TOWARDS AN ACCURATE LOW-TEMPERATURE THERMODYNAMIC MODEL FOR PERCHLORATE BRINES ON MARS. J. D. Toner[1], D. C. Catling[1], S. Halbert[1], and B. Light[2]
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Introduction: Perchlorate (ClO_4^-) has been directly measured in soils by the Phoenix Lander [1,2] and its presence is inferred from pyrolysis experiments in other locations [3,4], suggesting that perchlorate is globally distributed on Mars. Perchlorate salts have several properties that promote the formation of liquid water in the cold and dry conditions of present-day Mars. (1) Perchlorates have eutectic temperatures down to –75°C [5], which suggests that water could exist on the surface of present-day Mars in spite of global average temperatures near –55°C. (2) Perchlorate salts will spontaneously absorb water from the atmosphere via deliquescence, and, once brines are formed, they will resist evaporation [6]. (3) A recent study by [7] has found that perchlorate brines readily supercool below their eutectic until they transition into an amorphous glass near –120°C. The formation of liquid water in perchlorate brines on Mars is important for weathering of the Martian regolith and the habitability of soils.

To determine equilibrium ion chemistries, salt precipitates, and water activities in low-temperature perchlorate brines, semi-empirical thermodynamic models such as FREZCHEM have been used [5]. However, a recent study by [8] has found that FREZCHEM predictions for $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines are extremely sensitive to the accuracy of the experimental data used to parameterize FREZCHEM. This is problematic because experimental data for low-temperature perchlorate brines is limited to only a few studies [5], which sometimes disagree. Furthermore, when FREZCHEM is used to model the evolution of salt chemistries in Martian soils, Mg^{2+} activity coefficients with values up to 10^5 can occur and unusual $Ca(ClO_4)_2$-rich brines develop [8]. These effects are clearly artifacts of the FREZCHEM model.

Our goal in this study is to obtain accurate measurements of freezing-point depressions and salt solubilities for $NaClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, and mixtures of these salts. Using this experimental data, we will construct more accurate models of low-temperature perchlorate brines.

Methods:

Freezing-Point Depressions (FPDs). The activity of water (a_w) at low temperatures can be directly measured from the FPD of ice in salt solutions. This is because a_w for a solution in equilibrium with ice is a well-known function of temperature. To accurately measure FPDs, we have constructed a low-temperature copper reaction vessel. The vessel is cooled in a liquid N_2 bath and the temperature within the vessel is fixed by modulating the heat output from two cartridge heaters embedded in the vessel walls using a Lakeshore 340 Temperature Controller. Temperatures are monitored by a Platinum Resistance Thermometer (PRT) probe calibrated to an accuracy of 0.02°C. Salt solutions in the reaction vessel are vigorously stirred with a magnetic stir bar to ensure through mixing. FPDs are measured by equilibrating a solution-ice mixture in the vessel and then extracting a small fraction of the solution for later analysis of the salt content by gravimetric methods. Similarly, solubilities can be measured by equilibrating a solution-salt mixture in the vessel.

Analysis of Literature Thermodynamic Data. Current equilibrium models for perchlorate brines are based on experimentally determined water activities, but neglect apparent relative molar enthalpies (L_ϕ) measured at 25°C, which indicate the temperature dependence of thermodynamic parameters [9]. We use literature L_ϕ values [9] to guide the extrapolation of thermodynamic models from 25°C to lower temperatures.

Freezing-Point Depression Results: Preliminary results with the FPD vessel indicate that $Ca(ClO_4)_2$ FPDs in [10] and [11] typically differ from our results by ±4°C, although at low temperatures FPDs in [10] differ by >10°C (Fig. 2). For $Mg(ClO_4)_2$, our results differ from [12] and [11] by ±2.5°C. Our results agree well with the very accurate FPDs of [13], which unfortunately only extend up to 1 m concentration.

Modeling Low-Temperature Perchlorate Brines: We model perchlorate brines using the standard Pitzer model [14]. Following the approach used in FREZCHEM [5], we use model parameters at 25°C tabulated in [14] and extrapolate the model to low temperatures by fitting the model to water activities determined from FPD measurements. In contrast to FREZCHEM, we use only our FPD data and the very accurate data of [13], excluding the data of [10,11,12]. Furthermore, we use literature L_ϕ

values at 25°C to guide the extrapolation of our model to low temperatures, as described in [9]. Using this approach, our model predictions for $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines differ significantly from FREZCHEM (Fig. 2). FREZCHEM predicts that ion activity coefficients in 3.5 m $Mg(ClO_4)_2$ and 4 m $Ca(ClO_4)_2$ brines will increase exponentially as temperatures decrease, while our model indicates that ion activity coefficients remain similar to their values near 25°C at all temperatures. In general, ion activity coefficients predicted by FREZCHEM are up to 10X higher than in our model.

