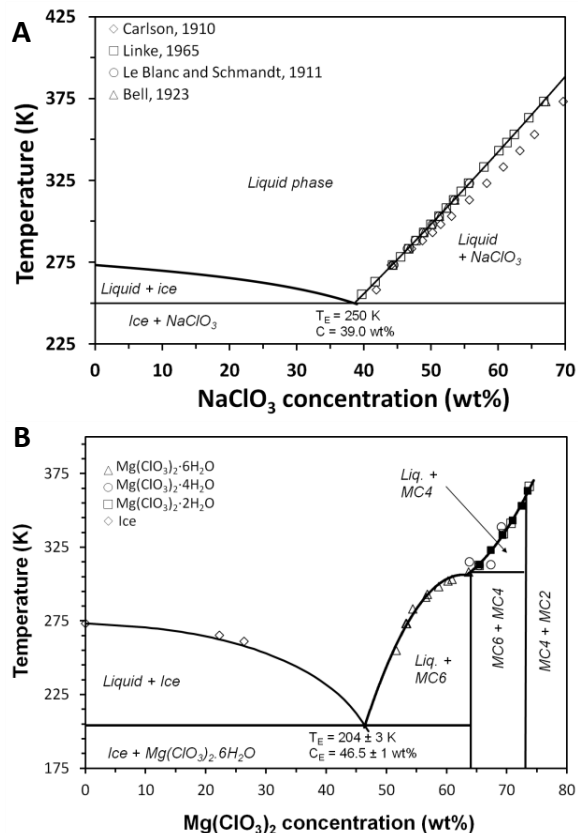


Figure 1. Stability diagram of $\text{Mg}(\text{ClO}_3)_2$ as a function of concentration versus temperature. Its low eutectic of $204 \pm 3\text{K}$ makes it possible for liquid to be present at the Phoenix landing site.

Geochemist's Workbench (GWB) *React* was used to model the precipitation of minerals as water was evaporated from the system. We have used an updated database that is based on the Pitzer method for determining the activity of water, which is more suited for highly concentrated solutions. Initial conditions were taken from [1] and [3] as described in Table 1. Three runs were performed. The "sulfate poor" model (Fig. 2A) assumes values from [1] and uses chlorate as the charge balance. The "sulfate heavy" model (Fig. 2B) uses the same initial values, except chlorate is fixed and sulfate is the charge balance. The "balanced" model (Fig. 2C) assumes more sulfate and magnesium as per the analysis in [3], while using chlorate as the charge balance.

	Fig 2A	Fig 2B	Fig 2C
Na ⁺	1.4	1.4	1.4
K ⁺	0.38	0.38	0.4
Ca ²⁺	0.58	0.58	0.75
Mg ²⁺	3.3	3.3	6.4
Cl ⁻	0.54	0.54	0.75
ClO ₄ ⁻	2.4	2.4	2.5
SO ₄ ²⁻	0.2	CB	5.3
ClO ₃ ⁻	CB	2.4	CB

Table 1. Initial concentrations (mM) used in GWB. CB stands for charge balance. Temperature was set to 7°C, pH was set at 7.7, and calcite was present at 4.5wt% in all runs.

Results: In the sulfate poor model (Fig. 2A), chlorate was more prevalent than perchlorate. In the sulfate heavy model, even with only a small amount of chlorate (Fig. 2B), Mg(ClO₃)₂ was still more dominant than perchlorate salts. Finally, in the balanced model, Mg(ClO₃)₂ precipitates at higher concentrations than any sulfate. In all runs KClO₄ is present, which is expected as this is the least soluble perchlorate. Similarly, magnesite is the dominant carbonate due to saturation of calcite. One thing to note is that these are done at 7°C, meaning that higher hydrates (if possible) would precipitate over their lower hydrate counterparts. For instance, epsomite is present rather than a higher hydrate simply because we do not have it in our database yet, though the outcome of cation-anion pairs would likely be similar.

