DELIQUESCENCE OF CALCIUM PERCHLORATE: AN INVESTIGATION OF STABLE AQUEOUS SOLUTIONS RELEVANT TO MARS. D. L. Nuding[1,2], R. V. Gough[1,3], V.F. Chevrier[4], M. A. Tolbert[1,3]. [1]Cooperative Institute for Research in Environmental Sciences, [2]Department of Atmospheric and Oceanic Sciences, [3]Department of Chemistry and Biochemistry; University of Colorado, Boulder, CO 80309. [4]W. M. Keck Laboratory for Space and Planetary Simulation. Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, USA.

Introduction: The Wet Chemistry Laboratory (WCL) aboard the Phoenix Mars Lander identified the presence of 0.5% perchlorate (ClO_4^-) [1]. Reanalysis of the Viking gas chromatography-mass spectrometry results also suggests perchlorate was present in the soil [2] and the Mars Science Laboratory (MSL) rover has potentially found perchlorate as well.

Perchlorate salts are known to readily absorb water vapor from the atmosphere and deliquesce into an aqueous solution [3,4]. We have previously performed laboratory studies to better understand the deliquescence (crystalline solid to aqueous salt) and also efflorescence (aqueous salt to crystalline solid) of several perchlorate salts at low temperatures. We found that $NaClO_4$ and $Mg(ClO_4)_2$ are highly deliquescent, forming aqueous solutions at humidity values as low as 40% RH and at temperatures as low as 223 K. We also observed a significant hysteresis that occurs during efflorescence of these salt solutions, expected due to the kinetic inhibition of crystal nucleation. The efflorescence relative humidity values of sodium and magnesium perchlorate solutions are 13% RH and 19% RH, respectively, indicating that perchlorate salts could exist as stable or metastable aqueous solutions over a wide range of Martian RH and temperature conditions [4].

Although the low temperature deliquescence of several perchlorate salts is now well characterized, instruments onboard Phoenix and MSL have identified calcium perchlorate ($Ca(ClO_4)_2$) as the likely parent salt. Calcium perchlorate is known for its highly deliquescent properties [5] and low eutectic point; however, the deliquescence and efflorescence of this salt have not yet been quantified.

Experiments and Results: To understand the likely phase of $Ca(ClO_4)_2$ on the Martian surface, we have used a Raman microscope equipped with an environmental cell to determine the deliquescent relative humidity (DRH) and efflorescent relative humidity (ERH) as a function of temperature (233 K to 273 K) and also hydration state.

We measured the deliquescence phase transitions of at least two hydration states. Figure 1 depicts a typical $Ca(ClO_4)_2$ deliquescence experiment starting with an anhydrous crystal particle. Here the experiment begins with dry $Ca(ClO_4)_2$ at 0.25% RH at 273 K. Immediately, the particle begins to uptake water and deliquesce into an aqueous phase. By 2% RH, both the Raman spectra and optical images suggest deliquescence is complete. Once deliquesced, the O-H stretch at 3550 cm^{-1} appears and the ClO_4^- stretch shifts from 990 cm^{-1} to 938 cm^{-1}. As the relative humidity is increased above the DRH value, the O-H stretch increases in height and width as demonstrated by the spectra in Figure 1. Visually, the particle darkens and

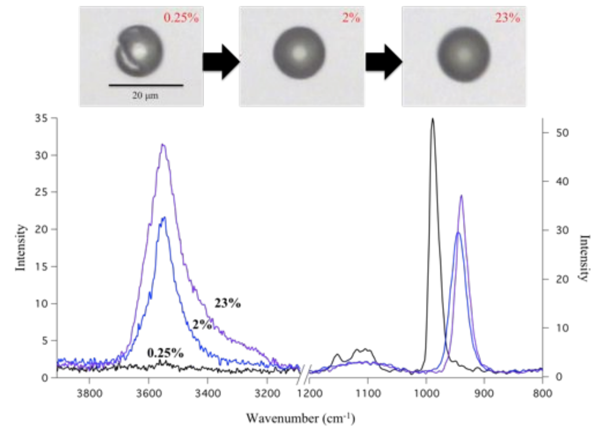

Figure 1 *Optical images and Raman spectra of a typical anhydrous $Ca(ClO_4)_2$ experiment at 273 K.*

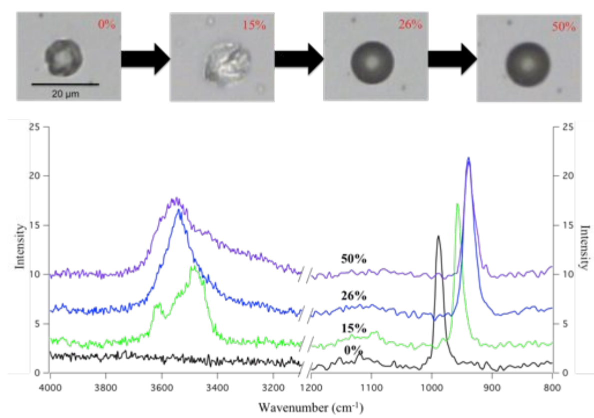

Figure 2 *Optical images and Raman spectra depicting the formation of a hydrated salt by 15% RH and the deliquescence of this hydrate by 26% RH. The temperature was held constant at 253 K. The spectra are offset for clarity.*

increases in volume as relative humidity is increased.