In contrast to ion activities, water activities in $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines show little change with temperature and are similar between FREZCHEM and our model. In general, a_w in our model is slightly higher than in FREZCHEM by about 0.01. This demonstrates that small differences in a_w correspond to much larger changes in solute activity for $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines. Given that an error in experimental FPDs of only 1°C causes an error in water activity between 0.005–0.01 (comparable to differences in Fig. 2), it is important to obtain highly accurate FPD measurements.

Conclusions: We have determined new, highly accurate FPD measurements for $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines. Using these measurements and L_ϕ values from the literature we construct a more accurate and thermodynamically consistent Pitzer model for low-temperature $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines. Our model predicts much lower ion activity coefficients than FREZCHEM, but similar water activities. Activities in concentrated perchlorate solutions are important for understanding the habitability of soils, salt phases present, and weathering reactions in the regolith.

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References: [1] Hecht M. H. et al. (2009) *Science*, 325, 5936. [2] Kounaves S. P. et al. (2010) *JGR*, 115, E00E10. [3] Navarro-González, R., E. et al. (2010), *JGR*, 115, E12010. [4] Leshin, L. A., et al. (2013), *Science*, 341, 6153. [5] Marion G. M. et al. (2010) *Icarus*, 207, 675-686. [6] Gough, R. V. et al. (2011), *EPSL*, 312(3-4), 371–377. [7] Toner, J. T. et al. in review, *Icarus*. [8] Toner, J. T. et al. in review, *GCA*. [9] Silvester, L. F. and Pitzer, K. S. (1978), *J. Soln. Chem.*, 7, 5. [10] Dobrynina, T. A. et al. (1984), *Russ. J. Inorg. Chem.*, 29(7), 1043-1045. [11] Pestova, O. N. et al. (2005), *Russ. J. Ap. Chem.*, 78, 409–413. [12] Dobrynina, T. A. et al. (1980), *Russ. J. Inorg. Chem.*, 25, 2233–2236. [13] Nicholson, D. E., and Felsing, W. A. (1950), *J. Am. Chem. Soc.*, 72(10), 4469–4471. [14] Pitzer, K. S. (1991), pp. 75–153, CRC Press.

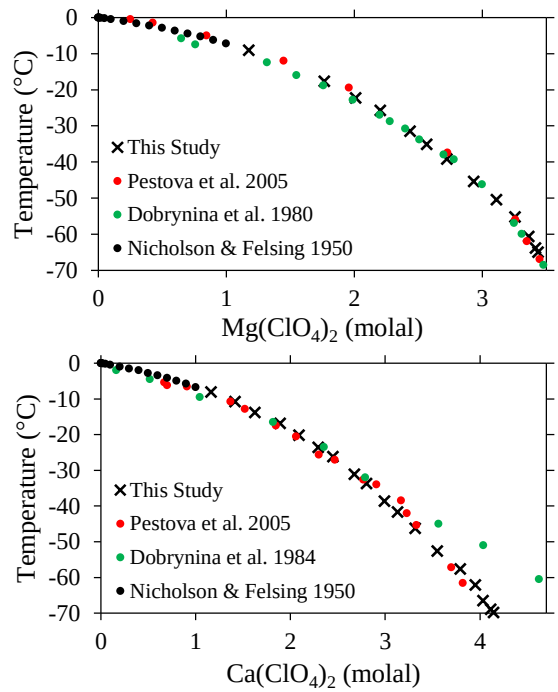

Fig. 1. FPDs for $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ brines determined in this study and from the literature.

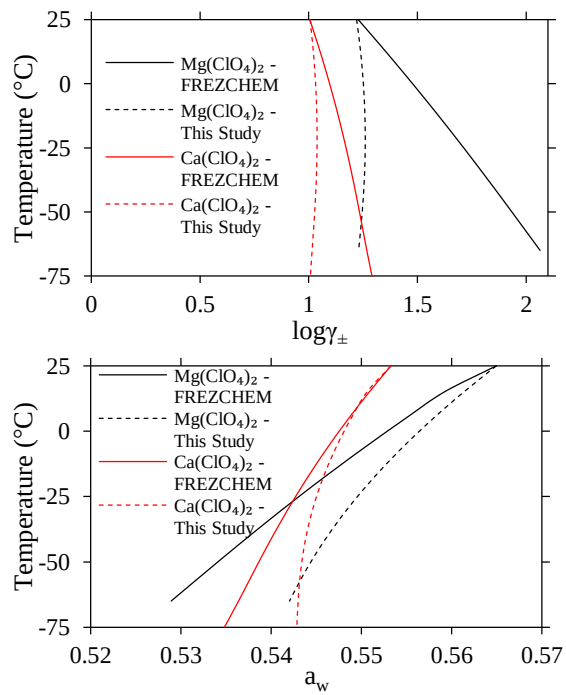

Fig. 2. The temperature dependence of mean ion activity coefficients ($\gamma_\pm$) and water activities (a_w) modeled in this study and in FREZCHEM for 3.5 m $Mg(ClO_4)_2$ and 4 m $Ca(ClO_4)_2$ brines at constant concentration.