Discussion: All models resulted in the presence of sulfate salts in high concentrations. They also revealed that given approximately equal concentrations of perchlorate and chlorate, chlorate will dominate. In most cases magnesium was the dominant cation associated with perchlorate and chlorate, and with their low eutectic temperatures (206 and 204 K respectively), there is a good possibility for the presence of liquid water on the surface of Mars today. Future work will be done to add calcium perchlorate to the mixture, as this also has a low eutectic temperature, though the likelihood of its presence is suspect given the saturation of calcite. Furthermore, we will begin testing these solutions under freezing conditions to better simulate the martian surface environment.

Conclusions: Mg(ClO₄)₂ has one of the lowest eutectic temperatures relevant to the Phoenix landing site, which, along with its low evaporation rates, suggests that it should be the dominant liquid phase [8]. However, based on geochemical modeling, it may not be the dominant salt present in the regolith. Further study is needed as each salt has a unique influence on eutectic temperatures that could potentially affect surface geochemistry. Future work will include similar modeling using the FREZCHEM model updated for chlorate to compare with GWB for evaporation and evaporation versus freezing.

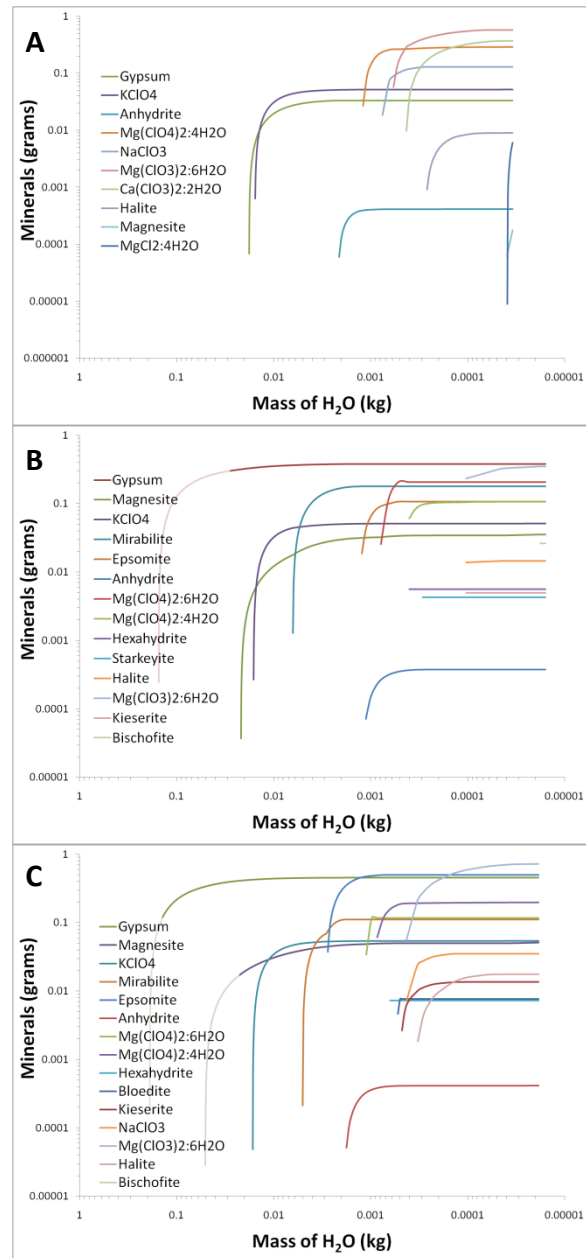


Figure 2. Results of GWB models showing mineral precipitation as water is lost through evaporation. Note the presence of a variety of salts, including carbonates, sulfates, chlorides, perchlorates, and chlorates. Calcite was present at 4.5wt% (45g) in all runs, but is not shown for clarity.

References: [1] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [2] Kounaves S. P. et al. (2009) *J. Geophys. Res.*, 114, E00A19. [3] Kounaves S. P. et al. (2010) *Geophys. Res. Lett.*, 37, L09201. [4] Kang N. et al. (2006) *Analytica Chimica Acta*, 567, 48-56. [5] Chevrier V. F. and Hanley J. (2009) #8009. *The New Martian Chemistry Workshop*. Medford, Massachusetts: LPI. [6] Hanley J. et al. (2012) *Geophys. Res. Lett.*, submitted. [7] Rao B. et al. (2010) *Environmental Science & Technology*, 44, 8429-8434. [8] Chevrier V. F. et al. (2009) *Geophys. Res. Lett.*, 36, L10202.