Figure 2 demonstrates the deliquescence of a $Ca(ClO_4)_2$ hydrate at 253 K. This experiment also starts with an anhydrous $Ca(ClO_4)_2$ crystal particle. As relative humidity is increased, deliquescence does not occur at this low temperature; rather, spectral and optical changes suggest that a hydrated salt forms at RH 15%. Sharp features indicative of crystalline water appear in the Raman spectrum in the O-H stretch region (3500 cm^{-1}) and there is a peak shift from 990 cm^{-1} to 958 cm^{-1} in a ClO_4^- stretch region. This change in hydration state is also verified by the optical microscope images by characteristic particle brightness. By 26% RH, optical images suggest deliquescence to an aqueous solution supported by the Raman O-H stretch broadening and the ClO_4^- stretch shifts to 938 cm^{-1}.

Experimental results are compared to the calculated thermodynamic stability diagram for the $Ca(ClO_4)_2 + H_2O$ system (Figure 3). This figure shows the stability regions of three hydration states that are expected to exist (anhydrous $Ca(ClO_4)_2$, $Ca(ClO_4)_2{\bullet}4H_2O$ and $Ca(ClO_4)_2{\bullet}8H_2O$). The symbols represent experimental deliquescence results of at least three averaged experiments with error bars represented by the standard deviation of the dataset. The deliquescence of anhydrous $Ca(ClO_4)_2$ occurs at very low RH in agreement with the thermodynamic model. At lower temperatures, we observe solid-solid phase transition to form a hydrate rather than deliquescence. Deliquescence of the hydrate occurs at higher RH, represented by the blue points in Figure 3.

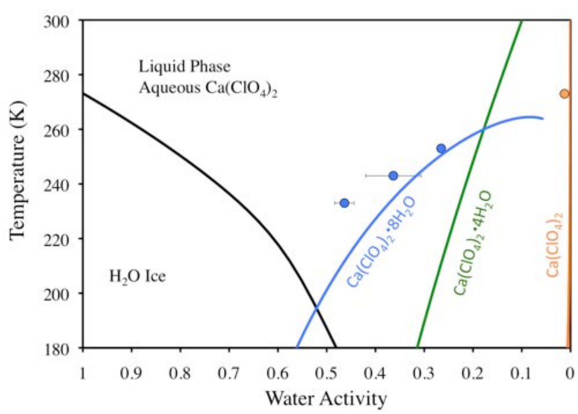

Figure 3 *Experimental DRH values (symbols) on a stability diagram for the $Ca(ClO_4)_2 + H_2O$ system. Thermodynamically predicted phase transitions are represented by the solid lines.*

Under all temperature conditions, $Ca(ClO_4)_2$ efflorescence is found to occur at relative humidity values far below where deliquescence occurs. The measured ERH values have an average value of 15% RH from 233 K to 263 K, but less than 1% RH have been observed at 273 K. This result confirms that all perchlorate salts studied thus far exhibit a significant hysteresis effect during crystallization and thus $Ca(ClO_4)_2$ readily forms supersaturated, metastable solutions.

Martian Implications: The recent detection of perchlorate by the Sample Analysis at Mars (SAM) suite aboard MSL, likely calcium perchlorate, further supports the widespread distribution of perchlorates on Mars. The experimental results presented allow us to predict the phase transition behavior of $Ca(ClO_4)_2$ at relevant Martian temperatures. Given that the surface RH on Mars likely varies from 0-100% throughout a diurnal cycle [6], it is likely that $Ca(ClO_4)_2$ salts could deliquesce, providing a mechanism for aqueous solution formation under present day Martian conditions.

The presence of liquid spheroids on the Phoenix lander strut [5] and Recurring Slope Lineae (RSL) [7] may be explained by $Ca(ClO_4)_2$ aqueous solutions. A better understanding of the RH conditions in the Martian subsurface are needed to accurately predict the duration of these stable, aqueous solutions.

Conclusion: We have experimentally examined the deliquescent and efflorescent properties of $Ca(ClO_4)_2$ under relevant Martian temperatures. A very low DRH of ~1% for the anhydrous $Ca(ClO_4)_2$ at 273 K could allow for formation of aqueous solutions under very low RH environmental conditions. However, regardless of hydration state and temperature over the range studied, $Ca(ClO_4)_2$ deliquesces at ≤50% RH and remains liquid until the RH decreases to a much lower value where the particle eventually effloresces. At 273 K, the ERH is less than 1% and on average, less than 15% for all temperatures studied. The experimental results were compared to a thermodynamic model for three hydration states of $Ca(ClO_4)_2$. As predicted, the higher hydration states were less deliquescent and the experimental results are in good agreement with the model results. Understanding RH phase transition range for $Ca(ClO_4)_2$ aqueous solutions, or any briny mixture, is important for characterizing the present-day water on Mars.

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